Appendix B
Quality Assurance Project Plan

Report

Quality Assurance Project Plan

Lower Fox River Operable Unit 1 and Lake Winnebago Long-term Monitoring

Project I.D.: 10G007

GW Partners, LLC
Neenah, Wisconsin

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Foth

Quality Assurance Project Plan

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Project ID: 10G007

Prepared for
GW Partners, LLC

Prepared by
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Appendices

List of Abbreviations, Acronyms, and Symbols

°C	degrees Celsius
Anchor	Anchor QEA, LLC
AOC	Administrative Order on Consent
BMP	Baseline Monitoring Program
CERCLA	Comprehensive Environmental Response, Compensation, Liability Act
CH2M HILL	CH2M HILL, Inc.
CLP	contract laboratory program
CMMP	Cap Monitoring and Maintenance Plan
COC	chain of custody
CUL	Cleanup Levels
CV	coefficient of variation
cy	cubic yards
DGPS	differential global positioning system
DMCM	Data Management Control Memo
DQO	data quality objective
eCOC	electronic chain of custody
EDD	electronic data deliverable
EDL	estimated detection limit
Foth	Foth Infrastructure & Environment, LLC
FR-LTMP	Long-Term Monitoring Plan for the Lower Fox River and Green Bay site
GPS	global positioning system
HASP	Health and Safety Plan
HRGC/MS	high-resolution gas chromatography/mass spectrometry
LCD	liquid crystal display
LCS	laboratory control sample
LFR	Lower Fox River
LIMS	laboratory information management system
LLBdM	Little Lake Butte des Morts
LOAEC	lowest observed adverse effects concentration
LTM	Long-term Monitoring
LTMP	Long-term Monitoring Plan
LTM Work Group	Long-term Monitoring Work Group
MDL	method detection limit
mg/kg	milligrams per kilogram
MDRD	minimum detectable relative difference
MNR	monitored natural recovery
NELAC	National Environmental Laboratory Accreditation Conference
ng/L	nanograms per liter
OU	Operable Unit

OU1-LTMP	Lower Fox River Operable Unit 1 – Long-term Monitoring Plan
PCB	polychlorinated biphenyl
PE	performance evaluation
PM	project manager
QA	quality assurance
QAM	quality assurance manager
QAPP	Quality Assurance Project Plan
QC	quality control
RA	remedial action
RAO	remedial action objective
RETEC	RETEC Group, Inc.
RG	Remediation Goals
RI/FS	remedial investigation/feasibility study
RMSE	Root mean squared error
ROD	Record of Decision
RPD	relative percent difference
RTK-GPS	real-time kinematic global positioning system
SDG	sample delivery group
Shaw	Shaw Environmental & Infrastructure, Inc.,
SOP	standard operating procedure
SOW	statement of work
SWAC	surface-weighted average concentration
TOC	total organic carbon
TSS	total suspended solids
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WDNR	Wisconsin Department of Natural Resources
WOE	weight-of-evidence
WSLH	Wisconsin State Lab of Hygiene
YOY	young-of-year

1 Purpose

Data generated during performance of the Lower Fox River (LFR) Operable Unit 1 (OU1) Long-term Monitoring Plan (LTMP) must be technically sound and legally defensible, and supported by defined and verified limits of confidence. This *Lower Fox River Operable Unit 1 and Lake Winnebago Long-term Monitoring – Quality Assurance Project Plan* (*QAPP*) specifies the quality control (QC) and quality assurance (QA) procedures to ensure the generation of valid data for the evaluation of the *Lower Fox River Operable Unit 1 – Long-term Monitoring Plan* (Foth and CH2M HILL, 2011a) (*OU1-LTMP*) objectives. The *QAPP* procedures herein are equivalent to those specified in the U.S. Environmental Protection Agency's (USEPA) QA/R-5 "EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations" and its promulgated updates.

It is the responsibility of all personnel involved in the *OU1-LTMP* to perform and document the required procedures designated within this document. This *QAPP* sets forth the data collection procedures and data evaluation process, which will ensure that appropriate levels of data quality are obtained throughout the program.

2 Project Description

2.1 Overview

The LFR extends 39 miles from the outlet of Lake Winnebago over a series of locks and dams to the mouth of the river where it discharges into Green Bay. The LFR is the most industrialized river in Wisconsin. Since the early 1900s, water quality has been degraded by expanding industries and communities discharging sewage and industrial wastes into the river. Polychlorinated biphenyls (PCB) were discovered in the LFR in the 1970s. Due to their persistence in the environment, PCBs remain the focus of current remediation efforts in the river. The river and bay are divided into five OUs (1 through 5) (Appendix A-2, Figure 1-1).

OU1 is also known as Little Lake Butte des Morts (LLBdM). The remedial action (RA) in OU1 began in 2004 and was completed in May 2009. It consisted of dredging approximately 375,000 cubic yards (cy) of sediment and placement of approximately 110 acres of engineered cap, 107 acres of 3-inch and 6-inch sand covers and 37 acres of residual sand cover, as referenced in OU1 annual RA summary reports.

The *OU1-LTMP* is focused solely on OU1 and Lake Winnebago but has been designed for consistency with the LTMP for the LFR and Green Bay Site (*FR-LTMP*) (Anchor et.al, 2009) which has already been submitted to the USEPA and the Wisconsin Department of Natural Resources (WDNR) (collectively, the "Response Agencies") for approval.

The *OU1-LTMP* was designed to quantifiably assess progress toward achieving the remedial action objectives (RAO) specified for OU1 in the *Record of Decision* (USEPA, 2002) (*ROD*) and the *Record of Decision Amendment* (USEPA, 2008) (*ROD Amendment*) issued by the Response Agencies under the authority of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended.

The data types consist of two media – water and fish tissue. Both media will be monitored at several stations from Lake Winnebago and OU1. Water and fish tissue data will be managed and statistically analyzed to assess the performance of the monitoring program and the more fundamental objective of monitoring progress toward achieving the RAOs.

2.2 Problem Statement

Data collected during the remedial investigation/feasibility study (RI/FS) and related investigations were used to define RAOs, Remediation Goals (RG), and Cleanup Levels (CUL) for the Site (USEPA, 2005). The RAOs, RGs, and CULs for the LFR are set forth in the *RODs* for OUs 1 and 2 and OUs 2 through 5 signed by the Response Agencies in December 2002 and June 2003, respectively.

As with other CERCLA sites, the *ROD* described the overall goals and objectives and selected a specific remedy that the Response Agencies believe will achieve the goals and objectives. Specifically, the *RODs* require that the remedies for the Site be designed to achieve CULs, and that achieving the CULs will result in achieving the RGs (target fish tissue concentrations) and RAOs (human and ecological risk reduction and surface water PCB load reductions to Green Bay). This translates into two types of remedy success measures: 1) remedy effectiveness

success (whether the CULs are met); and 2) achievement of risk reduction targets (whether the RA leads to the desired levels of risk reduction).

2.2.1 OU1 Remedy Effectiveness Success

A sediment verification sampling program was developed and approved by the Response Agencies as part of the OU1 Final Design and Remedial Action Work Plan to ensure that the CULs have been achieved at the completion of the RA. Long-term monitoring of water quality will be conducted in OU1 to verify that short-term and long-term improvements in sediment quality result in commensurate improvements in the water column. In a weight-of-evidence (WOE) evaluation, the combined verification and monitoring activities, as outlined in the *Lower Fox River Operable Unit 1 – Cap Monitoring and Maintenance Plan* (Foth and CH2M HILL, 2011b) (*CMMP*) and *OU1-LTMP*, will be used to determine whether RAs in OU1 (i.e., dredging, capping, cover, and monitored natural recovery [MNR]) have successfully implemented best reasonably available technology in order to achieve and maintain successful remedy effectiveness.

2.2.2 Achievement of OU1 Risk Reduction Targets

The primary objective of the *OU1-LTMP* is to develop a monitoring program to evaluate risk reduction success. The human and ecological receptors exposed to bioaccumulation pathways are the most sensitive endpoints for monitoring risk reduction success. Fish tissue concentrations will be monitored throughout OU1 and compared to levels below which human fish consumption advisories may be relaxed or eliminated, and target RGs for ecological risk are being addressed. In conjunction with the remedy effectiveness determinations described in the preceding section, the results of the long-term monitoring program will be used in a WOE evaluation to determine whether the combination of RAs approved by the Response Agencies have achieved risk reduction targets. OU1 data will be compared to "background" concentrations found in Lake Winnebago, and if the concentrations are comparable, then the comparison will also be a measure of achieving risk reduction targets.

2.2.3 OU1/Lake Winnebago Long Term Monitoring Objectives

Long-term monitoring data will be collected to evaluate progress toward achieving the RAOs of reduced risk to humans and the environment, as presented in the December 2002 *ROD* and the June 2008 *ROD Amendment*. The data collection effort is focused on water and fish tissue, these being critical components of the major bioaccumulation risk pathways. Water is a media of concern through which many aquatic organisms, including benthic and pelagic fish, may be exposed to PCBs. Water is also the media through which contaminants in the LFR are entrained and transported downstream. Fish are the medium of exposure for bioaccumulation risk in higher-level organisms, including humans, mammals, and birds, as well as the fish themselves.

2.3 Scope of Work

This Scope of Work (SOW) for the *OU1-LTMP* includes collection of water quality and fish tissue samples, submittal for analysis, and subsequent evaluation of the data. The results of this SOW will be compared to results of the OU1 baseline monitoring program (BMP) that were carried out in accordance with the *2006-2007 Lower Fox River Baseline Monitoring Plan* (Shaw and Anchor, 2006) (*LFR Baseline Monitoring Plan*). For comparison to the BMP results for

OU1 and Lake Winnebago, water samples for the *OU1-LTMP* will be collected at the same frequency as the BMP (i.e., monthly) and at the same transects in OU1 and Lake Winnebago as the BMP, during the 8 warm-weather months (April through November). Fish tissue samples for the *OU1-LTMP* will be collected from five fish species, which include a primary and secondary species for monitoring human health risk (walleye and bass, respectively) a primary and secondary species for monitoring ecological risk (carp and drum, respectively), and a young-of-year (YOY) forage fish to provide an early indication of ecosystem recovery (gizzard shad).

Descriptive statistics, distribution tests and correlation tests will be performed, as described in the *FR-LTMP*, or as modified through adaptive management processes with the Response Agencies. Data will be compared to numerical target concentrations, including ecological and human health risk goals and background criteria, and confidence levels will be assessed. Time trend analysis will be performed by comparing mean concentrations and percent reductions between baseline and long-term monitoring events (i.e., two-sample comparisons) and by using simple or multiple regression techniques.

3 Project Organization and Responsibility

This section describes the project organization, responsibilities, authorities, and lines of communication. The roles and responsibilities of key project personnel are described below.

3.1.1 Respondent Technical Team

3.1.1.1 Respondent Team Project Coordinator

The duties of the Respondent Team Project Coordinator include:

- Administration and management of long-term monitoring activities, including schedule and budget control.
- Authorization and coordination of subcontractors.
- Authority to stop work based on QC issues, health and safety issues, or other deficiencies that may compromise the safety of the field crew or the integrity of the long-term monitoring program.
- Ongoing communication with USEPA and WDNR regarding project status, problems encountered and recommended solutions, deviations from scope of work, and other related issues.
- Coordination and resolution of key technical issues with Respondent and Response Agency Teams.
- Coordinate document production.
- Prepare and submit progress reports.

3.1.1.2 Respondent Team Project Manager

The duties of the Respondent Team Project Manager (PM) include:

- Management of preparation of *OU1-LTMP* and data reports.
- Coordination and trouble-shooting of field activities, including recommendations for scope modifications as needed based on field conditions.
- Review and assessment of corrective action procedures in consultation with Project Coordinator.
- Oversight of water, fish tissue, and sediment quality data analysis and interpretation.
- Assignment of fish compositing groups in consultation with WDNR and USEPA PMs.

3.1.1.3 Field Quality Assurance Manager

The duties of the Field Quality Assurance Manager (QAM) include:

- Auditing of field activities to ensure compliance with *OU1-LTMP* requirements.
- Review of all field documentation for consistency, accuracy, and completeness, and to ensure any procedural modifications are appropriately documented and communicated.
- Reporting of deficiencies in field procedures or documentation to the PM to initiate corrective action procedures.

3.1.1.4 Data Quality Assurance Manager

The duties of the Analytical QAM include:

- Direct the review of QA plans and procedures.
- Schedule and coordinate the analytical laboratories and data validators.
- Oversee the tracking of samples and data from the time of field collection through laboratory reporting and database entry.
- Review laboratory data for compliance with *OU1-LTMP* and *QAPP* requirements.

3.1.1.5 Long-Term Monitoring Field Supervisors

The duties of the Field Supervisors include:

- On-site coordination and direction of field activities and personnel.
- Coordination of field and laboratory schedules.
- Oversight of field activities to ensure they are conducted in accordance with the *OU1-LTMP, QAPP,* and the *Lower Fox River Operable Unit 1 and Lake Winnebago Long-term Monitoring – Health and Safety Plan* (Foth, 2011b) (*HASP*).
- Authority to stop work based on QC issues, health and safety issues, or other deficiencies that may compromise the safety of the field crew or the integrity of the long-term monitoring program.
- Communication of field conditions and progress, problems encountered, and recommended scope modifications (if needed) to the project team.
- Oversee sampling subcontractors.

3.1.1.6 Corporate Health and Safety Manager

The duties of the Corporate Health and Safety Manager include:

- Remote supervision of field activities to ensure adherence to the *HASP*.
- Final authority on *HASP* issues and approval of significant modifications to the *HASP*, if needed, based on changed field conditions.

3.1.2 Subconsultants/Subcontractors

All subconsultants and subcontractors will be identified to the Response Agencies for review and approval prior to the beginning of field work.

3.1.2.1 Analytical Laboratory Project Managers

The duties of the Analytical Laboratory PMs include:

- Oversee laboratory QA/QC requirements for the project.
- Convey project requirements and objectives to laboratory staff and analysts.
- Provide technical guidance to the Consultant Team.
- Review laboratory data for compliance with *OU1-LTMP* and *QAPP* requirements.

3.1.2.2 Laboratory Quality Assurance Managers

The duties of the Laboratory QAMs include:

- Evaluate compliance with laboratory standards of practice and ensure that systems are in place to provide QA/QC as defined in the *OU1-LTMP* and *QAPP*.
- Initiate and oversee audits of corrective action procedures.
- Perform laboratory data quality reviews.
- Maintain laboratory documentation.

3.1.2.3 Data Quality Validator

The duties of the Data Quality Validator include:

- Provide independent third-party data validation at the following frequency:
  - One hundred percent of each media will be validated in the first week of sampling during each monitoring event, and when a substantive modification is made to the sampling method or analytical laboratory.

- If initial validation is acceptable, a minimum of 10% of each media will continue to be validated on an ongoing basis.

- Evaluate compliance with laboratory QA/QC criteria and other project requirements as defined in the *OU1-LTMP* and *QAPP*.

- Qualification of analytical data as needed to identify noncompliance with QA/QC criteria, and assessment of acceptability of data to fulfill project objectives.

3.1.3 Wisconsin Department of Natural Resources

As one of the lead Response Agencies, WDNR and its consultants will observe, review, and provide regulatory and technical comments to ensure the long-term monitoring program fulfills the requirements of the *ROD* and provides data necessary to evaluate attainment of RAOs in OU1. WDNR and USEPA have sole approval authority over any modifications to this Plan, including modifications to the frequency or intensity of sampling and the need for corrective action.

3.1.3.1 WDNR Project Coordinator

The duties of the WDNR Project Coordinator include:

- Review all project plans and data reports, and provide input to development of overall project strategies and technical approaches.

- Indicate the appropriate time to evaluate fish consumption advisories.

- Ensure *OU1-LTMP* meets the requirements of the *ROD*, and assist Consultant Team and WDNR staff in interpreting the intent of the *ROD*.

- Final review and approval of *OU1-LTMP* and data reports.

- Ongoing communication with Consultant Team Project Coordinator and PM.

3.1.3.2 WDNR Project Manager

The duties of the WDNR PM include:

- Scheduling and coordination of WDNR reviews and approvals of *OU1-LTMP* and data reports.

- Coordination of technical resources for WDNR and its consultants, and application of these resources to help support the design and implementation of the *OU1-LTMP*.

- Assist WDNR Project Coordinator with project administrative duties.

- Review progress reports detailing work accomplished.

3.1.3.3 WDNR Quality Assurance Manager

The duties of the WDNR QAM include:

- Review *OU1-LTMP* for technical accuracy and completeness.
- Provide technical assistance to the WDNR PM and Project Coordinator regarding analytical methods and QC procedures, including, if applicable, review and approval of the laboratory and subcontractor qualifications.
- Review of data validation results, data quality, and the need for and scope of corrective actions, if any.

3.1.4 U.S. Environmental Protection Agency

As one of the lead Response Agencies, USEPA and its consultants will observe, review, and provide regulatory and technical comments to ensure the long-term monitoring program fulfills the requirements of the *ROD* and provides data necessary to evaluate attainment of RAOs in OU1. USEPA and WDNR have sole approval authority over any modifications to the *OU1-LTMP* and *QAPP*, including modifications to the frequency or intensity of sampling and the need for corrective action.

3.1.4.1 USEPA Remedial Project Manager

The duties of the USEPA Remedial PM include:

- Review all project plans and data reports, and provide input to development of overall project strategies and technical approaches.
- Ensure *OU1-LTMP* meets the requirements of the *ROD.*
- Final review and approval of *OU1-LTMP*s and data reports.
- Ongoing communication with Consultant Team Project Coordinator and PM.

3.1.4.2 USEPA Quality Assurance Manager

The duties of the USEPA QAM include:

- Review *OU1-LTMP*s for technical accuracy and completeness.
- Provide technical assistance to the USEPA Remedial PM.

3.2 Communication Plan

3.2.1 Monthly Progress Reports

During periods of long-term monitoring activity (i.e., data collection, evaluation, and reporting), the Respondent Team Project Coordinator will provide written monthly progress reports to the

Response Agencies by the 10th day of every month. These progress reports will describe the status of long-term monitoring activities.

3.2.2 Monthly Meetings

During periods of long-term monitoring activity, the Project Coordinators will hold monthly progress report meetings or telephone conferences unless it is deemed unnecessary by the Response Agencies. Such meetings will begin 1 to 2 months prior to the beginning of field work. Briefings on the status of long-term monitoring activities and preliminary results, as available, will be provided during the meetings.

3.2.3 Long-Term Monitoring Work Group

In an effort to develop a coordinated and cost-effective long-term monitoring program that is consistent with the intent of the *ROD*, representatives and consultants from the Respondent Team and the Response Agencies formed the Long-Term Monitoring Work Group (LTM Work Group). From October 2004 to May 2009, the LTM Work Group held periodic meetings and conference calls to discuss monitoring objectives, field and analytical methods, data evaluation tools and techniques, and the design and implementation of the BMP. Draft notes from these meetings are maintained in the Response Agency project files. The LTM Work Group may continue to meet on a mutually agreeable schedule as needed to implement the long-term monitoring program. It is expected that meetings will be held to discuss the following:

- Adaptive management of field sampling, laboratory analysis, and data validation procedures.
- Review and evaluation of long-term water, fish tissue, and sediment analytical results as they become available.
- Ongoing assessment of the effects of sediment remediation, and progress toward achieving RAOs in the LFR and Green Bay.

3.2.4 Electronic Data Transmittal

Technical documents, reports, data, comments, schedules, meeting notices, and general project communications related to long-term monitoring activities will be distributed electronically to designated members and consultants of the Response Agencies. Documents that are too large to send via email will be posted on a shared access website. In such cases, an e-mail notification will be sent to the same persons with information on how to access those documents. Electronic copies (CD-ROM) of laboratory analytical data packages (in pdf format) will be provided to the Response Agencies upon receipt from the laboratory. Once the data have been checked and verified, they will also be provided to the Response Agencies in an electronic file format that can be loaded into a database for relational queries and numerical analysis.

3.2.5 Hard Copy Data Transmittal

For documents requiring hard copy distribution, one copy will be sent to each of the following Response Agency personnel:

- USEPA Remedial PM
- WDNR Project Coordinator
- WDNR PM
- WDNR QAM
- WDNR Oversight Consultant PM
- Other personnel, as appropriate

3.2.6 Notification Procedures

At least 15 days of notice shall be given to the WDNR Project Coordinator and the USEPA Remedial PM prior to beginning sampling. The notifications will include identification of subcontractors, schedule and contact information specific to the sampling event. In addition, the notification will include the laboratories Standard Operating Procedures (SOP), if they have not been previously provided or modified, to verify that the reporting limits will be as stated.

3.2.7 Modifications to the Long-term Monitoring Plan

Significant modifications to the *OU1-LTMP* may be provided to USEPA and WDNR for review and approval via revisions to the *OU1-LTMP* or Addenda to the *OU1-LTMP*. Modifications that will require USEPA and WDNR approval include the following:

- Major changes/revisions to the monitoring design.
- Major changes/revisions to the sampling or analytical methods.
- Major changes to project team personnel.
- Major changes/revisions to the statistical procedures for data quality assessment presented in Section 4.2.

Modifications may be required as a result of unexpected or changed field conditions; extreme weather or hydrologic events; or due to the results of ongoing discussions of monitoring strategies, techniques, and procedures during the CERCLA 5-year reviews.

4 Data Quality Objectives for Measurement Data

Data quality objectives (DQOs) are qualitative and quantitative statements that define the objectives of the project, identify the most appropriate types of data and data collection procedures, and specify acceptable error limits for decision making. The DQOs for this project were developed in accordance with USEPA Guidance for Data Quality Objectives Process, USEPA QA/G-4 (USEPA, 2000a) and USEPA Region 5 Instructions on the Preparation of the Superfund Division Quality Assurance Project Plan, Revision 0 (USEPA, 2000b).

The DQO process for the *OU1-LTMP* is presented below and was adapted from the *FR-LTMP*.

4.1 Step 1: State the Problem

The overall objective of the *OU1-LTMP* is to characterize long-term, post-remediation, water and fish tissue quality OU1 of the LFR. The combined baseline and long-term monitoring data will provide the Response Agencies with information to determine whether the implemented remedy meets RAOs, including remedy effectiveness criteria and risk reduction targets.

As stated in the *ROD,* the RAOs for this project which are relevant to the long-term monitoring program include:

- Reduction of water column PCB concentrations.
- Removal of human health fish consumption advisories.
- Achievement of safe ecological thresholds for fish-eating birds and mammals, and other ecological receptors.
- Reduction of LFR PCB loadings to Green Bay.

4.2 Step 2: Identify the Decisions

4.2.1 Risk Reduction Decisions

A key objective of the long-term monitoring program is to determine whether the RA has been successful at reducing risk to humans, fish and wildlife. In addition, reductions in sediment concentrations resulting from RA (i.e., dredging, capping, and cover) are expected to bring about similar levels of reduction in water and YOY fish as well as long-term improvements in MNR areas. The *OU1-LTMP* is designed to answer the following questions:

- Are fish tissue concentrations declining to levels that will allow human consumption at recreational and high intake rates?
- Are fish tissue concentrations declining to levels that will not impair fish and wildlife?
- Are fish tissue concentrations declining at rates that will achieve human health and ecological goals within 30 years?

- Are water and YOY fish PCB concentrations declining in response to sediment RAs and at levels commensurate with the sediment quality improvements brought about by the RAs?

- Are water and fish concentrations declining to levels comparable to relatively unimpacted background areas (e.g., Lake Winnebago)?

- Are water concentrations declining to levels comparable to field and laboratory blank contamination levels, indicative of ubiquitous low-level PCB contamination in the regional or global environment?

Ultimately, the achievement of human health and ecological risk-reduction goals will be based on fish tissue concentrations. However, water represents a medium through which fish are exposed to PCBs, and will therefore, be used as an indicator of bioaccumulation, an indicator that potentially responds more quickly to the effects of the RA. Water is also a medium through which PCBs are transported from the LFR to Green Bay.

4.2.2 Exit Criteria

The decisions outlined in the previous section are structured into a series of exit criteria to help determine when long-term monitoring goals have been achieved and monitoring may be reduced or eliminated. These exit criteria are also expressed as hypothesis statements that will be amenable to statistical testing. The default condition in the hypothesis statements is that the remedy has had no effect unless the preponderance of data indicates that it has. In other words, rejection of the null hypothesis provides evidence of remedial success.

1. **Comparison to Background Concentrations (All Media).** This criterion will be satisfied when it can be shown that OU1 water and fish tissue PCB concentrations are equivalent to ambient background water and fish tissue PCB concentrations in Lake Winnebago, which serves as the upstream reference area for fish and water for the LFR. In addition, Great Lakes reference concentrations for fish will be determined from a review of Wisconsin and Michigan fish contaminant databases in Lake Michigan and in relatively unimpacted tributaries of Lake Michigan representing a range of rural and urban land uses. Background criteria are established using the 90% upper prediction limit on the mean of the background data.

    - Null Hypothesis 1. Water and fish tissue contaminant concentrations are higher than reference areas.

    - Alternative Hypothesis 1. Water and fish tissue contaminant concentrations are equivalent to reference areas.

    Alternative Hypothesis 1 will be accepted when it can be shown that site monitoring data from a particular OU is equivalent to background data with an appropriate level of statistical confidence.

2. **Comparison to Risk-Based Target Concentrations (Human Health and Ecological Fish Species).** This criterion will be satisfied when it can be shown that OU1 concentrations have achieved levels that indicate fish consumption advisories may be reduced or eliminated and are protective of wildlife. The average fish concentration is the metric that will be compared to human health and ecological risk-reduction criteria; given that bioaccumulation exposures are represented by long-term average concentrations in the food source.

   - *Null Hypothesis 2a.* Human health index species concentrations are higher than risk-based goals for recreational and high-intake fish consumption.

   - *Alternative Hypothesis 2a.* Human health index species concentrations have achieved risk-based goals for recreational and high-intake fish consumption.

   - *Null Hypothesis 2b.* Ecological index species concentrations are higher than lowest observed adverse effects concentration (LOAEC) for protection of fish, birds, and mammals.

   - *Alternative Hypothesis 2b.* Ecological index species concentrations have achieved LOAECs for protection of fish, birds, and mammals.

   Alternative Hypotheses 2a or 2b will be accepted when it can be shown that the mean fish concentration in OU1 is below the risk-based target concentration with an appropriate level of statistical confidence.

   In addition, substitute human health species may be selected for monitoring after walleye have achieved their monitoring goals, to better support the evaluation of fish consumption advisories. The substitute fish species will be selected by the Response Agencies and Respondents prior to modifying the target fish species and size ranges.

3. **Comparison to SWAC-Reduction Targets (Water and YOY Species).** This criterion will be satisfied when it can be shown that OU1 concentrations have achieved the surface-weighted average concentration (SWAC)-reduction targets. To fulfill these criteria, water and YOY fish concentrations should achieve a 90% reduction relative to baseline conditions.

   - *Null Hypothesis 3.* Water and YOY fish concentrations have not been reduced to 10% of their initial baseline concentrations.

   - *Alternative Hypothesis 3.* Water and YOY fish concentrations are less than or equal to 10% of their baseline concentrations.

   Alternative Hypothesis 3 will be accepted when it can be shown that the mean water or YOY fish concentrations in OU1 is at or below the SWAC reduction target with an appropriate level of statistical confidence.

4. **Evaluation of Recovery Rate, i.e. Slope (All Fish Species and Water).** After a minimum of three sampling events, the rate of post-construction PCB concentration reductions will be analyzed using the appropriate statistical trend analysis. If the PCB reduction rate indicates risk-based concentrations, SWAC-reduction goals, or background conditions will be achieved within 30 years after remediation, then the monitoring schedule may be adjusted to more cost-effectively document this condition.

   - *Null Hypothesis 4.* Water and fish concentrations will not achieve risk-based goals, SWAC-reduction criteria, or background conditions within 30 years.

   - *Alternative Hypothesis 4.* Water and fish will achieve target concentrations within 30 years, indicating the RA has been successful.

   Alternative Hypothesis 4 will be accepted when it can be shown, using the appropriate statistical trend analysis, that target concentrations (whether based on acceptable risk levels, background, or SWAC reduction criteria) will be achieved in post-remediation Year 30 with an acceptable level of statistical confidence. Then, a follow-up confirmation sampling event will need to be scheduled to confirm the model predictions.

5. **Evaluation of Laboratory Blank Contamination Levels (Water).** If mean sample concentrations are less than three times the laboratory method blank concentrations, then analytical method performance will be evaluated to determine whether additional optimization is practicable, or alternatively, it will be concluded that concentrations have reached the limit of analytical capabilities for reliable determinations. If concentrations fall within this range of method blank contamination, then the *OU1-LTMP* goals will be determined to be met to the extent practicable using best available technology. The background contamination levels in field rinsate blanks should also be considered in this evaluation. The laboratory will effectively minimize blank contamination (e.g., by analyzing the most contaminated water samples last, etc.) in order to determine if the *OU1-LTMP* goals have or have not been met.

   - *Null Hypothesis 5.* Water concentrations are above the range of method blank contamination and can be reliably quantified.

   - *Alternative Hypothesis 5.* Water concentrations are within the range of method blank contamination and cannot be reliably quantified.

   Alternative Hypothesis 5 will be accepted when it can be shown that mean water concentration in a particular OU is less than three times the mean concentration in laboratory method blanks, provided further control of laboratory blank contamination is not practicable.

4.2.3 Weight-of-Evidence Evaluation

In addition to the exit criteria listed in the preceding section, a WOE evaluation of the *OU1-LTMP* results will be conducted in consultation with WDNR and USEPA during each CERCLA 5-year review to determine whether the preponderance of data indicates risk-reduction goals are or are not being achieved. This provides for adaptive management of the *OU1-LTMP* goals and objectives using the knowledge gained during the course of the monitoring program. Based on the WOE evaluation, the monitoring intensity may be increased, decreased, or eliminated in OU1. The WOE evaluation will consider the following:

- Achievement of significant progress toward risk reduction goals, including achievement of intermediate goals and relaxation of fish consumption advisories, even if high-intake fish consumption may not be achieved for all areas and all species.

- Evaluation of percent PCB concentration reductions in adult fish tissue compared to observed reductions in other media (e.g., water and YOY fish, which may respond more quickly to the RA), and whether further reductions over time would or would not be expected.

- Comparison of measured PCB reductions over time with predictions summarized in the RI/FS and *ROD*, and whether observed reductions are progressing faster or slower than expected.

- Stabilization of concentrations in a particular medium, with no significant change from one monitoring event to the next, indicating natural recovery processes associated with the RA have run their course and further monitoring would be of limited value (i.e., "flat line" condition).

4.3 Step 3: Identify Inputs to the Decision

4.3.1 Baseline Monitoring Data

The design of the *OU1-LTMP* has benefited from the data collected during the BMP as well as from ongoing review and discussion of the baseline data in the LTM Work Group. The BMP was conducted between August 2006 and July 2007. These data were analyzed to help develop a statistically based long-term monitoring program, to estimate sample sizes for long-term monitoring, and to define a baseline level of contamination for evaluating the recovery of water, fish tissue, and sediment concentrations in the years following the completion of the sediment RA. In addition to the baseline monitoring data, fish contaminant databases in state monitoring programs in Wisconsin (http://dnr.wi.gov/fish/consumption/) and other applicable fish or water quality databases will be consulted to complement the decision-making regarding background levels of PCBs in fish tissue.

4.3.1.1 Water Quality Summary

Stratification by Temperature

Analysis of the baseline monitoring data showed that the water column data have a bi-modal distribution, with higher concentrations during the warm weather months of April through November, and much lower concentrations during the winter, often ice-covered months of

December through March. Stratification of the data into these two groupings, therefore, improves the statistical characteristics of the data.

Distribution Tests
Water quality data from the warm weather months are well described by standard normal distributions (i.e., data are normally distributed at seven out of ten monitoring stations), whereas the year-round data set shows more significant deviations from normality (normally distributed at only three out of ten monitoring stations).

Statistical Variation
The coefficients of variation (CV) for total PCB concentrations in water in OU1 during the warm weather months (0.64) are also lower than the CVs for the year-round data set (1.01), indicating stratification of the warm-weather data helps to control statistical variability. For the warm-weather data set, the standard error on the mean total PCB concentration in water was 23% (Anchor et al., 2009).

4.3.1.2 Fish Tissue Summary

Distribution Tests
Analysis of the baseline monitoring data showed that fish tissue PCB concentrations (Aroclor analysis by USEPA method 8082) in OU1 are well described by standard normal distribution. The data are also well described by lognormal distributions; however, in general lognormal distributions do not improve the goodness-of-fit over normal distributions.

Statistical Variation
The standard errors on the mean total PCB concentrations in fish collected from OU1 are summarized below (Anchor et al., 2009):

- Walleye: 16%
- Bass: 19%
- Drum: 16%
- Carp: 24%
- Shad: 12%

Standard error (s.e.) is a function of both the standard deviation (s) and the number of samples (n), (s.e. = $s/\sqrt{n}$). Therefore, the statistical variation would decrease as more samples were collected, at roughly the rate of $1/\sqrt{n}$.

4.3.2 Existing Monitoring Guidance

Federal and state guidance documents were consulted in preparing the *OU1-LTMP*, including the following:

- USEPA, 2000c, Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1: Fish Sampling and Analysis

- Great Lakes Sport Fish Advisory Task Force, 1993, Protocol for a Uniform Great Lakes Sport Fish Consumption Advisory

- USEPA, 2005, Contaminated Sediment Remediation Guidance for Hazardous Waste Sites

4.3.3 Key Inputs to Monitoring Plan Design

A number of important considerations and monitoring strategies have been discussed in the LTM Work Group and have helped to guide the design of the *OU1-LTMP*. General programmatic monitoring strategies include the following:

- Archiving of Samples. Fish tissue and sediment samples will be archived (in frozen storage) in case additional or repeat analyses are called for during data review and evaluation. Samples will be archived for a minimum of one CERCLA 5-year review cycle. The status of the samples will be considered during the 5-year review process, at which time the samples may be designated for continued archiving over another review cycle, or else discarded.

- Expanded Baseline Monitoring Activities. The BMP was designed to be more broad-based than the long-term monitoring program; this strategy will provide flexibility to accommodate changing environmental conditions in the decades ahead, such as changes in fish species availability. For example, an expanded list of fish species was sampled during the BMP, including primary as well as secondary contingency species. During long-term monitoring, the primary fish species will be the main focus of the monitoring program. However, secondary species may also be analyzed in certain circumstances, for example: 1) if the primary species are sparse or unavailable; 2) to provide further support for human health fish consumption advisories; or 3) if the variability of the data for the primary species is higher than expected, compared to the baseline monitoring data, or if the statistical power is compromised by confounding variables or trends.

- State-of-the-Art Detection Limits. Because PCBs are difficult to detect in water at concentrations of environmental concern, a highly sensitive analytical method with ultra-low detection limits has been selected to carry the program forward into the future, in anticipation of declining concentrations in the future. Specifically, PCBs in water will be analyzed using high-resolution gas chromatography/mass spectrometry (HRGC/MS) by EPA Method 1668A, which provides the lowest commercially achievable detection limits at the present time. It should be noted, however, that analytical sensitivity is not just a function of instrument detection capabilities; it is also affected by sample volumes and blank contamination levels. Double (2 liter) sample volumes are being collected, and lab and field blank contamination levels are being monitored and evaluated to help control and optimize all aspects of analytical sensitivity.

- Control of Confounding Variables. The assessment of river recovery, as measured by decreasing water and fish tissue contaminant concentrations, may be confounded by random or systematic changes in other controlling variables. For example, PCB concentrations in water are affected by river temperature and turbidity, and possibly flow.

PCB concentrations in fish are affected by fish type, age, length, and fat content. As a result, field sampling and data analysis techniques will be utilized to control for the effects of confounding variables to the extent possible, thus providing a more accurate assessment of river recovery rates and magnitudes.

- Timing of Fish Sampling. Fish sampling will occur in late summer (August 15 to September 15) for the following reasons: 1) fish lipid content, which tends to concentrate PCBs, is typically highest in late summer and early fall after heavy spring and summer feeding, and therefore fish are expected to carry some of their highest PCB burdens during that time of year; 2) recreational fishing is popular at that time of year; 3) fish spawning periods are avoided; and 4) the state conducts many of its fish sampling programs and fish population surveys during that time, allowing for coordinated data collection activities. Sample collection activities may be extended an additional month (through October 15) if necessary to fill data gaps. In addition, if the walleye catch is found to be deficient and bass are substituted for the human health index species, bass fishing will be conducted in the following month of June to be consistent with the bass collection schedule used in the BMP.

- Timing of Water Sampling. Water samples will be collected monthly during the eight non-winter months from April through November. The four winter months are excluded from the monitoring program for the following reasons: 1) winter sampling from December through March presents a safety concern for the field crew due to severe weather conditions; 2) PCBs in the LFR are at their annual lowest concentrations in winter, such that the four winter months combined contribute less than 10% of the annual PCB mass load; 3) the lower PCB concentrations during the winter months are more difficult to quantify in the analytical lab, and therefore have greater uncertainty; and 4) PCB concentrations in winter are so low, relative to the rest of the year, that they result in a data set with a higher variance and non-normal statistical distributions, such that sampling the four additional months does not increase the statistical power for decision making. Samples will be collected systematically each month, at regular sampling intervals, to provide an unbiased and representative sample of the water year. Although "storm chasing" will not be practiced, the systematic sampling design is expected to capture a representative range of flow conditions during a particular monitoring year.

- Human Health Fish Species. Walleye were selected as the primary human health fish species because: 1) they are a regionally important and popular recreational fishery; 2) they were reliably present and relatively easily harvested in OU1 and Lake Winnebago and in most of the target size ranges during the BMP; and 3) walleye are widely distributed throughout the LFR and Green Bay. Consistent with the State Fish Advisory Program, individual walleye will be analyzed as skin-on fillet over a range of legal, harvestable sizes.

  Substitute human health species may be selected for monitoring after walleye have achieved their monitoring goals, to better support the evaluation of fish consumption advisories. The substitute fish species will be selected by the Response Agencies and Respondents prior to modifying the target fish species and size ranges.

- Ecological Fish Species. Carp was selected as the primary ecological species in the LFR because: 1) carp exhibit some of the highest PCB concentrations of the fish species sampled; 2) carp are a prey species for higher-order predators, such as eagles; 3) carp have an affinity for mud bottoms and may have more intimate contact with PCB-contaminated sediments; and 4) carp are easily and reliably harvested from OU1 and Lake Winnebago in the range of target fish sizes.

- YOY Fish Species. Gizzard shad were selected as the YOY fish species based on: 1) monitoring a juvenile life stage that does not carry a legacy PCB burden, and which may therefore respond more quickly to improving water quality conditions in the LFR; 2) its representativeness as a prey species for higher-order predators (i.e., fish-eating birds and mammals, as well as predatory fish); and 3) ease and reliability of harvesting.

- Fish Compositing Design. Ecological fish species will be composited for analysis because bioaccumulation is caused by the cumulative effects of long-term average dietary exposures. Fish composite groupings will be selected in consultation with the Response Agencies, and in accordance with the following general guidelines. Compositing will be performed using strict fish-length windows (typically 2-inch windows) to control for the effects of size and age on PCB concentration.

- Comparability of Background Stations. Procedures used for sampling background water and fish in Lake Winnebago will be the same as those used for OU1 to ensure comparability of data and accurate statistical comparisons. Ambient fish contaminant monitoring data from other Great Lakes sites and programs, when used to develop estimates of Great Lakes background concentrations, will be reviewed to ensure species, preparation methods, and analytical methods are comparable to those used in the *OU1-LTMP*.

- Location Control Requirements. Accurate sample location control is essential for ensuring quality data and reproducibility between field sampling events. More accurate and precise control is needed for water monitoring activities to be able to reoccupy monitoring stations and depths along the designated cross-sections every month and from one monitoring event to the next. A reduced level of accuracy is appropriate for the fish monitoring program because fish are transient and migratory. Therefore, water stations will be located to within a target accuracy of two meters; fish stations will be located to within a target accuracy of 10 meters.

4.4 Step 4: Define the Boundaries of the Study

The study area for the *OU1-LTMP* is bounded by the following geographic and temporal boundaries.

4.4.1 Geographic Boundaries

The study area encompasses the following:

- Upstream Reference Site – Lake Winnebago
- RA Area – OU1

4.4.2 Temporal Boundaries

Long-term monitoring will be for 30 years following completion of all remedial dredging, capping, and cover actions in OU1 unless it can be demonstrated to the satisfaction of the Agencies that risk-reduction goals have been or are being achieved, and monitoring may be modified or terminated earlier. Based on RI/FS predictions as well as experience at other sediment cleanup sites, the effects of the RA are expected to be fully realized within 30 years. The time frames estimated by the Response Agencies for achievement of the RAOs or significant progress toward RAOs are:

- Recreational anglers 10 years
- High-intake anglers 30 years
- Fish-eating birds and mammals 30 years

The RA in OU1 began in 2004 and was completed in May 2009. It consisted of dredging approximately 375,000 cy of sediment and placement of approximately 110 acres of engineered cap, 107 acres of 3- and 6-inch sand covers, and 37 acres of residual sand cover, as referenced in OU1 annual RA summary reports. Therefore, long-term monitoring in OU1 is expected to occur from 2010 through 2039. However, WDNR will continue monitoring the LFR and Green Bay as part of the State Fish Consumption Advisory Program even after the *OU1-LTMP* requirements have been fulfilled.

4.5 Step 5: Develop Decision Rules

Long-term monitoring will be conducted in accordance with the decision frameworks (flow charts) depicted on the following figures in Appendix A-2:

- Figure 1-4 Human health fish species
- Figure 1-5 Ecological fish species
- Figure 1-6 YOY fish species
- Figure 1-7 Water quality

4.5.1 General Rules

The collection and evaluation of long-term monitoring data is based on the following general rules:

1. **OU-by-OU Decisions.** Long-term monitoring decisions will be made at the scale of individual OUs. As a result, OU1 may fulfill exit criteria and be removed from the monitoring program sooner than other OUs.

2. **Maximum 30-Year Program Duration.** Monitoring will be conducted for 30 years after the RA unless it can be demonstrated that risk-reduction goals are being achieved to the satisfaction of the Agencies at an earlier period. Based on RI/FS predictions as well as experience at other sediment cleanup sites, the effects of the RA are expected to be fully realized within 30 years. WDNR will continue to

monitor the LFR as part of he State Fish Consumption Advisory Program even after the *OU1-LTMP* requirements have been fulfilled.

3. **Confirmation Sampling Requirement.** Monitoring data will be evaluated using the exit criteria listed in Section 4.2.2. If the average concentration (or 90th percentile concentration in the case of background) meets the exit criterion in a particular medium, this provides a minimum line of evidence that the *OU1-LTMP* targets have been achieved. Statistical certainty will be improved and WOE more clearly achieved if the average concentration meets the exit criterion a second consecutive time in a follow-up confirmation sampling round.

4. **Trend Analysis will not be used for Final Confirmation.** Exit criterion No. 4 (Evaluation of Recovery Rate) can be used as evidence to proceed to confirmation sampling, but cannot be used to establish final confirmation nor to justify termination of the monitoring program.

4.5.2 Fish Monitoring Rules

The collection and evaluation of fish monitoring data is based on the following:

1. **Minimum of 3 Events.** A minimum of three fish monitoring events (Years 0, 5, and 10) are required before a confirmation monitoring event can be scheduled for either human health or ecological risk.

2. **Walleye is Index Species for Human Health.** Walleye will be used as the primary sentinel species for evaluating human health risk.

3. **Consideration of Substitute Human Health Species.** After walleye have fully recovered to allow recreational and high-intake consumption by humans, consumption advisories may continue to be in effect for other fish species. WDNR and USEPA will review the long-term monitoring record as well as the State Fish Advisory database to determine whether one or more human health index species should be substituted for walleye in the monitoring program to further support fish consumption advisory evaluations.

4. **Lifting of Fish Consumption Advisories for PCBs.** If the WDNR removes all fish consumption advisories for PCBs for OU1 during implementation of the *OU1-LTMP*, then all fish tissue monitoring for human health risk may be terminated in OU1.

5. **Carp are Index Species for Ecological Risk.** Carp will be used as the sentinel species for ecological risk in OU1.

4.5.3 Young-of-Year Monitoring Rules

The collection and evaluation of YOY fish monitoring data is based on the following:

1. **Minimum of 1 Event.** At a minimum, YOY fish will be collected and analyzed in Year 0 to help support the WOE evaluation.

2. **Adaptive Management of YOY Monitoring Requirements.** WDNR and USEPA will review the monitoring data to determine whether significant progress toward SWAC-reduction goals is being achieved, relative to baseline concentrations, and whether monitoring should be continued, modified, or terminated.

4.5.4 Water Monitoring Rules

The collection and evaluation of water monitoring data is based on the following:

1. **Minimum of 2 Events.** A minimum of two water monitoring events (Years 0 and Year 5) are required before a confirmation monitoring event can be scheduled.

2. **Linked with Achievement of Fish Goals.** Water monitoring will be terminated when target fish tissue concentrations have been achieved for humans and wildlife, even if water monitoring goals have not yet been achieved, given that fish tissue quality provides a more direct and accurate measure of bioaccumulation risk.

If water or fish tissue concentrations are not declining, or are declining at a rate that indicates risk-reduction goals will not be achieved within the *ROD*-predicted time frames, then project assumptions will be reassessed, i.e., are the *ROD*-predicted recovery rates realistic, achievable, or necessary in light of the knowledge gained during the monitoring program? If project goals and assumptions remain valid, the data will be evaluated to determine the likely cause(s) of the delayed recovery, and whether revisions to the monitoring program (i.e., increased sampling intensity, improved characterization of ambient background conditions, etc.) should be considered. Such revisions would be discussed during the CERCLA 5-year reviews.

4.6 Step 6: Specify Limits on Decision Errors

The goal of the long-term monitoring program is to meet the statistical criteria in Sections 4.2.2. The monitoring program is expected to provide an appropriate level of statistical confidence for OU1 management decisions.

4.6.1 Minimum Detectable Relative Difference

The specified minimum detectable relative difference (MDRD) between two consecutive monitoring rounds is 50%. The monitoring program should be able to detect with statistical significance a 50% reduction in water or fish tissue concentrations over relatively short time periods (i.e., 5 years, from one monitoring event to the next).

In response to the anticipated 90% reduction in average surface sediment PCB concentrations following completion of the RA, combined with ongoing natural recovery processes in the river, order-of-magnitude reductions in water and fish tissue concentrations are expected to occur. One order-of-magnitude reduction is approximately equal to three 50% reductions. Therefore, an MDRD of 50% provides an appropriate level of sensitivity for monitoring the cumulative concentration reductions that are expected to result from the RA over the entire monitoring program (e.g., 30 years).

4.6.2 Statistical Confidence and Power

The goal of the long-term monitoring program is to collect water and fish tissue data that will achieve the following levels of statistical significance to support OU1 management decisions:

- Alpha (α) = 0.1 (90% confidence)
- Beta (β) = 0.2 (80% power)

4.7 Step 7: Optimize the Design

To achieve the DQOs specified for the *OU1-LTMP*, a sufficient number of water and fish tissue samples will be collected and analyzed using field and laboratory methods which provide adequate sensitivity for detection and quantitation of PCBs.

4.7.1 Number of Samples

The estimated number of water and fish samples required for OU1 management decisions is based on the desired MDRD, the desired level of statistical confidence and power, and an estimate of the variability of the data (as described by the CV of historical monitoring data). This analysis is based on a comparison of two populations (i.e., one monitoring event compared to a subsequent event), with each population or event having an associated variance. Such an approach is expected to provide a conservatively high estimate of sample size requirements for all types of OU1 management decisions because of the following considerations:

- If data from one monitoring event is compared to a fixed numerical criterion (e.g., a human health or ecological target concentration), fewer samples will be required to achieve the same confidence level.

- After three post-construction monitoring events are completed, two-sample comparisons will be augmented with regression-based analysis. As the size of the data set grows with each successive monitoring event, greater statistical power will generally be achieved (provided the variance of the data does not increase over the length of the monitoring record).

- Sample size estimates are based on a MDRD of 50% between two monitoring events. As the length of the monitoring record grows, larger reductions totaling 90% or more are expected over the long term. Larger reductions are more easily discerned using statistical methods.

- The sample size estimates developed for the *OU1-LTMP* do not consider ancillary variables that may influence PCB concentrations (e.g., fish length and lipid content, water temperature, and suspended solids content). If correlations can be established between PCBs and ancillary variables, a larger proportion of the sample variance may be predicted and controlled through the use of multivariate statistical techniques, such as multiple regression.

The relationship between sample size and statistical power follows USEPA (1998):

$N = (Z_{\alpha} + Z_{2\beta})^2 (CV/MDRD)^2$

Where:
N is number of samples,
Z_{α} and $Z_{2\beta}$ are Z statistics at the specified alpha and beta levels,
CV is the coefficient of variation of water or fish tissue data, and
MDRD is the minimum detectable relative difference.

The estimated sample size as a function of CV for either water or fish tissue data is provided in Table 1-7 (Appendix A-2). For comparison purposes, a range of confidence levels (alpha = 0.2, 0.1, and 0.05) is provided. The estimated sample sizes are based on an assumed normal distribution; both fish tissue data and seasonally stratified water data are reasonably described by normal distributions.

The statistical characteristics of the data collected in the BMP were used to estimate the sample sizes for the long-term monitoring program. The estimated level of statistical confidence provided by the baseline monitoring data, based on the sample size and the observed CV of these data, is summarized in Table 1-8 (Appendix A-2). For OU1, the baseline monitoring data consistently met or exceeded expectations for statistical power, as described below.

Water Sample Sizes. When monthly water samples are evaluated as a year-round data set, statistical power expectations for OU1 are met >80% of the time.

Without considering the effects of controlling variables, statistical power was improved by removing the winter months (December through March) from the data set. Statistical confidence levels of >90% were observed in OU1, in spite of having fewer samples in the data set. Lake Winnebago showed the lowest confidence levels (> 75%), likely due to the extremely low PCB concentrations and higher analytical uncertainty associated with this upstream background location.

In summary, the 8-month warm-weather data set exhibited better statistical power for detecting long-term reductions in PCB concentrations compared to the year-round data set. It is therefore recommended that long-term monitoring of the water column should be performed on a monthly basis from April through November. Additional sampling in the winter months is not likely to improve and may actually degrade statistical performance.

Fish Sample Sizes. The statistical confidence levels associated with human health fish species – walleye and bass – exceeded 90% for OU1 (Table 1-8, Appendix A-2). Statistical confidence levels associated with ecological fish species – carp and drum – exceeded 80%. Overall, these comparisons validate the continued use of the sample sizes specified in the BMP for all of the adult fish species except carp. In order to increase the statistical power of the carp data, the sample size will be increased from five to seven composite samples (comprised of 35 total fish) during the OU1 long-term monitoring.

Statistical confidence goals were met >95% in the gizzard shad OU1 data, the YOY species intended to serve as an early indicator of ecosystem recovery. Five of the OUs showed excellent power of discrimination, with over 95% confidence, whereas the other four OUs showed only modest power, with 80% to 90% confidence. Therefore, the gizzard shad sample size will be increased from five to seven composite samples during the long-term monitoring to improve statistical power, especially in OU1 (Table 1-8, Appendix A-2).

4.7.2 Analytical Sensitivity

To achieve the DQOs for this project, analytical methods must be sensitive enough to:

- Quantify upstream "background" concentrations in Lake Winnebago
- Quantify future PCB concentrations based on anticipated order-of-magnitude reductions

Water is the more difficult medium and requires greater analytical sensitivity because PCBs are extremely hydrophobic, i.e., they are poorly soluble in water. The method specified for water analysis in the long-term monitoring program is PCB congener analysis by HRGC/MS using EPA Method 1668A. The laboratory used in the BMP estimated detection limits (EDL) for individual congeners ranging from 0.0005 nanogram per liter (ng/L) to 0.003 ng/L, and reporting limits ranging from 0.02 to 0.03 ng/L. The PCB congener EDLs and reporting limits were enhanced by extraction of double sample volumes (2 liters per sample) as well as by installation of upgraded electronics for the mass spectrometer, resulting in state-of-the-art sensitivity for a commercial laboratory.

Minimum Number of Detected Congeners. Water column PCB data is expressed as total PCBs, which is the sum of all detected congeners using zero for undetected congeners below the EDL, and using estimated values between the EDL and the reporting limit. The congener compositions of the most highly contaminated samples in the BMP (i.e., those samples with the fewest number of undetected congeners and the least amount of "censoring") were evaluated to determine how many of the 209 possible congeners make up the bulk of the PCB mass. Water samples from August and September in OU3 and OU4 were analyzed for this purpose. It was determined that the top 20 to 25 congeners contributed 80% of the total PCB mass.

Based on this evaluation, the goal for the long-term monitoring program is to detect and quantify 25 congeners in each sample. With this level of detection, a majority of the PCB mass will be positively quantified. When PCB concentrations are very low, there may be too few congeners detected. Detections of fewer numbers of congeners may tend to bias results low because a larger fraction of the PCB mass would be undetected or "censored." However, as PCB congener levels decrease over time, it is likely that less than 25 congeners detected may become the norm. Therefore, although detection of 25 congeners may be a goal, it is not a requirement of the analysis; and when this occurs, it will be addressed collaboratively through adaptive management.

Analytical Sensitivity in Water. A review of the water data from the BMP shows EPA Method 1668A is sufficiently sensitive to meet the objectives of the long-term monitoring program, at least during the initial monitoring rounds. During the warm-weather months from April to November, between 49 and 132 congeners were detected in water samples from the LFR and

31 to 61 congeners were detected in Lake Winnebago (all statistics based on blank-corrected data). Good detection frequencies were achieved for total PCB concentrations as low as 0.1 ng/L. This level of sensitivity exceeded the expectations of the *LFR Baseline Monitoring Plan* by about an order of magnitude, which assumed accurate quantitations would be achievable down to about 1 ng/L.

In winter months, fewer numbers of congeners were detected overall. In Lake Winnebago, the number of detected congeners dropped below the minimum recommended detection frequency (less than 25 congeners) for 2 months.

Given the order of magnitude reductions in PCB concentrations which are predicted to occur in the decades following the RA, the sensitivity of the PCB analytical methods may need to be evaluated at some point in the future of the long-term monitoring program. However, data collected during the BMP indicates high-quality data should be obtained during the initial monitoring rounds using EPA Method 1668A, with the modifications as recommended in this plan.

Further improvements in sensitivity may be limited by trace levels of PCBs in the global and regional atmosphere, evidenced by ambient PCB concentrations in laboratory method blanks (approximately 0.1 ng/L to 0.3 ng/L) and field rinseate blanks (approximately 0.1 ng/L to 0.9 ng/L). Ongoing monitoring and evaluation of field and laboratory blank contamination is, therefore, a critical component of the long-term monitoring program. To this end, laboratory blank contamination will be controlled as practicable to 0.2 ng/L total PCBs or lower during the long-term monitoring program. This should be an achievable control limit based on the analytical laboratory's performance during the second half of the BMP, after a source of laboratory contamination was diagnosed and eliminated. As with other elements of the long-term monitoring program, adaptive management may be used to update this control limit if further reductions in PCB blank contamination can be reasonably achieved by the laboratory.

Analytical Sensitivity in Fish Tissue. PCB concentrations in fish tissue from the LFR and Green Bay during the BMP ranged from about 0.1 milligrams per kilogram (mg/kg) to 10 mg/kg (Aroclor basis), depending on the particular species and river reach. The detection limit achieved in the BMP for PCBs in fish tissue was 0.019 mg/kg. All fish species were at or near 100% detection in all parts of the LFR and Green Bay. In Lake Winnebago, more frequent non-detects were observed, especially in the human health species (50% non-detect for walleye, 40% non-detect for bass). Because PCB concentrations in the LFR and Green Bay are typically about an order of magnitude higher than those in Lake Winnebago, additional analytical sensitivity in Lake Winnebago does not appear to be warranted at this time.

5 Sampling Procedures

The following section presents the sampling procedures for the SOW field activities.

This section presents the anticipated sampling strategies to be employed during each monitoring event, including sample numbers, monitoring locations, sampling schedules, and field and laboratory procedures. These sampling strategies may be adjusted or modified through adaptive management and the CERCLA 5-year review process. For example, environmental media or fish species may be added, reduced, or discontinued based on an ongoing evaluation of progress toward risk reduction goals.

5.1 Water Quality Monitoring Plan

5.1.1 Number of Water Samples

Monthly water samples will be collected at all monitoring stations during the eight warm-weather months (April through November) during each monitoring year (eight samples at each of two stations). Sampling may not always be possible at all stations due to unforeseen field conditions; therefore, the "completeness" objective for the water quality sampling program will be a minimum of seven out of eight possible sampling events at each station.

5.1.2 Water Quality Monitoring Stations

In general, water monitoring stations are sited near the downstream boundaries of the OUs such that the net PCB contribution from each OU, and the effectiveness of the remedy in each OU, can be evaluated.

Water column samples will be collected and analyzed at one upstream reference location in Lake Winnebago and one station along OU1. The stations recommended for the long-term monitoring program are identical to those occupied during the BMP.

The water monitoring stations for the *OU1-LTMP* are listed below:

- Lake Winnebago (upstream reference station): Just above Neenah and Menasha Channels (Figure 2-2, Appendix A-2).

- OU1: Downstream of LLBdM and above the first Appleton Dam (Figure 2-3, Appendix A).

Figures 2-2 and 2-3 were taken from the *FR-LTMP*. A note regarding June sampling was added to each figure proceeding the issuance of the report. In addition, the transects are shown in cross section in two figures taken from Appendix G of the *LFR Baseline Monitoring Plan* (Figures 2-3 and 2-3, Appendix A-1).

5.1.3 Water Quality Monitoring Schedule

Sampling will be performed on a monthly basis from April through November in a given monitoring year (eight sampling events total). Sampling will be "systematic" in design, to provide representative and unbiased coverage. Specific runoff events will not be targeted but a

random and representative range of flows is expected to be captured during the course of the monitoring program. Water sampling will be scheduled during the first two weeks of each month. The six river water samples will be collected in order from upstream to downstream over as short a period of time as practical, typically 1 day.

5.1.4 Water Quality Sample Identification

Water quality samples will be coded as follows:

AAAA-YY-MMDD

where "AAAA" is a 3 to 4 letter code that identifies the OU (e.g., OU1) or subunit (OU2B); "YY" is the two-digit year (e.g., -10 for 2010, etc.); and "MMDD" is the month and day of the sample collection. For example, "OU1-10-0415" is a water sample from the OU1 station collected on April 15, 2010. This sample identification scheme is designed to sort alphabetically in time and space.

Field replicates will be coded in the initial letter string (e.g., OU1D or OU2BD) in order to preserve the time stamp at the end of the name. The code for field rinsate blanks will replace the OU designation at the beginning of the sample code and will retain the time stamp. For peristaltic pump and Niskin bottle rinsate blanks, respectively, the codes are as follows:

RBP-YY-MMDD
RBN-YY-MMDD

Each of the water quality samples will be composited from six separate aliquots from different distances and depths along the channel transect, as described below (Section 5.1.5). Each aliquot will be labeled with a consecutive letter (A, B, C, D, E, and F) progressing from top to bottom and west to east, in the following format:

AAAA-YY-MMDD-B

The six aliquots will be submitted separately to the analytical laboratory for compositing.

5.1.5 Water Quality Sampling Procedures

Water quality sampling procedures are described below.

5.1.5.1 Location Control

Water quality monitoring stations will be located to within a target accuracy of 2 meters using a handheld global positioning system (GPS) unit with differential GPS (DGPS) software calibrated to known shoreline benchmarks before and after each sampling transect. Water depths will be determined using either a lead line or a calibrated echo sounder recorded to the nearest 0.1 foot. Care shall be taken to avoid sediment surface disruption at the sampling point. Project-specific location control requirements, calibration protocols, and quality indicators are described in the *Location Control* SOP (Appendix B).

5.1.5.2 "Quarter Point" Sampling Procedures

Water quality samples will be collected according to the *Trace PCB Sampling of Surface Water* SOP (Appendix B). Area-weighted composite samples will be collected on specified transects to obtain representative water concentrations averaged over the cross-section of flow. Water quality sampling transects are located to the extent possible in relatively straight reaches with simple, U-shaped cross-sections, avoiding areas with shallow benches or protrusions that could cause eddies, wind waves, or other hydraulic complications. It is assumed that the flow in these sections is relatively uniform and well mixed. In a uniform, well-mixed cross-section, an area-weighted sampling design provides a reasonable approximation of a flow-weighted design.

Representative transects of OU1 and Lake Winnebago will be sampled in general accordance with U.S. Geological Survey (USGS) "quarter point" sampling procedures. The channel cross-sections are divided into three equal areas based on bathymetric data. Water sampling stations are positioned at the midpoint of each of the three flow areas; the coordinates of these stations are listed in Table 2-2 (Appendix A-2). In OU1 and Lake Winnebago, discrete water samples will be collected at 0.2 and 0.8 times the depth of the water column.

5.1.5.3 Sample Compositing

Discrete water subsamples will be collected at each of the six "quarter point" locations and depths (i.e., two depths x three stations = six subsamples for each transect), then shipped to the analytical laboratory where the compositing will be performed under clean laboratory conditions. A 1-liter bottle will be collected at each of the six subsampling locations/depths (six bottles total) and a second, redundant set of bottles will be collected and held in refrigerated storage near the sampling site until it has been determined that the original bottle set arrived safely at the analytical laboratory. Water quality sample compositing will be conducted in the laboratory, according to the laboratory SOPs referenced in Appendix C.

5.1.5.4 Field Equipment

Samples in OU1 and Lake Winnebago will be collected using a peristaltic pump with expendable tubing (i.e., used only once for each transect). Sample containers, holding times, and preservation requirements are provided in Table 2-6 (Appendix A-2).

5.1.5.5 Field Parameters

The following field parameters will be measured at each of the "quarter-point" locations on each sampling transect:

- Temperature
- Turbidity

These field parameters will be monitored in continuous casts from water surface to river bed to assess water column stratification and spatial heterogeneity in each cross section of the river or lake at the time of sampling. Water quality meter calibration and operation will follow the *Water Quality Meter Use* SOP (Appendix B).

5.2 Fish Tissue Monitoring Plan

5.2.1 Number of Fish Samples

Optimum Completeness Goal. The following number of fish samples will be targeted at each sampling station in OU1 and Lake Winnebago:

- Walleye (human health index species): 15 individual fish
- Carp (ecological index species): 35 individual fish, to be composited into seven groups of five fish each
- Gizzard shad (YOY forage fish): 175 individual fish, to be composited into seven groups of 25 fish each

Minimum Completeness Goal. Reasonable efforts will be made to obtain the optimum numbers of target species. However, if sufficient numbers of fish cannot be collected at certain sampling stations, after consideration of alternate fish sizes and other contingency actions to improve the harvest, the following minimum numbers of fish will be collected to satisfy project completeness goals, while still providing a reasonable level of statistical power:

- Walleye (human health index species): Minimum of eight individual fish
- Carp (ecological index species): Minimum of seven individual fish, to be analyzed separately (no compositing)
- Gizzard shad (YOY forage fish): Minimum of 25 individual fish, to be composited into five groups of five fish each

5.2.2 Fish Monitoring Stations

There are seven suggested fish monitoring stations in Lake Winnebago (Figure 2-2, Appendix A-2) and five suggested fish monitoring stations in OU1 (Figure 2-3, Appendix A-2), depending upon the fish species. Figures 2-2 and 2-3 were taken from the *FR-LTMP*. A note regarding June sampling was added to each figure proceeding the issuance of the report.

Recommended fish collection sites, based on the catches obtained during the BMP, are provided on these figures. However, fishing locations may be adjusted as needed in the field based on species availability, habitat, river conditions, seasonal migration patterns, or other field conditions. Because of these variables and habitat preferences, it is assumed that different species will be collected from different parts OU1 and Lake Winnebago. However, fish have free access within the entire OU1 or Lake Winnebago that they represent; therefore, they should be representative of the general environmental conditions in OU1 or Lake Winnebago.

5.2.3 Fish Collection Schedule

Fish will be collected in late summer/early fall, between August 15 and September 15. Every fish sampling event will target this same seasonal sampling window to control for seasonal

variability in the monitoring data. Sample collection activities may be extended an additional month (through October 15), if necessary, to fill data gaps.

If the walleye catch is found to be deficient and bass are substituted for the human health index species, then bass fishing should be conducted in June of the following year to be consistent with the bass collection schedule used in the BMP.

5.2.4 Target Fish Species and Size Ranges

Target fish species were selected based on the following criteria:

- Presence of fish consumption advisories (human health index species).
- Popular recreational fishery (human health index species).
- Key species evaluated in Human Health or Ecological Risk Assessments (RETEC, 2002).
- Common food source for upper-level animals, e.g., fish-eating mammals and birds (ecological index species).
- Availability in OU1 and Lake Winnebago based on recommendations from state fish biologists and experience during BMP.

A total of five fish species were analyzed during the BMP to provide greater flexibility during long-term monitoring. Four fish species will be analyzed during the long-term monitoring program, including a human health index species, two ecological index species, and a YOY forage fish species. The YOY forage fish species is intended to provide an early indication of recovery in the river because these fish best represent current conditions unburdened by legacy contaminants. The four primary species that will be targeted during the long-term monitoring program are:

- Walleye (human health index)
- Carp (ecological index for LFR)
- Drum (ecological index for Green Bay)
- Gizzard Shad (YOY forage fish)

The following secondary species may be considered if the corresponding primary species are difficult to obtain or unavailable during a particular monitoring event:

- Smallmouth Bass (human health index)
- Drum (ecological index for LFR)
- Carp (ecological index for Green Bay)

It is recommended that all secondary species be retained and archived during field collection activities until the entire catch is evaluated and it can be determined that the completeness objectives for the primary species are fulfilled.

5.2.5 Fish Tissue Sample Identification

With the exception of gizzard shad, each individual fish will be given a unique sample ID, as follows:

LLLL-YY-SP-NN

where [LLLL] is the location code describing OU1, [YY] is the two-digit year (i.e., 10 is 2010), [SP] is the species identification code (WA = walleye, SB = smallmouth bass, CA = carp, and DR = drum), and [NN] is a sequential number assigned to each individual fish in a given OU. For example, OU1-10-WA-23 is the twenty-third walleye collected in OU1 during a monitoring event in 2010. Gizzard shad from a particular sampling location will be bagged in groups of 25 fish or less and each bag of fish will be assigned a sample number in accordance with this convention (with the species code GS = gizzard shad).

Composite sample IDs will follow a similar convention as the IDs assigned to individual fish, except the last two characters will be changed to identify a composite sample:

LLLL-YY-SP-C#

where C# represents composite samples C1, C2, C3, etc. These IDs will be assigned in the laboratory where the compositing will be performed at the direction of the Respondent PM or his/her designee, in consultation with the Response Agencies.

Field replicate samples will be coded in the initial letter string (e.g., OU1D).

5.2.6 Fish Sampling and Preparation Methods

Fish sampling procedures are described below. Sample containers, holding times, and preservation requirements are provided in Table 2-6 (Appendix A-2).

5.2.6.1 Location Control

The beginning, end, and turning points of fishing transects will be located to within a target accuracy of 10 meters using a DGPS as well as references to shoreline landmarks. Project-specific location control requirements for fish sampling activities are described in the *Location Control* SOP (Appendix B). Because fish migrate freely within an OU, location control requirements are less stringent for fish collection.

5.2.6.2 Fish Sampling Methods

The following fish collection methods are recommended based on the experience gained during the BMP:

- Electrofishing (all species)
- Trawls (all species)
- Seine nets (gizzard shad)
- Rod and reel (bass and potentially other species)
- Gill nets (all species, if approved)

Rod and reel techniques were found to be productive for bass fishing in June but may also be productive for other species during the fall. Fyke nets and set lines were not generally productive. Methods may be modified as needed based on field conditions at the time of sampling.

The coordinates, time, and water depth of the starting point, ending point, and turning points for all fishing runs will be recording in field logs. Start and end times will also be marked on the hard copy print out from the echosounder. The coordinates, water depth, and time of deployment and recovery will be logged for stationary equipment, if used, such as set lines, fixed nets, etc.

The following data will be recorded for each individual fish (with the exception of gizzard shad):

- Unique individual sample ID
- Time of collection
- Length
- Weight
- Abnormalities (i.e., tumors, lesions)

Because of their small size and large numbers, YOY gizzard shad will not be logged individually. All gizzard shad fingerlings from a particular fishing location will be combined in a plastic bag and forwarded to the analytical lab for compositing. Fish collection, handling and preservation techniques are provided in the *Fish Collection* SOP (Appendix B).

5.2.6.3 Compositing

The Respondent PM or his/her designee, in consultation with the Response Agencies, will select the fish to be used for composite samples and will direct the laboratory in their preparation. See the *Biological Tissue and Plant Preparation* SOP (Appendix C) for further details on laboratory methods of preparing composite samples. Compositing is also described in Section 2.2.6.3, Appendix E, of the *OU1-LTMP*.

Carp and drum (ecological index species), and gizzard shad (YOY forage fish species) will be analyzed as composite samples. Carp composites will consist of seven composites with five individuals in each composite (i.e., 35 fish total), drum composites will consist of five composites with five individuals in each composite (i.e., 25 fish total), and gizzard shad composites will consist of seven composites with 25 individuals in each composite (i.e., 175 fish total). To the extent possible, fish will be collected that are representative of the size classes listed in Table 2-3 (Appendix A-2). Ideally, composites would be prepared for each of the five 2-inch classes in the target length window. However, some compositing classes may be represented by two or more samples, whereas other classes may contain no samples, depending on the catch.

The individual fish will be archived (frozen) until the fishing season is completed and the entire catch may be evaluated. Then the fish will be assigned to compositing groups. Similarly sized individuals (within 2-inch size classes, if possible) will be grouped together for compositing. To the extent possible, gizzard shad composites will be prepared using fish obtained from a single

fishing site. Carp and drum composites, on the other hand, may be combined from multiple fishing sites; the primary consideration for these larger and older fish is preparing composites based on a relatively narrow range of fish lengths. In no case will fish be composited across OUs (e.g., Lake Winnebago and OU1).

5.2.6.4 Fish Tissue Preparation

Walleye (and bass, if analyzed) will be prepared as skin-on fillets. These human health species will be analyzed on an individual basis to be consistent with methods used in the State Fish Consumption Advisory Program. Carp and drum (ecological species) and gizzard shad will be analyzed as composite samples of whole fish (see *Biological Tissue and Plant Preparation* SOP, in Appendix C).

5.2.6.5 Tissue Archiving

Aliquots of all homogenized fish tissue samples (including both individual and composited samples) will be set aside and archived (frozen) for possible future analysis. Fish tissue samples will be archived for a minimum of one CERCLA 5-year review cycle. The status of the samples will be considered during the 5-year review process, at which time the samples may be designated for continued archiving over another review cycle, or else discarded.

For human health species (i.e., walleye or bass), one fillet will be analyzed and the other side will be archived. For ecological species (i.e., carp and drum), each fish will be individually homogenized, then equal masses of tissue will be drawn from the individual samples to prepare the composite sample. The remainder of the individual samples will be archived for possible future analysis in case it is later determined that analysis of individual fish would be useful. For gizzard shad, an aliquot of each composited and homogenized sample will be set aside and archived.

6 Sample Custody

The primary objective of sample custody is to create an accurate, written, verifiable record, which can be used to trace the possession and handling of the samples from the moment of collection through data analysis and reporting. A sample is under a person's custody if:

1. It is in that person's possession;
2. It is in that person's view, after being in that person's possession;
3. It was in that person's possession and subsequently was placed in a secure area by that person; or
4. It is in a designated secure area.

6.1 Field Sample Custody Documentation

Chain of Custody (COC) forms will be required for all samples. The sample processing team will initiate COC forms. COC forms will contain the sample's unique identification number, sample date and time, sample description, sample type, preservation (if any), and analyses required. Original COC forms, signed by the field team, will accompany the samples to the laboratory. A copy of relinquished COC forms will be retained with the field documentation. COC forms will remain with the samples at all times. Samples and signed COC forms will remain in the possession of the field team until samples are delivered to the express carrier (e.g., Federal Express), hand delivered to the laboratory, or placed in secure storage (see *Sample Chain of Custody* SOP, in Appendix B).

6.2 Laboratory Sample Custody Documentation

Upon sample receipt, the laboratory sample custodian will verify package seals, open the packages, check temperature blanks (and record temperatures), verify sample integrity, and inspect contents against COC forms. Note that samples requiring preservation at 4 degrees Celsius (°C) may be recorded as "received on ice" if solid ice is present in the cooler at the time the samples are received, in lieu of temperature measurements, per Wisconsin Administrative Code Chapter NR 149.11(4). The laboratory PM will be contacted to resolve any discrepancies between sample containers and COCs. After confirming the shipment and COC are in agreement, the sample custodian will initiate an internal COC as well as supply the Laboratory QAM with a sample acknowledgement letter. If the sample temperatures are outside the required range, the laboratory will contact the Laboratory QAM to determine the proper course of action.

Samples will be logged into the Laboratory Information Management System (LIMS), which assigns a unique laboratory number to each sample. LIMS will be used by all laboratory personnel handling samples to ensure all sample information is tracked and recorded.

After the laboratory labels the samples, they will be moved to secured refrigerators where they will be maintained at 4°C or frozen, as appropriate. Access to refrigerators and freezers will be limited to authorized laboratory personnel.

6.3 Electronic Data Management

Field and laboratory sample data will be maintained in an EQuIS® relational database management system running in unison with an SQL Server® database. Data entering this system will follow uniform procedures for various data management stages including planning, collecting, receiving, reviewing, uploading and QA verification of data. Note, the data review stage occurs throughout the data management process including format and valid value review, completeness review, and data quality review. In addition, there is a procedure to track the status of the data management stages.

The data workflow process begins with sample planning and preparation of a field electronic data deliverable (field EDD) template and an electronic Chain of Custody (eCOC) developed specifically for Foth Infrastructure & Enviro nment, LLC (Foth) data requirements. Sampling personnel will populate the field EDD which will then be uploaded to the EQuIS database. Corresponding laboratory data will then be subsequently loaded from an electronic laboratory data deliverable (lab EDD) utilizing information from the eCOC. QA verification will be performed by generating and reviewing standard data reports defined in the project work plan. Documentation of QA activities will be recorded to an electronic form referred to as the Data Management Control Memo (DMCM) on an associated Sharepoint® database.

7 Analytical Procedures

The analytical parameters and methods specified for water and fish tissue analysis are the same as those used in the BMP. In water, PCB congeners will be analyzed using EPA Method 1668A to achieve ultra-low level detection limits. In fish, PCB Aroclors will be extracted using USEPA Method 3541 and analyzed using USEPA Method 8082 to ensure consistency with historical fish monitoring data and the state fish consumption advisory program.

7.1 Water Analytical Parameters

All water column samples will be analyzed for the following:

- PCB Congeners (209 total) by USEPA Method 1668A (HRGC/MS)
- Total suspended solids (TSS) by USEPA Method 160.2
- Total Organic Carbon (TOC) by USEPA Method 415.1

7.1.1 Water Methods and Reporting Limits

Analytical methods and reporting limits for water analysis are summarized in Table 2-7 (Appendix A-2). EDLs and reporting limits for PCB congeners by Method 1668A are listed in Table 2-8 (Appendix A-2). Two-liter samples will be analyzed to improve reporting limits.

7.2 Fish Tissue Analytical Parameters

Fish tissue samples will be analyzed using the following methods:

- Tissue Extraction (USEPA Method 3541)
- PCB Aroclors (USEPA Method 8082)
- Lipid Content (Randall et al., 1991)

7.2.1 Fish Tissue Methods and Reporting Limits

Analytical methods and reporting limits for tissue analysis are summarized in Table 2-7 (Appendix A-2).

Detected values above the method detection limit (MDL) but below the reporting limit (also known as the limit of quantitation) will be reported by the laboratory as estimated values with a "J" qualifier to indicate that the reported value is less accurate in this region of measurement. Matrix effects should be considered in assessing the laboratory's compliance with MDLs and reporting limits. The laboratory will provide a discussion of all failures to meet sensitivity specifications in the data package narrative. If a sample dilution results in non-detected values for analytes that had been detected in the original analysis, the results of the original run and the dilution will be reported with the appropriate notations in the case narrative.

7.3 Quality Assurance and Control Procedures

The overall QA objective for this project is to collect data of a known and high level of quality through the specification and implementation of QC procedures during field sampling, sample handling, laboratory analysis, and data management.

Location Control. Field sampling locations must be determined to within known accuracy specifications. Water quality monitoring stations will be located to a target accuracy of within 2 meters using a DGPS calibrated to known shoreline benchmarks before and after each sampling transect. The beginning, end, and turning points of fishing transects will be located to a target accuracy of within 10 meters using a DGPS, as well as references to shoreline landmarks (see *Location Control* SOP, in Appendix B).

Analytical Control. Analytical specifications, reporting limits, QC procedures, assessment criteria, and corrective actions are summarized in the following tables (Appendix A-2):

- Table 2-7. Laboratory Analytical Methods and Reporting Limits
- Table 2-8. PCB Congener Reporting Limits
- Table 2-9. Quality Control Procedures, Criteria, and Corrective Actions – PCB Aroclors and Conventionals
- Table 2-10. Quality Control Procedures, Criteria, and Corrective Actions – PCB Congeners

The identification of analytical laboratories to perform the required work in the *OU1-LTMP* will be provided to the Response Agencies for approval at least two months before sampling is initiated. It is acknowledged that laboratories may need to be changed, with Response Agency approval, over the duration of the multi-decadal monitoring program.

The QA program is designed to generate data of known and acceptable precision, accuracy, representativeness, comparability, and completeness, as described below.

7.3.1 Precision

Precision is a measure of reproducibility of sample results. All work will adhere to the established protocols presented in this Plan. Checks for field and analytical precision will include the analysis of field replicates for water and fish, as well as matrix spike/matrix spike duplicates.

Field Replicates for Water. To provide an overall assessment of the field and analytical precision associated with PCB congener analysis, field duplicate samples will be collected during each of the eight monitoring months. Four duplicates will be collected from Lake Winnebago.

Field Rinsate Blanks for Water. To provide an assessment of ambient field contamination caused by low but ubiquitous levels of PCBs in the regional background of OU1 and Lake Winnebago, field rinsate blanks will be collected. Two rinsate blanks will be collected each month, one from a clean unused section of Teflon® tubing and the second from a decontaminated Niskin bottle (if utilized), to assess both of the water sampling techniques. The

laboratory will provide ultra-pure water to the field crew for use in preparing rinsate blanks for high-resolution congener analysis.

In the lake and the river, all six sampling points on the transect (A through F) will be sampled, then a second circuit of the sampling points will be made to collect the six aliquots for the field replicate sample.

Field Replicates for Fish. Field replicate samples will be collected and prepared for both individual and composite samples of fish, as indicated in Table 2-4 (Appendix A-2). For those species analyzed on an individual basis (i.e., walleye or bass), a pair of fish specimens from the same haul, and nearly identical in size (i.e., within 1 inch in length, if possible), will be designated as a primary specimen and a replicate specimen. For those species analyzed on a composited basis (i.e., carp, drum, and gizzard shad), a replicate composite grouping will be prepared from a second group of fish in the same size class. For carp and drum, replicate composite groups may be prepared from multiple hauls, but they must be from the same monitoring event (i.e., within a 30 to 60 day collection period). For gizzard shad, replicate composite groups should be prepared from the same haul as the original sample, to the extent possible.

Evaluation and Response. Field replicate data will be evaluated during the CERCLA 5-year reviews. If significant discrepancies are evident in field replicate results, the field documentation will be reviewed to determine whether the discrepancies are potentially caused by field sampling error or alternatively, natural heterogeneities in environmental media which are beyond the control of the sampling crew. Note that it may not always be possible to differentiate these two potential sources of sampling variability. Appropriate modifications to the long-term monitoring program, if warranted, will be discussed in the 5-year reviews.

7.3.2 Accuracy

Accuracy is a measure of how close a measured result is to the true value. Both field accuracy (i.e., temperature and turbidity measurements) and analytical accuracy will be monitored through initial and continuing calibration of instruments. In addition, internal standards, matrix spikes, blank samples, laboratory control samples (LCS), and surrogate standards will be used to assess the accuracy of the analytical data.

Accuracy will be calculated in terms of percent recovery, as follows:

$$\%Recovery = [(A - X)/B] \times 100$$

where:

A = Value measured in spiked sample or standard
X = Value measured in original sample
B = True value of amount added to sample or true value of standard

This formula uses an assumption of constant accuracy between the original and spiked measurements.

7.3.3 Representativeness

Representativeness is the degree to which sampling data accurately and precisely represent site conditions. Representativeness is dependent on sampling and analytical variability and the variability of environmental media at the site.

7.3.3.1 Representativeness in Space

Accurate and precise location control is a fundamental requirement for obtaining representative water and sediment samples (see *Location Control* SOP, in Appendix B). Because fish swim freely within OUs/sub-units, and may congregate in different locations from season-to-season and year-to-year, lower levels of accuracy and precision for location control can be tolerated for fish collection.

Water Representativeness. Representativeness of water samples will be achieved through the use of modified USGS "quarter-point" sampling procedures which provide systematic characterization of water quality over the depth and across the width of the river and lake. Representativeness will be further assessed by analyzing the spatial variability of field parameter measurements (i.e., temperature and turbidity) at the time of sample collection.

Fish Representativeness. Representativeness of fish samples will be achieved by collecting specimens from a range of sizes and a cross-section of habitats that are frequented by the target fish species in OU1 and Lake Winnebago. Because fish are migratory, they provide spatial integration of contaminant exposures over the extent of their home range. A goal of the monitoring program is to characterize each fish station with fish specimens collected from at least three separate fishing sites within OU1 or Lake Winnebago. Collecting specimens from multiple fishing sites will help to provide representative geographic coverage of particular river and lake areas. If possible, depending on species availability, some specimens should be collected using a second, complementary fishing method (e.g., electrofishing and rod-and-reel) to evaluate the potential for field sampling bias (i.e., potential for one type of fishing gear to preferentially sample a particular habitat or size class).

7.3.3.2 Representativeness in Time

Representativeness of water samples will be achieved through the use of systematic monthly sampling over the eight-month monitoring period (April through November) when greater than 90% of the annual PCB load is discharged. Representativeness of fish samples will be achieved by targeting a late summer (August 15 to September 15) sampling window, as recommended by USEPA (2000c), and maintaining this same sampling window throughout all baseline and long-term monitoring events to minimize seasonal variability in fish lipid content and contaminant levels.

If walleye are relinquished in favor of bass, bass samples should be collected during the same late summer window, to the extent they are available. Bass samples should also be collected in Lake Winnebago during the following June to be consistent with the BMP. If possible, complementary data sets should be collected from these four stations in both the late summer window and the June window to better characterize seasonal differences in PCB and lipid

concentrations. If seasonal differences are not significant or are controllable using appropriate statistics, and if bass can be successfully obtained in the fall, the spring sampling event may be phased out.

7.3.4 Comparability

Comparability is the degree of confidence with which one data set can be compared to another, as discussed below.

Comparability Between Baseline and Long-Term Monitoring Programs. Internal consistency will be achieved by occupying the same sampling stations and performing the same field and analytical methods in the BMP and the LTMP. Specifically, comparability between baseline and long-term monitoring events will be ensured by:

- Occupying the same water monitoring stations and the same general fishing areas during all baseline and long-term monitoring events.
- Utilizing the same or similar field sampling and analytical techniques during all monitoring events.
- Collecting water data according to the same systematic monthly sampling schedule during all monitoring events (i.e., monthly sampling from April through November).
- Adhering to a fish sampling window between August 15 and September 15 during all monitoring events to minimize seasonal variations in tissue concentrations and fish lipid content.

Tissue Performance Evaluation Sample. Comparability of PCB Aroclor analysis between baseline and long-term monitoring programs will be further evaluated by preparing tissue performance evaluation (PE) samples from representative composite groupings of fish collected during the BMP with a typical site-specific Aroclor composition. Although a PE sample was not available for the BMP, two PE samples will be prepared for long-term monitoring. One PE sample will be prepared for OU1. The PE samples will be analyzed five times by the contract laboratory used in the BMP, then archived in the freezer for future use in the LTMP. When long-term monitoring activities are initiated, the selected contract laboratory (whether the same or a different laboratory) will also be required to analyze each of the tissue PE samples five times, and a statistical comparison of Aroclor results will be performed to assess comparability of labs and analytical methods.

Comparability with Historical Data. Historical data will be used in a more qualitative than quantitative manner because monitoring stations and field and analytical methods specified in this Plan are not always comparable to those used in historical studies of the LFR and Green Bay. Comparability with historical data will need to be determined on a case-by-case basis. Comparability issues may arise due to station positioning methods, sampling and processing methods, analytical methods, and the level of data quality review.

Comparability with past and ongoing studies will be improved by:

- Utilizing sample preparation and analytical methods which are comparable to past and ongoing studies, to the extent possible (e.g., use of USEPA Method 3541 for fish tissue extraction and USEPA Method 8082 for tissue analysis).

- Occupying sampling stations which are coincident with stations occupied during past and ongoing studies to the extent possible (e.g., collocation with the USGS Oil Depot station at the mouth of the LFR).

- Collecting fish species (e.g., walleye, carp, gizzard shad) that have been routinely collected in past monitoring studies, to the extent possible.

7.3.5 Completeness

7.3.5.1 Field Completeness

Field completeness is the percentage of stations or monitoring events successfully completed during the field program. For example, some samples may be lost, certain fish species may be sparse or unavailable in particular river reaches, and water sampling may be precluded at one or more stations because of severe weather or safety issues (e.g., wind, unstable ice, etc.).

The completeness of the field data is calculated using the following equation:

% Completeness = [(# Samples Collected) / (# Samples Planned)] × 100

Minimum Field Completeness Goals. The overall completeness goal for the water column sampling program is collection of valid water samples in at least 7 out of 8 warm-weather months (i.e., 88%). The overall completeness goal for the human health fish species (walleye) is collection of eight out of 15 specimens at a given sampling station (i.e., 53%). The overall completeness goal for ecological fish species (carp and drum) is collection of five individual fish as opposed to five composites of five fish each (i.e., 20% of the fish and 100% of the laboratory analyses). The overall completeness goal for gizzard shad is collection of five composites of five fish each as opposed to seven composites of 25 fish each (i.e., 14% of the specimens and 71% of the laboratory analyses).

These reduced numbers of samples should still provide sufficient statistical power to assess progress toward meeting RAOs. If completeness goals are not met for water, additional sampling may be required; if completeness goals are not met for fish, alternate species may need to be collected and analyzed. In the event completeness goals are not met for water or fish, appropriate contingency actions are described in Section 9.4.

Completeness Goal for Water Transects. The minimum completeness goal for any individual water sampling transect is collection of four out of six aliquots along the transect. For example, it is possible that the sampling crew could be driven off the water partway through a sampling transect due to foul weather. If at least four aliquots were obtained from the transect, these existing aliquots should be submitted to the analytical lab for compositing. If fewer than four

aliquots were obtained on a particular sampling day, the aliquots should be discarded and the transect should be completely resampled on a later day when the field crew can remobilize.

7.3.5.2 Laboratory Completeness

Laboratory completeness is a measure of the percentage of data that were successfully collected and analyzed as planned and not rejected during the validation process. Data qualified as estimated values using qualifiers such as "J" are still deemed acceptable and can still be used to make project decisions.

The completeness of the analytical data is calculated using the following equation:

% Completeness = [(# Valid Sample Results) / (# Samples Collected)] × 100

The overall completeness goal for the laboratory is 90%. All valid and usable data must have accompanying location control and field documentation.

8 Instrument Testing, Inspection and Maintenance

8.1 Field Instruments Calibration

Field instruments will be calibrated daily in accordance with manufacturers' specifications before the beginning of daily sampling activities (see *Water Quality Meter Use* SOP, in Appendix B). Standards used to calibrate the field instruments will be traceable to the standards of the National Institute of Standards and Technology whenever possible. The DGPS system will be checked against known benchmarks before and after each water sampling transect. Location control requirements, calibration protocols, and quality indicators are described in the *Location Control* SOP, in Appendix B.

8.2 Cleanliness Testing of Water Sampling Equipment

Field rinseate blanks will be collected from Niskin bottles (if utilized) and peristaltic pump equipment prior to water sampling to evaluate the potential for field blank contamination. Field rinseate blanks are described further in Section 7.3.1.

8.3 Laboratory Instruments Calibration

Records of calibration, repairs, or replacement will be filed and maintained by the designated laboratory personnel performing QC activities. These records will be filed at the location where the work is performed and will be subject to QA audit. The frequency and QC limits for the analytical instrument calibrations are provided in the relevant laboratory SOPs, in Appendix C.

8.4 Field Documentation

8.4.1 Field Log Books

Field Log Book entries will be described in as much detail as possible so that persons going to the site could reconstruct a particular situation without reliance on memory. Modifications to field sampling protocols must be documented in the Field Log Book. The Field Supervisor is responsible for ensuring that modifications to sampling protocols are documented in the Field Log Book (see *Field Log Book* SOP, in Appendix B).

8.4.2 Field Forms

Additional detailed sampling information may be recorded on separate field forms and referenced in the Field Log Book. The field team members will manage the raw data during field activities as overseen by the Field Supervisor. Periodically, the QAM will collect and compile the field data to maintain a current summary of field activities and measurements. All field sampling forms must include the project name, OU, date and time, sample location and sample number(s), and name and signature of the person completing the form.

8.4.3 Photographs

Photographs will be taken as needed to document field activities. Digital photograph files will be downloaded from the field camera to the project directory. The information listed below will be linked to each photograph.

- Name of person who took the picture
- Date and time photograph was taken
- Location and direction toward which the photograph was taken
- Description of the photograph

8.5 Laboratory Documentation

8.5.1 Laboratory Log Books

Workbooks, bench sheets, instrument log books, and instrument printouts will be used to trace the history of samples through the analytical process and document important aspects of the analytical work, including QC metrics. As such, all log books, bench sheets, instrument logs, and instrument printouts will be part of the permanent record of the laboratory.

Each page or entry will be dated and initialed by the analyst at the time of entry. Errors in entry will be crossed out in indelible ink with a single stroke, corrected without obliterating or overprinting the erroneous entry, and initialed and dated by the individual making the correction. Lining out unused portions and initialing by the person lining out the page will complete pages of log books that are not used.

The analyst will record information about the sample, analytical procedures, and results on laboratory forms or notebook pages and enter this information in LIMS. These notes will be dated and will also identify the analyst; instruments used, and instrument conditions.

Sufficient raw data records must be retained to permit reconstruction of initial instrument calibrations (e.g., calibration date, test method, instrument, analysis date, each analyte name, concentrations and responses, calibration curves, response factors, or unique equations or coefficients used to reduce instrument responses into concentrations).

Laboratory notebooks will be reviewed periodically by the laboratory group leaders for accuracy, completeness, and compliance with the requirements of this Plan. The laboratory group leader will verify all entries and calculations. If all entries on the pages are correct, the laboratory group leader will initial and date the pages. Corrective action will be taken for incorrect entries before the laboratory group leader signs the notebook.

8.5.2 Laboratory Project File

In accordance with analytical laboratory's records information management, documentation will be placed in secured project files which will be maintained by the laboratory records manager. These files will include the following:

- Agreements
- Correspondence
- Memos
- Notes and data
- Special instructions

Filed materials may only be removed by authorized personnel on a temporary basis, at which time the name of the person removing the file will be recorded. Laboratories will retain project files and data packages for a minimum of 10 years unless otherwise specified.

8.5.3 Electronic Data Storage

The analytical laboratories will provide the full data package, including chromatograms and raw data, in pdf format on a CD-ROM. These electronic data will be archived in project files for the duration of the long-term monitoring program. Laboratory instrument files and instrument software, including quantification program(s), will be archived at the analytical laboratories for a minimum of 10 years, which surpasses the National Environmental Laboratory Accreditation Conference (NELAC) standard for data storage. The laboratory will provide notice to the QAM or Project Coordinator before purging any instrument files or instrument software at the end of the archiving period.

8.6 Data Reporting

8.6.1 Field Data Reporting

Information collected in the field through visual observation, manual measurement, or field instrumentation will be recorded in field log books, data sheets, and/or field forms, then entered into an electronic database or spreadsheet. Data will be reviewed by the Field Supervisor for adherence to the requirements of this Plan. Any concerns identified as a result of this review will be discussed with the QAM, corrected if possible, and incorporated into the data evaluation process.

The Field QAM will review the accuracy and completeness of the field documentation, log book entries, and field forms. The field documents will be checked for the following:

- Completeness and readability
- Use of Plan-specified procedures, with any modifications appropriately documented and communicated
- Instrument calibration and maintenance records
- Correctness of sample locations
- Correctness of reporting units, calculations, and interpretations

Where appropriate, field data forms and calculations will be processed and included in appendices to the appropriate data report. Original Field Log Books and supporting documents will be kept in the project file.

8.6.2 Laboratory Data Reporting

Full "contract laboratory program (CLP)-equivalent" reporting is required for all water and fish tissue analyses. Whenever possible, analytical data will be transferred directly from the instrument to a computerized data system. Electronic data storage will be utilized. All

electronic data will be maintained in a manner that prevents inadvertent loss, corruption, and inappropriate alteration. Per the requirements of the Administrative Order on Consent (AOC), electronic data will be accessible and retrievable for a period of 10 years after project completion and the Response Agencies will be notified prior to destruction of any data files (USEPA, 2003).

Raw data will be examined to assess compliance with QC guidelines. Surrogate and matrix spike sample recoveries will be checked. Samples and laboratory blanks will be checked for possible contamination or interferences. Chromatograms and concentrations will be checked to ensure that sample results are within the calibration range; if necessary, dilutions will be performed when the sample concentration of a constituent exceeds the initial calibration range of instrument.

Deviations from guidelines will call for corrective action. Deviations determined to be caused by factors outside the laboratory's control, such as matrix interference, will be noted with an explanation in the report narrative. Calculations will be checked, as specified in the referenced analytical methods, and the report reviewed for discrepancies, errors or omissions.

The laboratory data report will be submitted to the Laboratory PM for review and approval. The Laboratory PM will review the package, conduct a forms review on 100% of definitive data, and ensure that any necessary corrections are made and that the package is complete. A copy of the data package will be maintained in the project file. Data packages will be made available, upon request, to the Response Agencies.

Laboratory data reports will include, at a minimum:

Case Narrative. Summary of activities that took place during the course of sample analysis, including the following information:

- Laboratory name and address
- Date of sample receipt
- Laboratory ID number cross-referenced to contractor ID number
- Analytical methods
- Deviations from specified protocol, if any
- Corrective actions taken
- Sample handling documents including; field and internal COC forms, air bills, or bills of lading from couriers

Chemical Analytical Results. The following information, as applicable, will be reported with the analytical results:

- Sample results with laboratory sample and client sample identification
- Detection and reporting limits
- Extraction and analysis times
- Sample volume
- Percent moisture
- Dilution factor
- Surrogate recovery
- LCS/LCD (liquid crystal display) accuracy and precision summary
- Matrix spike/matrix spike duplicate accuracy and precision summary
- Method blank summary
- Initial calibration summary–including concentration levels, retention times, response factors, and linearity demonstration
- Calibration blank summary
- Continuing calibration summary–including unique instrument/column identification, retention times, retention time windows, calibration factors, percent difference, or drift as appropriate to method
- Internal standard recoveries
- Degradation summary
- Analytical sequence
- Compound identification summary

8.6.3 Electronic Data Deliverable Format

An EDD file will be generated by the laboratory for every sample delivery group (SDG). These files will be incorporated into the LTM database. Each file will be named "*.txt," where "*" represents the batch SDG number. The USEPA Region 5 valid value list will be used for field and parameter names
(see http://www.epa.gov/region5superfund/edman/download/EDD%20V1_05.pdf).

9 Assessment and Oversight

Assessment and oversight activities are performed to determine whether the QC measures identified in the *OU1-LTMP* are implemented and documented as required. The Respondent Team Project Coordinator, PM, and Field Supervisors will perform assessment and oversight to check conformance to this *OU1-LTMP*. For example, during a review, the Field Supervisor may check that a sample has been processed and labeled correctly or that the field QC samples were collected at the appropriate frequency. The need for a check can be determined independently by the Project Coordinator or PM, or assigned by these persons to another team member.

Response Agency oversight activities may be performed by USEPA and WDNR. At all reasonable times, USEPA and WDNR personnel and their authorized representatives shall have the authority to enter and freely move about all on-site and off-site areas where work, if any, is being performed, for the purposes of inspecting conditions, activities, the results of activities, records, operating logs, field notes, and data related to these monitoring activities, provided project health and safety requirements are followed.

Aspects of the *OU1-LTMP* may be adaptively managed by the Respondents, Response Agencies, and their respective technical consultants. Using an adaptive management approach, information collected during the early stages of the monitoring program may be used to guide or improve the performance of later field or analytical tasks.

9.1 Field Audits

Planning, scheduling, and conducting QA audits and surveillance are required to verify that site activities are being performed in conformance with approved plans, standards, federal and state regulatory requirements, sound scientific practices, and contractual requirements. Planned and scheduled audits may be performed to verify compliance with aspects of the QA program and to evaluate the effectiveness of the QA program. Audits include an objective examination of work areas, activities, processes, review of documents and records, interviews with project personnel, and review of plans and standards.

Internal review of the sampling program will be conducted on a regular basis during the field activities. Reviewers will pay particular attention to the sampling program with respect to representativeness, comparability, and completeness of the specified measurements.

Field documentation (e.g., COC forms, field sampling forms, and log books) will be reviewed as it is generated, by the Field Supervisor or designee, for accuracy, completeness, and compliance with the requirements of this *OU1-LTMP*. The Field QAM, PM, or Project Coordinator will audit field sampling procedures periodically for compliance with *OU1-LTMP* procedures. The auditor will check that the following procedures are being properly implemented:

- Sampling protocols are being followed.
- Samples are placed in appropriate containers.
- Samples are stored and transported properly.
- Field documentation is complete, accurate, and legible.

Internal field audits will be conducted by one of the individuals listed above at the beginning of each new field activity (i.e., fish sampling; water sampling) and during a significant crew change (i.e., replacement of Field Supervisor). Additional field audits may be conducted on an as-needed basis if potential data quality issues are identified by field staff or during senior review of field reports and field documentation.

In addition to internal field audits, the USEPA and WDNR oversight team may also conduct field audits. At least 15 days of notice shall be given to the WDNR and USEPA Project Coordinators prior to beginning sampling. If necessary, corrective action shall be performed as provided in Section 9.3 of this Plan.

9.2 Laboratory Audits

The Laboratory QAM may conduct internal system audits. An internal audit is a qualitative evaluation of all components of the laboratory QC measurement system. The audit serves to determine whether measurement systems are being used appropriately. The system audits are conducted to evaluate the following:

- Sample handling procedures
- Calibration procedures
- Analytical procedures
- QC results
- Safety procedures
- Recordkeeping procedures
- Timeliness of analysis and reporting

The Laboratory QAM will evaluate laboratory precision and accuracy by comparing results of duplicate samples, QC samples, spikes, and blanks. When a beyond-control limit situation is encountered, analytical results will be checked by the Laboratory PM prior to distribution.

In addition, laboratories are subject to external audits. The focus of these audits is to assess general laboratory practices and conformance to the requirements of this *OU1-LTMP*. Laboratory audits may be performed by the Data QAM prior to the start of analyses for this project and at any time during the course of the project as deemed necessary.

External reviews of laboratory performance may also be conducted based on an evaluation of QC check samples analyzed as part of the USEPA and/or Wisconsin state certification requirements. In addition, performance audits may be conducted by sending double-blind PE samples (samples that are not discernable from routine field samples) to the analytical laboratory.

The USEPA and WDNR may also perform laboratory audits in addition to routine certification audits or PE sample results. Any discrepancies will be remedied as described in this Plan.

9.3 Corrective Actions

9.3.1 Field Corrective Action

Any project team member may initiate a field corrective action process. The corrective action process consists of identifying a problem, acting to eliminate the problem, monitoring the effectiveness of the corrective action, verifying that the problem has been eliminated, and documenting the corrective action.

Corrective actions include correcting COC forms; correcting problems associated with sample collection, packaging, shipping, or field record keeping; or additional training in sampling and analysis. Additional approaches may include re-sampling or evaluating and amending sampling procedures. The Field Supervisor will summarize the problem, establish possible causes, and designate the person responsible for a corrective action. The Field Supervisor will verify that the initial action has been taken, that it appears to be effective, and then follow up at a later date to verify that the problem has been resolved.

Technical staff and field personnel will be responsible for reporting suspected technical or QA nonconformances or suspected deficiencies to the Field Supervisor. The Field Supervisor will assess suspected problems in consultation with the Project Coordinator, PM, and/or Field QAM, as appropriate, and reach a coordinated decision based on the potential for the situation to impact data quality. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, a nonconformance report will be initiated by the Field Supervisor.

9.3.2 Stop Work Order

The Project Coordinator has the authority to stop work based on QC, health and safety, or other serious deficiencies that may compromise the integrity of the long-term monitoring program or the safety of the field crew. The decision to stop work will be determined on a case-by-case basis in consultation with the PM, Field QAM, Field Supervisor, and as appropriate, the WDNR Project Coordinator and USEPA Remedial PM. Stop work decisions may also be made on the basis of hazardous field conditions by the Field Supervisor, Corporate Health and Safety Manager, or the boat captain.

9.3.3 Laboratory Corrective Action

Corrective actions are required whenever an out-of-control event or potential out-of-control event is identified at the analytical laboratory during sample handling and preparation, instrument analysis, or data generation, or during the Respondent Team's oversight of these activities (see Tables 2-9 and 2-10, in Appendix A-2). The investigative and corrective actions taken are somewhat dependent on the severity of the problem and its potential to adversely impact data quality. Corrective actions may be necessary if the following situations occur:

- QC data are outside control limits for precision and accuracy.
- Blanks contain target analytes above acceptable levels.
- Undesirable trends are detected in spike recoveries or relative percent difference (RPD) between duplicates.

- Unusual changes in detection limits occur.

- Deficiencies are detected by the Laboratory QAM during internal or external audits or from results of PE samples.

Corrective action procedures are often handled at the bench level by the analyst who reviews preparation or extraction procedures for possible errors, and checks instrument calibrations, spike and calibration mixes, and instrument sensitivity. If problems persist or cannot be identified, matters are referred to the Laboratory QAM or Laboratory PM for further investigation. Full documentation of the corrective action procedures is filed with the Laboratory QAM after discussion with and approval by the Data QAM. If corrective actions are insufficient, the Project Coordinator or the Data QAM may issue a stop-work order. Corrective action may include the following:

- Re-analyzing the samples, if sample or extract volume is adequate and holding times have not lapsed.

- Performance of additional cleanup steps.

- Re-sampling and analyzing.

- Evaluating and amending sampling or analytical procedures.

- Accepting data and acknowledging a higher level of uncertainty.

If re-sampling is deemed necessary due to laboratory problems, the Respondent Team's Project Coordinator and PM will coordinate collection of additional sample material, and if appropriate, pursue cost recovery from the laboratory for the additional sampling effort. If a proposed corrective action results in a significant change or modification to the procedures defined in the *OU1-LTMP*, review and approval by the WDNR and USEPA may be required prior to implementing the recommended procedural modifications.

9.4 Field Contingency Plans

9.4.1 Water Sampling Contingency Plan

It is possible severe weather conditions (e.g., ice, high winds, etc.) or other safety concerns will preclude water sampling at one or more locations during the monitoring year (April through November). Water sampling will be targeted for the first 2 weeks of each month. If severe weather or other difficult field conditions delay sampling, sampling will be performed as soon as possible during the month. If sampling cannot be completed at all during the month, the monthly sampling event will be lost.

The overall completeness goal for the water column sampling program is collection of valid water samples in at least seven out of eight monitoring months (also see Section 7.3.5.1). If this

completeness goal is not met, the Respondents and Response Agencies will review the data and determine an appropriate corrective action. Corrective action may include:

- Acceptance of fewer than the required number of sampling events at certain stations for the monitoring year.
- Assignment of two sampling events in one month to make up for the deficiency.
- Extension of the monitoring program into the winter or the following spring.

9.4.2 Fish Sampling Contingency Plan

It is possible that a sufficient number of appropriately sized fish may not be obtainable for all species and all OUs during the August 15 though September 15 sampling window. Figure 3-1 (Appendix A-2) summarizes the steps that will be taken to optimize fish collection efforts, and a decision framework that will be followed to ensure that the most complete and representative fish data are obtained during each monitoring event. Sample collection activities may be extended an additional month (through October 15) if necessary to fill data gaps. In addition, if the walleye catch is found to be deficient and bass are substituted for the human health index species, bass fishing will be conducted in the following year during the month of June to be consistent with the bass collection schedule used in the BMP.

At the outset of the sampling effort, two days will be allocated for fish collection at each station. Electrofishing will be the primary fishing method, as it was consistently productive for nearly all of the target species during the BMP. Trawling, seine netting, and rod-and-reel may also be used at the discretion of the Field Supervisor or Field Biologist. Recommended fishing areas, based on experience gained during the BMP, are shown on Figures 2-2 through 2-8 (Appendix A-2). Fishing methods and locations may be modified as necessary to target the species and sizes needed at each station, and to adapt to field conditions and fish occurrence. All primary (walleye, carp, drum, gizzard shad) and secondary (bass) species within the Plan-specified size ranges (Table 2-3, Appendix A-2), as well as 2 inches shorter and 2 inches longer than the specified size ranges, will be collected and archived in the event that all target species and sizes are not obtainable.

The sampling crew will move to the next station as soon as the requisite species and sizes have been collected or after two days are spent at any station. During the BMP, a third fishing day was not generally productive. The sampling crew will complete the circuit of nine stations in this manner, with a maximum of two days at each station. If some stations still lack the full complement of target species and sizes, then a field contingency strategy will be implemented, as described below, to optimize follow-up sampling efforts.

1. **Resample Incomplete Stations.** Once the circuit of all fishing stations has been completed, the sampling crew will circle back and resample any stations where additional species or sizes are needed, on the premise that it may be helpful to let the water "rest" for a few weeks, especially during the transition from summer to fall. An additional one to two days will be allocated to any incomplete stations. Different

fishing techniques may need to be tried. If necessary, the fishing season may be extended as late as October 15.

2. **Expand Target Size Ranges**. If all sizes and species have not been collected after the second attempt, the target size ranges will be expanded plus or minus 2 inches to achieve the requisite numbers of fish to prepare the individual and composite samples.

3. **Reduce Sample Sizes**. If the requisite numbers of fish cannot be achieved even after expanding the target size ranges, then fewer fish will be analyzed for human health species, and fewer fish will be used to prepare the composite samples for ecological species. Sampling will be considered complete if each fishing station contains at least eight walleye (or bass), at least five carp or drum, and at least five composites of five gizzard shad each (i.e., at least 25 gizzard shad).

4. **Use Alternate Species.** If there are still insufficient numbers of target fish species, consideration will be given to the use of alternate species, especially if alternate species were collected and archived during sampling. Bass is the alternate species for walleye; drum is the alternate species for carp in the LFR, and carp is the alternate species for drum in Green Bay. If an alternate species is needed to replace gizzard shad, it would be an opportunistic decision at the time of sampling based on the availability of another small, YOY species (e.g., emerald shiner, walleye fingerlings, etc.).

10 Data Assessment and Analysis

Data assessment and analysis are essential functions in summarizing information to support conclusions. It is essential that these processes are performed accurately and accepted statistical techniques are used. The procedures to be used and information necessary to meet project requirements are outlined below.

10.1 Data Assessment

Data validation is the process by which data generated in support of this project are evaluated according to the QA/QC requirements of the *OU1-LTMP*. The data are evaluated for precision and accuracy against analytical protocol requirements. Nonconformance or deficiencies that could affect the precision or accuracy of the reported result are identified and noted, followed by an assessment of whether the result is sufficient to achieve project DQOs.

Data analysis includes procedures for summing total PCB concentrations, blank-correcting PCB congener results, and statistically analyzing the resultant data in space and time. Statistical analysis procedures include statistical distribution testing, correlations with controlling variables, trend analysis and regression, and PCB loading calculations.

10.1.1 Data Review and Validation

The data validation process is conducted to assess the effect of the overall sampling and analysis process on the usability of the data. There are two areas of review: laboratory PE and the effect of matrix and sampling interference. Evaluation of laboratory performance is a check for compliance with the method requirements and is a straightforward examination: the laboratory either did or did not analyze the samples within the QC limits of the analytical method and according to protocol requirements. For this project, holding time exceedances for PCBs will be qualified, rather than invalidated. The assessment of potential matrix and sampling effects consists of a QC evaluation of the sample analytical results as well as the results of blank, duplicate, and matrix spike samples; and assessing whether, or how much, the usability of the data could be affected.

All analytical data will be provided in a data package with supporting QC. Before the laboratory releases each data package, the Laboratory QAM will carefully review the sample and laboratory performance QC data to verify sample identity, the completeness and accuracy of the sample and QC data, and compliance with method specifications.

10.1.1.1 Field Screening Data

Field screening data include measurements of water temperature and turbidity, fish length and weight. These data will be validated by checking the completeness and accuracy of field measurements, field documentation, and location control. The calibration records for the water probe will be reviewed for accuracy, completeness, and adherence to the calibration schedule.

10.1.1.2 Data Validation and Verification

One hundred percent of the PCB laboratory data will undergo a forms review by the laboratory consistent with the procedures specified in this *OU1-LTMP*. Independent third-party data validation will be provided for 100% of each media in the first week of sampling, for each monitoring event, and when a substantive modification is made to the sampling method or analytical laboratory. This initial validation effort will allow for the early implementation of any corrective actions, if needed. If the initial validation is acceptable, a minimum of 10% of each media will continue to be validated on an ongoing basis unless problems are encountered that warrant increasing the data validation requirements.

Third-party data validation will follow USEPA's "Contract Laboratory Program National Functional Guidelines for Organic Data Review" (USEPA, 1999) and USEPA's "Contract Laboratory Program National Functional Guidelines for Inorganic Review" (USEPA, 2002) (National Functional Guidelines). This is consistent with USEPA Region 5 QAPP Guidance (USEPA, 2000a), which cites the National Functional Guidelines as appropriate for use in data validation at Superfund sites in this region.

Forms Review. One hundred percent of the laboratory data collected during the long-term monitoring program will undergo a forms review by the laboratory prior to submitting the results to the Data QAM and subsequently to the Data Validator. The data package supplied by the laboratory will be validated through the forms review process for compliance with the following:

- Holding times and sample temperature
- Surrogate recovery
- Matrix spike/matrix spike duplicate precision and accuracy
- LCS precision and accuracy
- Initial calibration and continuing calibration precision and accuracy
- Instrument tuning criteria (where applicable)
- Blank contamination
- Field duplicate precision and accuracy

The QC criteria to be implemented during the forms review process are presented in Table 2-9 and Table 2-10 (Appendix A-2).

Data Validation. The laboratory data packages will be sent directly to the Data QAM by the subcontract laboratories. The Data QAM will select 10% of the data (or 100% of the data during the first week of sampling) to be validated by an independent, third-party Validation Subcontractor. The Data QAM will provide the Validation Subcontractor with copies of the selected data packages. Once validated, the Validation Subcontractor will make copies of the data validation report as well as the summary forms and submit them to the Data QAM, then they will be forwarded to the USEPA PM, and the WDNR Project Coordinator. The acceptance criteria for data validation are those listed in Table 2-9 and Table 2-10 (Appendix A-2). The QC requirements specified in this Plan shall take precedence over the requirements of the National Functional Guidelines.

Data validation is at times based upon professional judgment. In order to achieve consistent data validation, data worksheets will be completed for each data validation effort. A data review worksheet is a summary form on which the data validator records data validation notes and conclusions specific to each analytical method. The worksheets will help the validator track and summarize the overall quality of the data. Sample results will then be assigned a degree of usability based upon the overall data quality. The Consultant Team will review the data validation results and assess how the data, as qualified by the data validation process, can be used to fulfill project objectives, i.e., to evaluate progress toward achieving RAOs in OU1.

Data Verification. After validation, the data will be compiled in an electronic database and the data will be verified to confirm:

- The correct samples were analyzed and the correct parameters were reported.
- EDDs and hard copy data deliverables are consistent.
- Results are consistent with expectations based on baseline monitoring results or the results of previous long-term monitoring events.

In the first two instances, the laboratory will be directed to correct any omissions or inconsistencies in reporting. If the data obtained from the laboratories are not consistent with expectations, based on prior sampling data, a more in-depth evaluation of the results will be performed to determine if the deviation is a real environmental phenomenon or an artifact of the sampling and analysis process.

Project-Specific Qualifiers. While maintaining consistency with the National Functional Guidelines, the Region 5 QAPP Guidance also allows for the definition of additional project-specific data qualifiers. For this program, a project-specific data qualifier will be used for total PCB concentrations in water (using EPA Method 1668A) for which the summation of total PCBs is based on less than 25 congener detected. A "Q##" flag will be assigned to blank-corrected total PCB concentrations that have been quantified using fewer than 25 detected congeners, where ## is a number less than 25 that represents the number of detected congeners in each flagged sample. For example, "Q15" indicates the total PCB concentration for that sample is based on the sum of 15 detected congeners. These summations are qualified because the PCB profile may be censored by the limits of analytical sensitivity, and therefore, the total PCB concentration may be biased low. However, as PCB congener levels decrease over time, it is likely that less than 25 congeners detected may become the norm. Therefore, although detection of 25 congeners may be a goal, it is not a requirement of the analysis, and when this occurs, it will be addressed collaboratively through adaptive management.

10.1.1.3 Reconciliation with Data Quality Objectives

The goal of the data collection effort is to acquire enough information and data to verify that sediment RAs in OU1 result in substantive reductions in water column and fish tissue PCB concentrations and loadings to Green Bay. Field and laboratory data will be evaluated in accordance with the DQOs. Progress toward achieving RAOs will be evaluated using the data analysis methods and statistical procedures described in Section 10.2. Determining whether the

data are sufficient to achieve project objectives will be the collective responsibility of the Respondents, the Consultant Team, the Response Agencies, and the Agencies Oversight Team.

10.2 Data Analysis

10.2.1 PCB Summation

In water samples, total PCBs will be summed using zero for congeners undetected at the EDL. In tissue samples, total PCBs will be summed using zero for Aroclors undetected at the MDL. Estimate (J-flagged) values between the EDL/MDL and the reporting limit will be included in the summation at full value.

10.2.1.1 Aroclors versus Congeners

It should be noted that total PCBs that are summed using congener data are not generally comparable to total PCBs that are summed using Aroclors. These different analytical techniques and quantitation methods respond differently to matrix interference, PCB weathering, and instrument sensitivity. Therefore, comparing water quality data that is reported as PCB congeners, as specified in this Plan, with historical data reported as PCB Aroclors is problematic, unless the bias between the two different analytical methods is adequately understood. As a result, historical data prior to the baseline monitoring event will generally not be used to assess time trends in water quality.

10.2.1.2 Analytical Sensitivity (Minimum Detected Congeners)

Based on an evaluation of the PCB congener compositions in the river reaches (OUs 3 and 4) and monitoring months (August and September) with the highest PCB concentrations during the BMP, it was determined that the top 25 congeners contributed at least 80% of the total PCB mass. Based on this evaluation, the goal for the long-term monitoring program is to detect and quantify 25 congeners in each sample. With this level of detection, a majority of the PCB mass will be positively quantified. Detections of fewer numbers of congeners may tend to bias results low because a larger fraction of the PCB mass would be undetected or "censored". However, as PCB congener levels decrease over time, it is likely that less than 25 congeners detected may become the norm. Therefore, although detection of 25 congeners may be a goal, it is not a requirement of the analysis, and when this occurs, it will be addressed collaboratively through adaptive management.

In addition, highly contaminated samples should be diluted such that the goal of 25 individual congeners continue to be detected in the diluted sample. In addition to this minimum congener detection goal, OU1 and Lake Winnebago water samples also need to be discernible from field and laboratory blank contamination, in which low levels of PCB congeners from the global and regional atmosphere are ubiquitously present.

A review of the water data from the BMP shows USEPA Method 1668A is sufficiently sensitive to meet the objectives of the *OU1-LTMP*, at least during the initial monitoring rounds. During the warm-weather months from April to November, between 49 and 132 congeners were detected in water samples from the LFR; 33 to 99 congeners were detected in water samples from Green Bay; and 31 to 61 congeners were detected in Lake Winnebago (all statistics based on blank-corrected data). Good detection frequencies were achieved for total PCB

concentrations as low as 0.1 ng/L. This level of quantitation exceeds the expectations of the BMP, which predicted reliable quantitations down to about 1 ng/L.

In summary, data collected during the BMP indicates high-quality data should be obtained during the initial long-term monitoring rounds using EPA Method 1668A. However, given the order of magnitude reductions in PCB concentrations which are predicted to occur in the decades following the RA, the sensitivity of the PCB analytical methods may need to be re-evaluated at some point in the future of the program. Through adaptive management, the Respondents and Response Agencies may convene to determine whether some type of corrective action is warranted to improve the estimate of total PCBs. Possible corrective actions may include:

- Qualify the PCB summation as "estimated" and report the number of detected congeners that contribute to the total value.

- Develop a correction factor to account for undetected PCB mass in the "censored" part of the data.

- Modify the field and/or analytical procedures in an attempt to achieve lower detection limits; the need for lower detection limits, and the ability to achieve lower detection limits, must be determined in consideration of ambient PCB levels in laboratory method blanks and field rinseate blanks.

10.2.2 Blank Correction for PCB Congeners

During the BMP, the lowest PCB congener concentrations in water samples were found at the upstream reference area (Lake Winnebago) and at the outermost station in Green Bay. At times, the concentrations in these areas approach the sensitivity of the HRGC/MS 1668A method, as well as ambient background levels of PCB contamination in the global and regional atmospheres. Following the sediment RA, concentrations are expected to decline further. As a result, blank correction of the PCB congener data must be carefully performed, especially in OUs with background or near-background concentrations.

During the BMP, blank correction was evaluated using three different correction procedures: 1) standard method following National Functional Guidelines (in which congener concentrations less than five times the method blank concentrations are corrected to nondetect); 2) blank subtraction method of Ferrario et al. 1997, also referenced in Section 17.6.1.4.4 of EPA Method 1668A (in which blank correction is based on the mean plus two standard deviations of the method blank data set during the period of analysis); and 3) a nonparametric modification of Ferrario et al. 1997 method (in which blank correction is based on the 95th percentile of the method blank data). In discussions of the LTM Work Group, the Ferrario method was determined to be superior to the standard method because the standard method resulted in too few congener detections and fragmented and unrealistic congener fingerprints after blank correction.

The Ferrario method is described in Section 17.6.1.4.4 of EPA Method 1668A:

> *Blank corrected results may be reported in addition to reporting of separate results for samples and blanks. The recommended procedure for blank correction is that a result is significantly above the blank level, and the level in the blank may be subtracted, if the result is greater than the mean plus 2 standard deviations of results of analyses of 10 or more blanks for a sample medium.*

The LTM Work Group decided that a nonparametric modification of the Ferrario method was appropriate due to concerns regarding treatment of censored values (i.e., non-detects) in the method blank data set, and the determination of means and standard deviations from censored data. As a result, the LTM Work Group decided to blank correct using the 95th percentile of the method blank data, rather than the mean plus two standard deviations. The percentile approach provides an equivalent level of statistical certainty but is unaffected by high percentages of undetected values in the method blank data set. In practice, the Ferrario method and the nonparametric modification of the Ferrario method showed very little difference in terms of blank-corrected total PCB concentrations in the baseline data set (typically less than a few percent RPD between the two calculations).

The blank correction procedures to be used in the long-term monitoring program will be the nonparametric modification of the Ferrario subtraction method. The procedure for nonparametric blank subtraction is described below:

1. Compile laboratory method blank data for EPA Method 1668A during the period of laboratory analysis corresponding to the 8 month monitoring period (April through November), plus 3 months before and 3 months after the monitoring period.

2. Prepare a time-series graph of the method blank data to determine whether there are any significant trends in blank concentrations, especially abrupt changes in blank concentrations that may be traceable to a change in laboratory procedures or equipment.

3. Determine whether there were any changes in chromatographic columns during the period of analysis, and ascertain the exact date of column replacement.

4. The method blank data set, and the associated statistical calculations and blank subtraction terms, must be calculated separately for any analysis periods in which different chromatographic columns were used, and for periods in which procedural modifications had a significant effect on method blank results, as per Items 2 and 3 above.

5. It is preferable to have at least 10 to 20 method blank results in every analysis period for which blank subtraction terms are being calculated. If there are fewer than ten results, two options are available: a) use the maximum blank concentration in the data set as the blank subtraction term; or b) consider pooling together some of the analysis periods, if appropriate, to provide more blank results in each period.

6. For each analysis period, calculate the 95th percentile concentration of the method blank data: [k=0.95(n+1)] where k is the rank of the sample corresponding to the 95^{th} percentile concentration, and n is the number of method blank samples in the analysis period. Fractional, non-integer ranks will be interpolated between the two closest data points. The 95th percentile method blank concentrations become the blank subtraction terms.

7. Subtract the 95th percentile method blank concentrations from the raw PCB concentrations for all samples analyzed during the corresponding period. The resultant values are the blank-corrected PCB concentrations. If the sample congener concentration is less than the corresponding 95th percentile blank values, the congener will be corrected to an undetected value. Undetected congeners do not contribute to the summation of total PCB concentrations.

Blank-corrected total PCB concentrations will be used in the statistical analyses described in the following section.

10.2.3 Statistical Analysis of Monitoring Data

Water, fish tissue, and sediment data will be statistically analyzed to assess the performance of the monitoring program and the more fundamental objective of monitoring progress toward achieving the RAOs. Descriptive statistics, distribution tests, and correlation tests will be performed. Long-term monitoring data will be compared to numerical target concentrations, including ecological and human health risk goals and background criteria, and confidence levels will be assessed. Time trend analysis will be performed by comparing mean concentrations and percent reductions between baseline and long-term monitoring events (i.e., two sample comparisons) and by using simple or multiple regression techniques. Finally, PCB mass loadings discharging from OU1 will be calculated.

10.2.3.1 Descriptive Statistics

For each round of long-term monitoring, descriptive statistics will be calculated for OU1 and Lake Winnebago for each fish species. Descriptive statistics will include mean, median, minimum and maximum, 10th, 25th, 50th, 75th, and 90th percentiles, percent nondetects, standard deviation and CV. These statistics will be used to verify the assumptions underlying the sampling design and to confirm that the expected level of statistical power is being achieved. These statistics will also be used to evaluate the achievement of human health and ecological target tissue goals, background criteria, and SWAC reduction targets.

10.2.3.2 Statistical Distribution Tests

Water and fish data will be subjected to statistical distribution tests to assess conformance with standard normal or lognormal distributions. Conformance with these distributions will allow the data to be analyzed using parametric testing procedures which are generally more powerful than nonparametric procedures. Distribution testing will utilize either numerical procedures (e.g., Shapiro-Wilk or D'Agostino Tests) or graphical procedures (e.g., normal probability plots).

10.2.3.3 Correlations with Controlling Variables

The data will be tested for statistical correlations between PCB concentrations and potential controlling variables. In particular, aqueous PCB concentrations will be tested for correlations with flow, temperature, and TSS concentrations. Fish tissue PCB concentrations will be tested for correlations with lipid content and fish length (a surrogate for fish age, as well as the primary basis for fish consumption advisories).

10.2.3.4 Estimating Statistical Confidence of Exit Decisions

This section provides guidance on estimating statistical confidence levels associated with achieving specified target concentrations, including risk-based concentrations, background criteria, and SWAC reduction targets. The compound probability associated with the *OU1-LTMP* requirement to achieve exit criteria in two successive monitoring rounds is also discussed.

Comparison to Target Concentrations. The statistical confidence associated with achieving a specified target concentration in a particular OU (whether it is a risk-based, background-based, or percent reduction target) is a function of the standard error of the mean concentration and the percent difference between the mean and the target concentration. If the mean concentration is equal to the target concentration, there is a 50% chance that the mean is at or below the target concentration. Statistical confidence improves as the mean concentration drops below the target concentration; and the greater the difference, the higher the confidence. Statistical confidence also improves as the standard error on the mean is reduced – a smaller standard error provides greater power of discrimination between the mean and the target concentration.

Compound Probability of Confirmation Monitoring. The statistical confidence of exit decisions is improved by requiring exit criteria to be achieved in two consecutive monitoring events (i.e., an initial event and a follow-up confirmation event). The compound probability of achieving exit criteria in two successive monitoring events will be considered in the evaluation of statistical confidence for exit decisions. For example, if exit criteria are met with 70% confidence (alpha = 0.3) in each of two successive monitoring events, the compound confidence level is 91% (alpha = 0.3 x 0.3 = 0.09).

10.2.3.5 Time Trend Analysis

A primary objective of the baseline and long-term monitoring programs is to evaluate risk reduction success as measured by declining PCB concentrations in water and fish tissue. The essence of this analysis is determining the significance and magnitude of decreasing trends in the monitoring data.

Comparison of Means. A simple test of significance is a comparison of mean PCB values between two monitoring events to determine if the mean value of the later event is significantly lower than the earlier event. If a decreasing trend is present, the power of this type of test will tend to increase as the time between monitoring events increases (i.e., the length of the monitoring record increases). Using this type of analysis, the estimated percent reduction and statistical significance of PCB concentration reductions between the baseline event and each successive monitoring event can be calculated. The results will be used to infer the magnitude

and statistical significance of the combined effects of active remediation and natural recovery on reducing PCB concentrations.

Simple Linear Regression. The data will be analyzed to determine an appropriate trend model. The default assumption is that PCB reductions will follow an exponential decay model. This model can be tested by fitting a linear regression through a plot of log PCB concentrations (in water, tissue, or sediment) versus time. A minimum of three rounds of post-construction monitoring data (i.e., Years 0, 5, and 10) will be needed to estimate the time rate of recovery in this way. Once the data are sufficient to estimate a model of PCB concentrations over time, the model can be used to predict future concentrations and compare predictions to risk reduction goals and other exit criteria. Time regressions will be performed separately for each OU and each fish species. For fish data, it may be appropriate to either stratify the data by size classes or normalize the data using lipid content or fish length, to reduce the effects of confounding variables. Nonparametric trend analysis may be considered if the data are poorly described by standard statistical distributions.

Multiple Regression. If warranted, more complex, multivariate statistical analysis procedures may be considered. In particular, multiple regression techniques may be useful if significant correlations are established with multiple controlling variables (LimnoTech, 2002, 2005).

Multiple linear regression provides a way to estimate the effects of an independent variable on water column PCB concentrations, such as the effect of sediment remediation, while controlling for the effects of other variables known to affect PCBs (such as flow, suspended solids, and seasonal temperature changes in water; or lipid content and fish length in tissue). As required for simple linear regression, a minimum of three rounds of post-construction monitoring data are also required for multiple regression. These data would be pooled to estimate the coefficients of an equation predicting PCB concentrations as a function of the independent variables mentioned above. Another independent variable would be a digital indicator to denote post-remediation conditions, equal to 0 for the baseline data and 1 for post-remediation data. The regression coefficient for this indicator would provide an estimate of the effect of remediation, after controlling for the effects of the other variables. A test of the hypothesis of "no effect of remediation" could be structured as a t-test of the null hypothesis that this coefficient is equal to zero.

A finding of a "significant effect" requires rejection of the null hypothesis at a given level of statistical confidence (i.e., probability of Type I error, which is the rejection of the hypothesis if it is true). The smaller the prediction error of the regression equation and the larger the number of data points in the monitoring program, the more accurately the effect of remediation can be estimated, thereby expanding the range of scenarios that can be judged "significantly different from zero." Similarly, smaller prediction errors and larger sample sizes also reduce the likelihood of accepting a null hypothesis of "no effect" if it is false, increasing the statistical power of the test.

Variations in the specification of the regression equation can be made, depending on what variables are known to affect PCB concentration and whether their effects are linear, nonlinear, or interactive. One important variation which is a commonly observed relationship in environmental data assumes the natural logarithm of PCB concentration is a linear function of its

determinants. The inclusion of variables and their functional forms should be dictated by scientific understanding of cause and effect relationships, supplemented by comparisons of goodness-of-fit of alternative forms of the equation. Variables should be retained in the regression equation if the hypothesis of "no effect" for each independent variable can be rejected at a high level of significance.

10.2.3.6 PCB Loading Calculations

One of the RAOs for the RA is to achieve a reduction of PCB loadings to Green Bay to accelerate natural recovery of bay sediment, water, and fish. To address this objective, PCB loads will be calculated at the downstream ends of the following reaches:

- Lake Winnebago (background loading to LFR)
- OU1

Loadings will be estimated using Beale's ratio estimator method. The Beale's method uses daily flow measurements and less frequent concentration measurements to estimate the average daily load. This estimate is computed as the average of loads for all days that both flow and concentration are measured, with a bias correction that accounts for higher- or lower-than average flows on the days when concentration was sampled. Richards (1999) provides formulas for the estimate of the average daily load and its root mean squared error (RMSE). Daily gaged flows are available at Rapide Croche, and can be scaled according to watershed area ratios to estimate daily flows at the four stations for which loads are to be estimated.

Analysis of baseline monitoring data (LimnoTech, 2008) indicates the aggregate PCB load discharged in the winter months from December through March contributes less than 10% of total annual load in the river, although these months represent one-third of the year. This study also showed that stratifying the data into the non-winter months from April through November provided more accurate loading estimates and lower RMSEs compared to loading estimates calculated over the entire year. Because only a small fraction of the PCB load is missed in the winter months, because the error on the loading estimate increases when winter months are included, and because field crews often face severe weather safety hazards during these months, winter sampling from December through March will not be performed during the long-term monitoring program. Therefore, the assessment of PCB loads will be based on the eight-month monitoring period from April through November. Baseline monitoring data will be truncated accordingly to conform to this monitoring period. If necessary, total annual PCB loads can also be estimated based on the proportion of the annual load that is discharged from December through March, as observed during the BMP.

11 Hydrographic Survey

Hydrographic survey, controlled with real-time kinematic global positioning system (RTK GPS) technology, will be used to assess cap integrity during the long term monitoring period. Multi-beam survey technology will be utilized during each event. Procedures implemented will adhere to USACE guidance contained in EM 1110-2-1003, Engineering and Design – Hydrographic Surveying (USACE, 2004).

Check-ins to known project control points with the system's RTK GPS shall occur at the start and end of each survey day. Checks shall be made to both the vertical (elevations) and horizontal (x,y coordinates) values at these known points. A target tolerance of +/- 0.08 feet from the recorded values shall be adhered to. Tolerances outside of this range shall be discussed and resolved with the Field Quality Assurance Manager prior to conduct of the survey. In addition, checks using a combination of RTK GPS water level and bar check or lead line, collection of survey data over a known reference surface, or fathometer comparison to the poled top of sediment measured depths shall be conducted daily to validate the hydrographic survey work on a system level.

Prior to each survey event, the speed of sound through the water column shall be measured, entered and applied either during the survey, or after the survey in post-processing.

A static bar shall be lowered under the transducer (center beam) to a measured increment. The depth displayed by the echo sounder will be noted and the sound velocity confirmed at that depth.

A patch test shall be performed prior to each year's survey and be used to calculate any misalignment that may occur between the X,Y,Z axis' of each sensor. These values will be dated, recorded in a standard notebook and kept with the survey vessel for reference.

All physical measurements taken during the survey preparation and conduct of the survey shall be recorded for reference and made available to the Field QAM upon request.

12 References

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Appendix A

Referenced Tables and Figures

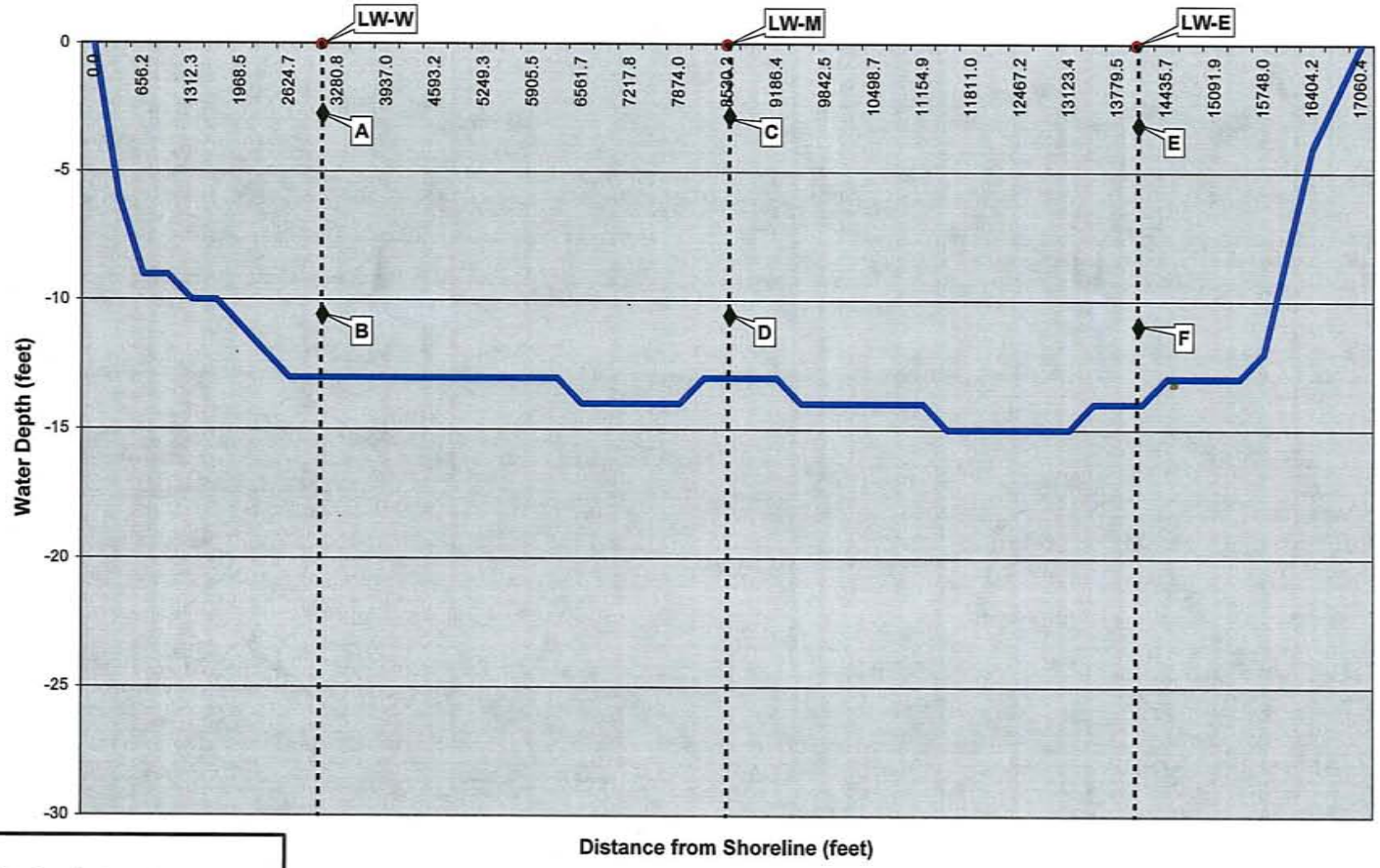
A-1 Figures (2) from Baseline Monitoring Plan (Shaw and Anchor, 2006)

A-2 Tables (10) and Figures (8) from FR-LTMP (Anchor QEA, LLC et al., 2009)

A-1

Figures (2) from Baseline Monitoring Plan
(Shaw and Anchor, 2006)

Lake Winnebago Cross Section



Legend

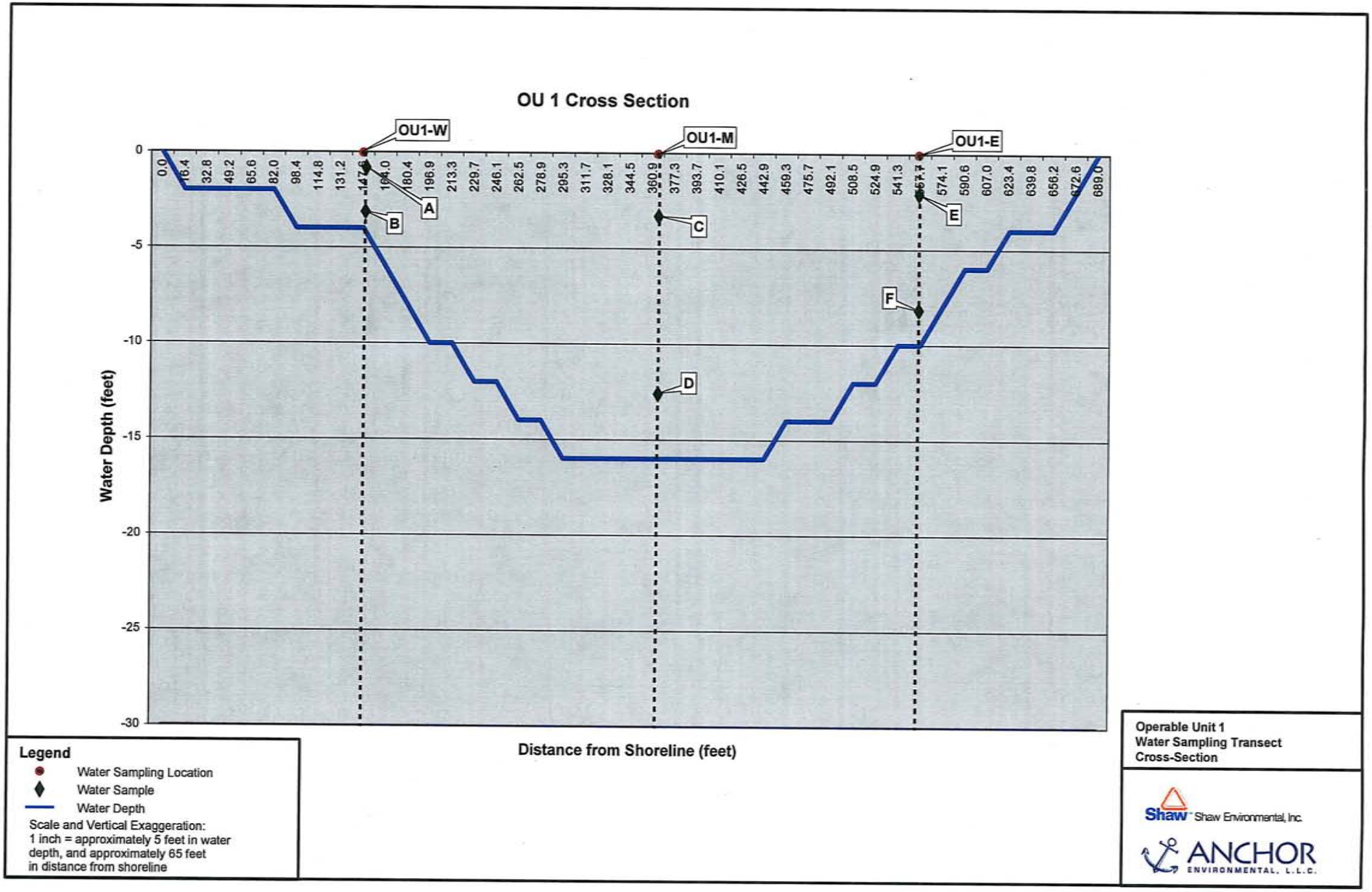
- Water Sampling Location
- Water Sample
- Water Depth

Scale and Vertical Exaggeration:
1 inch = approximately 5 feet in water depth, and approximately 1500 feet in distance from shoreline

Lake Winnebago
Water Sampling Transect
Cross-Section

Shaw Shaw Environmental, Inc.

ANCHOR ENVIRONMENTAL, L.L.C.


OU 1 Cross Section
OU1-W
OU1-M
OU1-E
A
B
C
D
E
F
0.0
16.4
32.8
49.2
65.6
82.0
98.4
114.8
131.2
147.6
164.0
180.4
196.9
213.3
229.7
246.1
262.5
278.9
295.3
311.7
328.1
344.5
360.9
377.3
393.7
410.1
426.5
442.9
459.3
475.7
492.1
508.5
524.9
541.3
557.7
574.1
590.6
607.0
623.4
639.8
656.2
672.6
689.0
0
-5
-10
-15
-20
-25
-30
Water Depth (feet)
Distance from Shoreline (feet)
Legend
Water Sampling Location
Water Sample
Water Depth
Scale and Vertical Exaggeration:
1 inch = approximately 5 feet in water depth, and approximately 65 feet in distance from shoreline
Operable Unit 1
Water Sampling Transect
Cross-Section
Shaw Shaw Environmental, Inc.
ANCHOR ENVIRONMENTAL, L.L.C.

A-2

Tables (10) and Figures (8) from FR-LTMP (Anchor QEA, LLC et al., 2009)

Table 1-7
Estimated Sample Sizes for Water and Fish Tissue Monitoring

Confidence (alpha)	Power (beta)	Coefficient of Variation							
		0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.2	0.2	1	2	2	3	5	6	8	10
0.1	0.2	2	3	5	7	9	12	15	19
0.05	0.2	3	5	7	10	14	18	23	29

Note:

Minimum Detectable Difference: 50%

Table 1-8
Estimated Statistical Confidence for Detecting 50 Percent Reduction in PCB Concentration

	n	LWB	OU 1	OU 2A	OU 2B	OU 2C	OU 3	OU 4	OU 5A	OU 5B	OU 5C
Water											
Year-Round	12	>75%	>80%	>80%	>90%	>80%	>80%	>80%	>95%	>80%	>95%
Apr. to Nov.	8	>75%	>90%	~90%	>90%	>80%	>90%	>90%	>95%	>80%	>90%
Fish											
Walleye	15	>95%	>95%	>95%	>95%	>90%	>90%	>95%	>95%	>95%	---
Bass	15	>95%	>90%	>95%	>95%	>95%	>95%	>95%	>95%	>90%	---
Carp	5	>95%	>80%	>70%	>95%	>95%	>95%	>95%	>95%	>70%	---
Drum	5	>95%	~95%	>90%	~90%	>90%	>80%	~95%	>95%	~95%	---
Gizzard Shad	5	>95%	>95%	>80%	>95%	>80%	>80%	>80%	>95%	>95%	---

Table 2-2
Water Sampling Locations

Transect	Position	X_WTM27	Y_WTM27	Latitude	Longitude	X_WTM8391	Y_WTM_8391
LW	W	625,571	392,512	44.1770	-88.4293	645,559	412,726
	M	626,486	393,942	44.1897	-88.4175	646,474	414,157
	E	627,390	395,354	44.2022	-88.4058	647,378	415,569
OU1	W	624,544	399,939	44.2440	-88.4403	644,531	420,154
	M	624,583	399,885	44.2435	-88.4399	644,571	420,100
	E	624,618	399,838	44.2431	-88.4394	644,606	420,053
OU2A	W	632,719	404,099	44.2800	-88.3369	652,707	424,314
	M	632,733	404,036	44.2794	-88.3368	652,721	424,251
	E	632,749	403,969	44.2788	-88.3366	652,736	424,184
OU2B	W	642,374	408,027	44.3135	-88.2149	662,362	428,242
	M	642,413	407,981	44.3131	-88.2145	662,400	428,197
	E	642,452	407,936	44.3127	-88.2140	662,440	428,151
OU2C	W	649,030	415,114	44.3759	-88.1295	669,017	435,329
	M	649,070	415,075	44.3756	-88.1290	669,057	435,290
	E	649,103	415,044	44.3753	-88.1286	669,090	435,259
OU3	W	653,989	422,665	44.4428	-88.0650	673,977	442,881
	M	654,035	422,628	44.4425	-88.0645	674,022	442,844
	E	654,090	422,584	44.4421	-88.0638	674,077	442,799
OU4	W	658,157	432,421	44.5297	-88.0097	678,144	452,637
	M	658,219	432,409	44.5296	-88.0089	678,206	452,625
	E	658,268	432,400	44.5295	-88.0083	678,255	452,615
OU5A	W	661,674	447,915	44.6683	-87.9606	681,661	468,130
	M	665,240	445,525	44.6460	-87.9164	685,227	465,741
	E	668,193	443,546	44.6275	-87.8798	688,180	463,762
OU5B	W	677,043	470,189	44.8651	-87.7591	697,029	490,405
	M	680,385	468,332	44.8475	-87.7175	700,371	488,548
	E	684,551	466,018	44.8257	-87.6657	704,538	486,234
OU5C	W	694,097	493,040	45.0661	-87.5347	714,083	513,255
	M	700,719	488,883	45.0269	-87.4523	720,705	509,099
	E	705,334	485,986	44.9995	-87.3950	725,319	506,202

Notes:
Quarter-point sampling location code: W = west, M = middle, E = east location in water sampling transect
All Wisconsin Transverse Mercator (WTM) coordinates are in meters

Table 2-3
Target Fish Species, Size Classes, and Compositing Plan

		2 - 4"	4 - 6"	6 - 8"	8 - 10"	10 - 12"	12 - 14"	14 - 16"	16 - 18"	18 - 20"	20 - 22"	22 - 24"	Skin-on Fillet	Whole Fish	No. Individuals (Target)	No. Individuals (Minimum)	No. Composites	No. Fish per Composite (Target)	No. Fish per Composite (Minimum)
Primary Species	**Objective**																		
Walleye	Human Health					▒	■	■	■	■	■	▒	X		15	8	0	n/a	n/a
Carp (OUs 1-4)	Ecological					▒	■	■	■	■	■	▒		X	35	7	7	5	1
Drum (OUs 4-5)	Ecological					▒	■	■	■	■	■	▒		X	25	5	5	5	1
Gizzard Shad	Young of Year	■	▒											X	175	25	7	25	5
Alternate Species	**Objective**																		
Smallmouth Bass	Human Health				▒	■	■	■	■	■	▒		X		15	15	0	n/a	n/a
Drum (OUs 1-3)	Ecological					▒	■	■	■	■	■	▒		X	25	5	5	5	1
Carp (OU 5)	Ecological					▒	■	■	■	■	■	▒		X	35	7	7	5	1

Notes:

■ Target Size Class

▒ Alternate Size Class

n/a = Walleye and Bass will not be composited

Table 2-4
Fish Tissue Sampling and Analysis Matrix

	Number of Composites	No. Fish / Composite	No. Individual Fish	Total Number Analyses	No. Field Replicates	Minimum Size (inches)	Maximum Size (inches)	Preparation Method	PCB Aroclors [8082/SLOH]	Lipid Content [EPA 2000]	Mercury [EPA 7471]	Archive [Freeze]
Walleye												
LWB-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X	X	X
OU1-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
OU2A-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
OU2B-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
OU2C-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X	X	X
OU3-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
OU4-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
OU5A-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
OU5B-YY-WA-000	n/a	n/a	15	15	1	12	22	SOF	X	X		X
WALLEYE SUBTOTAL:			**135**	**135**	**9**							
Carp												
LWB-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
OU1-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
OU2A-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
OU2B-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
OU2C-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
OU3-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
OU4-YY-CA-000	7	5	35	7	1	12	22	WF	X	X		X
CARP SUBTOTAL:			**245**	**49**	**7**							
Drum												
LWB-YY-DR-000	5	5	25	5	1	12	22	WF	X	X		X
OU4-YY-DR-000	5	5	25	5	1	12	22	WF	X	X		X
OU5A-YY-DR-000	5	5	25	5	1	12	22	WF	X	X		X
OU5B-YY-DR-000	5	5	25	5	1	12	22	WF	X	X		X
DRUM SUBTOTAL:			**100**	**20**	**4**							
Gizzard Shad												
LWB-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU1-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU2A-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU2B-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU2C-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU3-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU4-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU5A-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
OU5B-YY-GS-000	7	25	175	7	1	2	4	WF	X	X		X
GIZZARD SHAD SUBTOTAL:			**1,575**	**63**	**9**							

SUBTOTAL FISH ANALYSES (ALL SPECIES):	**267**	**29**
GRAND TOTAL FISH ANALYSES:	**296**	

Table 2-6
Sample Containers, Holding Times, and Preservation Requirements

Parameter	Analytical Method	Matrix	Container	Preservation	Minimum Sample	Maximum Holding
TOC - water	EPA 415.1	Water	Polyethylene / Glass	4'C, H2SO4 OR H3PO4 TO pH <2	100 mls	28 days
TSS	EPA 160.2	Water	1 Liter Polypropylene. Certified Clean	None	1,000 mls	7 days
PCB Congeners	EPA 1668	Water	2 Liter Amber Glass with Teflon lined cap. Certified clean	4'C. Residual chlorine will be tested at the lab upon receipt. If residual chlorine present, add 80 mg. Sodium Thiosulfate	1,000 mls	1 year
PCB Aroclors	SW 8082	Fish	Clean glass container or polyethylene bags	Stored frozen	20 grams	Stored frozen until extraction and analyzed within 40 days of extraction

Table 2-7
Analytical Methods, Detection Limits, and Control Limits

Analytical Parameter	Matrix	Proposed Laboratory	Analysis Methods	Laboratory SOP Number	Reporting Limit	Units
Aroclor 1016	Tissue	TBD	Method 8082	TBD	50	ug/kg
Aroclor 1221	Tissue	TBD	Method 8082	TBD	50	ug/kg
Aroclor 1232	Tissue	TBD	Method 8082	TBD	50	ug/kg
Aroclor 1242	Tissue	TBD	Method 8082	TBD	50	ug/kg
Aroclor 1248	Tissue	TBD	Method 8082	TBD	50	ug/kg
Aroclor 1254	Tissue	TBD	Method 8082	TBD	50	ug/kg
Aroclor 1260	Tissue	TBD	Method 8082	TBD	50	ug/kg
Lipids	Tissue	TBD	EPA 2000	TBD	0.1	%
TOC	Water	TBD	EPA 415.1	TBD	2	mg/L
TSS	Water	TBD	EPA 160.2	TBD	1	mg/L
PCB Congeners	Water	TBD	EPA 1668A	TBD	0.020 – 0.031 [See Table 2-8]	ng/L

Table 2-8
PCB Congener Reporting Limits

CAS Registry	Congener Number	Average EDL (ng/L)	Reporting Limit (ng/L)	Precision (%RPD) [1]	Accuracy (%R)
2051-60-7	1	0.00128	0.02	NA	50-150
2051-61-8	2	0.00114	0.02	NA	
2051-62-9	3	0.00105	0.02	NA	50-150
13029-08-8	4	0.01263	0.0314	NA	50-150
16605-91-7	5	0.0079	0.02	NA	
25569-80-6	6	0.00726	0.02	NA	
33284-50-3	7	0.00759	0.02	NA	
34883-43-7	8	0.0073	0.0269	NA	
34883-39-1	9	0.00763	0.02	NA	
33146-45-1	10	0.00783	0.02	NA	
2050-67-1	11	0.00755	0.0239	NA	
2974-92-7	12	0.0073	0.0259	NA	
2974-90-5	13	0.00729	0.0259	NA	
34883-41-5	14	0.00719	0.02	NA	
2050-68-2	15	0.00637	0.02	NA	50-150
38444-78-9	16	0.00731	0.02	NA	
37680-66-3	17	0.00589	0.02	NA	
37680-65-2	18	0.00487	0.0224	NA	
38444-73-4	19	0.00636	0.02	NA	50-150
38444-84-7	20	0.00216	0.02	NA	
55702-46-0	21	0.00223	0.02	NA	
38444-85-8	22	0.00234	0.02	NA	
55720-44-0	23	0.0024	0.02	NA	
55702-45-9	24	0.00427	0.02	NA	
55712-37-3	25	0.00203	0.02	NA	
38444-81-4	26	0.00224	0.02	NA	
38444-76-7	27	0.00416	0.02	NA	
7012-37-5	28	0.00216	0.02	NA	
15862-07-4	29	0.00224	0.02	NA	
35693-92-6	30	0.00487	0.0224	NA	
16606-02-3	31	0.0022	0.02	NA	
38444-77-8	32	0.00382	0.02	NA	
38444-86-9	33	0.00223	0.02	NA	
37680-68-5	34	0.00233	0.02	NA	
37680-69-6	35	0.00231	0.02	NA	
38444-87-0	36	0.00216	0.02	NA	
38444-90-5	37	0.00193	0.02	NA	50-150
53555-66-1	38	0.00221	0.02	NA	
38444-88-1	39	0.00205	0.02	NA	
38444-93-8	40	0.00226	0.02	NA	
52663-59-9	41	0.00226	0.02	NA	
36559-22-5	42	0.0025	0.02	NA	
70362-46-8	43	0.00207	0.02	NA	
41464-39-5	44	0.00203	0.02	NA	
70362-45-7	45	0.00236	0.02	NA	
41464-47-5	46	0.00275	0.02	NA	
2437-79-8	47	0.00203	0.02	NA	
70362-47-9	48	0.00226	0.02	NA	
41464-40-8	49	0.00193	0.02	NA	
62796-65-0	50	0.00227	0.02	NA	
68194-04-7	51	0.00236	0.02	NA	
35693-99-3	52	0.00217	0.02	NA	
41464-41-9	53	0.00227	0.02	NA	
15968-05-5	54	0.00342	0.02	NA	50-150

Table 2-8
PCB Congener Reporting Limits

CAS Registry	Congener Number	Average EDL (ng/L)	Reporting Limit (ng/L)	Precision (%RPD) [1]	Accuracy (%R)
74338-24-2	55	0.0017	0.02	NA	
41464-43-1	56	0.00168	0.02	NA	
70424-67-8	57	0.00167	0.02	NA	
41464-49-7	58	0.00163	0.02	NA	
74472-33-6	59	0.00164	0.02	NA	
33025-41-1	60	0.00165	0.02	NA	
33284-53-6	61	0.00158	0.02	NA	
54230-22-7	62	0.00164	0.02	NA	
74472-34-7	63	0.00156	0.02	NA	
52663-58-8	64	0.00164	0.02	NA	
33284-54-7	65	0.00203	0.02	NA	
32598-10-0	66	0.00155	0.02	NA	
73575-53-8	67	0.00146	0.02	NA	
73575-52-7	68	0.00151	0.02	NA	
60233-24-1	69	0.00193	0.02	NA	
32598-11-1	70	0.00158	0.02	NA	
41464-46-4	71	0.00226	0.02	NA	
41464-42-0	72	0.00161	0.02	NA	
74338-23-1	73	0.00207	0.02	NA	
32690-93-0	74	0.00158	0.02	NA	
32598-12-2	75	0.00164	0.02	NA	
70362-48-0	76	0.00158	0.02	NA	
32598-13-3	77	0.00145	0.02	NA	50-150
70362-49-1	78	0.00161	0.02	NA	
41464-48-6	79	0.00136	0.02	NA	
33284-52-5	80	0.00145	0.02	NA	
70362-50-4	81	0.0016	0.02	NA	50-150
52663-62-4	82	0.00358	0.02	NA	
60145-20-2	83	0.00371	0.02	NA	
52663-60-2	84	0.00362	0.02	NA	
65510-45-4	85	0.00256	0.02	NA	
55312-69-1	86	0.00257	0.02	NA	
38380-02-8	87	0.00257	0.02	NA	
55215-17-3	88	0.00319	0.02	NA	
73575-57-2	89	0.00346	0.02	NA	
68194-07-0	90	0.00268	0.02	NA	
68194-05-8	91	0.00319	0.02	NA	
52663-61-3	92	0.00324	0.02	NA	
73575-56-1	93	0.00313	0.02	NA	
73575-55-0	94	0.00342	0.02	NA	
38379-99-6	95	0.00313	0.02	NA	
73575-54-9	96	0.00238	0.02	NA	
41464-51-1	97	0.00257	0.02	NA	
60233-25-2	98	0.00318	0.02	NA	
38380-01-7	99	0.00255	0.02	NA	
39485-83-1	100	0.00313	0.02	NA	
37680-73-2	101	0.00268	0.02	NA	
68194-06-9	102	0.00318	0.02	NA	
60145-21-3	103	0.00293	0.02	NA	
56558-16-8	104	0.00231	0.02	NA	50-150
32598-14-4	105	0.00141	0.02	NA	50-150
70424-69-0	106	0.00157	0.02	NA	
70424-68-9	107	0.00139	0.02	NA	
70362-41-3	108	0.00154	0.02	NA	

Table 2-8
PCB Congener Reporting Limits

CAS Registry	Congener Number	Average EDL (ng/L)	Reporting Limit (ng/L)	Precision (%RPD) [1]	Accuracy (%R)
74472-35-8	109	0.00257	0.02	NA	
38380-03-9	110	0.00227	0.02	NA	
39635-32-0	111	0.00218	0.02	NA	
74472-36-9	112	0.00255	0.02	NA	
68194-10-5	113	0.00268	0.02	NA	
74472-37-0	114	0.00125	0.02	NA	50-150
74472-38-1	115	0.00227	0.02	NA	
18259-05-7	116	0.00256	0.02	NA	
68194-11-6	117	0.00256	0.02	NA	
31508-00-6	118	0.00131	0.02	NA	50-150
56558-17-9	119	0.00257	0.02	NA	
68194-12-7	120	0.0021	0.02	NA	
56558-18-0	121	0.00229	0.02	NA	
76842-07-4	122	0.00162	0.02	NA	
65510-44-3	123	0.0013	0.02	NA	50-150
70424-70-3	124	0.00154	0.02	NA	
74472-39-2	125	0.00257	0.02	NA	
57465-28-8	126	0.00159	0.02	NA	50-150
39635-33-1	127	0.00143	0.02	NA	
38380-07-3	128	0.0022	0.02	NA	
55215-18-4	129	0.00225	0.02	NA	
52663-66-8	130	0.00286	0.02	NA	
61798-70-7	131	0.00288	0.02	NA	
38380-05-1	132	0.00281	0.02	NA	
35694-04-3	133	0.00264	0.02	NA	
52704-70-8	134	0.00288	0.02	NA	
52744-13-5	135	0.00405	0.02	NA	
38411-22-2	136	0.003	0.02	NA	
35694-06-5	137	0.00215	0.02	NA	
35065-28-2	138	0.00225	0.02	NA	
56030-56-9	139	0.00242	0.02	NA	
59291-64-4	140	0.00242	0.02	NA	
52712-04-6	141	0.00256	0.02	NA	
41411-61-4	142	0.00283	0.02	NA	
68194-15-0	143	0.00288	0.02	NA	
68194-14-9	144	0.00396	0.02	NA	
74472-40-5	145	0.00307	0.02	NA	
51908-16-8	146	0.00232	0.02	NA	
68194-13-8	147	0.00233	0.02	NA	
74472-41-6	148	0.00404	0.02	NA	
38380-04-0	149	0.00233	0.02	NA	
68194-08-1	150	0.00294	0.02	NA	
52663-63-5	151	0.00405	0.02	NA	
68194-09-2	152	0.0029	0.02	NA	
35065-27-1	153	0.00198	0.02	NA	
60145-22-4	154	0.00347	0.02	NA	
33979-03-2	155	0.00281	0.02	NA	50-150
38380-08-4	156	0.00175	0.02	NA	50-150
69782-90-7	157	0.00175	0.02	NA	50-150
74472-42-7	158	0.00172	0.02	NA	
39635-35-3	159	0.00181	0.02	NA	
41411-62-5	160	0.00201	0.02	NA	
74472-43-8	161	0.00188	0.02	NA	
39635-34-2	162	0.00181	0.02	NA	

Table 2-8
PCB Congener Reporting Limits

CAS Registry	Congener Number	Average EDL (ng/L)	Reporting Limit (ng/L)	Precision (%RPD) [1]	Accuracy (%R)
74472-44-9	163	0.00225	0.02	NA	
74472-45-0	164	0.00215	0.02	NA	
74472-46-1	165	0.00205	0.02	NA	
41411-63-6	166	0.0022	0.02	NA	
52663-72-6	167	0.00154	0.02	NA	50-150
59291-65-5	168	0.00198	0.02	NA	
32774-16-6	169	0.00174	0.02	NA	50-150
35065-30-6	170	0.00198	0.02	NA	
52663-71-5	171	0.00255	0.02	NA	
52663-74-8	172	0.00258	0.02	NA	
68194-16-1	173	0.00255	0.02	NA	
38411-25-5	174	0.00239	0.02	NA	
40186-70-7	175	0.00229	0.02	NA	
52663-65-7	176	0.00182	0.02	NA	
52663-70-4	177	0.00256	0.02	NA	
52663-67-9	178	0.00246	0.02	NA	
52663-64-6	179	0.0018	0.02	NA	
35065-29-3	180	0.00167	0.02	NA	
74472-47-2	181	0.00239	0.02	NA	
60145-23-5	182	0.00232	0.02	NA	
52663-69-1	183	0.00229	0.02	NA	
74472-48-3	184	0.00169	0.02	NA	
52712-05-7	185	0.00229	0.02	NA	
74472-49-4	186	0.00184	0.02	NA	
52663-68-0	187	0.00217	0.02	NA	
74487-85-7	188	0.00176	0.02	NA	50-150
39635-31-9	189	0.0016	0.02	NA	50-150
41411-64-7	190	0.00185	0.02	NA	
74472-50-7	191	0.0018	0.02	NA	
74472-51-8	192	0.00195	0.02	NA	
69782-91-8	193	0.00195	0.02	NA	
35694-08-7	194	0.00209	0.02	NA	
52663-78-2	195	0.00229	0.02	NA	
42740-50-1	196	0.00313	0.02	NA	
33091-17-7	197	0.00229	0.02	NA	
68194-17-2	198	0.00311	0.02	NA	
52663-75-9	199	0.00311	0.02	NA	
52663-73-7	200	0.00229	0.02	NA	
40186-71-8	201	0.00228	0.02	NA	
2136-99-4	202	0.00241	0.02	NA	50-150
52663-76-0	203	0.00287	0.02	NA	
74472-52-9	204	0.00235	0.02	NA	
74472-53-0	205	0.00146	0.02	NA	50-150
40186-72-9	206	0.00146	0.02	NA	50-150
52663-79-3	207	0.00132	0.02	NA	
52663-77-1	208	0.00127	0.02	NA	50-150
2051-24-3	209	0.00096	0.02	NA	50-150

Notes:

[1] MS/MSD or LCS/LCSD not required by method

NA = Not applicable.

RPD = Relative percent difference.

Table 2-9
Quality Control Criteria – Standard Analyses

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
EPA Method 8082 w/ WSLOH Modification[1]	Aroclors 1016/1260	Five-point initial calibration (ICAL)	Initial calibration prior to sample analysis	Calibration factor of each peak < 20 % RSD	Correct problem, then repeat initial calibration
	Aroclors, 1221, 1232, 1242, 1248, 1254	One point midrange calibration standard	With each Aroclor 1016/1260 initial calibration	Calibration is acceptable if Aroclor 1016 and 1260 meet acceptance criteria.	None, use response factor from mid-range standard to quantify Aroclor if present
	All Aroclors	Qualitative match for Aroclor Identification	Every sample	Minimum 5 peak match for all Aroclors except Aroclor 1221 (3 peak match)	None, do not report as detected Aroclor
	All Aroclors	Retention time window	Each calibration verification	ICAL mean RT + 0.03 minutes	Correct problem, then reanalyze all samples analyzed since the last retention time check
	Aroclors 1016/1260	Calibration verification	After every 10 samples	Average RF of > 5 peaks < 15 % difference from ICAL mean RF	Correct problem, then repeat initial calibration verification and reanalyze all samples since last successful calibration verification
	Aroclors 1016/1260	Ending calibration verification	After all samples analyzed	Average RF of > 5 peaks < 15 % difference from ICAL mean RF	If sensitivity increased > 15 %, no reanalysis of undetected samples needed. If sensitivity decreased > 15 %, reanalyze samples.
	All Aroclors	Method blank (MB)	One per analytical batch of 20 samples or less	No analytes detected > RL	Correct problem, then repeat prep and analysis of method blank and all samples with detects < 20 X MB processed with the contaminated blank
	Aroclors 1254	LCS	One LCS per analytical batch of 20 samples or less	40-128%	Assess all other batch QC for same bias, if consistent bias present, repeat prep and analysis of LCS and all samples in the affected analytical batch
	All Aroclors	Surrogate spikes (TCMX, DCB)	Every sample, spiked sample, standard, and method blank	TCMX 40-136% DCB 47-145%	If both TCMX and DCB out of limit, re-extract and re-analyze sample
	Aroclor 1254	MS/MSD	One MS/MSD per every 20 project samples	43-130% recovery 56% RPD	If recovery is out of limit, qualify data and note in case narrative suspected matrix problem
	All Aroclors	Field Duplicates	Submitted blind to lab	< 35 % RPD	May request analysis of additional aliquot(s), data qualified as estimated during validation

1. The OU1 QAPP specifies analysis of PCB Aroclors in fish extract using the USEPA Method 8082.

Table 2-9
Quality Control Criteria – Standard Analyses

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
EPA Method 415.1	TOC (water)	Method Blank	1 with each batch of samples processed not to exceed 20 samples	Absolute value < RL of 2 mg/L, if sample level > 20 x MB, no action	Rerun all samples associated with unacceptable blank. If MB > MDL < RL, qualify sample levels < 20 x MB with "A"
	TOC (water)	Laboratory Control Sample	1 with each batch of samples processed not to exceed 20 samples	Percent recovery must be within laboratory control limits 80-120%	If not within laboratory control limits, rerun all associated samples
	TOC (water)	MS/MSD	1 per 10 samples, minimum of one per batch of samples processed	Percent recovery must be within laboratory control limits 80 -120% RPD < 20%	Flag data outside of limit
	TOC (water)	Update calibration factor with 3 standard plus blank.	Initially and as needed when calibration failures occur	See instrument manual	Correct problem, then repeat initial calibration
	TOC (water)	ICV	1 mid-level at beginning of every analytical run	± 10% of true value	Correct problem, then repeat calibration verification and reanalyze all samples not bracketed by an acceptable ICV
	TOC (water)	ICB	Immediately after ICV	Absolute value < RL of 2 mg/L	Correct problem, then repeat calibration verification and reanalyze all samples not bracket by acceptable ICB
	TOC (water)	CCV	1 mid-level every 10 samples	± 10% of true value	Correct problem, then reanalyze all samples not bracketed by an acceptable CCV
	TOC (water)	CCB	Immediately after CCV	Absolute value < RL of 2 mg/L. If sample level >10 x CCB, no action	Correct problem, then reanalyze all samples not bracketed by an acceptable CCB
	TOC (water)	Field Duplicate	Submitted blind to lab	<30% RPD	May request analysis of additional aliquot(s), data qualified as estimated during validation
EPA Method 160.2	Total suspended solids	Method Blank	1 with each batch of samples processed not to exceed 20 samples	< + RL	Reanalyze all samples associated with unacceptable MB
	Total suspended solids	Laboratory Control Sample	1 with each batch of samples processed not to exceed 20 samples	80-120%	Reanalyze all samples associated with unacceptable LCS
	Total suspended solids	Duplicate	1 with each batch of samples processed not to exceed 10 samples	< 10% RPD when results >5xs RL	Flag Parent result with appropriate qualifier

Table 2-10
Quality Control Criteria – PCB Congeners

Analytical Method	Calibration/ QC Check	Frequency	Acceptance Criteria	Corrective Action
EPA Method 1668, Revision A	Check of mass resolution mass accuracy (PFK) and gc performance	Every 12 hours	1) > 10,000 resolving power 2) < 5 ppm deviation from reference mass 3) < 40 % valley between PCBs 34 and 23 4) < 40 % valley between PCBs 187 and 182	1) Retune or service GC/MS system 2) Repeat check
	Initial 6-point calibration	Initially and as needed	1) %RSD for CCCs calculated by isotope dilution - < 20% 2) %RSD for CCCs calculated by internal standard - < 35% 3) %RSD for Labeled congeners calculated by internal standard - < 35%	1) Identify the root cause 2) Perform corrective action 3) Repeat the initial calibration
	Continuing calibration verification (CCV):	Every 12 hours	1) > 10,000 resolving power 2) < 5 ppm deviation from reference mass % D <20% for CCCs 3) Ion abundance ratios within limit in 1668A Table 8. 4) S/N > 10 for all targets and internal standards 5) %D for all target PCBs < 30% 6) % D for labeled internal standards < 50%	1) If %D > 30% for non-toxic/locs, but is < 60%, use shift response factor 2) Evaluate system, service as required 3) Repeat calibration check 4) Perform new initial calibration 5) Reanalyze affected samples
	Labeled congeners/internal standards	Twenty-eight 13C-labeled congeners added to every sample, QA sample, standard	1) %Recovery 30-140% on LCSs 2) %Recovery > 25% on samples, blanks	1) Check all calculations for error 2) Ensure that instrument performance is acceptable 3) Recalculate the data and/or reanalyze if either of the above checks reveal a problem 4) If any recovery is < 25%, evaluate labeled congener S/N and EDLs. If S/N > 10 and EDL< EML, report with qualifiers and discuss in narrative
	Method blank	One per batch of not more than 20 samples	1) Control method blank contamination to <0.2 ng/L total PCBs 2) Individual target compounds should be: - Less than the RL, or - Less than 10% of measured concentration in the associated sample, or - Not present in the associated sample 3) Verify that samples were analyzed in order from anticipated low to high concentrations [See Section 2.6.1.3 of the Plan] [Note: Blank correction procedures described in Section 4.2.2 of the Plan]	1) Service system/glassware to reduce lab contamination 2) Notify Data Quality Assurance Manager (QAM) 3) Reanalyze blank and all affected samples as directed by Data QAM and A/OT
	Ongoing Precision and Recovery (OPR)	One per batch of not more than 20 samples	1) All criteria specified in Table 6 of Method 1668A	1) Corrective action required may include: Re-extraction and Re-analysis of LCS and associated samples If batch is not re-extracted reasons for acceptance must be clearly presented in the project records and report If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints the OPR is reported and the failure is documented in the project narrative

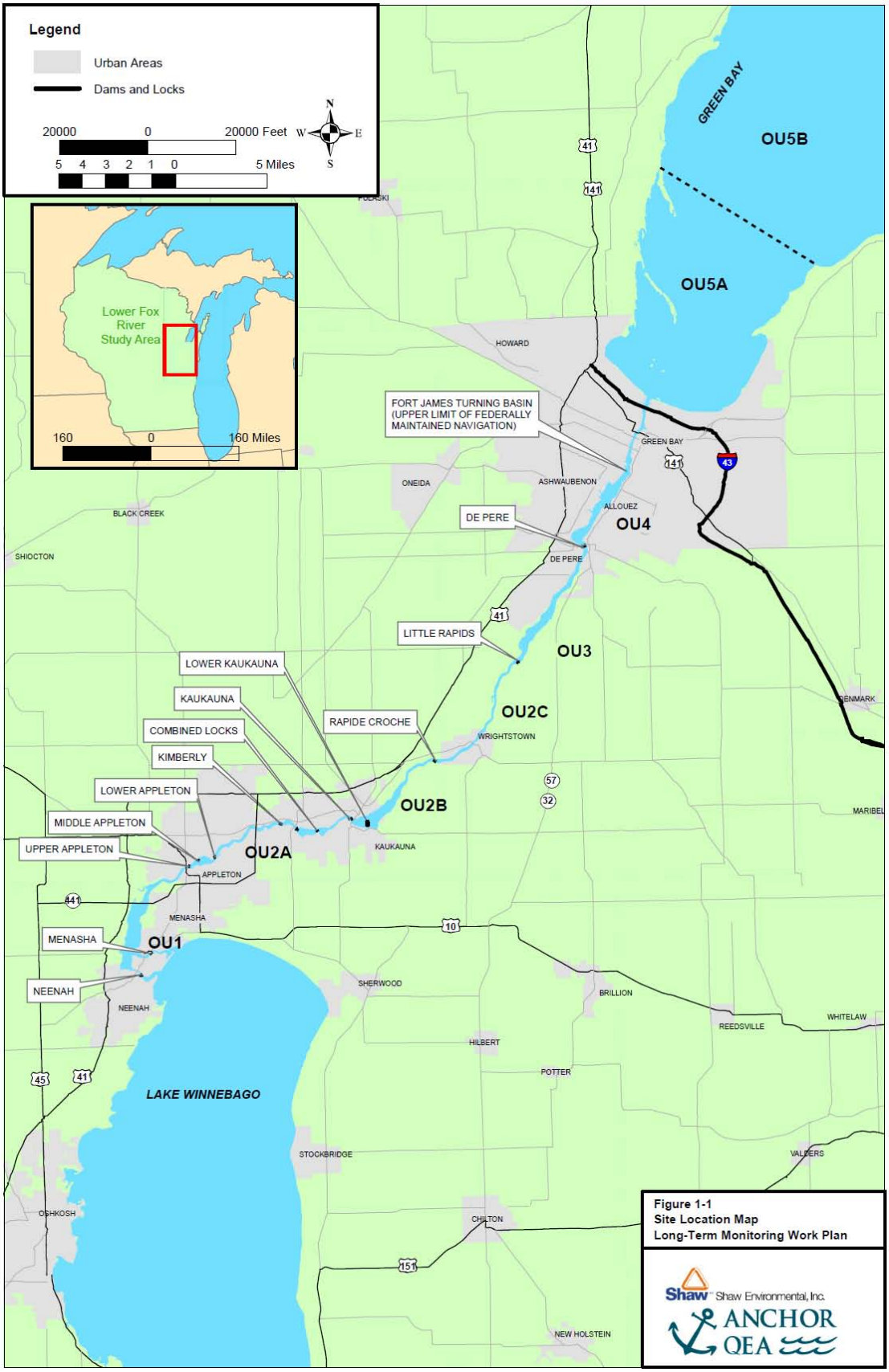


Figure 1-1
Site Location Map
Long-Term Monitoring Work Plan

Shaw Shaw Environmental, Inc.
ANCHOR QEA

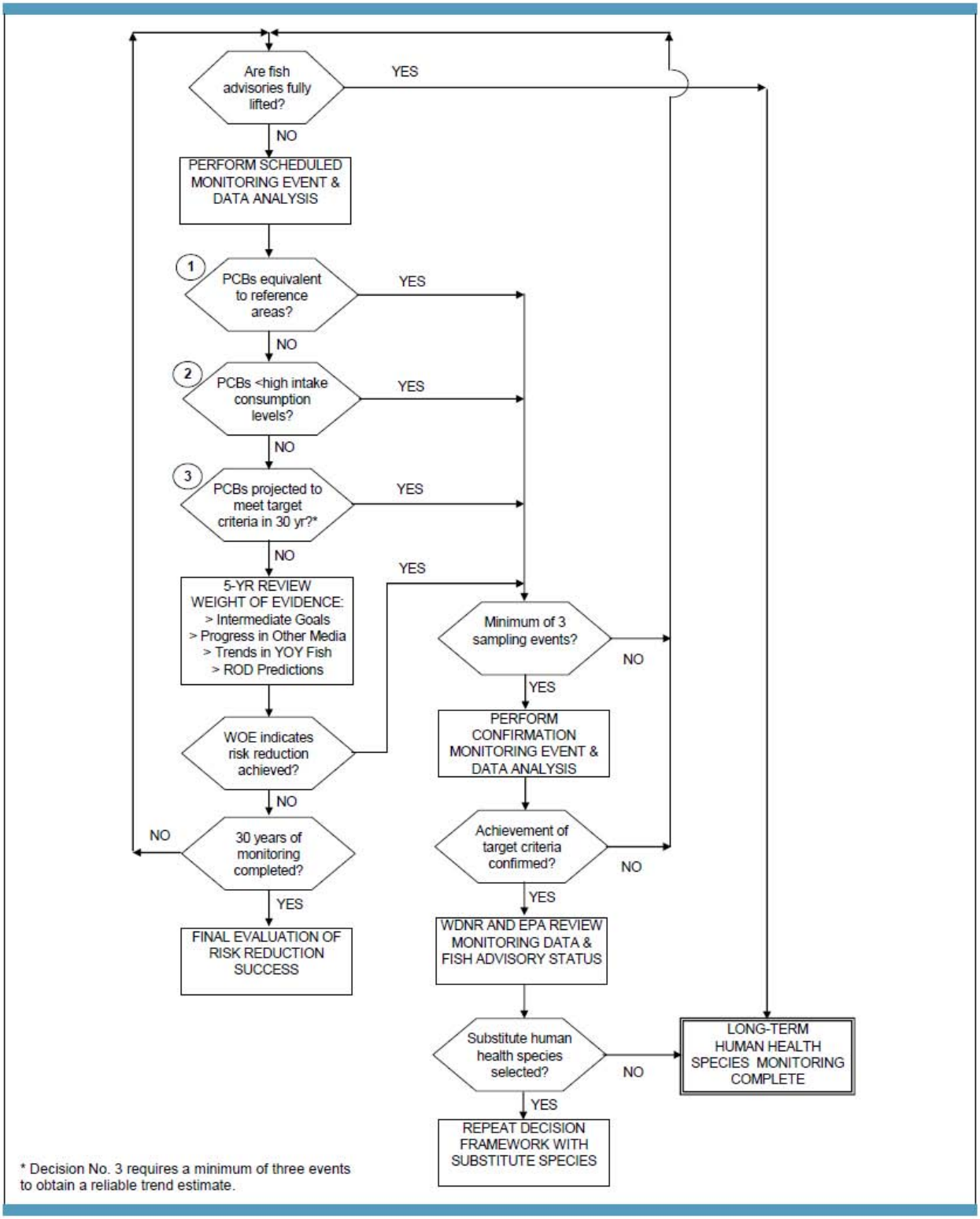


Figure 1-4

Decision Framework for Human Health Fish Species
Long-term Monitoring Plan
Lower Fox River

ANCHOR QEA

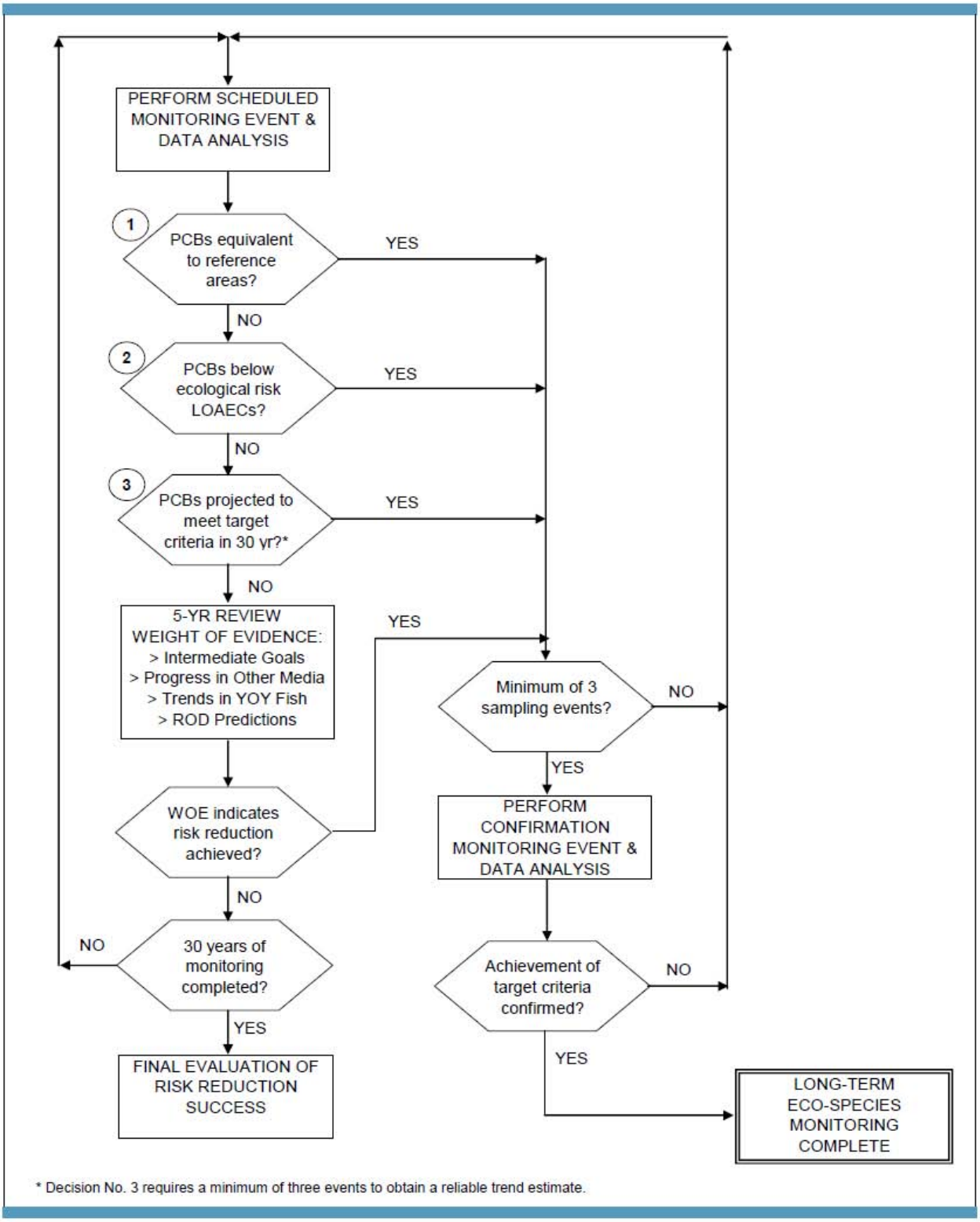
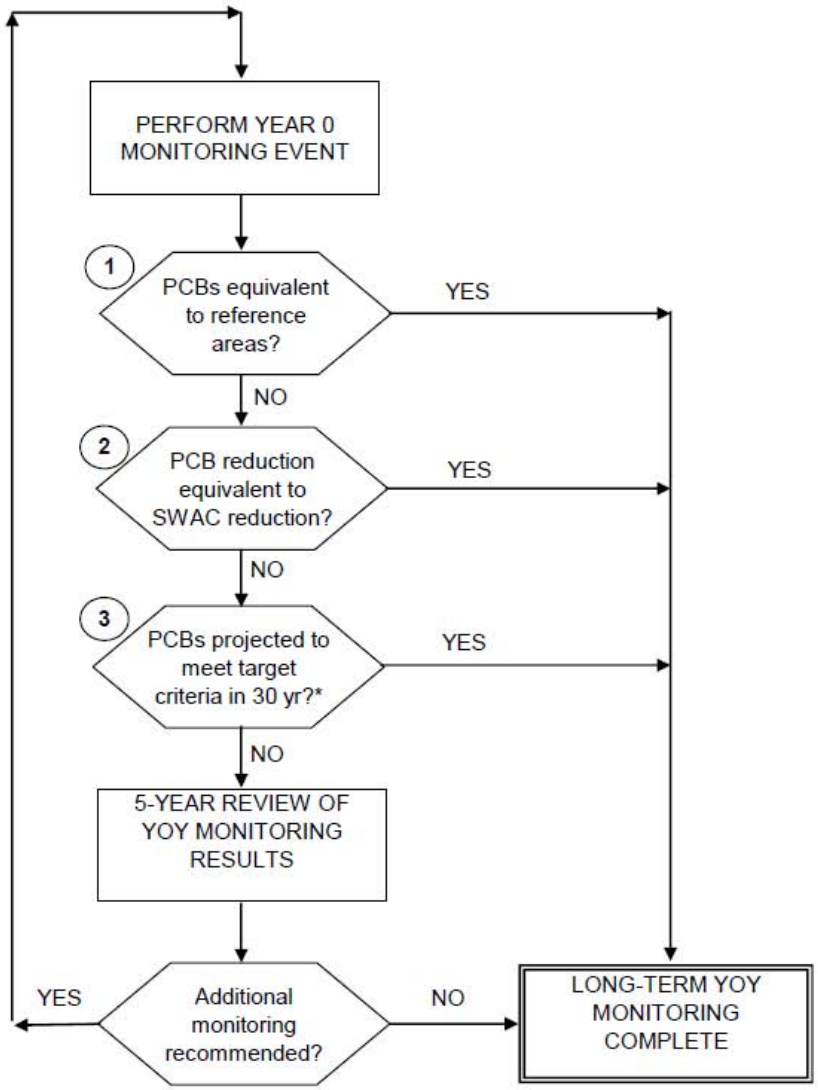


Figure 1-5
Decision Framework for Ecological Fish Species
Long-term Monitoring Plan
Lower Fox River

ANCHOR QEA



* Decision No. 3 requires a minimum of three events to obtain a reliable trend estimate.

Figure 1-6
Decision Framework for Young-of-Year Fish Species
Long-term Monitoring Plan
Lower Fox River

ANCHOR QEA

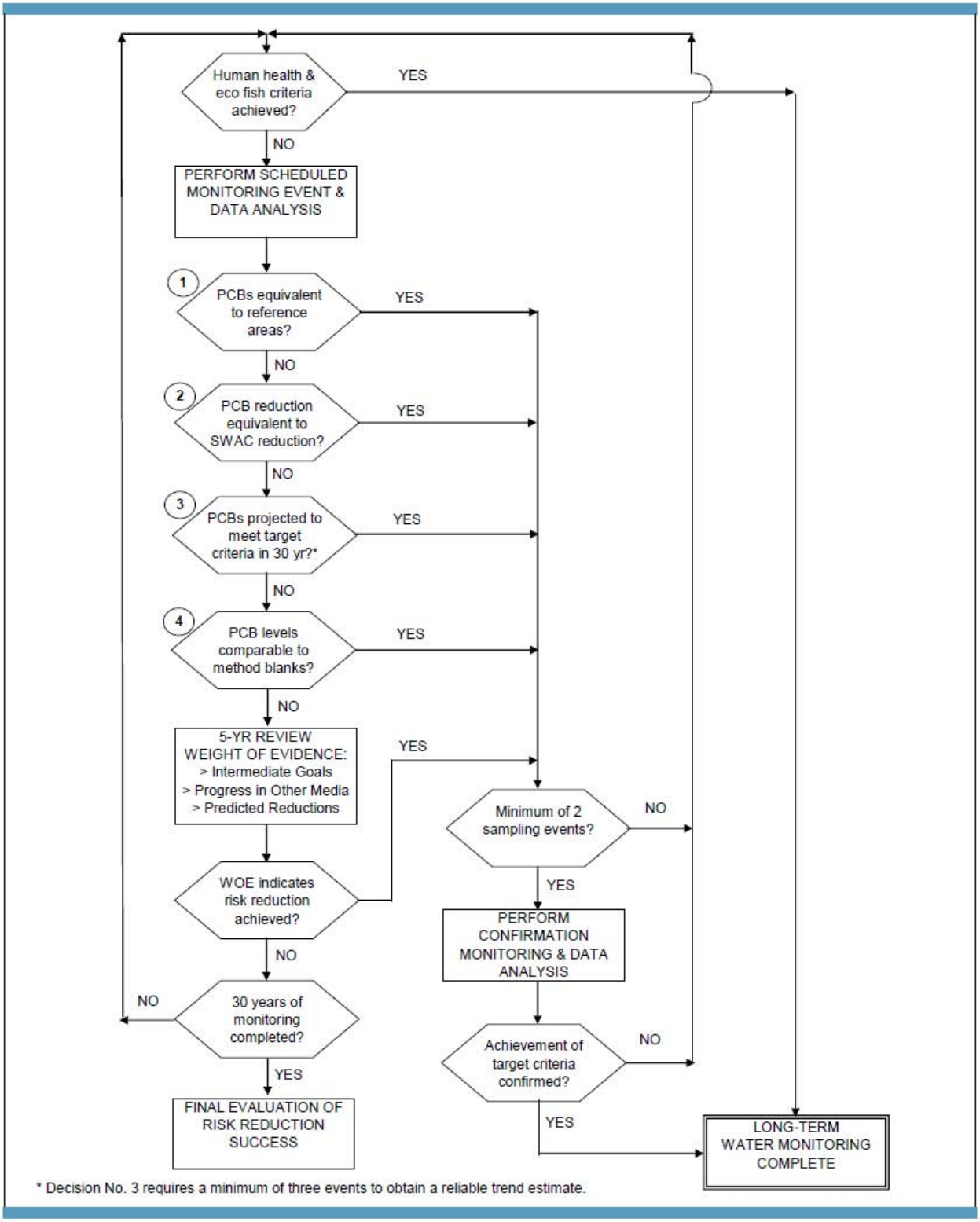


Figure 1-7
Decision Framework for Water Quality
Long-term Monitoring Plan
Lower Fox River

ANCHOR QEA

Legend

Water Quality Monitoring Stations

Water Sampling Location and Transect

Suggested Fishing Areas

Fall (Aug - Oct)

W = Walleye
B = Smallmouth Bass
D = Drum
C = Carp
G = Gizzard Shad

Spring (Jun)

w = Walleye
b = Smallmouth Bass
d = Drum
c = Carp

Note: June event is a contingency and is not anticipated.

Physical Features

Dock - Source: OSI 1998

Boat Landing

USACE Channel Definition

Dams

Shoreline

Water Depth Contour - 10-Foot Interval

Water Depth Contour - 2-Foot Interval

12000 0 12000 Feet

N W E S

OU1
JEFFERSON PARK
C
LW
DOTY PARK
PARK AVENUE
OSH-O-NEE
w,b,d
w,d
LAKE WINNEBAGO
SHERMAN ROAD
MURDOCK AVENUE
D,C,G
MILL STREET
FUGLEBURG
24TH AVENUE
G
W,D
D,C,G
b
b,d
NAGY PARK
COUNTY LINE ROAD
G
10
41
45
151
12
18
6

Figure 2-2
Lake Winnebago Sampling Stations
Long-Term Monitoring Work Plan

Shaw Shaw Environmental, Inc.
ANCHOR QEA

Legend

Water Quality Monitoring Stations

Water Sampling Location and Transect

Suggested Fishing Areas

Fall (Aug - Oct)

W = Walleye
B = Smallmouth Bass
D = Drum
C = Carp
G = Gizzard Shad

Spring (Jun)

Note: June event is a contingency and is not anticipated.

w = Walleye
b = Smallmouth Bass
d = Drum
c = Carp

Physical Features

Dock - Source: OSI 1998

Boat Landing

USACE Channel Definition

Dams

Shoreline

Water Depth Contour - 10-Foot Interval

Water Depth Contour - 2-Foot Interval

2000 0 2000 Feet

N W E S

LUTZ PARK
B,D,C
OU1
47
10
W,C
NINTH STREET
FRITZE PARK
W,D,C
B,C
114
LOCK STREET
JEFFERSON PARK
MENASHA DAM
TAYCOST
Lake Winnebago
W,B,D,C,G
DOTY PARK
NEENAH DAM
WINNECONNEAVE

Figure 2-3
Operable Unit 1 Sampling Stations
Long-Term Monitoring Work Plan

Shaw™ Shaw Environmental, Inc.
ANCHOR QEA

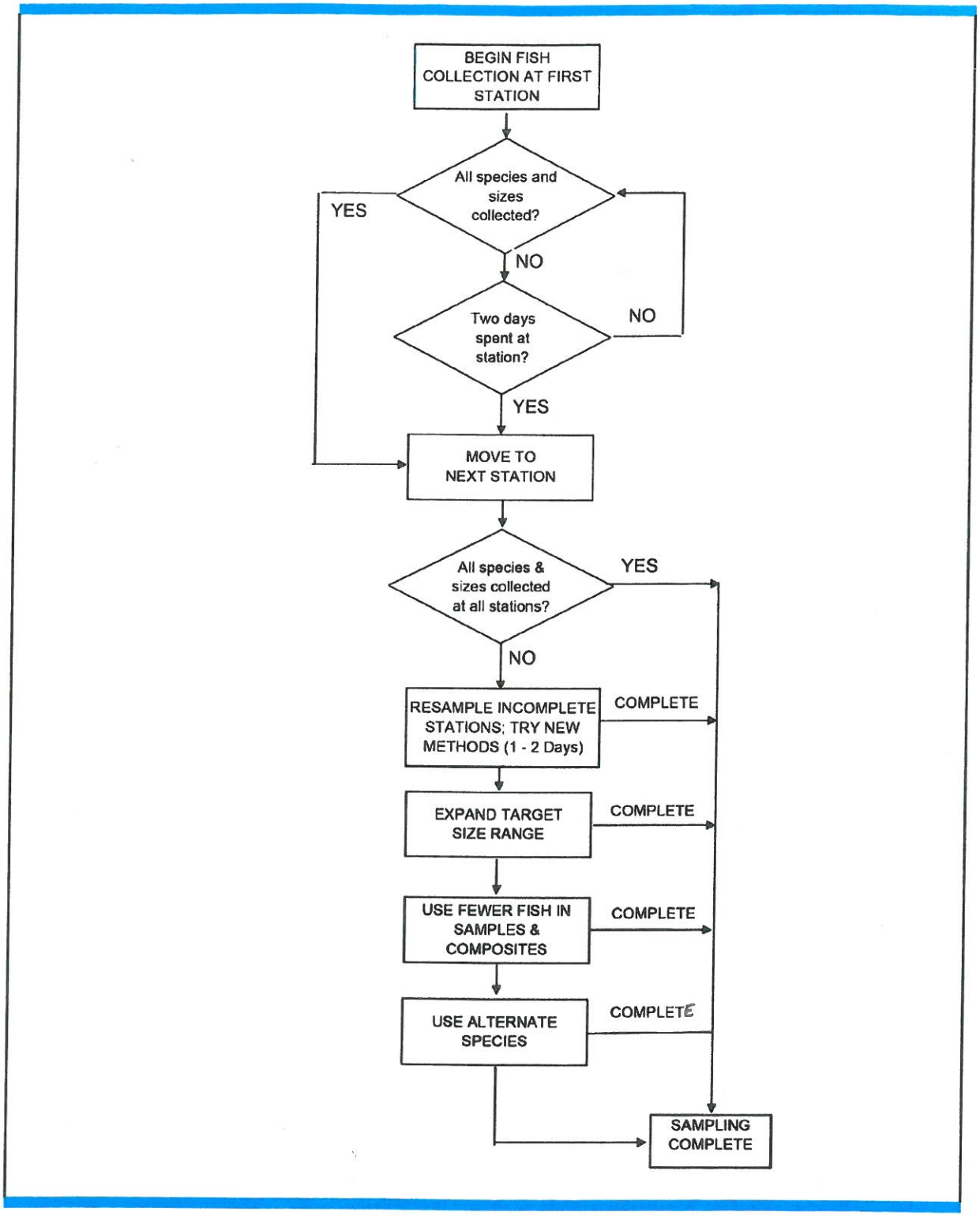


Figure 3-1
Field Decision Flow Chart for Fish Sampling
Long-term Monitoring Plan
Lower Fox River Remedial Design

Appendix B

Field Standard Operating Procedures

1. Location Control
2. Fish Collection
3. Sample Chain of Custody
4. Field Log Book
5. Water Quality Meter Use
6. Trace PCB Sampling of Surface Water
7. Shipping and Packaging of Non-Hazardous Samples

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Standard Operating Procedure

Location Control

Introduction

To meet the goals of water quality monitoring activities during the long-term monitoring, specifically for collection of water column samples for low-level polychlorinated biphenyls (PCB) congener analysis, precise positioning of vessel location is required. Both accuracy (i.e., ability to define position) and repeatability (i.e., ability to return to sample station) are essential. Positioning for all surveys and sampling techniques will be achieved using a handheld global positioning system (GPS) unit with differential GPS (DGPS) software capable of locating stations to within an accuracy and repeatability of ± 1 meter.

Water quality monitoring stations will be located to within a target accuracy of 2 meters. Fish tissue monitoring stations will be located using the same equipment; however, they will be located to within a target accuracy of 10 meters. Because fish migrate freely within an Operable Unit (OU), location control requirements are less stringent for fish collection.

Responsibility

The Field Supervisor will be responsible for ensuring the navigation system is checked against known benchmarks and location control data is collected at the required times and frequencies as specified in this Standard Operating Procedure (SOP).

Equipment and Supplies

For water column sampling during baseline monitoring, navigation of the sampling vessels to the predetermined sampling locations and maintaining a final position will be accomplished using a handheld Trimble 2005 GEOXT DGPS navigation system; this unit is specified to provide sub-meter accuracy. This DGPS unit is capable of using either U.S. Coast Guard beacons or Wide Area Augmentation System (WAAS) to achieve the required accuracy. The sampling team will also verify position with the Trimble 2005 GEOXT DGPS. Water surface elevation or vertical accuracy is not required for these sampling activities.

Survey Datum

Location control for all sample stations will use the Wisconsin Transverse Mercator (WTM) coordinate system referenced to the 1997 adjustments to the North American Datum (NAD) 83 (97) horizontal datum (i.e., WTM 83 [97]). The DGPS system will be referenced to the new Fox River monuments that were established by the Wisconsin Department of Natural Resources (WDNR) in 2003 (or an alternate monument that is tied to the same coordinate system and documented). These monuments were established using North American Vertical Datum (NAVD) 88 vertical datum and the WTM 83 (97) horizontal coordinate system.

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Procedures for Positioning Sample Vessel

- Prior to vessel departure at each transact, a calibration check shall be taken at the two known benchmarks nearest the transect(s) to be sampled. The acceptable tolerance for the benchmark check with the handheld DGPS unit shall be twice the instrument accuracy, or +/- 2 meters. These readings shall be recorded in a project field book by a project team member and stored electronically for later download. Location readings shall be recorded and compared to published values.

- Sample locations for each transect are from Table 2-2, Water Sample Locations, of the *Lower Fox River Baseline Monitoring Plan* (Shaw and Anchor, 2006).

- The vessel navigation and sample station positioning shall be accomplished using the DGPS methodology and the handheld display. Actual coordinates of sample station starting position shall be recorded by a project team member and stored electronically for later download. Location readings and time shall be recorded.

- The position of the DGPS unit on the vessel shall be as close to the sampling team as possible during water quality monitoring activities without compromising field operations, worker safety, or sample integrity (i.e., potential for cross-contamination).

- At a minimum, DGPS locations shall be recorded at the beginning and end of each hydrocast during water column profiling, and at the beginning and end of each subsampling event at a particular location and depth along a sampling transect (i.e., each transect consists of six subsamples, per U.S. Geological Survey (USGS) quarter-point sampling procedures). For prolonged sampling activities, intermediate DGPS location readings shall also be taken at approximately two minute intervals (more frequently if possible). These readings shall be recorded in a project field book by a project team member and stored electronically for later download. Location readings and time shall be recorded.

- After each sampling transect event, a calibration check shall be taken at one of the pre-determined benchmarks. This reading shall be recorded and compared to published values.

Measurement Tolerance

The field checks of DGPS locations against know benchmarks will be evaluated using the following tolerance intervals:

- Less than or equal to 2 meters – Accuracy within project control limits;

- >2 to 5 meters – Acceptable accuracy, locations of associated water sampling locations will be qualified as estimated;

- >5 meters – Unacceptable accuracy, corrective action required (see next section).

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Corrective Action

In the event the DGPS unit fails to agree to within 5 meters of the known locations at the two benchmarks assigned to a particular water sampling station, the following corrective actions will be implemented:

- Check the DGPS unit against an alternate benchmark in case the original benchmark is compromised by interference, obstruction, or other signal deterioration;
- Wait for a stronger satellite signal and re-check the unit; and
- Obtain and check a new DGPS unit.

References

Shaw Environmental & Infrastructure, Inc. and Anchor QEA, LLC. 2006. *Lower Fox River Baseline Monitoring Plan*. June 2006.

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Standard Operating Procedure

Fish Collection

Introduction

The predominant method of fish collection will be electrofishing. Gill netting, hook and line or trawling may be substituted. Fish will be composited according to the approved compositing plans outlined in the *Lower Fox River Operable Unit 1 – OU1-Long-term Monitoring Plan* (Foth and CH2M HILL, 2011).

Responsibility

Prior to electrofishing, the Field Supervisor will verify that all crew members will have reviewed and become familiar with the site *Health and Safety Plan* (Foth, 2011) (HASP)) in regards to boat and electrofisher operations. At all times that the boat is actively electrofishing, all crew members will wear rubber boots and the netters will wear rubber gloves rated for 5,000-volt protection.

Electrofishing activities will be conducted by a crew of three. The Field Supervisor will be in charge of all sampling activities. Two additional crew members will participate in the boat operation and/or dipnetting activities.

Equipment and Supplies

Fish will be collected using a boat of appropriate length and draft for site conditions fitted with a Coffelt VVP-15 electrofisher (or equivalent) to collect fish from shoreline habitats and shallow water shoals (generally less than 10 feet deep) in areas adjacent to deep water or the main channel. The Coffelt VVP-15 (or equivalent) can be set to 20-120 pulses per second (pps). Specifications of the boat and electrofishing equipment are presented in Table 1.

All vessels will have up to date U.S. Coast Guard-approved and required safety equipment, personal floatation devices (PFD), fire extinguishers, marine 5-watt output VHF communications equipment, and other equipment as described in the *HASP*. All personnel onboard vessels engaged in nighttime activities will wear attached strobe lights to their PFDs.

Prior to each water deployment, the Field Supervisor will confirm adequate cell phone signal and confirm the appropriate way to contact emergency personnel. Additionally, prior to the inception of work, Field Supervisor will coordinate with onsite Project Manager, or designee via cell phone or handheld radio, the location and duration of planned activities and confirm the Project Manager or designee is available for assistance in an emergency situation.

Prior to electrofishing the Field Supervisor will check through the materials and equipment check list to ensure that all gear is accounted for and in good working order and that all boat equipment required by the *HASP* are on board the vessel. The boat and electrofisher specifications are provided in Table 1.

Table 1

Boat and Electrofishing Equipment Specifications

Boat	Electrofisher	Other Equipment
Lowe Roughneck 2007 aluminum Jon boat	Coffelt VVP-15	Bow and stem-mounted safety switches
Length: 19.5 feet	Volts DC: 600	Circular ring and dropper electrodes:
Beam: 85 inch	Pulse/second: 20-120	Bow and stem mounted collection lights
Depth: 21 in / .53 m	Pulse width: 1-7 ms	Navigation lights
Max capacity: 898 lb /568 kg	Generator: 5,000 watt	Deck work lights
Bare hull weight: 277 lb / 126 kg		Fiberglass-insulated scapping nets
Engine: 2005 Mercury 40 hp		USGS-required safety equipment
VHF marine radio: 5-watt output		100-g aerated live well
Garmin eTrex Vista HCx		

Specific electrofishing equipment will include:

- Coffelt VVP-15 with extra fuses
- Generator rated at least 4,500-watts output
- Generator to electrofisher power cord
- Foot operated voltage cut-off safety switches
- Electrofisher output power cord
- Electrode array
- Fiberglass handle dip nets
- Sets of rubber gloves rated for 5,000 volts
- Pairs of rubber boots
- 100-gallon live well
- Headlamps
- Extra lights for night electrofishing
- Handheld spotlight

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Collection Procedures

Electrofishing

Electrofishing will be conducted at night to obtain the necessary sample sizes of each target fish species.

The electrofishing unit will be fished in a downstream direction, where appropriate. Collection procedures are as follows:

- Position the boat upstream (or downstream if needed) of the station.
- Adjust electrofisher volts, pulse rate, and pulse width settings to maintain an average 4-5 amp output.
- Record water temperature, air temperature, weather conditions, conductivity, and the electrical output of the electrofishing unit.
- Record the starting location of electrofishing station using a handheld global positioning system (GPS) unit with differential GPS (DGPS) software capable of delivering submeter accuracy (see *Location Control* Standard Operating Procedure [SOP]).
- Place the boat in gear, turn on the electrofishing unit and collection lights, record the start time, and proceed at a slow speed along the collection area. Use the boat to position the electrode array near any instream cover such as overhanging vegetation, instream trees, rocky substates, etc.
- All target species within reach of the netter will be captured and placed in a 100-gallon holding tank.
- At the end of electrofishing, place the boat in neutral, turn off the electrofisher and collection lights, record the stop time and the end location from the GPS.

Electrofishing will be conducted from August 15 to September 15 of each collection year and may be extended through October 15 to fill data gaps. Collections will be conducted over the course of five nights each week (i.e., one stations per night) until the number of target species are met.

Gill Netting

Gill net sampling activities will be conducted by a crew of three. A Field Supervisor will be in charge of all sampling activities. Two additional crew members will participate in the sampling activities.

Prior to Gill netting all crew members will have reviewed and be familiar with the site *HASP* in regards to boat operations. Gill nets will be used to sample in water depths up to approximately 30 feet, primarily in areas with slow to moderate current adjacent to deep water or the main river channel.

Equipment

Gill nets will have the following specifications:

- 100 to 300 feet long x 1.0 – 3.0 inch bar mesh

Netting will be treated with a black UV protectant and algaecide. The siuicing Gill nets will be anchored at both ends. All anchors will have an attached float with the name and address of the group deploying the nets along with the Scientific Collectors License number.

All vessels will have up to date U.S. Coast Guard-approved and required safety equipment, PFD, fire extinguishers, marine 5-watt output VHF communications equipment, and other equipment as described in the HASP. All personnel onboard vessels engaged in nighttime activities will wear attached strobe lights to their PFDs.

Prior to Gill netting, the Field Supervisor will check through the materials and equipment check list to ensure that all gear is accounted for and in good working order and that all boat equipment required by the *HASP* are on board the vessel.

References

Foth, 2011. *Lower Fox River Operable Unit 1 – Integrated Final Design and Remedial Action Work Plan for Post-2009 Response Work,* Appendix A, *Health and Safety Plan*. April, 2011.

Foth and CH2M HILL, Inc., 2011. *Lower Fox River Operable Unit 1 – Integrated Final Design and Remedial Action Work Plan for Post-2009 Response Work,* Appendix E, *OU1 Long-term Monitoring Plan*. April, 2011.

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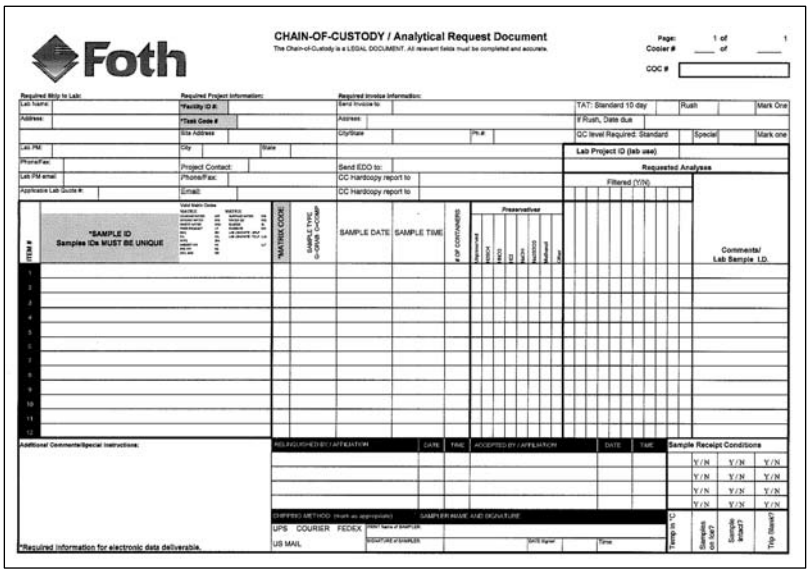
Standard Operating Procedure

Sample Chain of Custody

Introduction

As part of consulting services, Foth Infrastructure & Environment, LLC (Foth) collects a wide range of environmental samples. All samples collected must be accompanied by a chain of custody when submitted for analysis to ensure proper security and legal handling of samples.


CHAIN-OF-CUSTODY / Analytical Request Document

Proper documentation of sample custody is necessary to trace a sample from point of origin through the final report or completion of the project. Requiring samples to have a chain of custody ensures proper security and legal handling of samples as they move between the different parties that are responsible for their collection and analysis. A chain of custody is prepared by completing a chain of custody record form. Typically these forms are provided by the laboratory that is providing the sample bottles and analysis. If the laboratory does not supply a form, Foth has a generic chain of custody form which can be used. Chain of custody record forms will be filled out by the sampler(s) at the time of sampling and shipping.

This process is intended to be used for both paper and electronic chain of custody forms.

References

Not applicable.

Foth Infrastructure & Environment, LLC

Personnel Qualifications

The sampler(s) must be trained in properly filling out chain of custody forms.

Equipment and Supplies

- Electronic or paper copy of chain of custody form
- Pen

Procedures

Sample chain of custody documentation will be prepared by the sampler(s) immediately following the collection of samples. A chain of custody is a legal document. Therefore, it must be completed in pen. Foth also has an electronic chain of custody form that can be completed on the computer and printed. However, signatures on both electronic and paper chain of custody forms must be in ink. Once completed, the chain of custody will be placed in the master file.

Chain of custody forms will generally include the following information:

1. A unique chain of custody number
2. Laboratory shipping address
3. If using a laboratory chain of custody, use Foth as the company name, including branch office location
4. Project contact (in most cases, that will be the lab coordinator)
5. Contact phone number
6. Project number or scope ID
7. Project name
8. Project (site) license number (if applicable)
9. Project state
10. Name of sampler
11. Field ID and unique number (if applicable)
12. Sample description
13. Date sample collected
14. Time sample collected

15. Analyses requested
16. Sample matrix
17. Preservation of samples
18. Indicate whether or not sample was field filtered
19. Page numbers if more than one chain of custody
20. Address for where reports should be mailed
21. Address of where invoice should be sent
22. Regulatory program
23. Special quality assurance (QA) needs (turn around time)
24. Any request for data submitted by e-mail or any other format other than printed copy
25. Laboratory receiving information section completed by the laboratory
26. Shipping method and tracking numbers
27. Signature section for transfer of custody with date and time section

After collection, samples are securely stored and packaged as required by analytical protocol until delivered to the laboratory. The chain of custody document remains with the samples during transport and serves as a written record of sample possession and transference. A sample is considered to be in custody if it is in one's possession, is locked and sealed during shipment, or is placed in a secure area limited to authorized personnel. The chain of custody must be signed and dated by everyone who takes possession of the sample. If the electronic chain of custody form is used, a minimum of two printed copies must accompany the samples to the laboratory. All copies are signed and dated during sample transfer. Laboratory personnel will note any damaged sample containers, or discrepancies between the sample label and information on the chain of custody.

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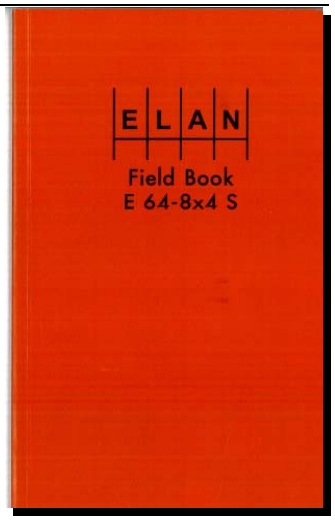
Standard Operating Procedure

Field Log Book



Introduction

Foth Infrastructure & Environment, LLC (Foth) gathers information for scientific and engineering evaluations. As part of the information gathering process, Field Log Books are often the sole source for interpretation of information. Field Log Books are legal documents.

The purpose of Field Log Book documentation is to collect information that is not documented in any standard form and that can be used by scientists and engineers to interpret data. Field Log Book entries show the importance of:

- Data collection objectives
- Developing and following site specific sampling plans
- Following regulatory regulations and permits
- Documenting pre-sampling preparations
- Changing environmental conditions
- Locations and types of forms used in documenting the field work of a project.

A Field Log Book entry is a process of systematic planning for determining the type, quantity, and quality of information collected that is necessary to make well-informed, valid, and defensible scientific and engineering decisions.

The objective of this Standard Operating Procedure (SOP) is to set the minimum criteria for content entry and form of a Field Log Book. This process is applicable during all Foth site operations. Additional requirements for documenting Field Log Books are often included in other SOPs and project-specific documentation.

Definitions

- Field Log Book – A Field Log Book is a bound notebook that is used at field sites and contains detailed information regarding site activities including dates, times, personnel names, activities conducted, equipment used, weather conditions, etc. A Field Log Book is used by a variety of different field personnel and is part of the project file. A Field Log Book is brought to the site activity. Field Log Books can be checked out from project file location for daily use. Field Log Books are kept in individual office sites when not in use.

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References

Not Applicable

Personnel Qualifications and Responsibilities

The project manager, or designee, is responsible for ensuring that project activities are conducted in accordance with this and other appropriate procedures. Project participants are responsible for documenting information in sufficient detail to provide objective documentation (i.e., check prints, calculations, reports, etc.) that meet the requirements of this SOP.

Equipment and Supplies

- Site-specific plans
- Bound, 8x4, water-resistant Field Log Book(s)
- Indelible black ink pen
- Ruler or similar scale

Procedures

Specifications for the Field Log Book:

1. Bound 8x4 book
2. Cover should have project name, project ID, and book number
3. Pages should be consecutively numbered
4. Table of contents and signature page should be on page 1
5. Name, address, and phone number(s) of key field contacts should be on page 1

Guidelines for simplifying entries:

1. Enter procedures for the first sample point, and then reference those procedures for subsequent entries on the same day if procedures did not change.

2. To eliminate redundancy, reference other locations if information is available.

Field Log Book entries should include, at a minimum, the following items. Additional entries may be required by a particular SOP.

1. Date, time, and type of field activities
2. Weather conditions
3. Field site conditions
4. Personnel on-site (Foth and non-Foth members)

5. Equipment used (Foth and/or clients or sub-consultants) and condition
6. Calibrations and calibration standards
7. Description of SOP followed or other procedures used
8. Description and reason of any variations from standard procedures in sampling plan
9. Tracking information for analytical sample containers and coolers
10. Reference of all standard forms used, chain of custody (COC), electronic data and its location
11. Sample point condition descriptions
12. Duplicates and field blank documentation
13. Problems and solutions encountered during field activities
14. Ending calibrations
15. Delivery and handling of samples

Field Log Book Documentation

Each site or operation where field activities are occurring will have Field Log Books. The details of all field activities shall be recorded in a Field Log Book. Multiple Field Log Books may be used depending upon the number of different types of field personnel conducting activities at the site. These Field Log Books shall be made part of the project master file and stored in project file 14350, Field Sampling Notes/Books.

The following requirements must be met when using a Field Log Book:

1. Enter events and entries in chronological order.

2. Record work, observations, quantity of materials, calculations, drawings, and related information directly in the Field Log Book. If data-collection forms are specified by an activity-specific work plan, the information on the form does not need to be duplicated in the Field Log Book. However, forms used to record site information must be referenced in the Field Log Book.

3. Ensure information is factual and unbiased.

4. Fill up all pages and use both sides of each page. Do not start a new page until the previous one is full or has been marked with a single diagonal line so that additional entries cannot be made.

5. Write in black, indelible ink. Do not write in pencil unless working in wet conditions.

6. Do not erase or blot out an entry. While changes to an entry may be made before it has been signed and dated, care must be taken not to obliterate what was originally written. Indicate deletions by a putting a single line through the material to be deleted and initial and date the change.

7. Do not remove any pages from the book.

8. Do not use loose paper and copy into the Field Log Book later.

9. Record sufficient information to completely document field activities.

10. Make sure entries are neat and legible.

11. Draw a diagonal line through the remainder of the final page at the end of the day.

12. Record the following information on a daily basis:
    a. Date and time
    b. Name of individual making entry
    c. Description of activity being conducted including well, boring, sampling, location number as appropriate
    d. Unusual site conditions
    e. Weather conditions (i.e., temperature, cloud cover, precipitation, wind direction, and speed) and other pertinent data
    f. People on site
    g. Level of personal protection to be used
    h. Arrival/departure of site visitors
    i. Arrival/departure of equipment
    j. Sample pickup (chain of custody) form numbers, carrier, time, electronic location of chain of custody
    k. Start and completion times of borehole/trench/monitoring well installation of sampling activity
    l. Heath and Safety issues
    m. Instrumentation calibration details

Signing and initialing requirements for Field Log Book entries:

1. Initial and date each page.

2. Sign and date the final page of entries for each day.

3. Initial and date all changes.

4. Multiple authors must sign out the Field Log Book by inserting the following:

   Above notes authored by:
   _____ (Sign name)
   _____ (Print name)
   _____ (Date)

5. A new author must sign and print his/her name before additional entries are made.

Entries into the Field Log Book shall be preceded with the time of the observation. The time should be recorded frequently and at the point of events or measurements that are critical to the activity being logged. All measurements made and samples collected must be recorded unless they are documented by automatic methods (i.e., data logger) or on a separate form required by a standard operating procedure. In such cases, the Field Log Book must reference the automatic data record or form.

While collecting samples, note observations such as color and odor of samples collected. Indicate the locations from which samples are being taken, sample identification numbers, the order of filling bottles, sample volumes, and parameters to be analyzed. If field duplicate samples are collected, note the duplicate pair sample identification numbers. If samples are collected that will be used for matrix spike and/or matrix spike/matrix spike duplicate analysis, record that information in the Field Log Book.

A sketch of the station location may be warranted. All maps or sketches made in the Field Log Book should have descriptions of the features shown and a directional indicator. Maps and sketches should be oriented so that north is towards the top of the page.

Other events and observations that should be recorded include, but are not limited to, the following:

1. Changes in weather that impact field activities
2. Subcontractor activities
3. Deviations from procedures outlined in any governing documents, including the reason for the deviation
4. Problems, downtime, or delays
5. Upgrade or downgrade of personal protective equipment

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Post-Operation

To guard against loss of data due to damage or disappearance of Field Log Books, copies of completed Field Log Books shall be securely stored within the project master file.

At the conclusion of each activity or phase of site work, or a complete Field Log Book, the individual responsible for the Field Log Book will ensure that all entries have been appropriately signed and dated and that corrections were made. Completed Field Log Books shall be made a part of the project master file and stored in project file 14350, Field Sampling Notes/Books.

Restrictions/Limitations

Field Log Books constitute the official record of on-site technical work, investigations, and data collection activities. Their use, control, and ownership are restricted to activities pertaining to specific field operations carried out by Foth personnel and their subcontractors. They are documents that may be used in court to indicate and defend dates, personnel, procedures, and techniques employed during site activities. Entries made in the Field Log Book should be factual, clear, precise, and as non-subjective as possible. Field Log Books, and entries within, shall not to be utilized for personal use.

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Standard Operating Procedure

Water Quality Meter Use

Introduction

This Standard Operating Procedure (SOP) is intended to provide general guidance and methods for using a field meter to measure water quality parameters from groundwater or surface water that is being purged, sampled, or monitored.

Scope

This procedure is applicable to all Foth projects where water quality monitoring is required using a water quality meter. The water quality meter may be a stand-alone meter or it may be a combined multi-probe unit used to measure temperature, pH, specific conductance, and/or other water quality parameters. The most common methods used for measuring water quality are instruments that measure in-situ parameters in one of the following two ways:

Water is extracted from its source using a pump and measured in a flow-through cell or in some instances captured and then measured in individual aliquots. This method is preferred when monitoring wells are sampled for laboratory analysis of chemical parameters, and groundwater purging is required.

The meter is submerged directly into the sample source, such as a monitoring well or surface water body, to collect in-situ monitoring parameters.

References

- U.S. Army Corps of Engineers, 2001, Requirements for the Preparation of Sampling and Analysis Plans, Appendix C, EM-200-1-3, Washington, D.C.
- American Society of Testing and Materials, Standard Guide for Selection of Purging and Sampling Devices for Ground-Water Monitoring Wells, D6634-01, West Conshohocken, PA.
- American Society of Testing and Materials, Standard Guide for Sampling Ground-Water Monitoring Wells, D4448-01, West Conshohocken, PA.

Definitions

- Water Quality Meter – A device used to measure specific field parameters indicative of water quality, such as temperature, pH, specific conductance, and/or other parameters. The meter may be stand-alone or it may be a combined multi-probe unit.

- Pump – An electric, compressed air, or inert gas-driven device that raises liquids by means of pressure or suction. The types of pumps that should be used for water quality monitoring should be chosen based on the well size and depth, the type of contaminants, and the specific factors affecting the overall performance of the sampling or monitoring effort. The types of pumps that may be used include centrifugal, peristaltic, centrifugal submersible, gas displacement, and bladder pumps.

- pH – The negative log of the hydrogen ion concentration (-log10 [H+]); a measure of the acidity or alkalinity of a solution, numerically equal to 7 for neutral solutions, increasing with increasing alkalinity and decreasing with increasing acidity. The scale is 0 to 14.

- Turbidity – A measure of overall water clarity determined by measurement of the degree to which light traveling through a water column is scattered by the suspended organic (including algae) and inorganic particles. Turbidity is commonly measured in Nephelometric Turbidity Units (NTU) but may also be measured in Jackson Turbidity Units (JTU).

- Specific Conductance (SC) – A measure of how well water can conduct an electrical current. Conductivity increases with increasing amount and mobility of ions such as chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, and iron, and can be used as an indicator of water pollution. The unit of conductance is expressed as microsiemens (1/1,000,000 siemen) per centimeter, or pS/cm.

- Oxidation-Reduction (Redox) Potential – A measure in volts of the affinity of a substance for electrons compared with hydrogen. Liquids that are more strongly electronegative than hydrogen (i.e., capable of oxidizing) have positive redox potentials. Liquids less electronegative than hydrogen (i.e., capable of reducing) have negative redox potentials.

- Dissolved Oxygen (DO) – Refers to the amount of oxygen expressed as milligrams per liter (mg/L) that is contained in particular water. The amount of oxygen that can be held by the water depends on the water temperature, salinity, purity, and pressure.

- Salinity – The amount of dissolved salts in water, generally expressed in parts per thousand (PPt).

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Responsibilities

Procedure Responsibility

The Long-term Monitoring Field Supervisor is responsible for maintenance, management, and revision of this procedure. Questions, comments, or suggestions regarding this technical SOP should be directed to the Long-term Monitoring Field Supervisor.

Project Responsibility

Foth employees performing this task, or any portion thereof, are responsible for meeting the requirements of this procedure. Foth employees conducting technical review of task performance are also responsible for following appropriate portions of this SOP.

For those projects where the activities of this SOP are conducted, the Project Manager or designee is responsible for ensuring that those activities are conducted in accordance with this and other appropriate procedures. Project participants are responsible for documenting information in sufficient detail to provide objective documentation (i.e., checkprints, calculations, reports, etc.) that the requirements of this SOP have been met. Such documentation shall be retained as project records.

Procedures

Equipment

The following equipment is recommended for use in performing water quality measurements:

- Water quality meter(s)
- Spare parts such as alkaline batteries (if used) and sensor probes
- Pump and discharge hose/line for use with a flow-through cell
- Paper towels or lint-free wipes
- Deionized water
- Sample gloves
- Calibration solutions for all parameters being measured; within expiration dates
- Plastic sheeting
- Logbook or log sheets

General Instructions

- Ensure that the measuring range of the instrument encompasses the expected sample concentration or units.

- Before going to the field, locate all necessary field supplies such as deionized water, calibration solutions, decontamination supplies, and spare parts.

- Consult the instrument's operation manual as well as the project-specific sampling plan to verify that you have prepared the proper equipment and supplies to successfully complete the work.

Calibration

*Calibration **must** be performed **at least once per day** during operation. Calibrate the meter according to the instrument's operating manual. If sampling and monitoring is being performed for long periods of time, periodically check the instrument calibration using the operating manual's recommended frequency.*

In order to avoid limiting the field personnel to one particular model, only general calibration instructions are presented in this procedure.

- Locate a clean, protected area in which to set up and calibrate the instrument. Ensure that sufficient supplies of de-ionized water, clean paper towels, buffer solutions, and standard solutions are available.

- Inspect the meter and probes for damage. Some of the probes are very delicate or have a thin membrane installed over the probe. Be careful when handling the meter/probes so as not to damage them. If damaged, replace probes in accordance with the instrument's operating manual or obtain a different meter.

- Turn on the meter and allow it to "warm-up" for the manufacturer-specified time (usually 15 to 30 minutes). Check the battery power to determine if the meter has sufficient power to operate for the monitoring period. Replace the batteries, if necessary.

- Calibrate the meter according to the instrument's operating manual. In general, calibration is performed by immersing the probe(s) in aliquots of calibration standard solution(s) and following certain meter keystrokes to set the calibration for each parameter. Do not immerse the probe into the stock container of the solution. Always transfer a small amount of the solution into a separate container to calibrate the probe(s). If calibrating for multiple parameters using more than one solution, be sure to wipe off and rinse the probe with deionized water between solutions.

- Recheck each parameter after calibration by immersing the probe into the calibration solution and reading it like a sample reading. If the agreement is not within 25% of the solution's known concentration, repeat the calibration process with a new solution aliquot.

- Discard the used calibration solution aliquots when finished into an appropriate waste container.

- Record the calibration data in the Field Log Book or log sheet.

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Operation of the Instrument

- If using a flow-through cell system, attach the extraction pump and lines in accordance with the pump and meter manufacturer's instructions. Allow the lines to fill and the probes to become immersed before switching the instrument to its measurement mode.
- If using a down-hole system, allow a few minutes for the probe to stabilize before taking a reading.
- Operate the meter in accordance with the instrument's operating manual.
- Collect the field parameter reading(s) per the project requirements, and record them in a Field Log Book or on log sheets.
- Decontaminate the meter before collecting data from the next sample source. For a flow-through system, flush the lines with three line volumes of deionized water or replace with new ones between samples.

Attachments

None.

Forms

None.

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Standard Operating Procedure

Trace PCB Sampling of Surface Water

Introduction

The objective of this Standard Operating Procedure (SOP) document is to provide methods, procedures, and guidance for sampling Trace polychlorinated biphenyls (PCB) in surface waters such as lakes, streams, pits, sumps, lagoons, and similar reservoirs for environmental analysis.

This process is applicable to all Foth Infrastructure & Environment, LLC (Foth) projects where low level PCB surface water sampling will be performed and where no other project/program plan or procedure is in place to direct those activities.

These procedures are modified based on Trace Metal sample collection techniques. When sampling requirements indicate that both trace metal and PCBs are to be sampled, Trace PCBs can be collected under the Trace Metal SOP.

Definitions

- "Clean Hands" is a gloved person (with shoulder length gloves, if needed). "Clean Hands" will only have contact with sample bottles.
- "Dirty Hands" is a gloved person and contacts all sampling material pumps and tubing.
- Composite Sample is a peristaltic pump with a flow weighted or time interval dependant sampling device that can composite samples into one container or into multiple containers enclosed within the device (i.e., ISCO sampler) or operated in manual mode to directly fill sample containers.

References

Foth, 2011. *Lower Fox River Operable Unit 1 – Integrated Final Design and Remedial Action Work Plan for Post-2009 Response Work,* Appendix A, *Health and Safety Plan*. April, 2011.

Foth and CH2M HILL, Inc., 2011. *Lower Fox River Operable Unit 1 – Integrated Final Design and Remedial Action Work Plan for Post-2009 Response Work,* Appendix E, *OU1 Long-term Monitoring Plan*. April, 2011.

Olson, Mark and, John F. De Wild. U.S. Geologic Survey Water Resource Division, "Low Level Collection Techniques and Species-Specific Analytical Methods for Mercury in Water, Sediment, and Biota." Reported in the U.S. Geologic Survey *Resource Investigations Report*, 99-4018B. 1999.

Shaw Environmental & Infrastructure, Inc. and Anchor QEA, LLC, 2006. *Lower Fox River Baseline Monitoring Plan*. June 2006.

Telliard, William A., et al. U.S. Environmental Protection Agency, Method 1669, "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels," July 1996.

Telliard, William A., et al. "Water Quality Criteria Levels," July 1996.

Note: List applicable regulatory standards, industry standards, other SOPs, reference book, etc.

Personnel Qualifications/Requirements

As directed in the Foth Project Planning Document (PPD) and appointed by the project manager (PM):

- *Health and Safety Plan* (Foth, 2011) (*HASP*).
- A minimum of two people are required to complete sampling with one person trained in this sampling technique.
- A third person will be needed to operate a vessel and operate a global positioning system (GPS).
- A boater safety course is required to operate the boat.

Equipment and Supplies

- Work boat (minimum 16 feet) cleaned prior to collecting samples, power washed inside and out if necessary. Boat should be equipped with sonar depth sounder and electric trolling motor.
- Proper safety precautions shall be maintained throughout sampling event including wearing of appropriate personal protective equipment (PPE), life jackets, and following all boating rules and regulations including Foth's boating Current Best Approach (CBA).
- Coolers containing sample bottles.
- Cooler of ice.

- Lab grade or reagent free deionized water for blanks supplied by the analytical lab.
- "PCB free" water for field decontamination procedures.
- Peristaltic pump (ISCO Sampler). Reference Owner's Manual for operations.
- Rod to measure depth and attach tubing for sample collection at predetermined depth.
- Battery: 12-volt marine to operate peristaltic pump or Honda generator.
- Trimble 2005 GEOXT Differential GPS (DGPS) software, or equivalent, as the primary GPS instrument for acquiring sample station locations.
- Hydrolab Series 5, or equivalent, will be used to take turbidity and temperature field readings. The Hydrolab Series 5 also has a pressure transducer for measuring depth. Daily calibrations of the Hydrolab Series 5 will occur prior to sample point data acquisition. Calibrations of all instruments shall be kept in the field book and shall contain, at a minimum, instrument serial number, make and model, manufacturer of standard(s), and standard lot number(s) and date of expiration. Calibration readings and any adjustments made to field instruments shall also be recorded. See Owner's Manual for calibration procedures. A calibration check will also be performed at the end of each day's activities to verify if any drift in the instrument readings has occurred. If unacceptable drift is detected, the drift will be recorded and equipment will be re-calibrated.
- Two sections of Teflon® lined tubing for each transect where a peristaltic pump is used. One section to be submerged to predetermined depth and the other, an approximate 4-foot section to discharge into sample bottles. A new section of tubing shall be used for each transect being sampled.
- Two-foot section of silicone tubing needed for peristaltic pump action. A new section of tubing shall be used for each transect being sampled.
- Tyvek® (or equivalent), nylon coveralls, waders or hip boots for sampling personnel. Face dust masks or full face shields may be worn by members of the sampling team if introduction of low level PCB contamination through respiration is suspected.

Safety Note

Surface water sampling can sometimes require the use of boats or access into or across bodies of water. Observe all boating safety considerations in the *HASP* including donning of proper life jackets.

"Quarter Point" Sampling Procedures

Area-weighted composite samples will be collected on specified transects to obtain representative water concentrations averaged over the cross-section of flow. Water quality sampling transects are located to the extent possible in relatively straight reaches with simple, U-shaped cross-sections, avoiding areas with shallow benches or protrusions that could cause eddies, wind waves, or other hydraulic complications. It is assumed that the flow in these sections is relatively uniform and well mixed. In a uniform, well-mixed cross-section, an area-weighted sampling design provides a reasonable approximation of a flow-weighted design.

Representative transects of Operable Unit 1 (OU1) and Lake Winnebago will be sampled in general accordance with U.S. Geological Survey (USGS) "quarter point" sampling procedures. The channel cross-sections are divided into three equal areas based on bathymetric data. Water sampling stations are positioned at the midpoint of each of the three flow areas. The coordinates of these stations are shown in Table 2-2, Appendix A, of the *Lower Fox River Operable Unit 1 – OU1 Long-term Monitoring Plan* (Foth and CH2M HILL, 2011) (*OU1-LTMP*). . In OU1 and Lake Winnebago, discrete water samples will be collected at 0.2 and 0.8 times the depth of the water column.

Sample Team Roles and PPE

- A three-person sampling team consisting of "Clean Hands," "Dirty Hands," and a boat driver who is an extra pair of hands in supporting the sampling effort.
  - All participants shall wear latex, nitrile or neoprene gloves. Nylon clothing, chest waders, or white Tyvek® coveralls, face dust mask or full face shields over life jackets and field clothing are recommended for all sampling team members if in PCB dust areas or PCB inhalation is a concern.
  - "Clean Hands" is a gloved person (with shoulder length gloves, if needed) who will only have contact with sample bottles.
  - "Dirty Hands" is a gloved person who will have contact with all sampling material, pump hose, and depth rod.

- The third person will handle driving of the boat, maintaining direction of route traveled during sampling into the waves/wind, or upstream in any current. Other duties of the third person include assisting with cooler manipulation, controlling the Teflon® lined tubing and the "PCB free" water while collecting field blanks, recording DGPS coordinates, starting the peristaltic pump (ISCO Sampler) or generator, and monitoring safety conditions of sampling team during each sampling event.

Sample Collection Using Peristaltic Pump

1. Sample team shall calibrate the DGPS instrument with two known benchmarks per OU, using the Wisconsin Department of Natural Resources' (WDNR) Fox River monuments, or other documented monuments, if WDNR monuments are not available in the project area.

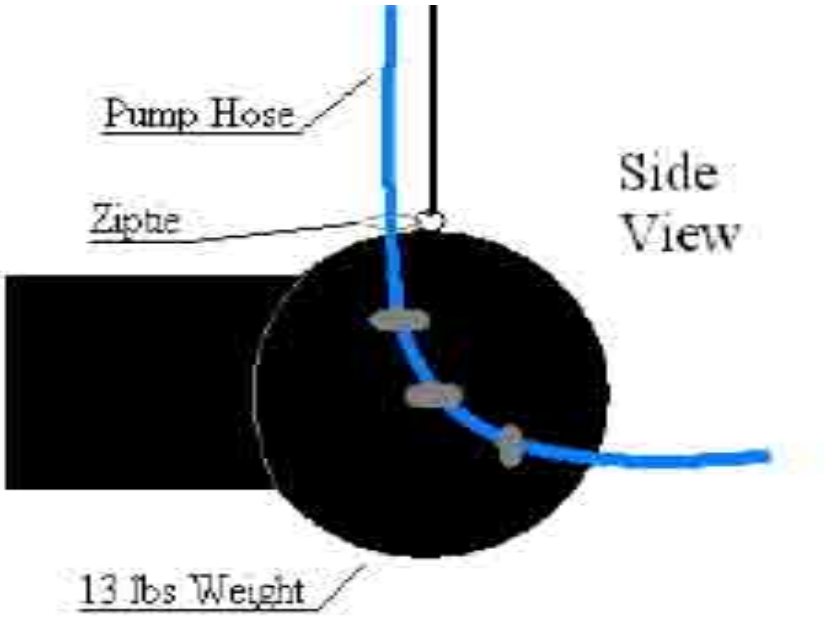
2. Sample team should ideally approach the predetermined sites using the DGPS instrument from down current or down wind to prevent vessel induced disturbance in the sampling area. No anchoring for sample collection. Sampling can take place from either the bow or stern of the boat. Bow or Stern should be oriented into the current or wind whenever possible. Work area shall be covered with plastic sheeting, if necessary, and duct taped to hold in place. Prepping the boat at each transect can be done on shore prior to launching.

3. Stratification measurements (turbidity and temperature) shall be measured at one meter intervals, starting at the surface and vertically measuring to within one meter of the bottom. DGPS measurements will be recorded at a minimum of 2-minute intervals to record drift from the starting position. Electronic sonar shall be used to verify total depth and as the measurements are recorded, care must be taken to not disturb bottom sediments. These measurements will be made before active sample collection begins for determining sample distribution. These results shall be recorded in the Field Log Book. Vessel control will be made with the engines or electric trolling motor to maintain as vertical as possible to the original starting DGPS location along each transect. Any variations in boat drift from targeted distances as a result of weather or boat traffic need to be documented in the Field Log Book.

4. Sampling equipment preparation of tubing and peristaltic pump, bottle prep, and sampling team gloving activities shall be completed before active sampling begins. Due to limited space in the boat and safety of sampling team, some of the preparation procedures can occur on shore prior to the launching of the boat. During actual collection of samples, the vessel direction must be maintained into the current or the wind with DGPS coordinates recorded.

5. Downrigger or similar mechanical method shall be used to maintain depth control during sample extraction activities. Any weight suspended shall track in the direction the boat is traveling by means of a tail fin or similar device. All operations involving contact with sample bottle and with transfer tubing shall be handled by individuals designated as "Clean Hands" and "Dirty Hands." "Clean Hands" is responsible for all activities that involve direct contact with sample. "Dirty Hands" is responsible for all activities that do not involve direct contact with sample. All sample collection participants may wear nylon clothing, chest waders, or white Tyvek® coveralls and gloves over life jackets and field clothing.

6. The peristaltic pump intake shall be deployed to a predetermined depth (20% and 80% of shallowest total depth measured during stratification measurements rounded to nearest ½ feet) by using a weight, downrigger ball, or secured measuring tool to maintain sample extraction depth. Two tubing volumes shall be purged through the tubing system prior to sample collection from predetermined depth. When a downrigger ball is used, it shall be setup in a manner that the tubing extends beyond the weight. If downrigger is not used, to prevent Teflon® lined tube from curling, a weight or length of PVC pipe needs to be used to keep intake tubing at desired depth. See Owner's Manual for operations of peristaltic pump. See diagram below for downrigger ball setup.



7. All measuring devices shall be zeroed at the surface before deployment to sample collection depth.

8. Collect the upper water column sample first.

9. "Dirty Hands" must open the cooler or storage container and remove the sample bottles from storage.

10. Sample bottle collection order: PCB bottle, and backup, total suspended solids (TSS) (unpreserved bottle), total organic carbon (TOC) (H2SO4 preserved bottle).

11. "Clean Hands" sample bottle shall remain in "Clean Hands" view at all times. "Dirty Hands" reseals the outer bag and places back in storage container.

12. "Dirty Hands" controls the discharge hose from the peristaltic pump while the "Clean Hands" opens the sample bottle cover. The sample bottle is filled after two tube volumes have been purged. The unpreserved PCB sample bottle is partially filled and rinsed with the sample water three times prior to sample collection.

13. Once the sample bottle lid has been replaced and all samples have been collected, the peristaltic pump can be turned off or moved to a lower depth in the water column, if required.

14. Return sample bottles to cooler on ice.

15. Document sample conditions, sample time, sample procedures, and any other observations pertinent to sample collection (wave action, boat activity, deviations from sampling plan, and DGPS coordinates after sampling for drift documentation during sampling). (See *Location Control* SOP.)

16. Ensure all samples are placed on ice.

17. Contracted lab shall composite samples from each transect prior to analysis per requirements in the *OU1-LTMP*.

Procedures for Additional Vertical Samples Collected at Individual Transect Location

- Repeat above procedure for samples at the next predetermined depth in the water column at the same transect location.

- Ensure a minimum of two tubing volumes are purged from depth before sample collection begins.

- Ensure that the bottom is not disturbed during drift by maintaining sonar depth.

- After all vertical samples are collected at transect location, rinse sample equipment with deionized water by pumping deionized water through peristaltic pump system.

- Store in plastic bag for transport to next transect location or secure and protect intake and discharge ends of tubing during travel from one point along the transect to the next.

- Procedure is then repeated for additional samples along each transect by repeating and recording stratification measurements at next sample along transect and sample prep procedures as necessary and drift control.

Procedures After Each Sample is Collected Along Individual Transect

- Procedure is then repeated for additional samples along each transect by repeating and recording stratification measurements at next sample along transect and sample prep procedures as necessary and drift control.

- Repeat stratification measurements at next sample along transect and sample prep procedures as necessary.

- Rinse sample equipment with deionized water. Pump deionized water through peristaltic pump system.

Decon Procedures After Each Transect and Before Next Transect Sampling Event

- The used Teflon® lined tubing and silicone tubing shall be discarded or dedicated to a transect.

- A decontamination area shall be determined by the sample team.

- Remove any particulate matter and other surface debris from peristaltic pump and any other dedicated equipment (weights, pipes, etc.) used during the sampling event using appropriate tools such as a brush and Alconox or Liquinox and rinse with deionized water.

- Let air dry in a clean area.

- Place sampling equipment in a double bag and then in a plastic container ready for next event.

Procedures for QA Sample Collection

- For Field Blank samples, use lab provided "PCB free" water and pass through a new section of tubing (Teflon® lined and silicone) prior to any sample collection.
- For replicate sample collection, sample bottle shall be alternated during sample collection.
- All samples shall be placed on ice.
- Contracted lab shall composite samples from each transect prior to analysis per requirements in the *OU1-LTMP*.

ID #: 1308
Revision #: 1
Date: 1/28/11
Geographic Area: General

Competency: Envir Sciences
TCL: JSK
Technical Expert: SDJ

Foth Infrastructure & Environment, LLC

Standard Operating Procedure

Shipping and Packaging of Non-Hazardous Samples

Introduction

The purpose of this Standard Operating Procedure (SOP) is to provide general instructions in the packaging and shipping of non-hazardous samples. The primary use of this SOP is for the transportation of samples collected on site to be sent off site for physical, chemical, and/or radiological analysis.

Non-hazardous samples are those that do not meet any hazard class definitions found in 49 Code of Federal Regulations (CFR) 107-178, including materials designated as Class 9 materials and materials that represent Reportable Quantities (hazardous substances).

Definitions

- Cooler/Shipping container – Any hard-sided insulated container meeting any state Department of Transportation (DOT) or International Air Transport Association's (IATA) general packaging requirements.

- Bubble Wrap – Plastic sheeting with entrained air bubbles for protective packaging purposes.

References

- 49 CFR Parts 107-178
- State DOT
- IATA
- Shipping carrier instructions

Personnel Qualifications

- NA

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Equipment and Supplies

- Shipping container
- Samples
- Ice
- Various types of packing supplies
- Plastic bags
- Zip-lock® plastic bags
- Custody seals

Packaging

1. Follow shipping instructions from contracting lab.

2. Use tape to seal off the cooler drain on the inside and outside to prevent leakage.

3. Place packing material on the bottom of the shipping container (cooler) to provide a soft impact surface.

4. Place a 55-gallon or equivalent plastic bag into the cooler (to minimize possibility of leakage during transit).

5. Starting with the largest glass container, wrap each container with sufficient bubble wrap to ensure the best chance to prevent breakage of the container.

6. Pack the largest glass containers in bottom of the cooler, placing packing material between each of the containers to avoid breakage from bumping.

7. Double-bag the ice (chips or cubes) in gallon or quart freezer Zip-lock® plastic bags and wedge the ice bags between the sample bottles. (Use “quality” ice, not ice from motel ice machine.)

8. Add bags of ice across the top of samples.

9. When sufficiently full, seal the inner protective plastic bag and place additional packing material on top of the bag to minimize shifting of containers during shipment.

10. Tape a gallon Zip-lock® bag to the inside of the cooler lid, place the completed chain of custody document inside, and seal the cooler shut.

11. Tape the shipping container (cooler) shut using packing tape, duct tape, or other tear-resistant adhesive strips. Taping should be performed to ensure the lid cannot open during transport.

12. Place a custody seal on two separate portions of the cooler to provide evidence that the lid has not been opened prior to receipt by the intended recipient.

Labeling

1. "This Side Up" arrow must be adhered to all sides of the cooler.

2. The name and address of the receiver and the shipper must be on the top of the cooler.

3. The air bill must be attached to the top of the cooler.

Shipping Documentation

1. If project has specific cooler shipment checklist requirements it shall be completed and kept in the project file. Custody seal numbers may need to be recorded and tracked.

2. Shipping tracking numbers should be kept in project file.

3. Shipping costs should be recorded and kept in project file.

Appendix C

Laboratory Standard Operating Procedures/Certifications

Pace Analytical Services, Inc.

C-01 Laboratory Certifications (2)

C-02 Quality Assurance Manuals (2)

C-03 Chain of Custody Form/Custody Seal

C-04 Measurement of Volatile Solids and Solids in Waters

C-05 Determination of Total Organic Carbon-Tekmar (EPA 415.1)

C-06 Determination of Total Organic Carbon-Apollo 9000 (SW846 9060A)

C-07 Biological Tissue and Plant Preparation

C-08 Determination of Lipids in Tissues, Fats, and Plants

C-09 Extraction of Biological Samples for Organochlorine Pesticides/PCBs

C-10 Extraction of PCBs in Tissue Using Automated Soxhlet

C-11 Analysis of PCBs by Gas Chromatography (SW846-8082A)

TestAmerica Laboratories, Inc.

C-12 Extraction of PCB Isomers for Analysis by Isotope Dilution HRGC/HRMS

C-13 Analysis of PCB Isomers by Isotope Dilution HRGC/HRMS

C-14 Record Retention and Document Storage

State of Wisconsin
Department of Natural Resources

WISCONSIN
DEPT. OF NATURAL RESOURCES

recognizes

Wisconsin Certification under NR 149

of

Pace Analytical Services, Inc. Green Bay

Laboratory Id: **405132750**

as a laboratory licensed to perform environmental sample analysis in support of covered environmental programs (ch. NR149.02 Note) for the parameter(s) specified in the attached Scope of Accreditation.

August 31, 2010

Expiration Date

August 31, 2009

Issued on

FORWARD

David Webb

David Webb, Chief
Environmental Science Services

Matthew J. Frank, Secretary
Department of Natural Resources

This certificate does not guarantee validity of data generated, but indicates the methodology, equipment, quality control practices, records, and proficiency of the laboratory have been reviewed and found to satisfy the requirements of ch. NR 149, Wis. Adm. Code.

Scope of Accreditation

Pace Analytical Services, Inc. Green Bay
1241 Bellevue Street
Green Bay, WI 54302

Laboratory Id: **405132750**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Aqueous (Non-potable Water)

Class: General Chemistry

Acidity as CaCO3 *by Titration*
Alkalinity *by Titration*
Ammonia as N *by Colorimetric*
Biochemical Oxygen Demand (BOD) *by BOD*
Bromide *by IC*
Carbonaceous Oxygen Demand (cBOD) *by BOD*
Chemical Oxygen Demand (COD) *by Colorimetric*
Chloride *by IC*
Cyanide, Total *by Colorimetric*
Fluoride *by IC*
Hardness, Total as CaCO3 *by ICP*
Kjeldahl Nitrogen, Total *by Colorimetric*
Nitrate *by IC*
Nitrate + Nitrite *by Colorimetric*
Nitrate + Nitrite *by IC*
Nitrite *by IC*
Organic Carbon, Total (TOC) *by Comb-Ox*
Phosphorus, Total *by Colorimetric*
Residue, Filterable (TDS) *by Solids*
Residue, Nonfilterable (TSS) *by Solids*
Residue, Total *by Solids*
Residue, Volatile (TVS) *by Solids*
Residue, Volatile, Nonfilterable (TVSS) *by Solids*
Sulfate *by IC*
Sulfide *by Titration*
Sulfides, Acid-Soluble and Acid-Insoluble *by Titration*

Class: Metals

Aluminum *by ICP*
Aluminum *by ICP-MS*
Antimony *by ICP*
Antimony *by ICP-MS*
Arsenic *by ICP*
Arsenic *by ICP-MS*
Barium *by ICP*
Barium *by ICP-MS*
Beryllium *by ICP*
Beryllium *by ICP-MS*
Boron *by ICP*
Cadmium *by ICP*
Cadmium *by ICP-MS*
Calcium *by ICP*
Calcium *by ICP-MS*
Chromium (Hexavalent) *by Colorimetric*
Chromium (Total) *by ICP*
Chromium (Total) *by ICP-MS*

Class: Metals

Cobalt *by ICP*
Cobalt *by ICP-MS*
Copper *by ICP*
Copper *by ICP-MS*
Iron *by ICP*
Iron *by ICP-MS*
Lead *by ICP*
Lead *by ICP-MS*
Magnesium *by ICP*
Magnesium *by ICP-MS*
Manganese *by ICP*
Manganese *by ICP-MS*
Mercury *by Hyd-CVAA*
Mercury *by ICP-MS*
Mercury *by UltraLow*
Molybdenum *by ICP*
Molybdenum *by ICP-MS*
Nickel *by ICP*
Nickel *by ICP-MS*
Potassium *by ICP*
Potassium *by ICP-MS*
Selenium *by ICP*
Selenium *by ICP-MS*
Silver *by ICP*
Silver *by ICP-MS*
Sodium *by ICP*
Sodium *by ICP-MS*
Strontium *by ICP*
Thallium *by ICP*
Thallium *by ICP-MS*
Tin *by ICP*
Titanium *by ICP*
Vanadium *by ICP*
Vanadium *by ICP-MS*
Zinc *by ICP*
Zinc *by ICP-MS*

Class: BNA Semivolatiles

* BNA ANALYTE GROUP *by GC/MS*

Class: Pesticides, Organochlorine

* PESTICIDES, ORGANOCHLORINE ANALYTE GROUP *by GC*

Class: Petroleum Hydrocarbons

Diesel Range Organics (DRO) *by GC*
Gasoline Range Organics (GRO) *by GC*

The laboratory named above is hereby licensed under ch. NR 149, Wis. Adm. Code for the parameters listed in this attachment.
* Analyte groups are defined and listed on the WI DNR Lab Certification website. See http://dnr.wi.gov/org/es/science/lc/ for details.

Scope of Accreditation

Pace Analytical Services, Inc. Green Bay
1241 Bellevue Street
Green Bay, WI 54302

Laboratory Id: **405132750**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Aqueous (Non-potable Water)

Class: Petroleum Hydrocarbons
Petroleum Volatile Organic Compounds (PVOC) *by GC*
Petroleum Volatile Organic Compounds (PVOC) *by GC/MS*
Class: PCBs as Aroclors
* PCB as AROCLORS ANALYTE GROUP *by GC*
Class: Volatile Organics
* VOC ANALYTE GROUP *by GC/MS*

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Scope of Accreditation

Pace Analytical Services, Inc. Green Bay
1241 Bellevue Street
Green Bay, WI 54302

Laboratory Id: **405132750**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Potable Water (Drinking Water)

Class: SDWA - Primary Non-metals
Nitrate + Nitrite - EPA 300.0
Nitrate - EPA 300.0
Nitrite - EPA 300.0

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Scope of Accreditation

Pace Analytical Services, Inc. Green Bay
1241 Bellevue Street
Green Bay, WI 54302

Laboratory Id: **405132750**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Solid (Waste, Soil & Tissue)

Class: General Chemistry

Ammonia as N *by Colorimetric*
Bromide *by IC*
Chloride *by IC*
Cyanide, Total *by Colorimetric*
Fluoride *by IC*
Kjeldahl Nitrogen, Total *by Colorimetric*
Nitrate *by IC*
Nitrate + Nitrite *by Colorimetric*
Nitrate + Nitrite *by IC*
Nitrite *by IC*
Organic Carbon, Total (TOC) *by Comb-Ox*
Phosphorus, Total *by Colorimetric*
Residue, Total *by Solids*
Sulfate *by IC*
Sulfide *by Titration*
Sulfides, Acid-Soluble and Acid-Insoluble *by Titration*

Class: Metals

Aluminum *by ICP*
Aluminum *by ICP-MS*
Antimony *by ICP*
Antimony *by ICP-MS*
Arsenic *by ICP*
Arsenic *by ICP-MS*
Barium *by ICP*
Barium *by ICP-MS*
Beryllium *by ICP*
Beryllium *by ICP-MS*
Boron *by ICP*
Cadmium *by ICP*
Cadmium *by ICP-MS*
Calcium *by ICP*
Calcium *by ICP-MS*
Chromium (Total) *by ICP*
Chromium (Total) *by ICP-MS*
Cobalt *by ICP*
Cobalt *by ICP-MS*
Copper *by ICP*
Copper *by ICP-MS*
Iron *by ICP*
Iron *by ICP-MS*
Lead *by ICP*
Lead *by ICP-MS*
Magnesium *by ICP*
Magnesium *by ICP-MS*
Manganese *by ICP*

Class: Metals

Manganese *by ICP-MS*
Mercury *by Hyd-CVAA*
Mercury *by ICP-MS*
Mercury *by UltraLow*
Molybdenum *by ICP*
Molybdenum *by ICP-MS*
Nickel *by ICP*
Nickel *by ICP-MS*
Potassium *by ICP*
Potassium *by ICP-MS*
Selenium *by ICP*
Selenium *by ICP-MS*
Silver *by ICP*
Silver *by ICP-MS*
Sodium *by ICP*
Sodium *by ICP-MS*
Strontium *by ICP*
Thallium *by ICP*
Thallium *by ICP-MS*
Tin *by ICP*
Titanium *by ICP*
Vanadium *by ICP*
Vanadium *by ICP-MS*
Zinc *by ICP*
Zinc *by ICP-MS*

Class: BNA Semivolatiles

* BNA ANALYTE GROUP *by GC/MS*

Class: Pesticides, Organochlorine

* PESTICIDES, ORGANOCHLORINE ANALYTE GROUP *by GC*

Class: Petroleum Hydrocarbons

Diesel Range Organics (DRO) *by GC*
Gasoline Range Organics (GRO) *by GC*
Petroleum Volatile Organic Compounds (PVOC) *by GC*
Petroleum Volatile Organic Compounds (PVOC) *by GC/MS*

Class: PCBs as Aroclors

* PCB as AROCLORS ANALYTE GROUP *by GC*

Class: Volatile Organics

* VOC ANALYTE GROUP *by GC/MS*

Class: Waste Characterization Extractions

Reagent Water Shake Extraction (ASTM Leach Test) *by Waste Extractions*

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Scope of Accreditation

Pace Analytical Services, Inc. Green Bay
1241 Bellevue Street
Green Bay, WI 54302

Laboratory Id: **405132750**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Solid (Waste, Soil & Tissue)

Class: Waste Characterization Extractions
SPLP Extraction *by Waste Extractions*
TCLP Extraction *by Waste Extractions*
Class: Waste Characterization Assays
Ignitability, Pensky-Martens Closed Cup *by Waste Assays*

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State of Wisconsin \ DEPARTMENT OF NATURAL RESOURCES

Jim Doyle, Governor
Matthew J. Frank, Secretary

101 S Webster St
PO Box 7921
Madison, WI 53707-7921
Telephone 608-266-2621
Fax 608-267-3579
TTY Access via relay - 711

August 31, 2009

FID: 405132750

MS. KATE GRAMS
PACE ANALYTICAL SERVICES, INC. GREEN BAY
1241 BELLEVUE STREET
GREEN BAY, WI 54302

Dear Ms. Kate Grams:

Enclosed is your new Laboratory Certification or Registration certificate. This certificate supersedes all previous certificates.

YOUR CERTIFICATE IS AN IMPORTANT DOCUMENT. PLEASE REVIEW IT CAREFULLY FOR ERRORS AND COMPARE IT TO YOUR PREVIOUS YEAR'S CERTIFICATE. MAKE SURE THAT THIS CERTIFICATE REFLECTS THE TESTS FOR WHICH YOU APPLIED TO BE CERTIFIED. If you believe your certificate contains errors, contact the Laboratory Certification and Registration Program immediately at (608) 267-7633 or by e-mail at LabCert@dnr.state.wi.us.

Sincerely,

David Webb

David Webb, Chief
Environmental Science Services
Bureau of Integrated Science Services

State of Wisconsin
Department of Natural Resources

WISCONSIN
DEPT. OF NATURAL RESOURCES

recognizes

Wisconsin Certification under NR 149

of

Pace Analytical Services, Inc.

Laboratory Id: **999407970**

as a laboratory licensed to perform environmental sample analysis in support of covered environmental programs (ch. NR149.02 Note) for the parameter(s) specified in the attached Scope of Accreditation.

August 31, 2010

Expiration Date

August 31, 2009

Issued on

David Webb, Chief
Environmental Science Services

Matthew J. Frank, Secretary
Department of Natural Resources

This certificate does not guarantee validity of data generated, but indicates the methodology, equipment, quality control practices, records, and proficiency of the laboratory have been reviewed and found to satisfy the requirements of ch. NR 149, Wis. Adm. Code.

Scope of Accreditation

Pace Analytical Services, Inc.
1700 Elm St SE. Suite 200
Minneapolis, MN 55414

Laboratory Id: **999407970**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Aqueous (Non-potable Water)

Class: General Chemistry
- Alkalinity *by Titration*
- Ammonia as N *by Colorimetric*
- Biochemical Oxygen Demand (BOD) *by BOD*
- Carbonaceous Oxygen Demand (cBOD) *by BOD*
- Chemical Oxygen Demand (COD) *by Colorimetric*
- Chemical Oxygen Demand (COD) *by Titration*
- Chloride *by Colorimetric*
- Cyanide, Amenable *by Colorimetric*
- Cyanide, Total *by Colorimetric*
- Hardness, Total as CaCO3 *by ICP*
- Nitrate *by Colorimetric*
- Nitrite *by Colorimetric*
- Oil&Grease, Hexane Ext. Material (HEM) *by HEM*
- Orthophosphate *by Colorimetric*
- Phenolics, Total *by Colorimetric*
- Phosphorus, Total *by Colorimetric*
- Residue, Filterable (TDS) *by Solids*
- Residue, Nonfilterable (TSS) *by Solids*
- Residue, Total *by Solids*
- Residue, Volatile (TVS) *by Solids*
- Residue, Volatile, Nonfilterable (TVSS) *by Solids*
- Sulfate *by Colorimetric*

Class: Metals
- Aluminum *by ICP*
- Aluminum *by ICP-MS*
- Antimony *by ICP*
- Antimony *by ICP-MS*
- Arsenic *by ICP*
- Arsenic *by ICP-MS*
- Barium *by ICP*
- Barium *by ICP-MS*
- Beryllium *by ICP*
- Beryllium *by ICP-MS*
- Boron *by ICP*
- Cadmium *by ICP*
- Cadmium *by ICP-MS*
- Calcium *by ICP*
- Chromium (Total) *by ICP*
- Chromium (Total) *by ICP-MS*
- Cobalt *by ICP*
- Cobalt *by ICP-MS*
- Copper *by ICP*
- Copper *by ICP-MS*
- Iron *by ICP*
- Iron *by ICP-MS*

Class: Metals
- Lead *by ICP*
- Lead *by ICP-MS*
- Magnesium *by ICP*
- Magnesium *by ICP-MS*
- Manganese *by ICP*
- Manganese *by ICP-MS*
- Mercury *by ICP-MS*
- Molybdenum *by ICP*
- Molybdenum *by ICP-MS*
- Nickel *by ICP*
- Nickel *by ICP-MS*
- Potassium *by ICP*
- Selenium *by ICP*
- Selenium *by ICP-MS*
- Silver *by ICP*
- Silver *by ICP-MS*
- Sodium *by ICP*
- Thallium *by ICP*
- Thallium *by ICP-MS*
- Tin *by ICP*
- Titanium *by ICP*
- Vanadium *by ICP*
- Vanadium *by ICP-MS*
- Zinc *by ICP*
- Zinc *by ICP-MS*

Class: BNA Semivolatiles
- * BNA ANALYTE GROUP *by GC/MS*

Class: PAH - Polynuclear Aromatic Hydrocarbons (BN)
- * PAH ANALYTE GROUP *by GC/MS*

Class: Petroleum Hydrocarbons
- Diesel Range Organics (DRO) *by GC*
- Gasoline Range Organics (GRO) *by GC*
- Petroleum Volatile Organic Compounds (PVOC) *by GC*
- Petroleum Volatile Organic Compounds (PVOC) *by GC/MS*

Class: PCB Congeners
- * PCB CONGENERS ANALYTE GROUP *by GC*
- * PCB CONGENERS ANALYTE GROUP *by GC/MS*
- * PCB CONGENERS ANALYTE GROUP *by HR-GC/MS*

Class: Dioxins and Furans
- * DIOXINS AND FURANS ANALYTE GROUP *by GC/MS*
- * DIOXINS AND FURANS ANALYTE GROUP *by HR-*

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Scope of Accreditation

Pace Analytical Services, Inc.
1700 Elm St SE. Suite 200
Minneapolis, MN 55414

Laboratory Id: **999407970**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Aqueous (Non-potable Water)

Class: Dioxins and Furans
GC/MS
Class: Volatile Organics
* VOC ANALYTE GROUP *by GC/MS*
Benzene *by GC*
Ethylbenzene *by GC*
Toluene *by GC*
m-Xylene *by GC*
o-Xylene *by GC*
p-Xylene *by GC*

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Scope of Accreditation

Pace Analytical Services, Inc.
1700 Elm St SE. Suite 200
Minneapolis, MN 55414

Laboratory Id: **999407970**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Solid (Waste, Soil & Tissue)

Class: General Chemistry
- Ammonia as N *by Colorimetric*
- Chemical Oxygen Demand (COD) *by Titration*
- Chloride *by Colorimetric*
- Cyanide, Total *by Colorimetric*
- Nitrate *by Colorimetric*
- Nitrite *by Colorimetric*
- Orthophosphate *by Colorimetric*
- Phenolics, Total *by Colorimetric*
- Phosphorus, Total *by Colorimetric*
- Sulfate *by Colorimetric*

Class: Metals
- Aluminum *by ICP*
- Aluminum *by ICP-MS*
- Antimony *by ICP*
- Antimony *by ICP-MS*
- Arsenic *by ICP*
- Arsenic *by ICP-MS*
- Barium *by ICP*
- Barium *by ICP-MS*
- Beryllium *by ICP*
- Beryllium *by ICP-MS*
- Boron *by ICP*
- Cadmium *by ICP*
- Cadmium *by ICP-MS*
- Calcium *by ICP*
- Chromium (Total) *by ICP*
- Chromium (Total) *by ICP-MS*
- Cobalt *by ICP*
- Cobalt *by ICP-MS*
- Copper *by ICP*
- Copper *by ICP-MS*
- Iron *by ICP*
- Iron *by ICP-MS*
- Lead *by ICP*
- Lead *by ICP-MS*
- Magnesium *by ICP*
- Magnesium *by ICP-MS*
- Manganese *by ICP*
- Manganese *by ICP-MS*
- Mercury *by ICP-MS*
- Molybdenum *by ICP*
- Molybdenum *by ICP-MS*
- Nickel *by ICP*
- Nickel *by ICP-MS*
- Potassium *by ICP*

Class: Metals
- Selenium *by ICP*
- Selenium *by ICP-MS*
- Silver *by ICP*
- Silver *by ICP-MS*
- Sodium *by ICP*
- Thallium *by ICP*
- Thallium *by ICP-MS*
- Tin *by ICP*
- Titanium *by ICP*
- Vanadium *by ICP*
- Vanadium *by ICP-MS*
- Zinc *by ICP*
- Zinc *by ICP-MS*

Class: BNA Semivolatiles
- * BNA ANALYTE GROUP *by GC/MS*

Class: PAH - Polynuclear Aromatic Hydrocarbons (BN)
- * PAH ANALYTE GROUP *by GC/MS*

Class: Petroleum Hydrocarbons
- Diesel Range Organics (DRO) *by GC*
- Gasoline Range Organics (GRO) *by GC*
- Petroleum Volatile Organic Compounds (PVOC) *by GC*
- Petroleum Volatile Organic Compounds (PVOC) *by GC/MS*

Class: PCBs as Aroclors
- * PCB as AROCLORS ANALYTE GROUP *by GC*

Class: PCB Congeners
- * PCB CONGENERS ANALYTE GROUP *by GC*
- * PCB CONGENERS ANALYTE GROUP *by GC/MS*
- * PCB CONGENERS ANALYTE GROUP *by HR-GC/MS*

Class: Dioxins and Furans
- * DIOXINS AND FURANS ANALYTE GROUP *by HR-GC/MS*

Class: Volatile Organics
- * VOC ANALYTE GROUP *by GC/MS*
- Benzene *by GC*
- Ethylbenzene *by GC*
- Toluene *by GC*
- m-Xylene *by GC*
- o-Xylene *by GC*
- p-Xylene *by GC*

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Scope of Accreditation

Pace Analytical Services, Inc.
1700 Elm St SE. Suite 200
Minneapolis, MN 55414

Laboratory Id: **999407970**
Expiration Date: **08/31/10**
Issued Date: **08/31/09**

Wisconsin Certification under NR 149
Matrix: Solid (Waste, Soil & Tissue)

Class: Waste Characterization Extractions
TCLP Extraction *by Waste Extractions*

The laboratory named above is hereby licensed under ch. NR 149, Wis. Adm. Code for the parameters listed in this attachment.
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Scope of Accreditation

Pace Analytical Services, Inc.
1700 Elm St SE. Suite 200
Minneapolis, MN 55414

Laboratory Id: **999407970**
Expiration Date: **08/31/10**
Issued Date: **01/13/10**

Wisconsin Certification under NR 149
Matrix: Potable Water (Drinking Water)

Class: SDWA - Primary Non-metals
- Cyanide - SM 4500-CN- C,E (18,19, or 20)
- Cyanide, Amenable - SM 4500-CN- C,G (18,19, or 20)
- Fluoride - SM 4500F- C (18,19, or 20)
- Nitrite - SM 4500-NO2- B (18,19, or 20)

Class: SDWA - Primary Metals
- Antimony - EPA 200.8
- Arsenic - EPA 200.8
- Barium - EPA 200.7
- Barium - EPA 200.8
- Beryllium - EPA 200.7
- Beryllium - EPA 200.8
- Cadmium - EPA 200.7
- Cadmium - EPA 200.8
- Chromium - EPA 200.7
- Chromium - EPA 200.8
- Copper - EPA 200.7
- Copper - EPA 200.8
- Lead - EPA 200.8
- Mercury - EPA 200.8
- Mercury - EPA 245.1
- Nickel - EPA 200.7
- Nickel - EPA 200.8
- Selenium - EPA 200.8
- Thallium - EPA 200.8

Class: SDWA - Secondary Metals
- Aluminum - EPA 200.8
- Calcium - EPA 200.7
- Iron - EPA 200.7
- Manganese - EPA 200.8
- Silver - EPA 200.8
- Sodium - EPA 200.7
- Zinc - EPA 200.8

Class: SDWA - SOC, Dioxin
- 2,3,7,8-TCDD (Dioxin) - EPA 1613

Class: SDWA - Trihalomethanes
- * THM ANALYTE GROUP - EPA 524.2

Class: SDWA - Volatile Organics
- * VOCS, REGULATED ANALYTE GROUP - EPA 524.2

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Pace Analytical™

QUALITY ASSURANCE MANUAL

Quality Assurance/Quality Control
Policies and Procedures
Revision 12.0

Pace Analytical Services – *Green Bay, WI*
1241 E Bellevue Street, Suite 9
Green Bay, WI 54302
920-469-2436

CORPORATE APPROVAL

Steve A. Vanderboom
President, CEO
1700 Elm Street SE, Suite 200
Minneapolis, MN 55414
(612) 607-1700

Date 1/30/09

Bruce Warden
Director of Quality, Safety, and Training
1700 Elm Street SE, Suite 200
Minneapolis, MN 55414
(612) 607-1700

Date 1/30/09

Any printed documents in use within a Pace Analytical Services, Inc. laboratory have been reviewed and approved by the persons listed on the cover page. They can only be deemed official if proper signatures are present.

This is **COPY#** 37 distributed on 2/16/10 by LAB and is _____ **CONTROLLED or** X **UNCONTROLLED.**

PACE ANALYTICAL SERVICES – *GREEN BAY, WI*
LOCAL APPROVAL

This document has been approved as the Quality Assurance Manual, effective 01/29/09, as indicated by the following signatures:

Laboratory General Manager 920-469-2436	01/29/09 Date
Laboratory Quality Manager 920-469-2436	1/29/09 Date
Laboratory Technical Director 920-469-2436	1/29/09 Date
Laboratory Technical Director 920-469-2436	1/29/09 Date
Laboratory Technical Director 920-469-2436	1/29/09 Date

Additional Signatures

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

Table of Contents

1.0 INTRODUCTION AND ORGANIZATIONAL STRUCTURE

"Working together to protect our environment and improve our health"

Pace Analytical Services Inc. - Mission Statement

1.1 Introduction to PASI

Pace Analytical Services, Inc. (PASI) is a privately held, full-service analytical testing firm operating a nationwide system of laboratories. PASI offers extensive services beyond standard analytical testing, including: bioassay for aquatic toxicity, air toxics, industrial hygiene testing, explosives, high resolution mass spectroscopy (including dioxins, furans and coplanar PCB's), radiochemical analyses, product testing, pharmaceutical testing, field services and mobile laboratory capabilities. PASI has implemented a consistent Quality System in each of its laboratories and service centers. In addition, the company utilizes an advanced data management system that is highly efficient and allows for flexible data reporting. Together, these systems ensure data reliability and superior on-time performance. This document defines the Quality System and QA/QC protocols.

Our goal is to combine our expertise in laboratory operations with customized solutions to meet the specific needs of our customers.

1.2 Statement of Purpose

To meet the business needs of our customers for high quality, cost-effective analytical measurements and services.

1.3 Quality Policy Statement and Goals of the Quality System

The PASI management is committed to maintaining the highest possible standard of service for our customers by following a documented quality system. The overall objective of this quality system is to provide reliable data through adherence to rigorous quality assurance policies and quality control procedures as documented in this Quality Assurance Manual.

All personnel within the PASI network are required to be familiar with all facets of the quality system and implement these policies and procedures in their daily work. This daily focus on quality is applied with initial project planning, continued through all field and laboratory activities, and is ultimately included in the final report generation.

PASI management demonstrates its commitment to quality by providing the resources, including facilities, equipment and personnel to ensure the adherence to these documented policies and procedures and to promote the continuous improvement of the quality system. All PASI personnel comply with all current applicable state, federal, and industry standards (such as the NELAC and ISO 17025 standards).

1.4 Pace Analytical Services Core Values

- **INTEGRITY**
- **VALUE EMPLOYEES**
- **KNOW OUR CUSTOMERS**
- **HONOR COMMITMENTS**
- **FLEXIBLE RESPONSE TO DEMAND**
- **PURSUE OPPORTUNITIES**
- **CONTINUOUSLY IMPROVE**

1.5 Code of Ethics

PASI's fundamental ethical principles are as follows:

- Each PASI employee is responsible for the propriety and consequences of his or her actions.
- Each PASI employee must conduct all aspects of Company business in an ethical and strictly legal manner, and must obey the laws of the United States and of all localities, states and nations where PASI does business or seeks to do business.
- Each PASI employee must reflect the highest standards of honesty, integrity and fairness on behalf of the Company with customers, suppliers, the public, and one another.

Strict adherence by each PASI employee to this Code of Ethics and to the Standards of Conduct is essential to the continued vitality of PASI.

Failure to comply with the Code of Ethics and Standards of Conduct will result in disciplinary action up to and including termination and referral for civil or criminal prosecution where appropriate. An employee will be notified of an infraction and given an opportunity to explain, as prescribed under current disciplinary procedures.

1.6 Standards of Conduct

1.6.1 Data Integrity

The accuracy and integrity of the analytical results produced at PASI are the cornerstones of the company. Lack of data integrity is an assault on our most basic values and puts PASI and its employees at grave financial and legal risk. Therefore, employees are to accurately prepare and maintain all technical records, scientific notebooks, calculations and databases. Employees are prohibited from making false entries or misrepresentations of data (e.g., dates, calculations, results or conclusions).

Managerial staff must make every effort to ensure that personnel are free from any undue pressures that may affect the quality or integrity of their work; including commercial, financial, over-scheduling and working condition pressures.

1.6.2 Confidentiality

PASI employees must not (directly or indirectly) use or disclose confidential or proprietary information except when in connection with their duties at PASI. This is effective over the course of employment and for a period of two years thereafter.

Confidential or proprietary information, belonging to either PASI and/or its customers, includes but is not limited to test results, trade secrets, research and development matters, procedures, methods, processes and standards, company-specific techniques and equipment, marketing and customer information, inventions, materials composition, etc.

1.6.3 Conflict of Interest

PASI employees must avoid situations that might involve a conflict of interest or appear questionable to others. The employee must be careful in two general areas:

- Participation in activities that conflict or appear to conflict with PASI responsibilities.

- Offering or accepting anything that might influence the recipient or cause another person to believe that the recipient may be influenced. This includes bribes, kickbacks or illegal payments.

Employees are not to engage in outside business or economic activity relating to a sale or purchase by the Company. Other questionable activities include service on the Board of Directors of a competing or supplier company, significant ownership in a competing or supplier company, employment for a competing or supplier company or participation in any outside business during the employee's work hours.

1.6.4 Compliance

All employees are required to read, understand and comply with the various components of the standards listed in this document. As confirmation that they understand this responsibility, each employee is required to sign an acknowledgment form (either hardcopy or in electronic database) annually (or as revisions become finalized) that becomes part of the employee's permanent record. Employees will be held accountable for complying with the Quality Systems as summarized in the Quality Assurance Manual.

1.7 Laboratory Organization

The PASI Corporate Office centralizes company-wide accounting, business development, financial management, human resources development, information systems, marketing, quality, safety, and training activities. PASI's Director of Quality, Safety & Training is responsible for assisting the development, implementation and monitoring of quality programs for the company. See Attachment IIB for the Corporate Organizational structure.

Each laboratory within the system operates with local management, but all share common systems and receive support from the Corporate Office.

A General Manager (GM) supervises each regional laboratory. Some operations may have an Assistant General Manager (AGM) in situations where the General Manager is responsible for multiple laboratory facilities and is not necessarily in the facility on a regular basis. Quality Managers (QM) at each lab report directly to their General Manager (or Assistant General Manager) but receive guidance and direction from the Director of Quality, Safety & Training.

The General Manager bears the responsibility for the laboratory operations and serves as the final, local authority in all matters. In the absence of the General Manager (and an Assistant General Manager), the Quality Manager serves as the next in command. He or she assumes the responsibilities of the GM until the GM is available to resume the duties of their position. In the absence of the GM and QM, management responsibility of the laboratory is passed to the Technical Director – provided such a position is identified – and then to the most senior department manager until the return of the GM or QM. The most senior department manager in charge may include the Client Services Manager or the Administrative Business Manager at the discretion of the General Manager.

A Technical Director who is absent for a period of time exceeding 15 consecutive calendar days shall designate another full-time staff member meeting the qualifications of the technical director to temporarily perform this function. The laboratory General Manager or Quality Manager has the authority to make this designation in the event the existing Technical Director is unable to do so. If this absence exceeds 65 consecutive calendar days, the primary accrediting authority shall be notified in writing.

The Quality Manager has the responsibility and authority to ensure the Quality System is implemented and followed at all times. In circumstances where a laboratory is not meeting the established level of quality or following the policies set for in this Quality Assurance Manual, the Quality Manager has the authority to halt laboratory operations should he or she deem such an action necessary. The QM will immediately

communicate the halting of operations to the GM and keep him or her posted on the progress of corrective actions. In the event the GM and QM are not in agreement as to the need for the suspension, the Chief Operating Officer and Director of Quality, Safety and Training will be called in to mediate the situation.

Under the direction of the General Manager, the technical staff of the laboratory is generally organized into the following functional groups:

- Organic Sample Preparation
- Wet Chemistry Analysis
- Metals Analysis
- Volatiles Analysis
- Semi-volatiles Analysis
- Radiochemical Analysis
- Product Testing
- Equipment Maintenance
- Microbiology

Appropriate support groups are present in each laboratory. The actual organizational structure for PASI – Green Bay is listed in Attachment IIA. In the event of a change in General Manager, Quality Manager or Technical Director(s), the laboratory will notify its accrediting authorities and revise the organizational chart in the Quality Assurance Manual (QAM) within 30 days. For changes in Department Managers or Supervisors or other laboratory personnel, no notifications will be sent to the laboratory's accrediting agencies; changes to the organizational chart will be updated during or prior to the annual review process. Changes or additions in these key personnel will also be noted by the additional signatures on the QAM Local Approval page. In any case, the QAM will remain in effect until the next scheduled revision.

1.8 Laboratory Job Descriptions

1.8.1 Senior General Manager

1. Oversees all functions of all the operations within their designated region.
2. Oversees the development of local General Managers within their designated region.
3. Oversees and authorizes personnel development including staffing, recruiting, training, workload scheduling, employee retention and motivation.
4. Oversees the preparation of budgets and staffing plans for all operations within their designated region.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.2 General Manager

1. Oversees all functions of the operations.
2. Authorizes personnel development including staffing, recruiting, training, workload scheduling, employee retention and motivation.
3. Prepares budgets and staffing plans.
4. Monitors the Quality Systems of the laboratory and advises the Quality Manager accordingly.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.3 Quality Manager

1. Oversees the laboratory Quality Systems while functioning independently from laboratory operations. Reports directly to the General Manager.
2. Monitors Quality Assurance policies and Quality Control procedures to ensure that the laboratory achieves established standards of quality.

3. Maintains records of quality control data and evaluates data quality.
4. Conducts periodic internal audits and coordinates external audits performed by regulatory agencies or customer representatives.
5. Reviews and maintains records of proficiency testing results.
6. Maintains the document control system
7. Assists in development and implementation of appropriate training programs.
8. Provides technical support to laboratory operations regarding methodology and project QA/QC requirements.
9. Maintains certifications from federal and state programs.
10. Ensures compliance with all applicable state, federal and industry standards.
11. Maintains the laboratory training records, including those in the Learning Management System (LMS).

1.8.4 Technical Director

1. Monitors the standards of performance in quality assurance and quality control data
2. Monitors the validity of analyses performed and data generated.
3. Reviews tenders, contracts and QAPPs to ensure the laboratory can meet the data quality objectives for any given project
4. Serves as the general manager of the laboratory in the absence of the GM, AGM and QM.
5. Provides technical guidance in the review, development and validation of new methodologies.

1.8.5 Administrative Business Manager

1. Responsible for financial and administrative management for the entire facility.
2. Provides input relative to tactical and strategic planning activities.
3. Organizes financial information so that the facility is run as a fiscally responsible business.
4. Works with staff to confirm that appropriate processes are put in place to track revenues and expenses.
5. Provide ongoing financial information to the General Manager and the management team so they can better manage their business.
6. Utilizes historical information and trends to accurately forecast future financial positions.
7. Works with management to ensure that key measurements (mileposts) are put in place to be utilized for tread analysis—this will include personnel and supply expenses, and key revenue and expense ratios.
8. Works with General Manager to develop accurate budget and track on an ongoing basis.
9. Works with entire management team to submit complete and justified capital budget requests and to balance requests across departments.
10. Works with project management team and administrative support staff to ensure timely and accurate invoicing.

1.8.6 Client Services Manager

1. Oversees all the day to day activities of the Client Services Department which includes Project Management and, possibly, Sample Control.
2. Responsible for staffing and all personnel management related issues for Client Services.
3. Serves as the primary senior consultant to customers on all project related issues such as set up, initiation, execution and closure.
4. Performs or is capable of performing all duties listed for that of Project Manager.

1.8.7 Project Manager

1. Coordinates daily activities including taking orders, reporting data and analytical results.
2. Serves as the primary technical and administrative liaison between customers and PASI.

3. Communicates with operations staff to update and set project priorities.
4. Provides results to customers in the requested format (verbal, hardcopy, electronic, etc.).
5. Works with customers, laboratory staff, and other appropriate PASI staff to develop project statements of work or resolve problems of data quality.
3. Responsible for solicitation of work requests, assisting with proposal preparation and project initiation with customers and maintain customer records.
4. Mediation of project schedules and scope of work through communication with internal resources and management.
5. Responsible for preparing routine and non-routine quotations, reports and technical papers.
6. Interfaces between customers and management personnel to achieve customer satisfaction.
7. Manages large-scale complex projects.
8. Supervises less experienced project managers and provide guidance on management of complex projects.
6. Arranges bottle orders and shipment of sample kits to customers.
7. Verifies login information relative to project requirements and field sample Chains-of-Custody.

1.8.8 Project Coordinator

1. Responsible for preparation of project specifications and provides technical/project support.
2. Coordinates project needs with other department sections and assists with proposal preparation.
3. Prepares routine proposals and invoicing.
4. Responsible for scanning, copying, assembling and binding final reports.
5. Other duties include filing, maintaining forms, process outgoing mail, maintaining training database and data entry.

1.8.9 Department Manager/Supervisor

1. Oversees the day-to-day production and quality activities of their assign department.
2. Ensures that quality assurance and quality control criteria of analytical methods and projects are satisfied.
3. Assesses data quality and takes corrective action when necessary.
4. Approves and releases technical and data management reports.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.10 Group Leader/Supervisor

1. Trains analysts in laboratory operations and analytical procedures.
1. Organizes and schedules analyses with consideration for sample holding times.
2. Implements data verification procedures by assigning data verification duties to appropriate personnel.
3. Evaluates instrument performance and supervises instrument calibration and preventive maintenance programs.
4. Reports non-compliance situations to laboratory management including the Quality Manager.

1.8.11 Laboratory Analyst

1. Performs detailed preparation and analysis of samples according to published methods and laboratory procedures.
2. Processes and evaluates raw data obtained from preparation and analysis steps.
3. Generates final results from raw data, performing primary review against method criteria.

4. Monitors quality control data associated with analysis and preparation. This includes examination of raw data such as chromatograms as well as an inspection of reduced data, calibration curves, and laboratory notebooks.
5. Reports data in LIMS, authorizing for release pending secondary approval.
6. Conducts routine and non-routine maintenance of equipment as required.
7. Performs or is capable of performing all duties associated with that of Laboratory Technician.

1.8.12 Laboratory Technician

1. Prepares standards and reagents according to published methods or in house procedures.
2. Performs preparation and analytical steps for basic laboratory methods.
3. Works under the direction of a Laboratory Analyst on complex methodologies.
4. Assists Laboratory Analysts on preparation, analytical or data reduction steps for complex methodologies.
5. Monitors quality control data as required or directed. This includes examination of raw data such as chromatograms as well as an inspection of reduced data, calibration curves, and laboratory notebooks.

1.8.13 Sample Management Personnel

1. Signs for incoming samples and verifies the data entered on the Chain-of-Custody forms.
2. Enters the sample information into the Laboratory Information Management System (LIMS) for tracking and reporting.
3. Stages samples according to EPA requirements.
4. Assists Project Managers and Coordinators in filling bottle orders and sample shipments.

1.8.14 Systems Administrator or Systems Manager

1. Assists with the creation and maintenance of electronic data deliverables (EDDs).
2. Coordinates the installation and use of all hardware, software and operating systems.
3. Performs troubleshooting on all aforementioned systems.
4. Trains new and existing users on systems and system upgrades.
5. Maintains all system security passwords.
6. Maintains the electronic backups of all computer systems.

1.8.15 Safety/Chemical Hygiene Officer

1. Maintains the laboratory Chemical Hygiene Plan.
2. Plans and implements safety policies and procedures.
3. Maintains safety records.
4. Organizes and/or performs safety training.
5. Performs safety inspections and provides corrective/preventative actions.
6. Assists personnel with safety issues (e.g. personal protective equipment).

1.8.16 Waste Coordinator

1. Evaluates waste streams and helps to select appropriate waste transportation and disposal companies.
2. Maintains complete records of waste disposal including waste manifests and state reports.
3. Assists in training personnel on waste-related issues such as waste handling and storage, waste container labeling, proper satellite accumulation, secondary containment, etc.
4. Conducts a weekly inspection of the waste storage areas of the lab.

1.9 Training and Orientation

Each new employee receives a five part orientation: human resources, ethics and data integrity, safety, Quality Systems, and departmental.

The human resources orientation includes benefits, salary, and company policies. All records are stored with Human Resources.

The ethics and data integrity training covers the obligations of each employee to ensure the defensibility of laboratory data. Employees are provided with general policies related to ethics in the laboratory and specific examples of improper practices that are unacceptable in any PASI facility. The employee is trained to make the right decisions with regards to laboratory practices and where to go for answers in circumstances where they may be unclear as to the correct protocol.

The safety orientation includes an in-depth review of the PASI Chemical Hygiene Plan/Safety Plan, which are consistent with the requirements of OSHA's Hazard Communication Program (29 CFR 1910.1200) and other pertinent regulations.

The Quality Systems orientation provides the new employee with information through an introduction to the Quality Assurance Manual and SOPs, acceptable record keeping practices, and the individual's responsibility to data quality. Quality Systems training is reinforced with the new employee as specific topics are covered during the departmental or analytical method training. Quality Systems training will address policies and practices that ensure the quality and defensibility of the analytical data. These topics include but are not limited to traceability of measurements, method calibration, calibration verification, accuracy, precision and uncertainty of measurements, corrective actions, documentation and root cause analysis.

The new employee's Department Supervisor provides the employee with a basic understanding of the role of the laboratory within the structure of PASI and the basic elements of that individual's position.

Supervised training uses the following techniques:

- Hands-on training
- Training checklists
- Lectures and training sessions
- Method-specific training
- Conferences and seminars
- Short courses
- Specialized training by instrument manufacturers
- Proficiency testing programs.

Group Supervisors/Leaders are responsible for providing documentation of training and proficiency for each employee under their supervision. The employee's training file indicates what procedures an analyst or a technician is capable of performing, either independently or with supervision. The files also include documentation of continuing capability (see Section 3.4 for details on Demonstration of Capability requirements). Training documentation files for each person are maintained by the Quality Office either in hardcopy format or within the Learning Management System (LMS).

All procedures and training records are maintained and available for review during laboratory audits. These procedures are reviewed/updated periodically by lab management. Additional information can be found in SOP S-ALL-Q-020 ***Orientation & Training Procedures*** or its equivalent revision or replacement.

1.10 Laboratory Safety

It is the policy of PASI to make safety and health an integral part of daily operations and to ensure that all employees are provided with safe working conditions, personal protective equipment, and requisite training to do their work without injury. Each employee is responsible for his/her own safety by complying with established company rules and procedures. These rules and procedures as well as a more detailed description of the employees' responsibilities are contained in the corporate Safety Manual and Chemical Hygiene Plan.

1.11 Security and Confidentiality

Security is maintained by controlled access to laboratory buildings. Exterior doors to laboratory buildings remain either locked or continuously monitored by PASI staff. Keyless door-lock combinations (and computer access codes/logins) are changed periodically. Posted signs direct visitors to the reception office and mark all other areas as off limits to unauthorized personnel. All visitors to the facility must sign the Visitor's Logbook maintained by the receptionist. A staff member will accompany them during the duration of their stay on the premises unless the GM, QM or TD specify otherwise. In this instance, the staff member will escort the visitor back to the reception area at the end of his/her visit where he/she signs out. The last staff member to leave their department for the day should ensure that all outside access points to that area are secure.

Additional security is provided where necessary, e.g., specific secure areas for sample, data and customer report storage, as requested by customers or cases where national security is of concern. These areas are lockable within the facilities, or are in secure offsite storage. Access is limited to specific individuals or their designees. Security of sample storage areas is the responsibility of the Sample Custodian. Security of samples and data during analysis and data reduction is the responsibility of Group Supervisors. Security of customer report archives is the responsibility of the Client Services Manager. These secure areas are locked whenever these individuals or their designees are not present in the facility.

Access to designated laboratory sample storage locations is limited to authorized personnel only. Provisions for lock and key access are provided. No samples are to be removed without proper authorization. If requested by customer or contract, samples are not to be removed from secure storage areas without filling out the associated internal Chain-of-Custody records.

Standard business practices of confidentiality are applied to all documents and information regarding customer analyses. Specific protocols for handling confidential documents are described in PASI SOPs. Additional protocols for internal identification of samples and data by number only are implemented as required under contract specific Quality Assurance Project Plans (QAPPs).

All information pertaining to a particular customer, including national security concerns will remain confidential. Data will be released to outside agencies only with written authorization from the customer or where federal or state law requires the company to do so (i.e. federal or state subpoena).

2.0 SAMPLE CUSTODY

2.1 Sampling Support

Each individual PASI laboratory provides shipping containers, sample containers (including applicable chemical preservatives), custody documents, and field quality control samples (e.g., trip blanks) to support field-sampling events. Guidelines for sample container types, preservatives, and holding times for a variety of methods are listed in Attachment VIII. Note that all analyses listed are not necessarily performed at all PASI and there may be additional laboratory analyses performed that are not included in these tables. PASI – Green Bay may provide pick-up and delivery services to their customers when needed. PASI – Green Bay may provide pick-up and delivery services to customers when needed.

2.2 Field Services Division

Pace Analytical has a large Field Services Division which is based in their Minneapolis facility as well as limited field service capabilities in some of the other facilities. Field Services provides comprehensive nationwide service offerings including:

- Stack Testing
- Ambient Air
- CEM Certification Testing
- Air Quality Monitoring
- Onsite Analytical Services- FTIR and GC
- Real-time Process Diagnostic/Optimization Testing
- Wastewater, Groundwater and Drinking Water Monitoring
- Storm water and Surface Water Monitoring
- Soil and Waste Sampling
- Mobile Laboratory Services

The Field Services Division operates under the PASI Corporate Quality System, with applicable and necessary provisions to address the activities, methods, and goals specific to Field Services for a unit specific Quality Program. All procedures and methods used by Field Services are documented in Standard Operating Procedures and Procedure Manuals.

2.3 Project Initiation

Prior to accepting new work, the laboratory reviews performance capability. The laboratory establishes that sufficient resources (personnel, equipment capacity, analytical method capability, etc.) are available to complete the required work. The customer needs and data quality objectives are defined and appropriate environmental test methods are assured to meet customer's requirements by project managers or sales representative. Project Managers review laboratory certifications. Members of the management staff review current instrument capacity, personnel availability and training, analytical procedures capability and projected sample load. Management then informs the sales and client services personnel whether or not the laboratory can accept the new project via written correspondence, email, and/or daily operations meetings.

The laboratory maintains records of all such reviews, including discussions with customers. Routine analytical project documentation of quotes, notes, dates, initials and/or recordings is maintained in a project folder by project management. Conditions for new and more complex contracts are determined by the General Managers and sales representatives. Quality Management is consulted on technical requirements and operations staff provides input on volume capacities. Evidence of these reviews is maintained in the form of awarded Request for Proposals (RFPs), signed quotes or contracts, and a Customer Relationship Management (CRM) database. If a review identifies a potential mismatch between

customer requirements and laboratory capabilities and/or capacities, Pace will specify its level of commitment by listing these exceptions to the requirements within the RFP, quote or contract.

Additional information regarding specific procedures for reviewing new work requests can be found in SOP S-ALL-Q-006 ***Review of Analytical Requests*** or its equivalent revision or replacement.

2.4 Chain-Of-Custody

A chain-of-custody (COC) (see Attachment VII) document provides the legal documentation of samples from time of collection to completion of analysis. Importance is stressed on completeness of COCs. PASI has implemented Standard Operating Procedures to ensure that sample custody traceability and responsibility objectives are achieved for every project.

Field personnel or client representatives complete a chain-of-custody form for all samples. Samples are received by the laboratory accompanied by these forms.

If sample shipments are not accompanied by the correct documentation, the Sample Receiving department notifies a Project Manager. The Project Manager then obtains the correct documentation/information from the customer in order for analysis of samples to proceed.

The sampler is responsible for providing the following information on the chain-of-custody form:

- Customer project name
- Project location or number
- Field sample number/identification
- Date and time sampled
- Sample type (matrix)
- Preservative
- Requested analyses
- Sampler signature
- Relinquishing signature
- Date and time relinquished
- Sampler remarks (if applicable)
- Custody Seal Number (if applicable)
- Regulatory Program Designation
- The state where the samples were collected to ensure all applicable state requirements are met
- Turnaround time requested
- Purchase order number

The record is filled out completely and legibly with indelible ink. Errors are corrected by drawing a single line through the initial entry and initialing and dating the change. All transfers of samples are recorded on the chain-of-custody in the “relinquished” and “received by” sections. All information except signatures is printed.

Additional information can be found in SOP S-ALL-C-001 ***Sample Management*** or its equivalent revision or replacement.

2.5 Sample Acceptance Policy

In accordance with regulatory guidelines, PASI complies with the following sample acceptance policy for all samples received.

If the samples do not meet the sample receipt acceptance criteria outlined below, the laboratory is required to document all non-compliances, contact the customer, and either reject the samples or fully document

any decisions to proceed with analyses of samples which do not meet the criteria. Any results reported from samples not meeting these criteria are appropriately qualified on the final report.

All samples must:

- Have unique customer identification that are clearly marked with durable waterproof labels on the sample containers and that match the chain of custody.
- Have clear documentation on the chain of custody related to the location of the sampling site with the time and date of sample collection.
- Have the sampler's name and signature
- Have the requested analyses clearly marked
- Have clear documentation of any special analysis requirements (data deliverables, etc.);
- Be in appropriate sample containers with clear documentation of the preservatives used.
- Be correctly preserved unless method allows for laboratory preservation.
- Be received within holding time. Any samples with hold times that are exceeded will not be processed without prior customer permission.
- Have sufficient sample volume to proceed with the analytical testing. If insufficient sample volume is received, analysis will not proceed without customer approval.
- Be received within appropriate temperature ranges - not frozen but ≤6°C (See Note 1), unless program requirements or customer contractual obligations mandate otherwise (see Note 2). The cooler temperature is recorded directly on the COC and the SCUR. Samples that are delivered to the lab immediately after collection are considered acceptable if there is evidence that the chilling process has been started, for example by the arrival of the samples on ice. If samples arrive that are not compliant with these temperature requirements, the customer will be notified. The analysis will NOT proceed unless otherwise directed by the customer. If less than 72 hours remain in the hold time for the analysis, the analysis may be started while the customer is contacted to avoid missing the hold time. Data will be appropriately qualified on the final report.

  Note 1: Temperature will be read and recorded based on the precision of the measuring device. For example, temperatures obtained from a thermometer graduated to 0.1°C will be read and recorded to ±0.1°C. Measurements obtained from a thermometer graduated to 0.5°C will be read to ±0.5°C. Measurements read at the specified precision are not to be rounded down to meet the≤6°C limit (i.e. 6.2°C rounded and recorded as 6°C).

  Note 2: Some microbiology methods allow sample receipt temperatures of up to 10°C. Consult the specific method for microbiology samples received above 6°C prior to initiating corrective action for out of temperature preservation conditions.

Upon sample receipt, the following items are also checked and recorded:

- Presence of custody seals or tapes on the shipping containers
- Sample condition: Intact, broken/leaking
- Sample holding time
- Sample pH when required
- Appropriate containers

Samples for drinking water analysis that are improperly preserved, or are received past holding time, are rejected at the time of receipt, with the exception of VOA samples that are tested for pH at the time of analysis.

Additional information can be found in SOP S-ALL-C-001 ***Sample Management*** or its equivalent revision or replacement.

2.6 Sample Log-in

After sample inspection, all sample information on the chain-of-custody is entered into the Laboratory Information Management System (LIMS).

This permanent record documents receipt of all sample containers including:

- Customer name and contact
- Customer number
- Pace Analytical project number
- Pace Analytical Project Manager
- Sample descriptions
- Due dates
- List of analyses requested
- Date and time of lab receipt
- Field ID code
- Date and time of collection
- Any comments resulting from inspection for sample rejection

All samples received are logged into the LIMS system within one working day of receipt. Sample login may be delayed due to customer clarification of analysis needed, corrective actions for sample receipt non-conformance, or other unusual circumstances. If the time collected for any sample is unspecified and Pace is unable to obtain this information from the customer, the laboratory will use 08:00 as the time sampled. All hold times will be based on this sampling time and qualified accordingly if exceeded.

The Laboratory Information Management System (EPIC Pro) automatically generates a unique identification number for each sample created in the system. The LIMS sample number follows the general convention of BB-XXXXX-YYY. The BB represents the laboratory identification within Pace's laboratory network. The 5 digit "X" number represents the project number followed by a 3 digit sample number. The project number is a sequential number that is assigned as a new project is created. The sample number corresponds to the number of samples submitted by the client. In addition to the unique sample ID, there is a sample container ID that consists of the sample number, the container type (ex. BP1U), and bottle 1 of Y, where Y represent the total number of containers of that particular type. Together the sample LIMs number and sample container ID number create a unique barcode encryption that can be linked to the sample analysis requested by the client. This unique identification number is placed on the sample container as a durable label and becomes the link between the laboratory's sample management system and the client's field identification; it will be a permanent reference number for all future interactions.

Sample labels are printed from the LIMS system and affixed to each sample container.

Samples with hold times that are near expiration date/time may be sent directly to the laboratory for analysis at the discretion of the Project Manager and/or General Manager.

Additional information can be found in SOP S-ALL-C-001 ***Sample Management*** or its equivalent revision or replacement.

2.7 Sample Storage

2.7.1 Storage Conditions

Samples are stored away from all standards, reagents, or other potential sources of contamination. Samples are stored in a manner that prevents cross-contamination (e.g. volatile samples are stored separate from other samples). All sample fractions, extracts, leachates and

other sample preparation products are stored in the same manner as actual samples or as specified by the analytical method.

2.7.2 Temperature Monitoring

Samples are taken to the appropriate storage location (ambient, refrigerator, freezer) immediately after sample receipt and check-in procedures are completed. All sample storage areas are located in limited access areas and are monitored to ensure sample integrity.

The temperature of each refrigerated storage area is maintained at ≤6°C unless state or program requirements differ. The temperature of each freezer storage area is maintained at < - 10°C unless state or program requirements differ. The temperature of each storage area is monitored and recorded each workday. If the temperature falls outside the acceptable limits, the following corrective actions are taken and appropriately documented:

- The temperature is rechecked after two hours to verify temperature exceedance. Corrective action is initiated if necessary.
- The Quality Manager and/or laboratory management are notified if the problem persists.
- The samples are relocated to a proper environment if the temperature cannot be maintained after corrective actions are implemented.
- The affected customers are notified.
- Documentation is provided on analytical report.

2.7.3 Hazardous Materials

Pure product or potentially heavily contaminated samples are tagged as "hazardous" or "lab pack" and are stored separately from other samples.

2.7.4 Foreign/Quarantined Soils

Depending on the soil disposal practices of the laboratory, foreign soils and soils from USDA regulated areas are segregated. The USDA requires these samples to be incinerated or sterilized by an approved treatment procedure.

Additional information can be found in SOP S-ALL-C-001 ***Sample Management and*** SOP S-GB-S-001 ***Regulated Soil*** or its equivalent revision or replacement.

2.8 Sample Protection

PASI laboratory facilities are operated under controlled access to ensure sample and data integrity. Visitors must register at the front desk and be properly escorted.

Samples are removed from storage areas by designated personnel and returned to the storage areas, if necessary, immediately after the required sample quantity has been taken.

Upon customer request, additional and more rigorous chain of custody protocols for samples and data can be implemented. For example, some projects may require complete documentation of sample custody within the secure laboratory.

Additional information can be found in SOP S-ALL-C-001 ***Sample Management*** or its equivalent revision or replacement.

2.9 Subcontracting Analytical Services

Every effort is made to perform chemical analyses for PASI customers within the laboratory that receives the samples. When subcontracting to a laboratory other than the receiving laboratory (inside or outside the PASI network) becomes necessary, a preliminary verbal communication with an appropriate laboratory is undertaken. Customers are notified in writing of the lab's intention to subcontract any portion of the testing to another laboratory. Work performed under specific protocols may involve special considerations.

Prior to subcontracting samples to a laboratory outside Pace Analytical, the potential sub-contract laboratory will be pre-qualified by verifying that the subcontractor meets the following criteria:

- All certifications required for the proposed subcontract are in effect,
- Sufficient professional liability and other required insurance coverage is in effect, and
- Is not involved in legal action by any federal, state, or local government agency for data integrity issues and has not been convicted in such investigation at any time during the past 5 years.

Additional information can be found in SOP S-ALL-Q-027 ***Evaluation & Qualification of Vendors*** or its equivalent revision or replacement. The contact and preliminary arrangements are made between the PASI Project Manager and the appropriate subcontract laboratory personnel. The specific terms of the subcontract laboratory agreement include :

- Method of analysis
- Number and type of samples expected
- Project specific QA/QC requirements
- Deliverables required
- Laboratory certification requirement
- Price per analysis
- Turnaround time requirements

Chain-of-custody forms are generated for samples requiring subcontracting to other laboratories. Sample receiving personnel re-package the samples for shipment, create a transfer chain-of-custody form and record the following information:

- Pace Analytical Laboratory Number
- Matrix
- Requested analysis
- Special instructions (quick turn-around, required detection or reporting limits, unusual information known about the samples or analytical procedure).
- Signature in "Relinquished By"

All subcontracted sample data reports are sent to the PASI Project Manager.

Any Pace Analytical work sent to other labs within the PASI network is handled as subcontracted work (also known as inter-regional) and all final reports are labeled clearly with the name of the laboratory performing the work. Any non-NELAC work is clearly identified. PASI will not be responsible for analytical data if the subcontract laboratory was designated by the customer.

Additional information can be found in SOP S-ALL-Q-017 ***Subcontracting Samples*** or its equivalent revision or replacement.

2.10 Sample Retention and Disposal

Samples (and sample by-products) must be retained by the laboratory for a period of time necessary to protect the integrity of the sample or sample by-product (e.g. method holding time) and to protect the interests of the laboratory and the customer.

Unused portions of samples are retained by each laboratory based on program or customer requirements for sample retention and storage. The sample retention time is a minimum of 45 days from receipt of the samples. Samples requiring storage beyond this time due to special requests or contractual obligations will not be stored under temperature controlled conditions unless the laboratory has sufficient capacity and their presence does not compromise the integrity of other samples.

After this period expires, non-hazardous samples are properly disposed of as non-hazardous waste. The preferred method for disposition of hazardous samples is to return the excess sample to the customer. If it is not feasible to return samples, or the customer requires PASI to dispose of excess samples, PASI will arrange for proper disposal by an approved contractor.

Additional information can be found in SOP S-ALL-S-002 ***Waste Handling*** and S-ALL-C-001 ***Sample Management*** or their equivalent revisions or replacements.

3.0 ANALYTICAL CAPABILITIES

3.1 Analytical Method Sources

PASI laboratories are capable of analyzing a full range of environmental samples from a variety of matrices, including air, surface water, wastewater, groundwater, soil, sediment, biota, and other waste products. The latest valid editions of methodologies are applied from regulatory and professional sources including EPA, ASTM, USGS, NIOSH, and State Agencies. Section 11 of this manual is a representative listing of general analytical protocol references. PASI discloses in writing to its customers and regulatory agencies any instances in which modified methods are being used in the analysis of samples.

In the event of a customer-specific need, instrumentation constraint or regulatory requirement, PASI laboratories reserve the right to use valid versions of methods that may not be the most recent edition available.

3.2 Analytical Method Documentation

The primary form of documentation of analytical methods is the Standard Operating Procedure (SOP). SOPs contain pertinent information as to what steps are required by an analyst to successfully perform a procedure. The required contents for the SOPs are specified in the company-wide SOP for Preparation of SOPs (S-ALL-Q-001).

The SOPs may be supplemented by other training materials that further detail how methods are specifically performed. This training material will undergo periodic, documented review along with the other Quality System documentation.

3.3 Analytical Method Validation

In some situations, PASI develops and validates methodologies that may be more applicable to a specific problem or objective. When non-standard methods (e.g. methods other than EPA, NIOSH, ASTM, AOAC, etc.) are required for specific projects or analytes of interest, or when the laboratory develops a method, or modifies a standard method, the laboratory validates the method prior to applying it to customer samples. Method validity is established by meeting criteria for precision and accuracy as established by the data quality objectives specified by the end user of the data. The laboratory records the validation procedure, the results obtained and a statement as to the usability of the method. The minimum requirements for method validation include determination of the limit of detection and limit of quantitation, evaluation of precision and bias, and evaluation of selectivity of each analyte of interest.

3.4 Demonstration of Capability (DOC)

Analysts complete an initial demonstration of capability (IDOC) study prior to performing a method or when there is a change in instrument type, personnel or test method (when a defined ‘work cell’ is in operation, the entire work cell must meet the criteria). The mean recovery and standard deviation of each analyte, taken from 4 replicates of a quality control standard is calculated and compared to method criteria (if available) or established lab criteria for evaluation of acceptance. Each laboratory maintains copies of all demonstrations of capability and corresponding raw data for future reference and must document the acceptance criteria prior to the analysis of the DOC. Demonstrations of capability are verified on an annual basis.

Alternative demonstration of capability procedures may be used for IDOC for methods that don’t lend themselves to the “4 replicate” approach. For methods that only measure precision, the precision of four laboratory duplicate pairs will be assessed. The relative percent differences must be within the method acceptance limits. For procedures like TCLP or SPLP, the analyst will demonstrate making the buffered solution and performing the tumbling process. The trainer or supervisor will sign-off on demonstration of

capability of the tumbling process. Additional demonstration of capability options will be specified in Section 14 – Method Performance of the applicable method SOP.

For Continuing Demonstrations of Capability, the laboratories may use Performance Testing (PT) samples or any of the approaches utilized for IDOCs. For methods or procedures that do not lend themselves to the "4 replicate" approach, the demonstration of capability requirements will be specified in Section 14 – Method Performance of the applicable SOP.

Pace Analytical utilizes a peer review system for data review and approval. The data review staff are qualified to validate data conversion, transcription, and reporting in addition to assessing deviations from the standard operating procedures. The data review staff are familiar with the analytical method procedures with documentation maintained in their training files. The data reviewers also utilize a method specific checklist which contains the quality control acceptance criteria. Deviations from the standard operating procedure are documented on the checklist by the analyst. Further data review guidance is provided in SOP S-GB-Q-003 Data Reduction, Validation and Reporting in the Environmental Lab.

3.5 Regulatory and Method Compliance

PASI understands that expectations of our customers commonly include the assumption that laboratory data will satisfy specific regulatory requirements. Therefore PASI attempts to ascertain, prior to beginning a project, what applicable regulatory jurisdiction, agency, or protocols apply to that project. This information is also required on the Chain-of-Custody submitted with samples.

PASI makes every effort to detect regulatory or project plan inconsistencies, based upon information from the customer, and communicate them immediately to the customer in order to aid in the decision-making process. PASI will not be liable if the customer chooses not to follow PASI recommendations.

It is PASI policy to disclose in a forthright manner any detected noncompliance affecting the usability of data produced by our laboratories. The laboratory will notify customers within 30 days of fully characterizing the nature of the nonconformance, the scope of the nonconformance and the impact it may have on data usability.

4.0 QUALITY CONTROL PROCEDURES

4.1 Data Integrity System

The data integrity system at PASI provides assurances to management that a highly ethical approach is being applied to all planning, training and implementation of methods. Data integrity is crucial to the success of our company and Pace Analytical is committed to providing a culture of quality throughout the organization. To accomplish this goal, PASI has implemented a data integrity system that encompasses the following four requirements:

1. A data integrity training program: Standardized training is given to each new employee and a yearly refresher is presented to all employees. Key topics within this training include:
   - Need for honesty in analytical reporting
   - Process for reporting data integrity issues
   - Specific examples of unethical behavior and improper practices
   - Documentation of non-conforming data that is still useful to the data user
   - Consequences and punishments for unethical behavior
   - Examples of monitoring devices used by management to review data and systems
2. Signed data integrity documentation for all employees: This includes a quiz following the Ethics training session and written agreement to abide by the Code of Ethics and Standards of Conduct explained in the employee manual The quiz along with the employee's electronic signature of agreement are maintained within the Learning Management System.
3. In-depth, periodic monitoring of data integrity: Including peer data review and validation, internal data audits, proficiency testing studies, etc.
4. Documentation of any review or investigation into possible data integrity infractions. This documentation, including any disciplinary actions involved, corrective actions taken, and notifications to customers must be available for review for lab assessors and must be retained for a minimum of five years.

PASI management makes every effort to ensure that personnel are free from any undue pressures that affect the quality of their work including commercial, financial, over-scheduling, and working condition pressures.

Corporate management also provides all PASI facilities a mechanism for confidential reporting of data integrity issues that ensures confidentiality and a receptive environment in which all employees are comfortable discussing items of ethical concern. The anonymous message line is monitored by the Corporate Director of Quality, Safety and Training who will ensure that all concerns are evaluated and, where necessary, brought to the attention of executive management and investigated. **The message line voice mail box is available at 612-607-6427.**

4.2 Method Blank

A method blank is used to evaluate contamination in the preparation/analysis system. The method blank is processed through all preparation and analytical steps with its associated samples.

A method blank is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (e.g. volatiles), a method blank is processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The method blank consists of a matrix similar to the associated samples that is known to be free of the analytes of interest. Laboratories will characterize a representative matrix as "clean" if the matrix contains contaminants at less than ½ the laboratory's reporting limit.

Each method blank is evaluated for contamination. The source of any contamination is investigated and documented corrective action is taken when the concentration of any target analyte is detected above the

reporting limit and is greater than 1/10 of the amount of that analyte found in any associated sample for Inorganic Analysis. The source of any contamination is investigated and documented corrective action is taken when the concentration of any target analyte is detected above the reporting limit and is greater than 1/20 of the amount of that analyte found in any associated sample for Organic Analysis. Corrective actions include the re-preparation and re-analysis of all the samples (where possible) along with the full set of required quality control samples. Data qualifiers must be applied to any result reported that is associated with a contaminated method blank.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.3 Laboratory Control Sample

The Laboratory Control Sample (LCS) is used to evaluate the performance of the entire analytical system including preparation and analysis.

An LCS is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (e.g. volatiles), an LCS will be processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The LCS consists of a matrix similar to the associated samples that is known to be free of the analytes of interest that is then spiked with known concentrations of target analytes.

The LCS contains **all** analytes specified by a specific method or by the customer or regulatory agency (which may include full list of target compounds, with certain exceptions. These exceptions may include analyzing only specific Aroclors when PCB analysis is requested or not spiking with all EPA Appendix compounds when a full Appendix list of compounds is requested). In the absence of specified components, the lab will spike with the following compounds:

- For multi-peak analytes (e.g. PCBs, technical chlordane, toxaphene), a representative standard will be processed.
- For methods with long lists of analytes, a representative number of target analytes may be chosen. The following criteria is used to determine the number of LCS compounds used:
    - For methods with 1-10 target compounds, the lab will spike with all compounds
    - For methods with 11-20 target compounds, the lab will spike with at least 10 compounds or 80%, whichever is greater
    - For methods with greater than 20 compounds, the lab will spike with at least 16 compounds.

The LCS is evaluated against the method default or laboratory-derived acceptance criteria. Method default control limits will be used until the laboratory has a minimum of 20 (preferably greater than 30) data points from which to derive internal criteria. Any compound that is outside of these limits is considered to be ‘out of control’ and must be qualified appropriately. Any associated sample containing an ‘out-of-control’ compound must either be re-analyzed with a successful LCS or reported with the appropriate data qualifier.

For LCSs containing a large number of analytes, it is statistically likely that a few recoveries will be outside of control limits. This does not necessarily mean that the system is out of control, and therefore no corrective action would be necessary (except for proper documentation). NELAC has allowed for a minimum number of marginal exceedances, defined as recoveries that are beyond the LCS control limits (3X the standard deviation) but less than the marginal exceedance limits (4X the standard deviation). The number of allowable exceedances depends on the number of compounds in the LCS. If more analyte recoveries exceed the LCS control limits than is allowed (see below) or if any one analyte exceeds the marginal exceedance limits, then the LCS is considered non-compliant and corrective actions are necessary. The number of allowable exceedances is as follows:

- >90 analytes in the LCS- 5 analytes
- 71-90 analytes in the LCS- 4 analytes
- 51-70 analytes in the LCS- 3 analytes
- 31-50 analytes in the LCS- 2 analytes
- 11-30 analytes in the LCS- 1 analyte
- <11 analytes in the LCS- no analytes allowed out)

A matrix spike (MS) can be used in place of a non-compliant LCS in a batch as long as the MS passes the LCS acceptance criteria (this is a NELAC allowance). When this happens, full documentation must be made available to the data user. If this is not allowed by a customer or regulatory body, the associated samples must be rerun with a compliant LCS (if possible) or reported with appropriate data qualifiers.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is used to determine the effect of the sample matrix on compound recovery for a particular method. The information from these spikes is sample or matrix specific and is not used to determine the acceptance of an entire batch (see LCS).

A **Matrix Spike/Matrix Spike Duplicate** (MS/MSD) set is processed at a frequency specified in a particular method or as determined by a specific customer. This frequency will be specified in the applicable method SOP or customer QAPP. In the absence of such requirements, an MS/MSD set is routinely analyzed once per every 20 samples per general matrix (i.e. soil, water, biota, etc.) per method.

The MS and MSD consist of the sample matrix that is then spiked with known concentrations of target analytes. Lab personnel spike customer samples that are specifically designated as MS/MSD samples or, when no designated samples are present in a batch, randomly select samples to spike that have adequate sample volume or weight. Spiked samples are prepared and analyzed in the same manner as the original samples and are selected from different customers if possible.

The MS and MSD contain all analytes specified by a specific method or by the customer or regulatory agency. In the absence of specified components, the lab will spike with the same number of compounds as previously discussed in the LCS section.

The MS and MSD are evaluated against the method or laboratory-derived criteria. Any compound that is outside of these limits is considered to be ‘out of control’ and must be qualified appropriately. Batch acceptance, however, is based on method blank and LCS performance, not on MS/MSD recoveries. The spike recoveries give the data user a better understanding of the final results based on their site-specific information.

A matrix spike and sample duplicate will be performed instead of a matrix spike and matrix spike duplicate when specified by the customer or method.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.5 Surrogates

Surrogates are compounds that reflect the chemistry of target analytes and are typically added to samples for organic analyses to monitor the effect of the sample matrix on compound recovery.

Surrogates are added to each customer sample (for organics), method blank, LCS and MS prior to extraction or analysis. The surrogates are evaluated against the method or laboratory-derived acceptance criteria. Any surrogate compound that is outside of these limits is considered to be ‘out of control’ and must be qualified appropriately. Samples with surrogate failures are typically re-extracted and/or re-

analyzed to confirm that the out-of-control value was caused by the matrix of the sample and not by some other systematic error. An exception to this would be samples that have high surrogate values but no reportable hits for target compounds. These samples would be reported, with a qualifier, because the implied high bias would not affect the final results.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.6 Sample Duplicate

A sample duplicate is a second portion of sample that is prepared and analyzed in the laboratory along with the first portion. It is used to measure the precision associated with preparation and analysis. A sample duplicate is processed at a frequency specified by the particular method or as determined by a specific customer.

The sample and duplicate are evaluated against the method or laboratory-derived criteria for relative percent difference (RPD). Any duplicate that is outside of these limits is considered to be 'out of control' and must be qualified appropriately.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.7 Internal Standards

Internal Standards are method-specific analytes added to every standard, method blank, laboratory control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes. At a minimum, the laboratory will follow method specific guidelines for the treatment of internal standard recoveries as they are related to the reporting of data.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.8 Field Blanks

Field blanks are blanks prepared at the sampling site in order to monitor for contamination that may be present in the environment where samples are collected. These field quality control samples are often referenced as field blanks, rinseate blanks, or equipment blanks. The lab analyzes these field blanks as normal samples and informs the customer if there are any target compounds detected above the reporting limit.

4.9 Trip Blanks

Trip blanks are blanks that originate from the laboratory as part of the sampling event and are used to monitor for contamination of samples during transport. These blanks accompany the empty sample containers to the field and then accompany the collected samples back to the lab. These blanks are routinely analyzed for volatile methods where ambient background contamination is likely to occur.

4.10 Limit of Detection (LOD)

PASI laboratories are required to use a documented procedure to determine a limit of detection (LOD) for each analyte of concern in each matrix reported. All sample-processing steps of the preparation and analytical methods are included in this determination. For any test that does not have a valid LOD, sample results below the limit of quantitation (LOQ) cannot be reported.

The LOD is initially established for the compounds of interest for each method in a clean matrix with no target analytes present and no interferences at a concentration that would impact the results. The LOD is then determined every time there is a change in the test method that affects how the test is performed or

when there has been a change in the instrument that affects the sensitivity. If required by customer, method or accreditation body, the LOD will be re-established annually for all applicable methods.

Unless otherwise noted, the method used by PASI laboratories to determine LODs is based on the Method Detection Limit (MDL) procedure outlined in 40 CFR Part 136, Appendix B. Where required by regulatory program or customer, the above referenced procedure will be followed.

Where specifically stated in the published method, LODs (or MDLs) will be performed at the listed frequency.

The validity of the LOD must be verified by detection (a value greater than zero) of the analytes in a QC sample in each quality system matrix. The QC sample must contain the analyte at no more than 3X the LOD for a single analyte test and 4X the LOD for multiple analyte tests. This verification must be performed on each instrument used for sample analysis and reporting of data. The validity of the LOD must be verified as part of the LOD determination process. This verification must be done prior to the use of the LOD for sample analysis.

An LOD study is not required for any analyte for which spiking solutions or quality control samples are not available (e.g. temperature).

The LOD, if required, shall be verified annually for each quality system matrix, technology and analyte. In lieu of performing full LOD (MDL) studies annually, the lab can verify the LOD (MDL) on an annual basis, providing this verification is fully documented and does not contradict other customer or program requirements that the lab must follow. The requirements of this verification are:

- The spike concentration of the verification must be no more than 3X times the LOD for single analyte tests and 4X the LOD for multiple analyte tests.
- The lab must verify the LOD on each instrument used for the reporting of sample data.
- The lab must be able to qualitatively identify all target analytes in the verification standard (distinguishable from noise).

Additional information can be found in SOP S-ALL-Q-004 ***Method Detection Limit Studies*** or its equivalent revision or replacement.

4.11 Limit of Quantitation (LOQ)

A limit of quantitation (LOQ) for every analyte of concern must be determined. For PASI laboratories, this LOQ is referred to as the RL, or Reporting Limit. This RL is based on the lowest calibration standard concentration that is used in each initial calibration. Results below this level are not allowed to be reported without qualification since the results would not be substantiated by a calibration standard. For methods with a determined LOD, results can be reported out below the LOQ but above the LOD if they are properly qualified (e.g. J flag).

There must be a sufficient buffer between the LOD and the limit of quantitation (LOQ). The LOQ must be higher than the LOD.

To verify the LOQ, the laboratory will prepare a sample in the same matrix used for the LCS. The sample will be spiked with target analytes at the concentration(s) equivalent to or less than the RL(s). This sample must undergo the routine sample preparation procedure including any routine sample cleanup steps. The sample is then analyzed and the recovery of each target analyte determined. The recovery for each target analyte must meet the laboratories current control limits.

Additional information can be found in SOP S-ALL-Q-004 ***Method Detection Limit Studies*** or its equivalent revision or replacement.

4.12 Estimate of Uncertainty

PASI laboratories can provide an estimation of uncertainty for results generated by the laboratory. The estimate quantifies the error associated with any given result at a 95% confidence interval. This estimate does not include bias that may be associated with sampling. The laboratory has a procedure in place for making this estimation. In the absence of a regulatory or customer-specific procedure, PASI laboratories base this estimation on the recovery data obtained from the Laboratory Control Spikes. The uncertainty is a function of the standard deviation of the recoveries multiplied by the appropriate Student's t Factor at 95% confidence. Additional information pertaining to the estimation of uncertainty and the exact manner in which it is derived are contained in the SOP S-GB-Q-010 ***Estimation of Uncertainty*** or its equivalent revision or replacement.

The measurement of uncertainty is provided only on request by the customer, as required by specification or regulation and when the result is used to determine conformance within a specification limit.

4.13 Proficiency Testing (PT) Studies

PASI laboratories participate in the NELAC-defined proficiency testing program. PT samples are obtained from approved providers and analyzed and reported at a minimum of two times per year for the relevant fields of testing per matrix.

The lab initiates an investigation whenever PT results are deemed 'unacceptable' by the PT provider. All findings and corrective actions taken are reported to the Quality Manager. A corrective action plan (including re-analysis of similar samples) is initiated and this report is sent to the appropriate state accreditation agencies for their review.

PT samples are treated as typical customer samples, utilizing the same staff, methods, equipment, facilities, and frequency of analysis. PT samples are included in the laboratory's normal analytical processes and do not receive extraordinary attention due to their nature.

Comparison of analytical results with anyone participating in the same PT study is prohibited prior to the close of the study.

Additional information can be found in SOP S-ALL-Q-010 ***PE/PT Program*** or its equivalent revision or replacement.

4.14 Rounding and Significant Figures

In general, the PASI laboratories report data to no more than three significant digits. Therefore, all measurements made in the analytical process must reflect this level of precision. In the event that a parameter that contributes to the final result has less than three significant figures of precision, the final result must be reported with no more significant figures than that of the parameter in question. The rounding rules listed below are descriptive of the LIMS and not necessarily of any supporting program (Excel, etc.).

Rounding

PASI-Green Bay follows the odd / even guidelines for rounding numbers:

- If the figure following the one to be retained is less than five, that figure is dropped and the retained ones are not changed (with three significant figures, 2.544 is rounded to 2.54).
- If the figure following the ones to be retained is greater than five, that figure is dropped and the last retained one is rounded up (with three significant figures, 2.546 is rounded to 2.55).

- If the figure following the ones to be retained is five and if there are no figures other than zeros beyond that five, then the five is dropped and the last figure retained is unchanged if it is even and rounded up if it is odd (with three significant figures, 2.525 is rounded to 2.52 and 2.535 is rounded to 2.54).

Significant Digits

PASI-Green Bay follows the following convention for reporting to a specified number of significant figures. Unless specified by federal, state or local requirements or on specific request by a customer, the laboratory reports:

- Values > 10 – Reported to 3 significant digits
- Values ≤ 10 – Reported to 2 significant digits

5.0 DOCUMENT MANAGEMENT AND CHANGE CONTROL

5.1 Document Management

Additional information can be found in SOP S-ALL-Q-002 Document Management or its equivalent revision or replacement.

Pace Analytical Services, Inc. has an established procedure for managing documents that are part of the quality system. The list of managed documents includes, but is not limited to, Standard Operating Procedures, Quality Assurance Manuals, quality policy statements, training documents, work-processing documents, charts, posters, memoranda, notices, forms, software, and any other procedures, tables, plans, etc. that have a direct bearing on the quality system.

A master list of all managed documents is maintained at each facility identifying the current revision status and distribution of the controlled documents. This establishes that there are no invalid or obsolete documents in use in the facility. All documents are reviewed periodically and revised if necessary. Obsolete documents are systematically discarded or archived for audit or knowledge preservation purposes.

Each managed document is uniquely identified to include the date of issue, the revision identification, page numbers, the total number of pages and the issuing authorities. For complete information on document numbering, refer to SOP S-ALL-Q-003 Document Numbering.

As an alternative to the hard copy system of controlled documents, secured electronic copies of controlled documents may be maintained on the local or wide-area network (LAN or WAN). These document files must be read-only for all personnel except the Quality Department and system administrator. Other requirements for this system are as follows:

- Electronic documents must be readily accessible to all facility employees.
- Electronic documents (i.e. pdf's) must be locked from printing. All hardcopy SOPs must be obtained from the Quality Department.

5.1.1 Quality Assurance Manual (QAM)

The Quality Assurance Manual is the company-wide document that describes all aspects of the quality system for PASI. The base QAM template is distributed by the Corporate Quality Department to each of the regional Quality Managers. The regional management personnel modify the necessary and permissible sections of the base template and submit those modifications to the Corporate Director of Quality for review. Once approved and signed by both the CEO and the Director of Quality, the General Manager, Quality Manager and Technical Director(s) sign the Quality Assurance Manual. Each regional Quality Manager is then in charge of distribution to employees, external customers or regulatory agencies and maintaining a distribution list of controlled document copies. The Quality Assurance Manual template is reviewed on an annual basis by all of the PASI Quality Managers and revised accordingly by the Director of Quality, Safety and Training.

5.1.2 Standard Operating Procedures (SOPs)

SOPs fall into two categories: company-wide documents (starting with the prefix S-ALL-) and facility-specific documents (starting with the individual facility prefix).

The purpose of the company-wide SOPs is to establish policies and procedure that are common and applicable to all PASI facilities. Company-wide SOPs are document-controlled by the corporate quality office and signed copies are distributed to all of the regional Quality Managers.

The regional management personnel sign the company-wide SOPs. The regional Quality Manager is then in charge of distribution to employees, external customers or regulatory agencies and maintaining a distribution list of controlled document copies.

Regional PASI facilities are responsible for developing facility-specific SOPs applicable to their respective facility. The regional facility develops these facility-specific SOPs based on the corporate-wide SOP template. This template is written to incorporate a set of minimum method requirements and PASI best practice requirements. The regional facilities may add to or modify the corporate-wide SOP template provided there are no contradictions to the minimum method or best practice requirements. Facility-specific SOPs are controlled by the regional Quality Manager according to the corporate document management policies.

SOPs are reviewed every two years at a minimum (a more frequent review may be required by state or federal agencies or customers). A review of the document does not necessarily constitute a re-issue of a new revision. Documentation of this review and any applicable revisions are made in the last section of each SOP. This provides a historical record of all revisions.

All copies of superseded SOPs are removed from general use and the original copy of each SOP is archived for audit or knowledge preservation purposes. This ensures that all PASI employees use the most current version of each SOP and provides the Quality Manager with a historical record of each SOP.

Additional information can be found in SOP S-ALL-Q-001 Preparation of SOPs or its equivalent revision or replacement.

5.1.3 Other Documentation

Additional documents such as Forms and Spreadsheets are controlled through the document management system.

5.2 Document Change Control

Changes to managed documents are reviewed and approved in the same manner as the original review. Any revision to a document requires the approval of the applicable signatories. After revisions are approved, a revision number is assigned and the previous version of the document is officially retired. Copies may be kept for audit or knowledge preservation purposes.

All controlled copies of the previous document are replaced with controlled copies of the revised document and the superseded copies are destroyed or archived. All affected personnel are advised that there has been a revision and any necessary training is scheduled.

6.0 EQUIPMENT AND MEASUREMENT TRACEABILITY

Each PASI facility is equipped with sufficient instrumentation and support equipment to perform the relevant analytical testing or field procedures performed by each facility. Support equipment includes chemical standards, thermometers, balances, disposable and mechanical pipettes, etc. This section details some of the procedures necessary to maintain traceability and perform proper calibration of instrumentation and support equipment. See Attachment III for a list of equipment currently used at the (Green Bay) PASI facility.

6.1 Standards and Traceability

Each PASI facility retains all pertinent information for standards, reagents and chemicals to assure traceability to a national standard. This includes documentation of purchase, receipt, preparation and use.

Upon receipt, all purchased standard reference materials are recorded into a standard logbook or database and assigned a unique identification number. The entries include the facility's unique identification number, the chemical name, manufacturer name, manufacturer's identification numbers, receipt date and expiration date. Vendor's certificates of analysis for all standards, reagents, or chemicals are retained for future reference.

Subsequent preparations of intermediate or working solutions are also documented in a standard logbook or database. These entries include the stock standard name and lot number, the manufacturer name, the solvents used for preparation, the solvent lot number and manufacturer, the preparation steps, preparation date, expiration dates, preparer's initials, and a unique PASI identification number. This number is used in any applicable sample preparation or analysis logbook so the standard can be traced back to the standard preparation record. This process ensures traceability back to the national standard.

All prepared standard or reagent containers include the PASI identification number, the standard or chemical name, the date of preparation, the date of expiration, the concentration with units, and the preparer's initials. This ensures traceability back to the standard preparation logbook.

If a second source standard is required to verify an existing calibration or spiking standard, this standard is purchased from a different supplier. If no second source is available, a second standard from a different lot may be purchased from the same supplier if the lot can be demonstrated as prepared independently from other lots.

Additional information concerning standards and reagent traceability can be found in the SOP S-ALL-Q-025 Standard and Reagent Preparation and Traceability or its equivalent revision or replacement.

6.2 General Analytical Instrument Calibration Procedures

All types of support equipment and instrumentation are calibrated or checked before use to ensure proper functioning and verify that the laboratory's requirements are met. All calibrations are performed by, or under the supervision of, an experienced analyst at scheduled intervals against either certified standards traceable to recognized national standards or reference standards whose values have been statistically validated.

Calibration standards for each parameter are chosen to establish the linear range of the instrument and must bracket the concentrations of those parameters measured in the samples. The lowest calibration standard is the lowest concentration for which quantitative data may be reported. Data reported below this level is considered to have less certainty and must be reported using appropriate data qualifiers (e.g. J flag) or explained in a narrative. The Minnesota Department Health requires that the reporting limit be verified upon initial calibration and monthly there after. The reporting limit verification must be within ± 40% of the true value of the reporting limit standard. The reporting limit may need to be adjusted accordingly to meet this criteria. The highest calibration standard is the highest concentration for which quantitative data may be reported. Data reported above this level is considered to have less certainty and must be reported using appropriate data

qualifiers (e.g. E flag) or explained in the narrative. Any specific method requirement for number and type of calibration standards supersedes the general requirement. Instrument and method specific calibration criteria are explained within the specific analytical standard operating procedures for each facility.

Instrumentation or support equipment that cannot be calibrated to specification or is otherwise defective is clearly labeled as out-of-service until it has been repaired and tested to demonstrate it meets the laboratory's specifications. All repair and maintenance activities including service calls are documented in the maintenance log. Equipment sent off-site for calibration testing is packed and transported to prevent breakage and is in accordance with the calibration laboratory's recommendations.

In the event that recalibration of a piece of test equipment indicates the equipment may have been malfunctioning during the course of sample analysis, an investigation is performed. The results of the investigation along with a summary of the information reviewed are documented and maintained by the Quality Manager. If the investigation indicates sample results have been impacted, the customer is notified within 30 days. This allows for sufficient investigation and review of documentation to determine the impact on the analytical results. Instrumentation found to be consistently out of calibration is either repaired and positively verified or replaced.

Raw data records are retained to document equipment performance. Sufficient raw data is retained to reconstruct the instrument calibration and explicitly connect the continuing calibration verification to the initial calibration.

6.2.1 General Organic Calibration Procedures

Calibration standards are prepared at a minimum of five concentrations for organic analyses. Results from all calibration standards must be included in constructing the calibration curve with the following exceptions:

- The lowest level calibration standard may be removed from the calibration as long as the remaining number of concentration levels meets the minimum established by the method and standard operating procedure. For multi-parameter methods, this may be done on an individual analyte basis. The reporting limit must be adjusted to the lowest concentration included in the calibration curve.
- The highest level calibration standard may be removed from the calibration as long as the remaining number of concentration levels meets the minimum established by the method and standard operating procedure. For multi-parameter methods, this may be done an individual analyte basis. The upper limit of quantitation must be adjusted to the highest concentration included in the calibration curve.
- Multiple points from either the high end or the low end of the calibration curve may be excluded as long as the remaining points are contiguous in nature and the minimum number of levels remain as established by method or standard operating procedure. The reporting limit or quantitation range, which is appropriate, must be adjusted accordingly.
- Results from a concentration level between the lowest and highest calibration levels can be excluded from the calibration curve for an acceptable cause with approval from the responsible department supervisor if the results for all analytes are excluded and the point is replaced by re-analysis. Re-analysis must occur within the same 12 hour tune time period for GC/MS methodologies and within 8 hours of the initial analysis for non-GC/MS methodologies. All samples analyzed prior to the re-analyzed calibration curve point must be re-analyzed after the calibration curve is completed.

Initial calibration curves are evaluated against appropriate statistical models as required by the analytical methods. Curves that do not meet the appropriate criteria require corrective action that may include re-running the initial calibration curve. All initial calibrations are verified with a standard obtained from a second manufacturer or second lot from the same manufacturer if the lot can be demonstrated as prepared independently from other lots prior to the analysis of samples.

Sample results are quantitated from the initial calibration unless otherwise required by regulation, method, or program.

The calibration curve is periodically verified by the analysis of a mid-level continuing calibration verification (CCV) standard during the course of sample analysis. Calibration verification is performed at the beginning and end of each analytical batch (except if an internal standard is used only one verification at the beginning of the batch is needed), whenever it is expected that the analytical system may be out of calibration, if the time period for calibration has expired, or for analytical systems that contain a calibration verification requirement. This verification standard must meet acceptance criteria in order for sample analysis to proceed.

In the event that the CCV does not meet the acceptance criteria, a second CCV may be injected as part of the diagnostic evaluation and corrective action investigation. If the second CCV is acceptable, the analytical sequence is continued. If both CCVs fail, the analytical sequence is terminated. All samples analyzed since the last compliant CCV are re-analyzed for methodologies utilizing external calibration.

When instruments are operating unattended, the autosamplers may be programmed to inject consecutive CCVs as a preventative measure against CCV failure with no corrective action. In this case, both CCVs must be evaluated to determine potential impact to the results. A summary of the decision tree and necessary documentation are listed below:

- If both CCVs meet the acceptance criteria, the analytical sequence is allowed to continue without corrective action. (The 12 hour clock begins with the injection of the second CCV.)
- If the first CCV does not meet the acceptance criteria and the second CCV is acceptable, the analytical sequence is continued and the results are reported.
- If the first CCV meets the acceptance criteria and the second CCV is out of control, the samples preceded by the out of control CCV must be re-analyzed in a compliant analytical sequence.
- If both CCVs are out of control, all samples since the last acceptable CCV must be re-analyzed in a compliant analytical sequence.

Some analytical methods require that samples be bracketed by passing CCVs analyzed both before and after the samples. This is specific to each method but, as a general rule, all external calibration methods require bracketing CCVs. Most internal standard calibrations do not require bracketing CCVs.

Some analytical methods require verification based on a time interval; some methods require a frequency based on an injection interval. The type and frequency of the calibration verifications is dependent on both the analytical method and possibly on the quality program associated with the samples. The type and frequency of calibration verification will be documented in the method specific SOP employed by each laboratory.

6.2.2 General Inorganic Calibration Procedures

The instrument is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. A calibration blank is also included. Initial calibration curves are evaluated against appropriate statistical models as required by the analytical methods. The number of calibration standards used depends on the specific method criteria or customer project requirements, although normally a minimum of three standards is used.

The ICP and ICP/MS can be standardized with a zero point and a single point calibration if:

- Prior to analysis, the zero point and the single point calibration are analyzed and a linear range is established,
- Zero point and single point calibration standards are analyzed with each batch

- A standard corresponding to the LOQ is analyzed with the batch and meets the established acceptance criteria
- The linearity is verified at the frequency established by the method or manufacturer.

All initial calibrations are verified with a standard obtained from a second manufacturer or second lot from the same manufacturer if the lot can be demonstrated as prepared independently from other lots prior to the analysis of samples. Sample results are quantitated from the initial calibration unless otherwise required by regulation, method, or program.

During the course of analysis, the calibration curve is periodically verified by the analysis of calibration verification standards. A calibration verification standard is analyzed within each analytical batch at method/program specific intervals to verify that the initial calibration is still valid. The CCV is also analyzed at the end of the analytical batch.

A calibration blank is also analyzed with each calibration verification standard to verify the cleanliness of the system. All reported results must be bracketed by acceptable CCVs and CCBs. Instrument and method specific calibration acceptance criteria are explained within the specific analytical standard operating procedures for each facility.

Interference check standards are also analyzed per method requirements and must meet acceptance criteria for metals analyses.

6.3 Support Equipment Calibration Procedures

All support equipment is calibrated or verified at least annually using NIST traceable references over the entire range of use. The results of calibrations or verifications must be within the specifications required or the equipment will be removed from service until repaired. The laboratory maintains records to demonstrate the correction factors applied to working thermometers.

Prior to use on each working day, balances, ovens, refrigerators, freezers, and water baths are checked in the expected use range with NIST traceable references in order to ensure the equipment meets laboratory specifications.

6.3.1 Analytical Balances

Each analytical balance is checked and calibrated annually by a qualified service technician. The calibration of each balance is checked each day of use with weights traceable to NIST. Calibration weights are ASTM Class 1 (or other class weights that have been calibrated against a NIST standard weight) and are re-certified annually against a NIST traceable reference. Some accrediting agencies may require more frequent checks. If balances are calibrated by an external agency, verification of their weights must be provided. All information pertaining to balance maintenance and calibration is recorded in the individual balance logbook and/or is maintained on file in the Quality department.

6.3.2 Thermometers

Certified, or reference, thermometers are maintained for checking calibration of working thermometers. Reference thermometers are provided with NIST traceability for initial calibration and are re-certified, at a minimum, yearly with equipment directly traceable to NIST.

Working thermometers are compared with the reference thermometers annually according to corporate metrology procedures. Each thermometer is individually numbered and assigned a correction factor based on the NIST reference source. In addition, working thermometers are visually inspected by laboratory personnel prior to use and temperatures are documented.

Laboratory thermometer inventory and calibration data are maintained in the Quality department.

6.3.3 pH/Electrometers

The meter is calibrated before use each day, using fresh buffer solutions. Additional information regarding Ph/Electrometers can be found in SOP S-ALL-GB-I-015 ***Measurement of pH in Water, Soil, and Waste***.

6.3.4 Spectrophotometers

During use, spectrophotometer performance is checked at established frequencies in analysis sequences against initial calibration verification (ICV) and continuing calibration verification (CCV) standards.

6.3.5 Mechanical Volumetric Dispensing Devices

Mechanical volumetric dispensing devices including bottle top dispensers, pipettes, and burettes, excluding Class A volumetric glassware, are checked for accuracy on a quarterly basis. Non-Class A glassware and disposable pipettes must be calibrated once per lot prior to first use. The accuracy of glass microliter syringes is verified and documented prior to use.

Additional information regarding calibration and maintenance of laboratory support equipment can be found in SOP S-ALL-Q-013 Support Equipment or its equivalent revision or replacement.

6.4 Instrument/ Equipment Maintenance

The objectives of the Pace Analytical maintenance program are twofold: to establish a system of instrument care that maintains instrumentation and equipment at required levels of calibration and sensitivity, and to minimize loss of productivity due to repairs.

The Laboratory Operations Manager and department manager/supervisors are responsible for providing technical leadership to evaluate new equipment, solve equipment problems and coordinate instrument repair and maintenance. The analysts have a primary responsibility to perform routine maintenance.

To minimize downtime and interruption of analytical work, preventative maintenance is routinely performed on each analytical instrument. Up-to-date instructions on the use and maintenance of equipment are available to staff in the department where the equipment is used.

Department manager/supervisors are responsible for maintaining an adequate inventory of spare parts required to minimize equipment downtime. This inventory includes parts and supplies that are subject to frequent failure, have limited lifetimes, or cannot be obtained in a timely manner should a failure occur.

All major equipment and instrumentation items are uniquely identified to allow for traceability. Equipment/instrumentation are, unless otherwise stated, identified as a system and not as individual pieces. The laboratory maintains equipment records that include the following:

- The name of the equipment and its software
- The manufacturer’s name, type, and serial number
- Approximate date received and date placed into service
- Current location in the laboratory
- Condition when received (new, used, etc.)
- Copy of any manufacturer’s manuals or instructions
- Dates and results of calibrations and next scheduled calibration (if known)
- Details of past maintenance activities, both routine and non-routine
- Details of any damage, modification or major repairs

All instrument maintenance is documented in maintenance logbooks that are assigned to each particular instrument or system.

When maintenance is performed to repair an instrument problem, depending on the initial problem, demonstration of return to control may be satisfied by the successful analysis of a reagent blank or continuing calibration standard. The entry must include a summary of the results of that analysis and verification by the analyst that the instrument has been returned to an in-control status. In addition, each entry must include the initials of the analyst making the entry, the dates the maintenance actions were performed, and the date the entry was made in the maintenance logbook, if different from the date(s) of the maintenance.

Any equipment that has been subjected to overloading or mishandling, or that gives suspect results, or has been shown to be defective, is taken out of service and clearly identified. The equipment shall not be used to analyze customer samples until it has been repaired and shown to perform satisfactorily.

7.0 CONTROL OF DATA

Analytical results processing, verification and reporting are procedures employed that result in the delivery of defensible data. These processes include, but are not limited to, calculation of raw data into final concentration values, review of results for accuracy, evaluation of quality control criteria and assembly of technical reports for delivery to the data user.

All analytical data undergo a well-defined, well-documented multi-tier review process prior to being reported to the customer. This section describes procedures used by PASI for translating raw analytical data into accurate, final sample reports and PASI data storage policies.

7.1 Analytical Results Processing

When analytical, field, or product testing data is generated, it is either recorded in a bound laboratory logbook (e.g. Run log or Instrument log) or copies of computer-generated printouts are appropriately labeled and filed. These logbooks and other laboratory records are kept in accordance with each facility's Standard Operating Procedure for documentation storage and archival. If the lab chooses to minimize paper usage, these records can be kept as electronic records. In this case, the laboratory must ensure that there are sufficient redundant electronic copies so no data is lost due to unforeseen computer issues.

The primary analyst is responsible for initial data reduction and review. This includes confirming compliance with required methodology, verifying calculations, evaluating quality control data, noting discrepancies in logbooks and as footnotes or narratives, and uploading analytical results into the LIMS.

The primary analyst then compiles the initial data package for verification. This compilation must include sufficient documentation for data review. It may include standard calibrations, chromatograms, manual integration documentation, electronic printouts, chain-of-custody forms, and logbook copies.

Some agencies or customers require different levels of data reporting. For these special levels, the primary analyst may need to compile additional project information, such as initial calibration data or extensive spectral data, before the data package proceeds to the verification step.

7.2 Data Verification

Data verification is the process of examining data and accepting or rejecting it based on pre-defined criteria. This review step is designed to ensure that reported data are free from calculation and transcription errors, that quality control parameters are evaluated and that any discrepancies are properly documented.

Analysts performing the analysis and subsequent data reduction have primary responsibility for quality of the data produced. The primary analyst initiates the data verification process by reviewing and accepting the data, provided QC criteria have been met for the samples being reported. Data review checklists, either hardcopy or electronic, are used to document the data review process. The primary analyst is responsible for the initial input of the data into the LIMS.

The completed data package is then sent to a designated qualified reviewer (this cannot be the primary analyst). The following criteria have been established to qualify someone as a data reviewer. To perform secondary data reviewer, the reviewer must:

1. Have a current Demonstration of Capability (DOC) study on file and have an SOP acknowledgement form on file for the method/procedure being reviewed; or, See Note
2. Have a DOC on file for a similar method/technology (i.e. GC/MS) and have an SOP acknowledgment form on file for the method/procedure being reviewed; or, See Note
3. Supervise or manage a Department and have an SOP acknowledgment form on file for the method/procedure being reviewed; or,

4. Have significant background in the department/methods being reviewed through education or experience and have an SOP acknowledgment form on file for the method/procedure being reviewed.

Note: Secondary reviewer status must be approved personally by the Quality Manager or General Manager in the event that this person has no prior experience on the specific method or general technology (i.e. GC/MS).

This reviewer provides an independent technical assessment of the data package and technical review for accuracy according to methods employed and laboratory protocols. This assessment involves a quality control review for use of the proper methodology and detection limits, compliance to quality control protocol and criteria, presence and completeness of required deliverables, and accuracy of calculations and data quantitation. The reviewer also validates the data entered into the LIMS.

Once the data have been technically reviewed and approved, authorization for release of the data from the analytical section is indicated by initialing and dating the data review checklist or otherwise initialing and dating the data (or designating the review of data electronically). The Operations or Project Manager examines the report for method appropriateness, detection limits and QC acceptability. Any deviations from the referenced methods are checked for documentation and validity, and QC corrective actions are reviewed for successful resolution.

7.3 Data Reporting

All data segments pertaining to a particular PASI project number are delivered to the Client Services Department (Project Manager) for assembly into the final report. All points mentioned during technical and QC reviews are included in a case narrative if there is potential for data to be impacted.

Final reports are prepared according to the level of reporting required by the customer and can be transmitted to the customer via hardcopy or electronic deliverable. A standard PASI final report consists of the following components:

1. A title which designates the report as “Final Report”, “Laboratory Results”, “Certificate of Results”, etc.
2. Name and address of laboratory (or subcontracted laboratories, if used).
3. Phone number and name of laboratory contact where questions can be referred.
4. A unique number for the report (project number). The pages of the report shall be numbered and a total number of pages shall be indicated (usually in the cover letter).
5. Name and address of customer and name of project (if applicable).
6. Unique identification of samples analyzed (including customer sample numbers).
7. Identification of any sample that did not meet acceptable sampling requirements (from NELAC or other governing agency), such as improper sample containers, holding times missed, sample temperature, etc.
8. Date and time of collection of samples, date of sample receipt by the laboratory, dates of sample preparation and analysis, and times of sample preparation and analysis when the holding time for either is 72 hours or less.
9. Identification of the test methods used.
10. Identification of sampling procedures if sampling was conducted by the laboratory.
11. Deviations from, additions to, or exclusions from the test methods. These can include failed quality control parameters, deviations caused by the matrix of the sample, etc., and can be shown as a case narrative or as defined footnotes to the analytical data.
12. Identification of whether calculations were performed on a dry or wet-weight basis.
13. Reporting limits used.
14. Final results or measurements, supported by appropriate chromatograms, charts, tables, spectra, etc.
15. A signature and title of person accepting responsibility for the content of the report (can be an equivalent electronic identification) and date report was issued.
16. A statement clarifying that the results of the report relate only to the samples tested or to the samples as they were received by the laboratory.
17. If necessary, a statement indicating that the report must not be reproduced except in full, without the written approval of the laboratory.
18. Identification of all test results provided by a subcontracted laboratory or other outside source.

19. Identification of results obtained outside of quantitation levels.

Any changes made to a final report shall be designated as "Revised" or equivalent wording. The laboratory must keep sufficient archived records of all lab reports and revisions. For higher levels of data deliverables, a copy of all applicable raw data is sent to the customer along with a final report of results. When possible, the PASI facility will provide electronic data deliverables (EDD) as required by contracts or upon customer request.

Customer data that requires transmission by telephone, telex, facsimile or other electronic means undergoes appropriate steps to preserve confidentiality.

The following positions are the only approved signatories for PASI final reports:

- Senior General Manager
- General Manager
- Quality Manager
- Client Services Manager
- Project Manager
- Project Coordinator

7.4 Data Security

All data including electronic files, logbooks, extraction/digestion/distillation worksheets, calculations, project files and reports, and other information used to produce the technical report are maintained secured and retrievable by the PASI facility.

7.5 Data Archiving

All records compiled by PASI are maintained legible and retrievable and stored secured in a suitable environment to prevent loss, damage, or deterioration by fire, flood, vermin, theft, and/or environmental deterioration. Records are retained for a minimum of five years unless superseded by federal, state, contractual, and/or accreditation requirements. These records may include, but are not limited to, customer data reports, calibration and maintenance of equipment, raw data from instrumentation, quality control documents, observations, calculations and logbooks. These records are retained in order to provide for possible historical reconstruction including sampling, receipt, preparation, analysis and personnel involved. NELAP-related records will be made readily available to accrediting authorities. Access to archived data is documented and controlled by the Quality Manager or a designated Data Archivist.

Records that are computer-generated have either a hard copy or electronic write-protected backup copy. Hardware and software necessary for the retrieval of electronic data is maintained with the applicable records. Archived electronic records are stored protected against electronic and/or magnetic sources.

In the event of a change in ownership, accountability or liability, reports of analyses performed pertaining to accreditation will be maintained by the acquiring entity for a minimum of five years. In the event of bankruptcy, laboratory reports and/or records will be transferred to the customer and/or the appropriate regulatory entity upon request.

7.6 Data Disposal

Data that has been archived for the facility's required storage time may be disposed of in a secure manner by shredding, returning to customer, or utilizing some other means that does not jeopardize data confidentiality. Records of data disposal will be archived for a minimum of five years unless superseded by federal, contractual, and/or accreditation requirements.

8.0 QUALITY SYSTEM AUDITS AND REVIEWS

8.1 Internal Audits

8.1.1 Responsibilities

The Quality Manager is responsible for designing and/or conducting internal audits in accordance with a predetermined schedule and procedure. Since internal audits represent an independent assessment of laboratory functions, the auditor must be functionally independent from laboratory operations to ensure objectivity. The auditor must be trained, qualified and familiar enough with the objectives, principles, and procedures of laboratory operations to be able to perform a thorough and effective evaluation. The Quality Manger evaluates audit observations and verifies the completion of corrective actions. In addition, a periodic corporate audit will be conducted by the Director of Quality, Safety and Training and/or designee. The corporate audits will focus on the execution of the Quality System as outlined in this manual but may also include other quality programs applicable to each laboratory.

8.1.2 Scope and Frequency of Internal Audits

Internal systems audits are conducted yearly at a minimum. The scope of these audits includes evaluation of specific analytical departments or a specific quality-related system as applied throughout the laboratory.

Examples of system-wide elements that can be audited include:

- Quality Systems documents, such as Standard Operating Procedures, training documents, Quality Assurance Manual and all applicable addenda
- Personnel and training files.
- General laboratory safety protocols.
- Chemical handling practices, such as labeling of reagents, solutions, standards, and associated documentation.
- Documentation concerning equipment and instrumentation, calibration/maintenance records, operating manuals.
- Sample receipt and management practices.
- Analytical documentation, including any discrepancies and corrective actions.
- General procedures for data security, review, documentation, reporting and archiving.
- Data integrity issues such as proper manual integrations.

When the operations of a specific department are evaluated, a number of additional functions are reviewed including:

- Detection limit studies
- Internal chain-of-custody documentation
- Documentation of standard preparations
- Quality Control limits and Control charts

Certain projects may require an internal audit to ensure laboratory conformance to site work plans, sampling and analysis plans, QAPPs, etc.

A representative number of data audits are completed annually. The report format of any discrepancy is similar to that of other internal audits.

The laboratory, as part of their overall internal audit program, ensures that a review is conducted with respect to any evidence of inappropriate actions or vulnerabilities related to data integrity. Discovery and reporting of potential data integrity issues are handled in a confidential manner until

such time as a follow up evaluation, full investigation, or other appropriate actions are completed and the issues clarified. All investigations that result in findings of inappropriate activity are fully documented, including the source of the problem, the samples and customers affected, the impact on the data, the corrective actions taken by the lab and which final reports had to be re-issued. Customers are notified within 30 days when the investigation indicates analytical results are affected.

8.1.3 Internal Audit Reports and Corrective Action Plans

Additional information can be found in SOP S-ALL-Q-011 *Audits and Inspections* or its equivalent revision or replacement.

A full description of the audit, including the identification of the operation audited, the date(s) on which the audit was conducted, the specific systems examined, and the observations noted are summarized in an internal audit report. Although other personnel may assist with the performance of the audit, the Quality Manager writes and issues the internal audit report identifying which audit observations are deficiencies that require corrective action.

When audit findings cast doubt on the effectiveness of the operations or on the correctness of validity of the laboratory's environmental test results, the laboratory will take timely corrective action and notify the customer in writing within 3 business days, if investigations show that the laboratory results may have been affected.

Once completed, the internal audit report is issued jointly to the Laboratory General Manager and the manager(s)/supervisor(s) of the audited operation at a minimum. The responsible manager(s)/supervisor(s) responds within 14 days with a proposed plan to correct all of the deficiencies cited in the audit report. The Quality Manager may grant additional time for responses to large or complex deficiencies (not to exceed 30 days). Each response must include timetables for completion of all proposed corrective actions.

The Quality Manager reviews the audit responses. If the response is accepted, the Quality Manager uses the action plan and timetable as a guideline for verifying completion of the corrective action(s). If the Quality Manager determines that the audit response does not adequately address the correction of cited deficiencies, the response will be returned for modification.

To complete the audit process, the Quality Manager performs a re-examination of the areas where deficiencies were found to verify that all proposed corrective actions have been implemented. An audit deficiency is considered closed once implementation of the necessary corrective action has been verified. If corrective action cannot be verified, the associated deficiency remains open until that action is completed.

8.2 External Audits

PASI laboratories are audited regularly by regulatory agencies to maintain laboratory certifications, and by customers to maintain appropriate specific protocols.

Audit teams external to the company review the laboratory to assess the existence of systems and degree of technical expertise. The Quality Manager and other QA staff host the audit team and assist in facilitation of the audit process. Generally, the auditors will prepare a formalized audit report listing deficiencies observed and follow-up requirements for the laboratory. In some cases, items of concern are discussed during a debriefing convened at the end of the on-site review process.

The laboratory staff and supervisors develop corrective action plans to address any deficiencies with the guidance of the Quality Manager. The Laboratory General Manager provides the necessary resources for staff to develop and implement the corrective action plans. The Quality Manager collates this information

and provides a written report to the audit team. The report contains the corrective action plan and expected completion dates for each element of the plan. The Quality Manager follows-up with the laboratory staff to ensure corrective actions are implemented.

8.3 Quarterly Quality Reports

The Quality Manager is responsible for preparing a quarterly report to management summarizing the effectiveness of the laboratory Quality Systems. This status report will include:

- Results of internal systems or performance audits
- Corrective action activities
- Discussion of QA issues raised by customers
- Results of third party or external audits
- Status of laboratory certifications
- Proficiency Testing Study Results
- Results of internal laboratory review activities
- Summary of holding time violations
- Method detection limit study status
- Training activity summary
- SOP revision summary
- 3P Implementation summary (internal program)
- Other significant Quality System items

The Corporate Director of Quality, Safety & Technology utilizes the information from each laboratory to make decisions impacting the Quality Systems of the company as a whole. Each General Manager utilizes the quarterly report information to make decisions impacting Quality Systems and operational systems at a local level.

Additional information can be found in SOP S-ALL-Q-014 *Quality System Review* or its equivalent revision or replacement.

8.4 Annual Managerial Review

A managerial review of Quality Systems is performed on an annual basis at a minimum. This allows for assessing program effectiveness and introducing changes and/or improvements.

The managerial review must include the following topics of discussion:

- Policy and procedure suitability
- Manager/Supervisor reports
- Internal audit results
- Corrective and preventative actions
- External assessment results
- Proficiency testing studies
- Sample capacity and scope of work changes
- Customer feedback, including complaints

This managerial review must be documented for future reference by the Quality Manager and copies of the report are distributed to laboratory staff. The laboratory shall ensure that any actions identified during the review are carried out within an appropriate and agreed timescale.

8.5 Customer Service Reviews

As part of the annual managerial review listed previously, the sales staff is responsible for reporting on customer feedback, including complaints. The acquisition of this information is completed by performing surveys.

The sales staff continually receives customer feedback, both positive and negative, and reports this feedback to the lab management in order for them to evaluate and improve their management system, testing activities and customer service.

In addition, the labs must be willing to cooperate with customers or their representatives to clarify customer requests and to monitor the lab's performance in relation to the work being performed for the customers.

9.0 CORRECTIVE ACTION

Additional information can be found in SOP S-ALL-Q-012 ***Corrective Action/Preventive Action Process*** or its equivalent revision or replacement.

During the process of sample handling, preparation and analysis, certain occurrences may warrant the necessity of corrective actions. These occurrences may take the form of analyst errors, deficiencies in quality control, method deviations, or other unusual circumstances. The Quality System of PASI provides systematic procedures for documentation, monitoring and completion of corrective actions. This can be done using PASI's LabTrack system that lists among other things, the deficiency by issue number, the deficiency source, responsible party, root cause, resolution, due date, and date resolved.

9.1 Corrective Action Documentation

The following items are examples of laboratory deviations or non-conformances that warrant some form of documented corrective action:

- Quality Control data outside of acceptance criteria
- Sample Acceptance Policy deviations
- Missed holding times
- Instrument failures (including calibration failure)
- Sample preparation or analysis errors
- Sample contamination
- Errors in customer reports
- Audit findings (internal and external)
- Proficiency Testing (PT) sample failures
- Customer complaints or inquiries

Documentation of corrective actions may be in the form of a comment or footnote on the final report that explains the deficiency (e.g. matrix spike recoveries outside of acceptance criteria) or it may be a more formal documentation (either paper system or computerized spreadsheet). This depends on the extent of the deficiency, the impact on the data, and the method or customer requirements for documentation.

The person who discovers the deficiency or non-conformance initiates the corrective action documentation on the Non-Conformance Corrective/ Preventative Action report and/or LabTrack. The documentation must include the affected projects and sample numbers, the name of the applicable Project Manager, the customer name and the sample matrix involved. The person initiating the corrective action documentation must also list the known causes of the deficiency or non-conformance as well as any corrective/preventative actions that they have taken. Preventive actions must be taken in order to prevent or minimize the occurrence of the situation.

In the event that the laboratory is unable to determine the cause, laboratory personnel and management staff will start a root cause analysis by going through an investigative process. During this process, the following general steps must be taken into account: defining the non-conformance problem, assigning responsibilities, determining if the condition is significant, and investigating the root cause of the nonconformance problem. General non-conformance investigative techniques follow the path of the sample through the process looking at each individual step in detail. The root cause must be documented within Lab Track or on the Corrective/Preventative Action Report.

After all the documentation is completed, the routing of the Corrective/Preventative Action Report and /or Lab Track will continue from the person initiating the corrective action, to their immediate supervisor or the Project Manager and finally to the Quality Manager, who is responsible for final review and signoff of all formal corrective/preventative actions.

9.2 Corrective Action Completion

9.2.1 Quality Control outside of acceptance criteria

The analyst that is generating or validating Analytical data is responsible for checking the results against established acceptance criteria (quality control limits). The analyst must immediately address any deficiencies discovered. Method blank, LCS or matrix spike failures are evaluated against method, program, and customer requirements and appropriate footnotes are entered into the LIMS system. Some deficiencies may be caused by matrix interferences. Where possible, matrix interferences are confirmed by re-analysis.

Quality control deficiencies must be made known to the customer on the final report for their review of the data for usability. If appropriate, the supervisor is alerted to the QC failure and if necessary a formal corrective action can be initiated. This may involve the input of the Quality Manager or the General Manager.

The department supervisor and/or Operations Manager are responsible for evaluating the source of the deficiency and for returning the analytical system to control. This may involve instrument maintenance, analytical standard or reagent evaluation, or an internal audit of the analytical procedure.

See applicable analytical SOPs for further guidance on QC acceptance criteria.

9.2.2 Sample Acceptance Policy deviations

Any deviation from the Sample Acceptance Policy listed in this Manual must be documented on the Chain-of-Custody or other applicable form by the sample receiving personnel or by the Project Manager. Analysts or supervisors that discover such deviations must contact the sample receiving personnel or appropriate Project Manager so they can initiate the proper documentation and customer contact. If a more formalized corrective action must be documented, the Quality Manager is made aware of the situation.

The customer is notified of these deviations as soon as possible so they can make decisions on whether to continue with the sample analysis or re-sample. Copies of this documentation are included in the project file.

9.2.3 Missed holding times

In the event that a holding time requirement has been missed, the analyst or supervisor must complete a formal corrective action form. The Project Manager and the Quality Manager must be made aware of these hold time exceedances.

The Project Manager must contact the customer for appropriate decisions to be made with the resolution documented and included in the customer project file. The Quality Manager includes a list of all missed holding times in their Quarterly Report to the corporate office.

9.2.4 Instrument Failures

In the event of an instrument failure that either causes the necessity for re-analysis or questions the validity of generated results, a formal corrective action must be initiated. The analyst and supervisor evaluate any completed data for validity and usability. They are also responsible for returning the instrument to valid operating condition and for documenting that the system is in control (e.g. acceptable calibration verification).

9.2.5 Sample Preparation or Analysis errors

When there is an error in the preparation or analysis of samples, the analyst evaluates the impact on the usability of the analytical data with the assistance of the supervisor or manager. The affected samples will be re-processed or re-analyzed under acceptable conditions. In the event that no additional sample is available for re-analysis, the customer must be contacted for their decision on how to proceed. Documentation may take the form of footnotes or a formal corrective action form.

9.2.6 Errors in customer reports

When an error on the customer report is discovered, the Project Manager is responsible for initiating a formal corrective action form that describes the failure (e.g. incorrect analysis reported, reporting units are incorrect, reporting limits do not meet objectives). The Project Manager is also responsible for revising the final report if necessary and submitting it to the customer.

9.2.7 Audit findings

The Quality Manager is responsible for documenting all audit findings and their corrective actions. This documentation must include the initial finding, the persons responsible for the corrective action, the due date for reporting back to the auditing body, the root cause of the issue, and the corrective action taken to resolve the findings. The Quality Manager is also responsible for providing any back-up documentation used to prove that a corrective action has been completed.

9.2.8 Proficiency Testing failures

Any PT result returned to the Quality Manager as "not acceptable" requires an investigation and applicable corrective actions. The operational staff is made aware of the PT failures and they are responsible for reviewing the applicable raw data and calibrations and list possible causes for error. The Quality Manager reviews their findings and initiates another external PT sample or an internal PT sample to try and correct the previous failure. Replacement PT results must be monitored by the Quality Manager and reported to the applicable regulatory authorities.

9.2.9 Customer Complaints

Project Managers are responsible for issuing corrective action forms for customer complaints. As with other corrective actions, the possible causes of the problem are listed and the form is passed to the appropriate analyst or supervisor. After the corrective actions have been listed, the Project Manager reviews the corrective action to determine if the customer needs or concerns are being addressed.

9.3. Preventive Action Documentation

Pace laboratories can take advantage of several available information sources in order to identify needed improvements in all of their systems (technical, managerial, quality, etc.). These sources may include:

- Management Continuous Improvement Plan (CIP) metrics which are used by all production departments within Pace. When groups compare performance across the company, ways to improve systems are discovered. These improvements can be made within a department or lab-wide.
- Annual managerial reviews- part of this NELAC-required review is to look at all processes and procedures used by the lab over the past year and to determine ways to improve these processes in the future.
- Quality systems reviews- any frequent checks of quality systems (monthly logbook reviews, etc.) can uncover issues that can be corrected or adjusted before they become a larger issue.

When improvement opportunities are identified or if preventive action is required, the lab can develop, implement, and monitor preventive action plans.

10.0 GLOSSARY

3P Program	The Pace Analytical continuous improvement program that focuses on Process, Productivity and Performance. Best Practices are identified that can be used by all PASI labs.
Accuracy	The agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator.
Aliquot	A portion of a sample taken for analysis.
Analyte	The specific chemical species or parameter an analysis seeks to determine.
Batch	Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.
Blank	A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.
Blind Sample	A sample for submitted for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test analyst or laboratory proficiency in the execution of the measurement process.
Calibration	To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard must bracket the range of planned or expected sample measurements.
Calibration Curve	The graphic representation of known values, such as concentrations for a series of calibration standards and their instrument response.
Chain-of-Custody (COC)	A record that documents the possession of samples from the time of collection to receipt in the laboratory. This record generally includes the number and type of containers, mode of collection, collector, time of collection, preservation, and requested analyses.
Confirmation	Verification of the identity of a component through the use of an alternate scientific approach from the original method. These may include, but are not limited to: • second-column confirmation • alternate wavelength • derivatization derivative • mass spectral interpretation • additional cleanup procedures
Contract Required Detection Limit (CRDL)	Detection limit that is required for EPA Contract Laboratory Program (CLP) contracts.
Contract Required Quantitation Limit (CRQL)	Quantitation limit (reporting limit) that is required for EPA Contract Laboratory Program (CLP) contracts.
Comparability	An assessment of the confidence with which one data set can be compared to another. Comparable data are produced through the use of standardized procedures and techniques.

Completeness	The percent of valid data obtained from a measurement system compared to the amount of valid data expected under normal conditions. The equation for completeness is: % Completeness = (Valid Data Points/Expected Data Points)*100
Calibration Verification	The process of verifying a calibration by analysis of standards and comparing the results with the known amount.
Control Chart	A graphic representation of a series of test results, together with limits within which results are expected when the system is in a state of statistical control (see definition for Control Limit)
Control Limit	A range within which specified measurement results must fall to verify that the analytical system is in control. Control limit exceedances may require corrective action or require investigation and flagging of nonconforming data.
Corrective Action	The action taken to eliminate the causes of a nonconformity, defect, or other undesirable situation in order to prevent recurrence.
Corrective and Preventative Action (CAPA)	The primary management tools for bringing improvements to the quality system, to the management of the quality system's collective processes, and to the products or services delivered which are an output of established systems and processes.
Data Quality Objective (DOQ)	Systematic strategic planning tool based on the scientific method that identifies and defines the type, quality, and quantity of data needed to satisfy a specified use or end user.
Data Reduction	The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more usable form.
Demonstration of Capability	A procedure to establish the ability of the analyst to generate acceptable accuracy.
Detection Limit (DL)	General term for the lowest concentration or amount of the target analyte that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value. See definitions for Method Detection Limit and Limit of Detection.
Document Control (Management)	Procedures to ensure that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled (managed) to ensure use of the correct version at the location where the prescribed activity is performed.
Dry Weight	The weight after drying in an oven at a specified temperature.
Duplicate or Replicate Analysis	The identically performed measurement on two or more sub-samples of the same sample within a short interval of time
Environmental Sample	A representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. Environmental samples can generally be classified as follows: • Non Potable Water (Includes surface water, ground water, effluents, water treatment chemicals, and TCLP leachates or other extracts) • Drinking Water - Delivered (treated or untreated) water designated as potable water • Water/Wastewater - Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents • Sludge - Municipal sludges and industrial sludges. • Soil - Predominately inorganic matter ranging in classification from sands to clays. • Waste - Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes
Equipment Blank	A sample of analyte-free media used to rinse common sampling equipment to check effectiveness of decontamination procedures.
Field Blank	A blank sample prepared in the field by filling a clean container with reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken.

Field Measurement	Determination of physical, biological, or radiological properties, or chemical constituents that are measured on-site, close in time and space to the matrices being sampled/measured, following accepted test methods. This testing is performed in the field outside of a fixed-laboratory or outside of an enclosed structure that meets the requirements of a mobile laboratory.
Holding Time	The maximum time that samples may be held prior to preparation and/or analysis as defined by the method.
Homogeneity	The degree to which a property or substance is uniformly distributed throughout a sample.
Initial Calibration (ICAL)	The process of analyzing standards, prepared at specified concentrations, to define the quantitative response relationship of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a calibration verification standard do not conform to the requirements of the method in use or at a frequency specified in the method.
Internal Standards	A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.
Intermediate Standard Solution	Reference solutions prepared by dilution of the stock solutions with an appropriate solvent.
Laboratory Control Sample (LCS)	A blank sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. Sometimes referred to as Laboratory Fortified Blank, Spiked Blank or QC Check Sample.
Limit of Detection (LOD)	An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte and matrix specific and may be laboratory-dependent.
Limit of Quantitation (LOQ) .	The minimum levels, concentrations or quantities of a target variable (e.g. target analyte) that can be reported with a specified degree of confidence
Laboratory Information Management System (LIMS)	A computer system that is used to maintain all sample information from sample receipt, through preparation and analysis and including sample report generation.
Learning Management System (LMS)	A web-based database used by the laboratories to track and document training activities. The system is administered by the corporate training department and each lab's learn centers are maintained by a local administrator.
Lot	A quantity of bulk material of similar composition processed or manufactured at the same time.

Matrix	The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions are used: • **Aqueous or Non-Potable Water**: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts. • **Drinking Water**: any aqueous sample that has been designated a potable or potentially potable water source. • **Saline/Estuarine**: any aqueous sample from an ocean or estuary, or other saltwater source. • **Non-aqueous liquid**: any organic liquid with <15% settleable solids. • **Biological Tissue**: any sample of a biological origin such as fish tissue, shellfish or plant material. Such sample can be grouped according to origin. • **Solid**: includes soils, sediments, sludges, and other matrices with >15% settleable solids. • **Chemical Waste**: a product or by-product or an industrial process that results in a matrix not previously defined • **Air and Emissions**: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas vapor that are collected with a sorbent tube, impinger solution, filter, or other device.
Matrix Spike (MS)	A sample prepared by adding a known quantity of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the matrix on a method's recovery efficiency. (sometimes referred to as Spiked Sample or Fortified Sample)
Matrix Spike Duplicate (MSD)	A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of precision of the recovery of each analyte. (sometimes referred to as Spiked Sample Duplicate or Fortified Sample Duplicate)
Method Blank	A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures: and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Method Detection Limit (MDL)	One way to establish a Limit of Detection (LOD); defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.
Performance Based Measurement System (PBMS)	An analytical system wherein the data quality needs, mandates or limitations of a program or project are specified and serve as criteria for selecting appropriate test methods to meet those needs in a cost-effective manner.
Precision	The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.
Preservation	Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.
Proficiency Testing	A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.
Protocol	A detailed written procedure for field and/or laboratory operation that must be strictly followed.
Quality Assurance Project Plan (QAPP)	A formal document describing the detailed quality control procedures required by a specific project.
Quality Assurance (QA)	An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Control (QC)	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.
Quality Control Sample	A sample used to assess the performance of all or a portion of the measurement system. QC samples may be Certified Reference Materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking.
Quality Assurance Manual	A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users.
Quality System	A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.
Random Error	The EPA has established that there is a 5% probability that the results obtained for any one analyte will exceed the control limits established for the test due to random error. As the number of compounds measured increases in a given sample, the probability for statistical error also increases.
Raw Data	Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g. tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.
Reagent Grade	Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.
Reference Standard	A standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived.
Reporting Limit (RL)	The level at which method, permit, regulatory and customer-specific objectives are met. The reporting limit may never be lower than the Limit of Detection (i.e. statistically determined MDL). Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified. There must be a sufficient buffer between the Reporting Limit and the MDL.
Representativeness	A quality element related to the ability to collect a sample reflecting the characteristics of the part of the environment to be assessed. Sample representativeness is dependent on the sampling techniques specified in the project work plan.
Sample Delivery Group (SDG)	A unit within a single project that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days. Data from all samples in an SDG are reported concurrently.
Sample Tracking	Procedures employed to record the possession of the samples from the time of sampling until analysis, reporting and archiving. These procedures include the use of a Chain-of-Custody Form that documents the collection, transport, and receipt of compliance samples to the laboratory. In addition, access to the laboratory is limited and controlled to protect the integrity of the samples.
Sensitivity	The capability of a method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.
Standard	A substance or material with properties known with sufficient accuracy to permit its use to evaluate the same property in a sample.

Standard Blank	A calibration standard consisting of the same solvent/reagent matrix used to prepare the calibration standards without the analytes. It is used to construct the calibration curve by establishing instrument background.
Standard Operating Procedure (SOP)	A written document which details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks
Stock Standard	A concentrated reference solution containing one or more analytes prepared in the laboratory using an assayed reference compound or purchased from a reputable commercial source.
Surrogate	A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.
Systems Audit	An on-site inspection or assessment of a laboratory's quality system.
Traceability	The property of a material or measurement result defining its relationship to recognized international or national standards through an unbroken chain of comparisons.
Training Document	A training resource that provides detailed instructions to execute a specific method or job function.
Trip Blank	This blank sample is used to detect sample contamination from the container and preservative during transport and storage of the sample. A cleaned sample container is filled with laboratory reagent water and the blank is stored, shipped, and analyzed with its associated samples.
Uncertainty Measurement	The parameter associated with the result of a measurement that characterized the dispersion of the values that could be reasonably attributed to the measurand (i.e. the concentration of an analyte).

11.0 REFERENCES

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- "Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods." SW-846.
- "Methods for Chemical Analysis of Water and Wastes", EPA 600-4-79-020, 1979 Revised 1983, U.S. EPA.
- U.S. EPA Contract Laboratory Program Statement of Work for Organic Analysis
- U.S. EPA Contract Laboratory Program Statement of Work for Inorganic Analysis
- "Standard Methods for the Examination of Water and Wastewater." Current Edition APHA-AWWA-WPCF
- "Annual Book of ASTM Standards", Section 4: Construction, Volume 04.04: Soil and Rock; Building Stones, American Society of Testing and Materials.
- "Annual Book of ASTM Standards", Section 11: Water and Environmental Technology, American Society of Testing and Materials.
- "NIOSH Manual of Analytical Methods", Third Edition, 1984, U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health.
- "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", U.S. EPA, Environmental Monitoring and Support Laboratory – Cincinnati (September 1986).
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- Methods for Non-conventional Pesticides Chemicals Analysis of Industrial and Municipal Wastewater, Test Methods, EPA-440/1-83/079C
- Environmental Measurements Laboratory (EML) Procedures Manual, HASL-300, US DOE, February, 1992.
- Requirements for Quality Control of Analytical Data, HAZWRAP, DOE/HWP-65/R1, July, 1990.
- Requirements for Quality Control of Analytical Data for the Environmental Restoration Program, Martin Marietta, ES/ER/TM-16, December, 1992.
- Quality Assurance Manual for Industrial Hygiene Chemistry, AIHA, 1988
- National Environmental Laboratory Accreditation Conference, Constitution, Bylaws, and Standards. Most recent
- ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories.

12.0 REVISIONS

The PASI Corporate Quality and Safety Manager files both a paper copy and electronic version of a Microsoft Word document with tracked changes detailing all revisions made to the previous version of the Quality Assurance Manual. This document is available upon request. All revisions are summarized in the table below.

Document Number	Reason for Change	Date
Quality Assurance Manual Revision 10.0	Throughout the document, Pace was replaced with PASI or in some cases with Pace Analytical. Also, corrections were made to wording, grammar, spelling, and formatting. SECTION 1: • Updated the PASI mission statement • Deleted Financial Responsibility, Drug-Free Workplace, Non-Harassment, Proper and Professional Conduct, Protection of Property, and Communication sections. • Added Assistant General Manager/ Operations Manager, Technical Director, Administrative Business Manager, Project Manager, Project Coordinator, Field Analyst, Laboratory Technician & Field Technician job descriptions • Added detailed Chain of Command to Laboratory Organization section • Updated the Training and Orientation section to reflect current practices • Deleted a portion of the Laboratory Safety section and added a reference to the Safety Manual and Chemical Hygiene Plan. SECTION 2: • Switched the order of Chain of Custody and Sample Acceptance Policy sections • Added details of project review documentation to Project Initiation section • Added steps to sample log in SECTION 3: • Deleted reference to local addenda for companywide SOPs • Rearranged sentences • Added “PASI will not be liable if the customer chooses not to follow PASI recommendations” to the Regulatory and Method Compliance section. SECTION 4: • Added details to the documentation of review or investigation of possible data integrity. • Corrected wording in Method Blank section • Deleted from LCS/LCSD section an out-of-control statement that said affected samples associated with a failing LCS must be re-analyzed SECTION 5: • Added “Electronic documents must be readily accessible to all facility employees” to Documents Management section • Updated the Standard Operating Procedure section to describe the new PASI corporate SOP Templates and distribution. SECTION 6: • Re-organized & re-named sections • Updated the interpretation of the Calibration Verification policy • Added clarification to the definition of the Second Source Standard • Revised Single Point Calibration procedure to address NELAC requirement • Incorporated Spare Parts into Instrument/ Equipment Maintenance SECTION 7:	20Jun2006

Document Number	Reason for Change	Date
	• Updated Analytical Results Processing section to clarify data documentation policy. • Deleted "All data that are manually entered into the LIMS is reviewed at a rate of 100%" and deleted the use of checklists statement from Data Verification section • Integrated paragraphs for better flow • Deleted item # 15, "If required, a statement of the estimated uncertainty of the test results." from the Data Reporting section • Added Data Security section to describe PASI data security practices • Added fire, flood, and vermin protection requirement to Data Archiving section • Added statement to Data Archiving section describing that NELAP related records are available to accrediting authorities. • Added Data Disposal section SECTION 8: • Deleted first paragraph stating that Pace labs are subject to internal and external audits and reviews. • Added description of PASI internal audit program and investigations • Added requirement that corrective action be taken and customer notified within 3 days if audit findings show that test results may have been affected • Updated requirement for manager(s)/supervisor(s) to respond to audit findings with a plan to correct all deficiencies within 14 days. Statement included that allows Quality Manager to grant additional time for response. • Added to Annual Managerial Review section that "The laboratory shall ensure that any actions identified during the review are carried out within an appropriate and agreed timescale." SECTION 9: • Added documentation requirement for reporting discovery of deficiency or non-conformance, must be documented "on the Non-Conformance Corrective/ Preventative Action report and/or QA Trak." • Added "Preventative actions must be taken in order to prevent or minimize the occurrence of the situation." • Added a paragraph to describe the new PASI Root Cause Analysis procedure. SECTION 10: • Added the following definitions: Contract Required Detection Limit (CRDL), Contract Required Quantitation Limit (CRQL), Corrective and Preventative Action (CAPA), Non Potable Water (to Environmental Sample definition), Intermediate Standard Solution, Quality Control Sample, Stock Standard, Uncertainty Measurement, Working Standard Solution, SECTION 11: • Added ISO/IEC 17025:2005 reference Appendix: • Added Appendix I: Quality Control Calculations	
Quality Assurance Manual Revision 11.0	Overall conversion to template format. Removed all references to Addenda. Changes required based on conversion are not explicitly noted unless change represents a significant policy change. SECTION 1: • Add comment to address continuous improvement to quality system. • Changed statement of purpose in Section header to "Mission Statement". • Added requirements for appointment when Technical Director absent.	17Sep2007

Document Number	Reason for Change	Date
	• Added requirements for notification to AA's and updates to organizational charts when management changes. • Added Client Services Manager job description. SECTION 2: • Changed temperature requirements to "Not Frozen but ≤6°C". • Added flexible section concerning default sampling time in absence of customer-specified time. • Added flexible section to address sample and container identification by the LIMS. • Changed sample retention requirement to 45 days from receipt of samples. Added comment allowing for storage outside of temperature controlled conditions. SECTION 3: • Inserted allowance for use of older methods. • Changed references to work processing and training documents to allow for use of LMS and other types of training media. • Inserted allowance for alternative DOCs where spiking not possible. SECTION 4: • Inserted reference to Anonymous Message line. • Inserted reference to the use of default control limits. • Inserted allowance for release of data without corrective action for obvious matrix interferences. • Inserted reference to the treatment of internal standards. • Inserted allowance for use of MDL annual MDL verification in lieu of full 40 CFR Part 136 annual MDL studies. • Inserted general procedure for LOQ verification SECTION 5: • Added general process for approval and use of QAM template. • Removed specific reference of Work Process Manuals. Left flexible section to include all other controlled documentation. SECTION 6: • No changes noted. SECTION 7: • Added qualifications for secondary reviewers. SECTION 8: • Changed frequency listing for Corporate Audits. SECTION 9: • Changed references from QA Track to Lab Track – left flexible to accommodate information still in QA Track. SECTION 10: • No changes noted. SECTION 11: • No changes noted. ATTACHMENTS: • Standardized format for Attachments.	
Quality Assurance Manual Revision 12.0	General: replaced the word 'client' with 'customer', where applicable. SECTION 1: • Section 1.6.4: added language for clarity	13Nov2008

Document Number	Reason for Change	Date
	• Added new section 1.8.1; responsibilities of Senior General Managers. • Section 1.8.3: added reference to LMS. • Added new section 1.8.17: responsibilities of Waste Coordinators. • Section 1.9, last paragraph: changed 'annually' to 'periodically'. Next to last paragraph- added reference to LMS. SECTION 2: • Incorporated optional language into section 2.1 for laboratories with field services staff supervised by the laboratory • Added new section 2.2 entitled Field Services. • Section 2.3: added reference to the new Review of Analytical Requests SOP. • Changed optional text in 2.6 to explain how EpicPro assigns unique ID # to projects and samples including the unique container ID • Section 2.7.2: changed freezer temp requirement to match SOP. SECTION 3: • Section 3.4: Included optional language for performing IDOCs for tests not amenable to spiking using the "4 replicate" approach. SECTION 4: • Section 4.1: expanded language to allow electronic signature and storing of integrity training documentation within the LMS • Section 4.10: revised and added language regarding LOD studies, initial verification and annual verification, where applicable. • Section 4.11: changed PRL to RL. • Section 4.13: added editable line regarding PT study information. Changed wording to say approved PT providers are utilized • Section 4.14: added sentence regarding rounding rules listed applying only to LIMS. SECTION 5: • Section 5.1, last bullet point: changed language to reflect that SOPs must be locked from printing if controlled electronically. SECTION 6: • Section 6.3.1: adjusted language about classes of weights potentially used. • Section 6.3.3: removed customer-specific requirement to re-calibrate every four hours but added space for this to be added back in where applicable. • Added reference to Attachment III in the introductory paragraph to this section. SECTION 7: • Sections 7.1-7.3: added language for those labs that are minimizing or eliminating the need for paper copies. • Section 7.2: clarified language in numbered items so that it does not appear that all 4 criteria must be applicable at one time. • Section 7.3: added list of approved signatories for final reports. SECTION 8: • Section 8.1.2, last paragraph: revised language regarding data integrity issues and added a timeframe to notify customers of affected data. • Added section 8.5 "Customer Service Reviews"- ISO requirement SECTION 9: • Added new section 9.3 regarding Preventive Action. SECTION 10: • No revisions.	

Document Number	Reason for Change	Date
	SECTION 11: • No revisions. Attachments: • Attachment IIb: updated corporate org chart • Attachment VIII: revised to match the current Analytical Guides.	

ATTACHMENT I

Quality Control Calculations

PERCENT RECOVERY (%REC)

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

NOTE: The SampleConc is zero (0) for theLCS and Surrogate Calculations

PERCENT DIFFERENCE (%D)

$$\%D = \frac{MeasuredValue - TrueValue}{TrueValue} * 100$$

where:
TrueValue = Amount spiked (can also be the $\overline{CF}$ or $\overline{RF}$ of the ICAL Standards)
Measured Value = Amount measured (can also be the CF or RF of the CCV)

PERCENT DRIFT

$$\%Drift = \frac{CalculatedConcentration - TheoreticalConcentration}{TheoreticalConcentrtion} * 100$$

RELATIVE PERCENT DIFFERENCE (RPD)

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

where:
R1 = Result Sample 1
R2 = Result Sample 2

CORRELATION COEFFICIENT (R)

$$CorrCoeff = \frac{\sum_{i=1}^{N} W_i * (X_i - \overline{X}) * (Y_i - \overline{Y})}{\sqrt{\left(\sum_{i=1}^{N} W_i * (X_i - \overline{X})^2\right) * \left(\sum_{i=1}^{N} W_i * (Y_i - \overline{Y})^2\right)}}$$

With:	N	Number of standard samples involved in the calibration
	i	Index for standard samples
	Wi	Weight factor of the standard sample no. i
	Xi	X-value of the standard sample no. i
	X(bar)	Average value of all x-values
	Yi	Y-value of the standard sample no. i
	Y(bar)	Average value of all y-values

ATTACHMENT I (CONTINUED)

Quality Control Calculations (continued)

STANDARD DEVIATION (S)

$$S = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{(n-1)}}$$

where:
n = number of data points
X_i = individual data point
$\overline{X}$ = average of all data points

AVERAGE ($\overline{X}$)

$$\overline{X} = \frac{\sum_{n=1}^{i} X_i}{n}$$

where:
n = number of data points
X_i = individual data point

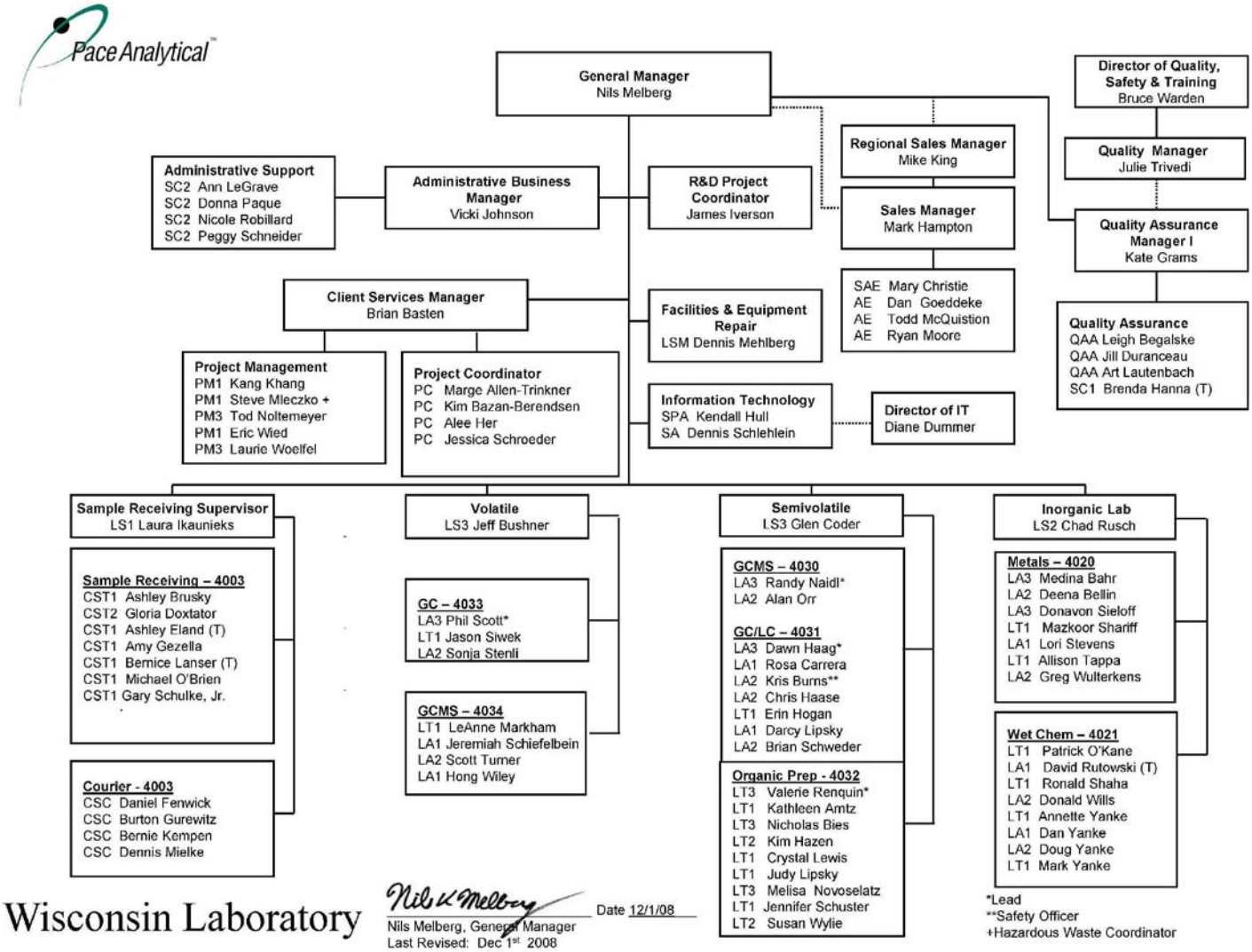
RELATIVE STANDARD DEVIATION (RSD)

$$RSD = \frac{S}{\overline{X}} * 100$$

where:
S = Standard Deviation of the data points
$\overline{X}$ = average of all data points

ATTACHMENT IIA

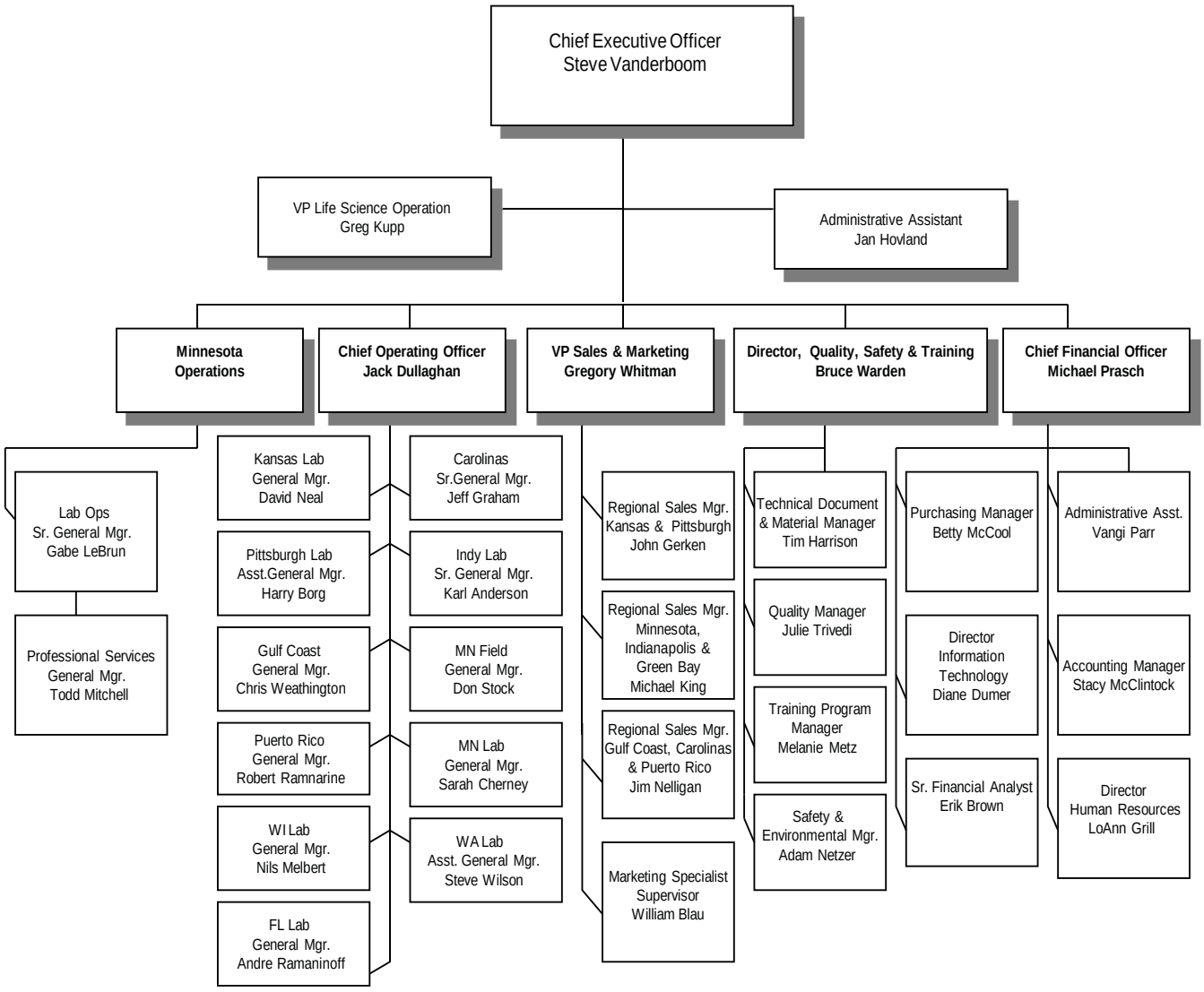
PASI – *GREEN BAY ORGANIZATION CHART*



ATTACHMENT IIB

PASI – CORPORATE ORGANIZATIONAL CHART

CORPORATE/MANAGEMENT STRUCTURE



_____ Date: _____
Steve Vanderboom, Chief Executive Officer **Dec. 2008**

ATTACHMENT III

PASI – GREEN BAY EQUIPMENT LIST

Analytical Instrument/Peripherals	Analysis
Thermo Scientific ICAP 6500 ICP Spectrometer	Metals
ICPMS Thermo Scientific Xseries 2	Metals
PE FIMS (Flow Injection Hg System)	Mercury
PE FIMS (Flow Injector Mercury System)	Mercury
Hot Block Metals Digestion System	Metals Dig.
Hot Block Metals Digestion System	Metals Dig.
Hot Block Metals Digestion System	Metals Dig.
Hot Block Metals Digestion System	Metals Dig.
Hot Block Metals Digestion System	Metals Dig.
Denver Instrument XE-310 Top Loading Balance	
Mettler AJ 100	
American Scientific Balance	
A&D Balance	
Ohaus Analytical Balance	
Ohaus Analytical Balance	
Ohaus Analytical Balance	
Tekran-2500 Low-level Mercury Analyzer	1631E
Tekran 2600 Low Level Automated Mercury Analyzer	1631E
HP 5890 Series II GC	Pesticide
HP 6890 Series GC	Toxaphene
HP 6890 Series GC	PCB
HP 5890 Series GC	Pest/Tox (Screener)
HP 5890 Series II GC	Pesticide
HP 6890 Series GC	PCB
HP 6890 Series GC	PCB
HP 5890 Series II GC	PCB
HP 5890 Series II GC HP 5972 Mass Selective Detector	BNA
HP 6890 GC HP 5973 Mass Selective Detector	PAH
HP 6890 GC HP 5973 Mass Selective Detector	PAH
HP 6890 GC HP 5973 Mass Selective Detector	PAH
HP 5890 Series II GC HP 5972 Mass Selective Detector	BNA Screener

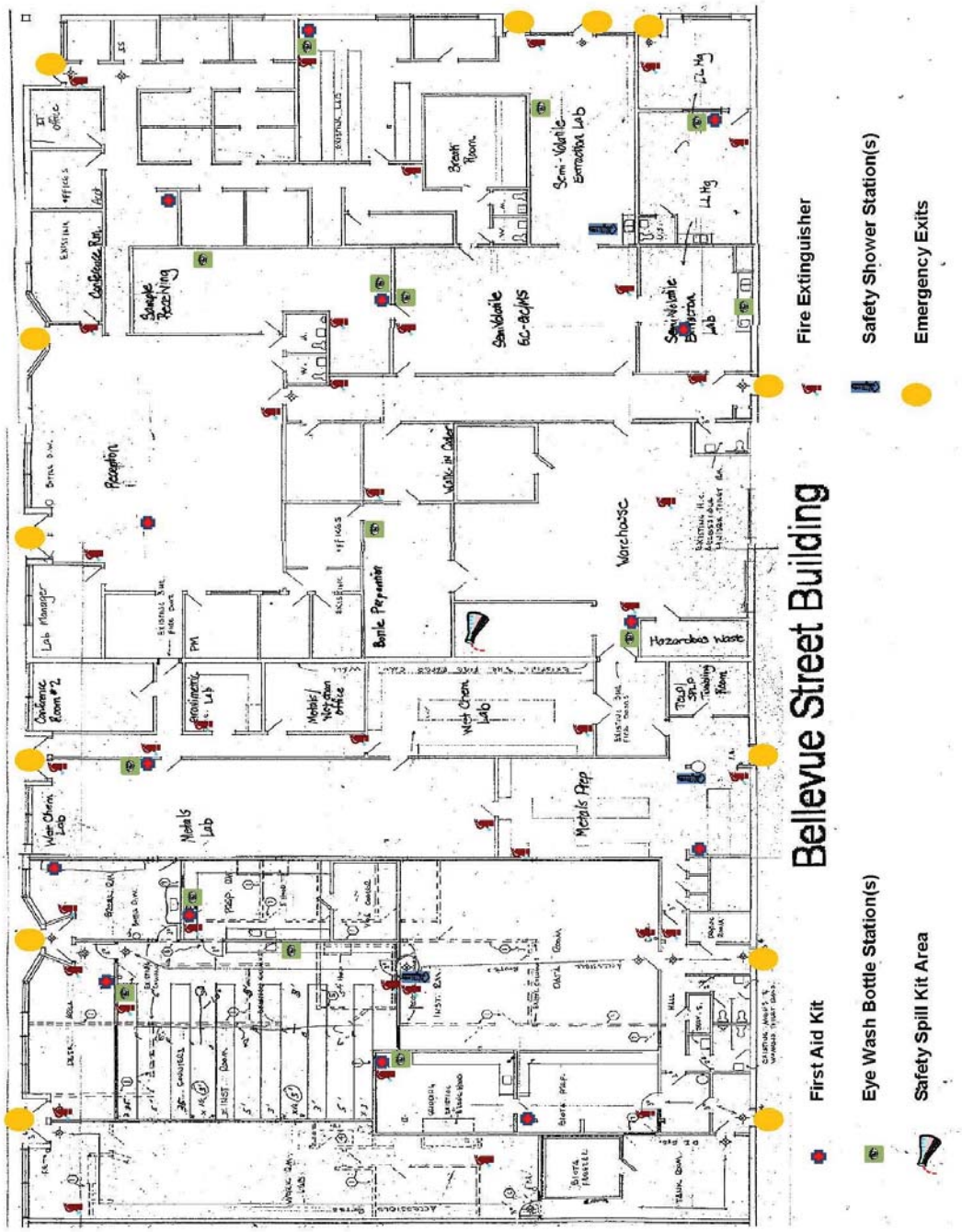
HP 5890E GC	
HP 5972A Mass Selective Detector	BNA/Phenols
HP 5890 Series II GC	DRO/TPH
HP 5890 Series II GC	DRO/TPH
HP 5890 Series II GC	DRO/TPH
HP 5890 Series II GC	DRO/TPH
HP 5890 GC	Alcohol
Lab-Line Automated Separatory Funnel Extractor	SVOA Ext.
Lab-Line Automated Separatory Funnel Extractor	SVOA Ext.
Lab-Line Automated Separatory Funnel Extractor	SVOA Ext.
Zymark TurboVap II Concentration Workstation	SVOA Ext.
Zymark TurboVap II Concentration Workstation	SVOA Ext.
Zymark TurboVap II Concentration Workstation	SVOA Ext.
Zymark TurboVap II Concentration Workstation	SVOA Ext.
Zymark TurboVap II Concentration Workstation	SVOA Ext.
Lab-Line 9334 Sonicator	SVOA Ext.
Fisher Isotemp Muffle Furnace	
Ohaus Analytical Balance	
Mettler Toledo AnalyticalBalance	
MettlerAE 200 Analytical Balance	
Sargent Welch TL 4000 DR Balance	
Mettler PM 480 Balance	
J2 Scientific Accuprep MPS GPC Cleanup System	SVOA Ext.
J2 Scientific Accuprep MPS GPC Cleanup System	SVOA Ext.
CEM Mars Xtraction Microwave System Model # 907501	SVOA Ext.
American Scientific Oven DK-42	
Scientific Products Oven DK-43	
Soxtherm Accelerated Soxhlet Extractor	SVOA Ext.
Soxtherm Accelerated Soxhlet Extractor	SVOA Ext.
Soxtherm Accelerated Soxhlet Extractor	SVOA Ext.
Soxtherm Accelerated Soxhlet Extractor	SVOA Ext.
Six place Soxhlet heater mantles and Glassware	SVOA Ext.
Sonifier Cell Disruptors with Horns	SVOA Ext.
Sonifier Cell Disruptors with Horns	SVOA Ext.
Sonifier Cell Disruptors with Horns	SVOA Ext.
HP 5890 Series II GC	
HP 5972 MSD	SW8260
Agilent 6850 GC	
Agilent 5975 MSD	SW8260
HP 5890 Series II GC	
HP 5972 MSD	SW8260
HP 6890 GC	
HP 5973 MSD	SW8260

HP 5890 Series II GC	
HP 5972 MSD	SW8260
HP 6890 GC	
HP 5973 MSD	SW8260
Agilent Technologies 6850 Network GC System	
Agilent Technologies 5975B MSD	SW8260
HP 6890 GC	
HP 5973 MSD	SW8260
HP 6890 GC	
HP 5973 MSD	SW8260
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 Series II GC with PID/FID	BTEX/TPH/GRO
HP 5890 GC with FID	Methane, Ethane, Ethene
HP 5890 GC with FID	VOA Screen
HP 5890 GC with FID	VOA Screen
Mettler/Toledo Top Loading Balance	
Sartouius PT-210 Top Loading Balance	
Dohrmann DC-80 Total Organic Carbon Analyzer (TOC)	TOC
Horiba TOC Detector	TOC
Rosemount/Dohrmann TOC Boatsampler	TOC
Lachat Quik Chem 8000	CN, Alk, TKN, NH3, Phenolics, Total Phos, NO2-NO3
Lachat MICRO DIST Rapid Distillation System	Distillation
Lachat MICRO DIST Rapid Distillation System	Distillation
Lachat MICRO DIST Rapid Distillation System	Distillation
Dionex DX-120 Ion Chromatograph	Anions
Dionex DX-120 Ion Chromatograph	Anions
HACH DR 2000 Direct Reading Spectrophotometer	COD, Hex. Cr, Ferrous Fe, Color
Fisher Model FW 99-20-1385 Stereomaster Stereoscope	Bact

YSI 5000 Oxygen Meter	BOD
YSI 5010 5010 Oxygen Probe	BOD
HACH Turbidimeter	Turbidity
Accumet 30 Conductivity Meter	Conductivity
Blue M Bacteriological Incubator Model C-4008-Q	BOD
Millipore Incubator	BOD
Precision Scientific Low Temperature Incubator	BOD
National Steril-Quick Autoclave Model 704-9000-D	Autoclave
Precision Scientific – Flashpoint Instrument	Flashpoint
Fisher Scientific – Flashpoint Instrument	Flashpoint
Orion 720A – pH meter	pH
Corning 320 pH Meter	pH
Millipore YT31 ORA HW Rotary Agitator	TCLP/SPLP
TDS Oven	TDS
TSS Oven - Yamato DKN 600	TSS
Solids Oven	Solids
Total Solids Oven	Total Solids
Hot Block Digestion System	TKN, Total Phos
Hot Block Digestion System	TKN, Total Phos
Lindberg Muffle Furnace	
Mettler/Toledo Top Loading Balance	
Mettler/Toledo Top Loading Balance	
Satorius Top Loading Balance	
Mettler/Toledo Analytical Balance	
Ohaus Analytical Balance	
Ohaus Analytical Balance	
Mettler -Toledo PB602S Balance	
Tekmar/Dohrmann Apollo 9000Total Organic Carbon Analyzer (TOC)	TOC
Dohrmann 183 S/SS Soil TOC Oven	TOC
Teledyne Model 14-9600-100 Total Organic Carbon Analyzer	TOC
Milton Roy Spectronic 21D Spectrophotometer	AVS/SEM

ATTACHMENT IV

PASI – GREEN BAY FLOOR PLAN



ATTACHMENT V

PASI – GREEN BAY SOP LIST

SOP Number	SOP Name
S-GB-ALL-C-001-REV.01	Sample Management
S-ALL-C-002-Rev.0	Bottle Order Database
S-GB-ALL-C-003-REV.01	Subcontracting Samples
S-GB-ALL-C-004-REV.02	Bottle Preparation
S-ALL-C-005-Rev.00	Operation of PacePort Customer Feedback Form
S-ALL-C-006-Rev.00	Review of Analytical Requests
S-GB-C-001-Rev.02	Procedure to Preserve Samples for Volatile Organic Analysis of Solid Matrices by Method 5035
S-GB-C-002-Rev.02	Extruding Sample from 25 g EnCores for Volatile and Semivolatile Analyses
S-GB-C-003-Rev.02	Tedlar Bag Preservation by Methanol
S-GB-C-005-Rev.02	Maintenance of Ice Chests and Shipping Containers
S-GB-C-007-Rev.02	Laboratory Tracking of Samples
S-GB-C-008-REV.0	Measurement of Percent Moisture in Soils and Solids
T-ALL-C-001-Rev.01	Project Management
GB-I-026-Rev.2	Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma Mass Spectroscopy
S-GB-I-028-REV.2	Soil Fraction Preparation for Lead Analysis
GB-I-036-REV.2	The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy
S-GB-I-039-REV.1	Mercury Analysis by Cold-Vapor Atomic Fluorescence Spectrometry - Automated Tekran 2600
S-GB-I-053-Rev.0	Acid Volatile Sulfide / Simultaneously Extracted Metals
S-ALL-GB-M-002-Rev.1	Determination of Metals by Inductively Coupled Plasma (ICP) Spectroscopy by 6010B
S-GB-M-001-REV.00	Mercury Analysis by Cold-Vapor Atomic Fluorescence Spectrometry
S-GB-M-002-REV.00	Methyl Mercury Analysis by Cold-Vapor Atomic Fluorescence Spectrometry
S-GB-M-003-REV.00	Mercury Analysis by Cold-Vapor Atomic Fluorescence Spectrometry Solids - Manual System
S-GB-M-004-REV.00	The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy (7470A/7471B)
S-GB-M-005-REV.00	Determination of Metals by Inductively Coupled Plasma (ICP) Spectroscopy by 6010C
S-GB-M-006-REV.00	Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma Mass Spectroscopy - 6020A
S-GB-M-007-REV.00	Determination of Trace Metals in Waters and Wastes by Inductively Coupled Plasma Mass Spectroscopy - 6020
S-GB-M-008-REV.00	Cleaning Metals Glassware
S-GB-M-009-REV.00	Hardness by Calculation
S-GB-M-011-REV.00	The Determination of Mercury in Biological Samples by Cold Vapor Atomic Absorption Spectroscopy
S-ALL-GB-I-014-Rev.3	Measurement of Volatile Solids and Solids in Water
S-ALL-GB-I-015-Rev.00	Measurement of pH in Water, Soil, and Waste
S-ALL-GB-I-016-Rev.00	Measurement of Specific Conductance in Water
S-GB-I-001-Rev.4	Total Sulfide, Iodometric Titration
S-GB-I-002-Rev.2	Flash Point (Pensky-Martens Closed Cup Method For Ignitability
S-GB-I-004-Rev.02	Acidity
S-GB-I-006-REV.01	Amenable Cyanide
S-GB-I-009-Rev.2	Ion Chromatography
S-GB-I-010-REV.1	Wet Chemistry Glassware Cleaning

S-GB-I-013-Rev.01	Free Liquids
S-GB-I-014-Rev.01	Alkalinity
S-GB-I-015-Rev.01	Oxidation - Reduction Potential (Eh) Measurement
S-GB-I-016-Rev.01	Specific Gravity
S-GB-I-017-Rev.01	Ferrous Iron
S-GB-I-018-Rev.01	Total Alkalinity Analyzed by Lachat 8000 Flow Injection
S-GB-I-019-Rev.02	Fecal Coliform Determination Using the Membrane Filter Technique
S-GB-I-020-Rev.02	Color Determination in Aqueous Samples
S-GB-I-023-Rev.02	Heterotropic Plate Count
S-GB-I-024-REV.2	Colisure Presence/Absence Test for Detection and Identification of Coliform Bacteria and *Escherichla coli* in Drinking Waters
S-GB-I-025-Rev.2	TCLP - Toxicity Characteristic Leaching Procedure
S-GB-I-027-Rev.01	Dissolved Oxygen
S-GB-I-030-Rev.01	Turbidity (Nephelometric)
S-GB-I-031-REV.01	Determination of Total Organic Carbon Using the DC-80 Instrument
S-GB-I-037-REV.01	The Determination of Total Organic Carbon Using the Walkley-Black Procedure
S-GB-I-042-Rev.01	The Determination of Total Organic Carbon Using the Apollo 9000 Instrument for MDEQ RRD Operational Memorandum No. 2
S-GB-I-043-Rev.01	Total Cyanide using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection following SW846 9012A and EPA Method 335.4
S-GB-I-044-Rev.01	Biochemical Oxygen Demand
S-GB-I-045-Rev.01	Chromium, Hexavalent-Colorimetric
S-GB-I-046-Rev.02	Total Phenolics using Micro-Distillation and Lachat 8000 Flow Injection
S-GB-I-047-Rev.01	Total Kjeldahl Nitrogen using Block Digestion and Analyzed by Lachat 8000 Flow Injection following EPA Method 351.2
S-GB-I-048-Rev.01	Ammonia using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection following EPA Method 350.1
S-GB-I-049-Rev.01	Total Phosphorus using Block Digestion and Analyzed by Lachat 8000 Flow Injection following EPA Method 365.4
S-GB-I-051-REV.01	Nitrate and Nitrite Analyzed by Lachat 8000 Flow Injection
S-GB-I-052-REV.01	Chemical Oxygen Demand, Colorimetric, Manual (Chemetric Vials)
S-GB-I-057-REV.00	SPLP - Synthetic Precipitation Leaching Procedure
S-GB-I-058-REV.00	ASTM Shake Extraction of Solid Waste with Water
S-GB-I-059-Rev.00	The Determination of Total Organic Carbon Using the Apollo 9000 Instrument
S-GB-O-005-REV.02	Soil/Semisolid Sample Preparation for the Analysis of Gasoline Range Organics and Petroleum Volatile Organics by Wisconsin Modified GRO
S-GB-O-006-Rev.02	Modified Method for Determination of Gasoline Range Organics
S-GB-O-008-REV.02	Total Petroleum Hydrocarbons - Gasoline by Gas Chromatography Using Flame-ionization Detectors
S-GB-O-009-REV.02	Aromatic Volatiles by Gas Chromatography Using Photo-ionization Detectors
S-GB-O-010-Rev.02	Aqueous Sample Preparation for the Analysis of Gas Range Organics and Petroleum Volatile Organics
S-GB-O-017-REV.02	Analysis of Dissolved Methane, Ethane, and Ethene in Ground Water by Static Headspace and Gas Chromatography
S-ALL-GB-O-001-Rev.00	Determination of Semi-Volatile Organics by GC/MS (8270)
S-ALL-GB-O-003-Rev.00	Separatory Funnel Extraction
S-ALL-GB-O-005-REV.00	Ultrasonic Extraction
S-ALL-GB-O-008-REV.00	Determination of Semi-Volatile Organics by gc/ms (Selective Ion Monitoring)
S-GB-O-015-REV.02	Cleaning of Glassware Used in the Analysis of Semivolatile Range Organics
S-GB-O-018-REV.1	Determination of DRO Sample Weight and Methylene Chloride Addition
S-GB-O-019-REV.02	WI Modified Method for Determination of Diesel Range Organics
S-GB-O-023-Rev.04	Total Petroleum Hydrocarbons
S-GB-O-025-Rev.01	Alcohols & Glycols by Direct Injection GC/FID
S-GB-O-026-REV.03	Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography

S-GB-O-027-REV.2	Analysis of Organochlorine Pesticides by Gas Chromatography
S-GB-O-028-REV.02	Preparation of Anhydrous Sodium Sulfate and Sand for Extraction Purposes
S-GB-O-031-REV.1	Extraction of Biological Samples for Organochlorine Pesticides/PCBs
S-GB-O-032-REV.1	Gel Permeation Chromatography
GB-O-033-Rev.0	Extraction of Biological Samples for Base Neutral/Acid and PAH-SIM Analysis
S-GB-O-034-REV.1	Sulfuric Acid Cleanup
S-GB-O-035-REV.1	Mercury Cleanup for the Removal of Sulfur from PCB Samples
S-GB-O-036-REV.1	Florisil Cleanup for PCBs
S-GB-O-037-REV.1	Florisil Cartridge Cleanup
S-GB-O-038-Rev.02	Silica Gel Cleanup for Organic Analysis
S-GB-O-039-REV.1	Copper Cleanup for the Removal of Sulfur from PCB Samples
S-GB-O-040-REV.02	Extraction of Wipes and Oil for PCB Analysis
S-GB-O-041-REV.02	Extraction of PCBs Using the Automated Soxhlet
S-GB-O-043-Rev.01	Extraction of Toxaphene Using the Automated Soxhlet
S-GB-O-044-REV.1	Determination of Low Level PAHs by GC/MS-SIM in Solid and Biological Matrices
S-GB-O-045-REV.1	Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acids in Solid Matrices
S-GB-O-047-REV.00	Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography following 8082A
S-GB-ALL-O-002-REV.01	Determination of Volatile Organics by GC/MS
S-GB-O-001-REV.03	Sample Screening Volatile Organics Prior to Preparation
S-GB-O-012-REV.02	Cleaning of Syringes Used in the Analysis of Volatile Organics
ALL-IT-001-Rev.1	System Security and Integrity
S-ALL-IT-002-Rev.1	Server Back-UP
S-ALL-GB-IT-002-Rev.02	Server Back-UP - Green Bay Addendum
T-ALL-IT-001-rev.04	EPIC Pro 01: Basic System Functions
T-ALL-IT-002-rev.05	EPIC Pro 02: Client Setup
T-ALL-IT-004-rev.03	EPIC Pro: PMs / Sales II
T-ALL-IT-005-rev.04	EPIC Pro: Login
T-ALL-IT-006-rev.04	EPIC PRO: Lab Prep
T-ALL-IT-007-rev.03	EPIC Pro: Analyst / Lab Management
T-ALL-IT-008-rev.05	EPIC Pro: PM - Additional Knowledge
T-ALL-IT-009-rev.01	EPIC Pro: Detection, Reporting and Control Limits
T-ALL-IT-010-rev.02	EPIC Pro: Standard Traceability
S-ALL-Q-001-Rev.7	Preparation of Standard Operating Procedures
S-ALL-Q-002-Rev.02	Document Management
S-ALL-Q-003-REV.2	Document Numbering
S-ALL-Q-004-Rev.4	Method Detection Limit Studies
ALL-Q-005-Rev.2	Purchasing of Laboratory Supplies
S-ALL-GB-Q-005-REV.04	Purchasing of Laboratory Supplies - Green Bay Addendum
ALL-Q-006-Rev.1	Receipt and Storage of Laboratory Supplies
S-ALL-GB-Q-006-Rev.1	Receipt and Storage of Laboratory Supplies - Green Bay Addendum
S-ALL-Q-007-Rev.01	EPIC Pro: Acode Validation
S-ALL-Q-009-Rev.02	Laboratory Documentation
S-ALL-Q-010-REV.2	Proficiency Testing Program
ALL-Q-011-Rev.1	Audits and Inspections
ALL-Q-012-Rev.0	Corrective Action / Preventative Action Process
S-ALL-GB-Q-012-Rev.02	Corrective Action / Preventative Action Process - Green Bay Addendum
S-ALL-Q-013-REV.1	Support Equipment
ALL-Q-014-Rev.1	Quality system Review

All-Q-016-Rev.0	Manual Integration
S-ALL-Q-018-Rev.02	Monitoring Storage Units
S-ALL-Q-020-REV.1	Orientation and Training Procedures
S-ALL-Q-021-Rev.02	Sample Homogenization and Sub-Sampling
ALL-Q-022-Rev.1	3P Program Continuous Process Improvement
ALL-Q-025-Rev.1	Standard and Reagent Management and Traceability
S-ALL-GB-Q-025-REV.01	Standard and Reagent Management and Traceability - Green Bay Addendum
S-ALL-Q-027-REV.0	Evaluation and Qualification of Vendors
S-ALL-Q-028-Rev.0	Use and Operation of Lab Track System
S-ALL-Q-029-REV.0	MintMiner Data File Review
S-ALL-Q-030-Rev.01	Operation of Data Checker for Epic Pro
S-GB-Q-001-REV.01	Employee Master Signature Log
S-GB-Q-002-Rev.01	Training Record Files Maintained by the QAO
S-GB-Q-003-Rev.00	Data Reduction, Validation, and Reporting
S-GB-Q-004-Rev.01	Laboratory Notebooks and Logbooks
S-GB-Q-005-Rev.01	Precision and Accuracy Measurement and Evaluation
S-GB-Q-006-Rev.01	Data Archiving
S-GB-Q-007-Rev.01	Method of Syringe Technique
S-GB-Q-008-Rev.02	Preventative, routine, and non-routine maintenance
S-GB-Q-009-Rev.01	Common Laboratory Calculations and Statistical Evaluation of Data
S-GB-Q-010-Rev.01	Estimation of Measurement Uncertainty
S-ALL-S-001-REV.1	Hazard Assessment
ALL-S-002-Rev.0	Waste Handling
S-GB-ALL-S-002-REV.03	Waste Handling - Green Bay Addendum
S-GB-S-001-REV.2	Regulated Soil Handling (Green Bay Location)
S-GB-S-002-REV.01	Control of Hazardous Energy Program - Lockout/Tagout
GB-S-003-Rev.0	Electrical Generator Procedure
S-GB-S-004-Rev.01	Rescue Alert System Operation
S-GB-E-001-Rev.01	Use and Maintenance of the NANOpure Infinity Water Purification System
S-GB-E-002-Rev.01	Operation of Waste Disposal Equipment
S-GB-L-001-REV.1	Biological Tissue and Plant Preparation
S-GB-L-002-REV.1	Small Rodent Handling and Homogenization
S-GB-L-003-REV.1	The Determination of Lipids in Tissues, Fats, and Plants
S-GB-L-004-REV.1	Determination of Percent Solids in Tissue Samples
S-GB-L-005-REV.0	Reagent Water Quality
S-GB-L-006-REV.00	Procedure for Handling Aqueous Organic Extractable Samples Containing Sediment

ATTACHMENT VI

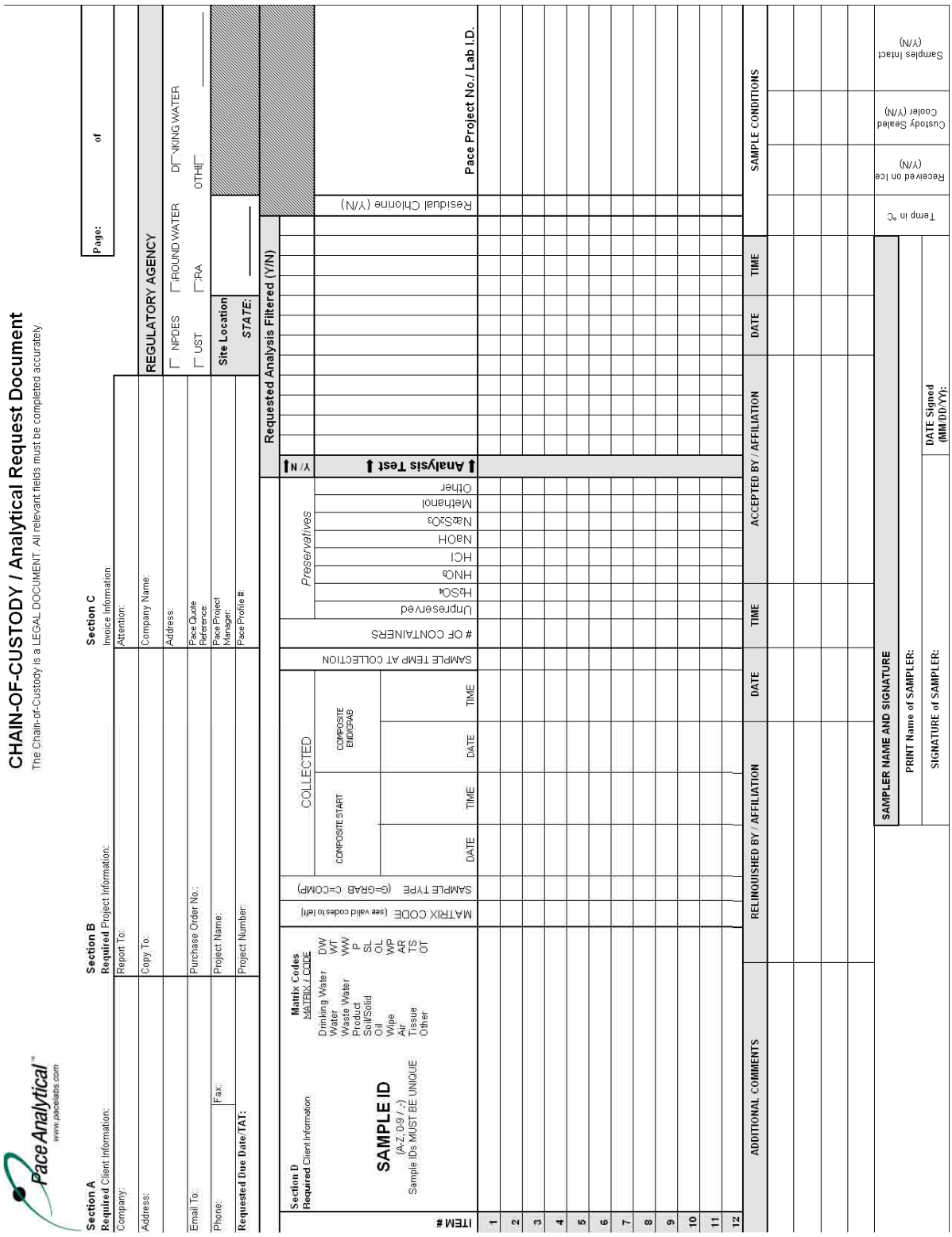
PASI – GREEN BAY CERTIFICATION LIST

Accrediting Authority	Program Category	Accrediting Agency	Certification #
Florida (NELAP)	Biological Tissue	Dept of Health, Bureau of Laboratories	E87948
Florida (NELAP)	Hazardous Waste - Solid	Dept of Health, Bureau of Laboratories	E87951
Florida (NELAP)	Hazardous Waste - Solid	Dept of Health, Bureau of Laboratories	E87948
Florida (NELAP)	Waste Water	Dept of Health, Bureau of Laboratories	E87951
Florida (NELAP)	Waste Water	Dept of Health, Bureau of Laboratories	E87948
Georgia	Hazardous Waste - Solid - NELAP stipulation	Environmental Protection Division	E87951
Georgia	Waste Water -NELAP stipulation	Environmental Protection Division	E87948
Georgia	Hazardous Waste - Solid - NELAP stipulation	Environmental Protection Division	E87951
Georgia	Waste Water - NELAP stipulation	Environmental Protection Division	E87948
Illinois (NELAP)	Hazardous Waste - Solid	Illinois EPA	200051
Illinois (NELAP)	Hazardous Waste - Solid	Illinois EPA	200050
Illinois (NELAP)	Waste Water	Illinois EPA	200050
Illinois (NELAP)	Waste Water	Illinois EPA	200051
Kentucky	UST	Environmental and Public Protection Cabinet	82
Kentucky	UST	Environmental and Public Protection Cabinet	83
Louisiana (NELAP)	Hazardous Waste - Solid	Department of Environmental Quality	04168
Louisiana (NELAP)	Waste Water	Department of Environmental Quality	04168
Louisiana (NELAP)	Biological Tissue	Department of Environmental Quality	04168
Louisiana (NELAP)	Hazardous Waste - Solid	Department of Environmental Quality	04169
Louisiana (NELAP)	Waste Water	Department of Environmental Quality	04169
Minnesota	Hazardous Waste	Dept of Health	055-999-334
Minnesota	Waste Water	Dept of Health	055-999-334
Minnesota	UST	Department of Health	055-999-334
New York (NELAP)	Solid - Hazardous Waste - NELAP	Dept of Health	11887
New York (NELAP)	Solid - Hazardous Waste - NELAP	Dept of Health	11888
New York (NELAP)	Waste Water - NELAP	Dept of Health	11888

New York (NELAP)	Waste Water - NELAP	Dept of Health	11887
North Carolina	Waste Water	Dept of Environment, Health & Natural Resources	503
North Dakota	Hazardous Waste	Dept of Health Chemistry Division	R-150
North Dakota	Hazardous Waste	Dept of Health Chemistry Division	R-200
North Dakota	Waste Water	Dept of Health Chemistry Division	R-150
North Dakota	Waste Water	Dept of Health Chemistry Division	R-200
South Carolina	Hazardous Waste	Dept of Hlth & Environmental Control	83006001
South Carolina	Waste Water	Dept of Hlth & Environmental Control	83006001
US Dept of Agriculture	Foreign Soil Permit	Dept of Argiculture	S-76505
Wisconsin	Drinking Water	Dept of Natural Resources	405132750
Wisconsin	Drinking Water	Dept of Agriculture, Trade & Consumer Protection	105-444
Wisconsin	Hazardous Waste	Dept of Natural Resources	405132750
Wisconsin	Waste Water	Dept of Natural Resources	405132750

ATTACHMENT VII

PASI – CHAIN OF CUSTODY



ATTACHMENT VIII
METHOD HOLD TIME, CONTAINER AND PRESERVATION GUIDE

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
2, 3, 7, 8-TCDD	1613B	Soil	8oz Glass	None	90/40 Days
2, 3, 7, 8-TCDD	1613B	Water	1L Glass	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	90/40 Days
2, 3, 7, 8-TCDD	8290	Water	1L Glass	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	30/45 Days
Acidity	SM2310B	Water	Plastic/Glass	$\leq 6^oC$	14 Days
Alkalinity	SM2320B/310.2	Water	Plastic/Glass	$\leq 6^oC$	14 Days
Alpha Emitting Radium Isotopes	9315/903.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Anions by IC, including Br, Cl, F, NO_2, NO_3, SO_4	300.0/300.1/ SM4110B	Water	Plastic/Glass	$\leq 6^oC$	Br, Cl, F, SO_4 (28 Days) NO_2, NO_3 (48 Hours)
Aromatic and Halogenated Volatiles	8021	Soil	5035 vial kit	See 5035 note*	14 days
Aromatic and Halogenated Volatiles	601/602/8021	Water	40mL vials	pH<2 HCl; $\leq 6^oC$; $Na_2S_2O_3$ if Cl present	14 Days
Bacteria, Total Plate Count	SM9221D	Water	Plastic/WK	$\leq 6^oC$; $Na_2S_2O_3$	24 Hours
Base/Neutrals and Acids	8270	Soil	8oz Glass	$\leq 6^oC$	14/40 Days
Base/Neutrals and Acids	625/8270	Water	1L Glass	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	7/40 Days
Base/Neutrals, Acids & Pesticides	525.1/525.2	Water	1L Glass	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	7/30 Days
BOD/cBOD	SM5210B	Water	Plastic/Glass	$\leq 6^oC$	48 hours
BTEX/Total Hydrocarbons	TO-3	Air	Summa Canister	None	14 Days
BTEX/Total Hydrocarbons	TO-3	Air	Tedlar Bag	None	48 Hours
Chloride	SM4500Cl/9250/ 9251/9252	Water	Plastic/Glass	None	28 Days
Chlorinated Herbicides	8151	Soil	8oz Glass Jar	$\leq 6^oC$	7/40 Days
Chlorinated Herbicides	8151	Water	1L Amber Glass	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	7/40 Days
Chlorinated Herbicides	515.1	Water	1L Amber Glass	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	14/28 Days
Chorine, Residual	SM4500Cl	Water	Plastic/Glass	None	15 minutes
COD	SM5220C/ 410.3/410.4	Water	Plastic/Glass	pH<2 H_2SO_4; $\leq 6^oC$	28 Days
Color	SM2120B,C,E	Water	Plastic/Glass	$\leq 6^oC$	48 Hours
Condensable Particulate Emissions	EPA 202	Air	Solutions	None	6 Months
Cyanide, Reactive	SW846 chap.7	Water	Plastic/Glass	None	28 Days
Cyanide, Total and Amenable	SM4500CN/9010/ 9012/335.4	Water		pH>12 NaOH; $\leq 6^oC$; ascorbic acid if Cl present	14 Days, 24 Hours if Sulfide present
Diesel Range Organics	8015	Soil	8oz Glass Jar	$\leq 6^oC$	14/40 Days
Diesel Range Organics	8015	Water	1L Glass	$\leq 6^oC$	7/40 Days
Dioxins & Furans	TO-9	Air	PUF	None	30/45 Days
EDB & DBCP	504.1/8011	Water	40mL vials	$\leq 6^oC$; $Na_2S_2O_3$ if Cl present	14 Days
Explosives	8330/8332	Water	1L Glass	$\leq 6^oC$	7/40 Days
Explosives	8330/8332	Soil	8oz Glass Jar	$\leq 6^oC$	14/40 Days
Ferrous Iron	SN3500Fe-D	Water	Glass	None	Immediate
Flashpoint/Ignitability	1010/1030	Water	Plastic/Glass	None	28 Days
Fluoride	SM4500Fl-C,D	Water	Plastic	None	28 Days
Gamma Emitting Radionuclides	901.1	Water	Plastic/Glass	pH<2 HNO_3	180 days
Gas Range Organics	8015	Water	40mL vials	pH<2 HCl	14 Days
Gasoline Range Organics	8015	Soil	5035 vial kit	See 5035 note*	14 days
Gross Alpha (NJ 48Hr Method)	NJAC 7:18-6	Water	Plastic/Glass	pH<2 HNO_3	48 Hrs

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Gross Alpha and Gross Beta	9310/900.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Haloacetic Acids	552.1/552.2	Water	40mL Amber vials	NH_4Cl; ≤6°C	14/7 Days
Hardness, Total ($CaCO_3$)	SM2340B,C/130.1	Water	Plastic/Glass	pH<2 HNO_3	6 Months
Hexavalent Chromium	7196/218.6/ SM3500Cr	Water	Plastic/Glass	≤6°C	24 Hours
Hydrogen Halide & Halogen Emissions	EPA 26	Air	Solutions	None	6 Months
Lead Emissions	EPA 12	Air	Filter/Solutions	None	6 Months
Low Level Mercury	1631	Water	Glass	BrCl	90 days (if preserved and oxidized)
Mercury	7471	Soil	8oz Glass Jar	≤6°C	28 days
Mercury	7470/245.1/245.2	Water	Plastic/Glass	pH<2 HNO_3	28 Days
Metals	7300/7303	Air	Filters	None	6 Months
Metals (and other ICP elements)	6010	Soil	8oz Glass Jar	None	6 months
Metals (and other ICP elements)	6010/6020/200.7/ 200.8	Water	Plastic/Glass	pH<2 HNO_3	6 Months
Methane, Ethane, Ethene	RSK-175	Water	40mL vials	HCl	14 Days
Methane, Ethane, Ethene	EPA 3C	Air	Summa Canister	None	14 Days
Methane, Ethane, Ethene	EPA 3C	Air	Tedlar Bag	None	48 Hours
Nitrogen, Ammonia	SM4500NH3/350.1	Water	Plastic/Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Nitrogen, Kjeldahl	SM4500-Norg; 351.1/351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Nitrogen, Nitrate	SM4500-NO3/ 352.1	Water	Plastic/Glass	≤6°C	48 Hours
Nitrogen, Nitrate & Nitrite	SM4500-NO3/ 353.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Nitrogen, Nitrite	SM4500-NO2/ 353.2	Water	Plastic/Glass	≤6°C	48 Hours
Nitrogen, Organic	SM4500-Norg/ 351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Non-Methane Organics	EPA 25C	Air	Summa Canister	None	14 Days
Non-Methane Organics	EPA 25C	Air	Tedlar Bag	None	48 Hours
Odor	SM2150B	Water	Glass	≤6°C	24 Hours
Oil and Grease/HEM	1664A/SM5520B/ 9070	Water	Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Organochlorine Pesticides & PCBs	TO-4	Air	PUF	None	7/40 Days
Organochlorine Pesticides & PCBs	8081/8082/608	Water	1L Glass	≤6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Organochlorine Pesticides & PCBs	8081/8082	Soil	8oz Glass Jar	≤6°C	14/40 Days
Organophosphorous Pesticides	8141	Soil	8oz Glass Jar	≤6°C	14/40 Days
Organophosphorous Pesticides	8141	Water	1L Amber Glass	≤6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Oxygen, Dissolved (Probe)	SM4500-O	Water	Glass	None	15 minutes
Paint Filter Liquid Test	9095	Water	Plastic/Glass	None	N/A
Particulates	PM-10	Air	Filters	None	6 Months
Permanent Gases	EPA 3C	Air	Summa Canister	None	14 Days
Permanent Gases	EPA 3C	Air	Tedlar Bag	None	48 Hours
pH	SM4500H+B/9040/ 9041/150.2	Water	Plastic/Glass	None	15 minutes
Phenol, Total	420.1/420.4/9065/ 9066	Water	Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Phosphorus, Orthophosphate	SM4500P/365.1/365.3	Water	Plastic	Filter; ≤6°C	Filter within 15 minutes, Analyze within 48 Hours
Phosphorus, Total	SM4500P/ 365.1/365.3/365.4	Water	Plastic/Glass	pH<2 H_2SO_4; ≤6°C	28 Days
Polynuclear Aromatic Hydrocarbons	TO-13	Air	PUF	None	7/40 Days
Polynuclear Aromatic Hydrocarbons	8270 SIM	Soil	8oz Glass Jar	≤6°C	14/40 Days
Polynuclear Aromatic Hydrocarbons	8270 SIM	Water	1L Glass	≤6°C; $Na_2S_2O_3$ if Cl present	7/40 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Radioactive Strontium	905.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-226 Radon Emanation Technique	903.1	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-228	9320/904.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Silica, Dissolved	SM4500Si-D	Water	Plastic	≤6°C	28 Days
Solids, Settleable	SM2540F	Water	Glass	≤6°C	48 Hours
Solids, Total	SM2540B	Water	Plastic/Glass	≤6°C	7 Days
Solids, Total Dissolved	SM2540C	Water	Plastic/Glass	≤6°C	7 Days
Solids, Total Suspended	SM2540D	Water	Plastic/Glass	≤6°C	7 Days
Solids, Total Volatile	SM2540E	Water	Plastic/Glass	≤6°C	7 Days
Specific Conductance	SM2510B/9050/120.1	Water	Plastic/Glass	≤6°C	28 Days
Stationary Source Dioxins & Furans	EPA 23	Air	XAD Trap	None	30/45 Days
Stationary Source Mercury	EPA 101	Air	Filters	None	6 Months, 28 Days for Hg
Stationary Source Metals	EPA 29	Air	Filters	None	6 Months, 28 Days for Hg
Stationary Source PM10	EPA 201A	Air	Filters	None	6 Months
Stationary Source Particulates	EPA 5	Air	Filter/Solutions	None	6 Months
Sulfate	SM4500SO4/9036/ 9038/375.2/ASTMD516	Water	Plastic/Glass	≤6°C	28 Days
Sulfide, Reactive	SW-846 Chap.7	Water	Plastic/Glass	None	28 Days
Sulfide, Total	SM4500S/9030	Water	Plastic/Glass	pH>9 NaOH; ZnOAc; ≤6°C	7 Days
Sulfite	SM4500SO3	Water	Plastic/Glass	None	15 minutes
Surfactants	SM5540C	Water	Plastic/Glass	≤6°C	48 Hours
Total Organic Carbon (TOC)	SM5310B,C,D/ 9060	Water	Glass	pH<2 H_2SO_4 or HCl; ≤6°C	28 Days
Total Organic Halogen (TOX)	SM5320/9020/ 9021	Water	Glass; no headspace	≤6°C	14 Days
Tritium	906.0	Water	Glass	pH<2 HNO_3	180 days
Turbidity	SM2130B/180.1	Water	Plastic/Glass	≤6°C	48 Hours
Uranium Radiochemical Method	908.0/ASTM D5174-97	Water	Plastic/Glass	pH<2 HNO_3	180 days
Volatiles	TO-14	Air	Summa Canister	None	30 Days
Volatiles	TO-14	Air	Tedlar Bag	None	48 Hours
Volatiles	TO-15	Air	Summa Canister	None	30 Days
Volatiles	8260	Soil	5035 vial kit	See 5035 note*	14 days
Volatiles	8260	Water	40mL vials	pH<2 HCl; ≤6°C; $Na_2S_2O_3$ if Cl present	14 Days
Volatiles	624	Water	40mL vials	pH<2 HCl; ≤6°C; $Na_2S_2O_3$ if Cl present	14 Days (7 unpreserved)
Volatiles	524.1/524.2	Water	40mL vials	pH<2 HCl; ≤6°C; $Na_2S_2O_3$ if Cl present	14 Days
Alaska DRO	AK102	Soil	8oz Glass	≤6°C	14/40 Days
Alaska DRO	AK102	Water	1L Glass	pH<2 HCl; ≤6°C	14/40 Days
Alaska RRO	AK103	Soil	8oz Glass	≤6°C	14/40 Days
Alaska GRO	AK101	Soil	5035 vial kit	See 5035 note*	14 Days
Alaska GRO	AK101	Water	40mL vials	pH<2 HCl; ≤6°C	14 Days

5035 Note: 5035 vial kit typically contains 2 vials water, preserved by freezing **or**, 2 vials aqueous sodium bisulfate preserved at 4°C, **and** one vial methanol preserved at ≤6°C **and** one container of unpreserved sample stored at ≤6°C.

QUALITY ASSURANCE MANUAL

Quality Assurance/Quality Control
Policies and Procedures

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612-607-1700

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Date: September 9 2009

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PACE ANALYTICAL SERVICES – MINNESOTA
LOCAL APPROVAL

This document has been approved as the Quality Assurance Manual, effective 10 September 2009, as indicated by the following signatures:

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Additional Signatures

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

Table of Contents

1.0 INTRODUCTION AND ORGANIZATIONAL STRUCTURE

"Working together to protect our environment and improve our health"

Pace Analytical Services Inc. - Mission Statement

1.1 Introduction to PASI

Pace Analytical Services, Inc. (PASI) is a privately held, full-service analytical testing firm operating a nationwide system of laboratories. PASI offers extensive services beyond standard analytical testing, including: bioassay for aquatic toxicity, air toxics, industrial hygiene testing, explosives, high resolution mass spectroscopy (including dioxins, furans and coplanar PCB's), radiochemical analyses, product testing, pharmaceutical testing, field services and mobile laboratory capabilities. PASI has implemented a consistent Quality System in each of its laboratories and service centers. In addition, the company utilizes an advanced data management system that is highly efficient and allows for flexible data reporting. Together, these systems ensure data reliability and superior on-time performance. This document defines the Quality System and QA/QC protocols.

Our goal is to combine our expertise in laboratory operations with customized solutions to meet the specific needs of our customers.

1.2 Statement of Purpose

To meet the business needs of our customers for high quality, cost-effective analytical measurements and services.

1.3 Quality Policy Statement and Goals of the Quality System

The PASI management is committed to maintaining the highest possible standard of service for our customers by following a documented quality system. The overall objective of this quality system is to provide reliable data through adherence to rigorous quality assurance policies and quality control procedures as documented in this Quality Assurance Manual.

All personnel within the PASI network are required to be familiar with all facets of the quality system and implement these policies and procedures in their daily work. This daily focus on quality is applied with initial project planning, continued through all field and laboratory activities, and is ultimately included in the final report generation.

PASI management demonstrates its commitment to quality by providing the resources, including facilities, equipment and personnel to ensure the adherence to these documented policies and procedures and to promote the continuous improvement of the quality system. All PASI personnel comply with all current applicable state, federal, and industry standards (such as the NELAC and ISO 17025 standards).

1.4 Pace Analytical Services Core Values

- **INTEGRITY**
- **VALUE EMPLOYEES**
- **KNOW OUR CUSTOMERS**
- **HONOR COMMITMENTS**
- **FLEXIBLE RESPONSE TO DEMAND**
- **PURSUE OPPORTUNITIES**
- **CONTINUOUSLY IMPROVE**

1.5 Code of Ethics

PASI's fundamental ethical principles are as follows:

- Each PASI employee is responsible for the propriety and consequences of his or her actions.
- Each PASI employee must conduct all aspects of Company business in an ethical and strictly legal manner, and must obey the laws of the United States and of all localities, states and nations where PASI does business or seeks to do business.
- Each PASI employee must reflect the highest standards of honesty, integrity and fairness on behalf of the Company with customers, suppliers, the public, and one another.

Strict adherence by each PASI employee to this Code of Ethics and to the Standards of Conduct is essential to the continued vitality of PASI.

Failure to comply with the Code of Ethics and Standards of Conduct will result in disciplinary action up to and including termination and referral for civil or criminal prosecution where appropriate. An employee will be notified of an infraction and given an opportunity to explain, as prescribed under current disciplinary procedures.

1.6 Standards of Conduct

1.6.1 Data Integrity

The accuracy and integrity of the analytical results produced at PASI are the cornerstones of the company. Lack of data integrity is an assault on our most basic values and puts PASI and its employees at grave financial and legal risk. Therefore, employees are to accurately prepare and maintain all technical records, scientific notebooks, calculations and databases. Employees are prohibited from making false entries or misrepresentations of data (e.g., dates, calculations, results or conclusions).

Managerial staff must make every effort to ensure that personnel are free from any undue pressures that may affect the quality or integrity of their work; including commercial, financial, over-scheduling and working condition pressures.

1.6.2 Confidentiality

PASI employees must not (directly or indirectly) use or disclose confidential or proprietary information except when in connection with their duties at PASI. This is effective over the course of employment and for a period of two years thereafter.

Confidential or proprietary information, belonging to either PASI and/or its customers, includes but is not limited to test results, trade secrets, research and development matters, procedures, methods, processes and standards, company-specific techniques and equipment, marketing and customer information, inventions, materials composition, etc.

1.6.3 Conflict of Interest

PASI employees must avoid situations that might involve a conflict of interest or appear questionable to others. The employee must be careful in two general areas:

- Participation in activities that conflict or appear to conflict with PASI responsibilities.

- Offering or accepting anything that might influence the recipient or cause another person to believe that the recipient may be influenced. This includes bribes, kickbacks or illegal payments.

Employees are not to engage in outside business or economic activity relating to a sale or purchase by the Company. Other questionable activities include service on the Board of Directors of a competing or supplier company, significant ownership in a competing or supplier company, employment for a competing or supplier company or participation in any outside business during the employee's work hours.

1.6.4 Compliance

All employees are required to read, understand and comply with the various components of the standards listed in this document. As confirmation that they understand this responsibility, each employee is required to sign an acknowledgment form (either hardcopy or in electronic database) annually (or as revisions become finalized) that becomes part of the employee's permanent record. Employees will be held accountable for complying with the Quality Systems as summarized in the Quality Assurance Manual.

1.7 Laboratory Organization

The PASI Corporate Office centralizes company-wide accounting, business development, financial management, human resources development, information systems, marketing, quality, safety, and training activities. PASI's Director of Quality, Safety & Training is responsible for assisting the development, implementation and monitoring of quality programs for the company. See Attachment IIB for the Corporate Organizational structure.

Each laboratory within the system operates with local management, but all share common systems and receive support from the Corporate Office.

A General Manager (GM) supervises each regional laboratory. Some operations may have an Assistant General Manager (AGM) in situations where the General Manager is responsible for multiple laboratory facilities and is not necessarily in the facility on a regular basis. Quality Managers (QM) at each lab report directly to their General Manager (or Assistant General Manager) but receive guidance and direction from the Director of Quality, Safety & Training.

The General Manager bears the responsibility for the laboratory operations and serves as the final, local authority in all matters. In the absence of the General Manager (and an Assistant General Manager), the Quality Manager serves as the next in command. He or she assumes the responsibilities of the GM until the GM is available to resume the duties of their position. In the absence of the GM and QM, management responsibility of the laboratory is passed to the Technical Director – provided such a position is identified – and then to the most senior department manager until the return of the GM or QM. The most senior department manager in charge may include the Client Services Manager or the Administrative Business Manager at the discretion of the General Manager.

A Technical Director who is absent for a period of time exceeding 15 consecutive calendar days shall designate another full-time staff member meeting the qualifications of the technical director to temporarily perform this function. The laboratory General Manager or Quality Manager has the authority to make this designation in the event the existing Technical Director is unable to do so. If this absence exceeds 65 consecutive calendar days, the primary accrediting authority shall be notified in writing.

The Quality Manager has the responsibility and authority to ensure the Quality System is implemented and followed at all times. In circumstances where a laboratory is not meeting the established level of quality or following the policies set for in this Quality Assurance Manual, the Quality Manager has the authority to halt laboratory operations should he or she deem such an action necessary. The QM will immediately

communicate the halting of operations to the GM and keep him or her posted on the progress of corrective actions. In the event the GM and QM are not in agreement as to the need for the suspension, the Chief Operating Officer and Director of Quality, Safety and Training will be called in to mediate the situation.

Under the direction of the General Manager, the technical staff of the laboratory is generally organized into the following functional groups:

- Organic Sample Preparation
- Wet Chemistry Analysis
- Metals Analysis
- Volatiles Analysis
- Semi-volatiles Analysis
- Radiochemical Analysis
- Product Testing
- Equipment Maintenance
- Microbiology

Appropriate support groups are present in each laboratory. The actual organizational structure for PASI – Minnesota is listed in Attachment IIA. In the event of a change in General Manager, Quality Manager or Technical Director(s), the laboratory will notify its accrediting authorities and revise the organizational chart in the Quality Assurance Manual (QAM) within 30 days. For changes in Department Managers or Supervisors or other laboratory personnel, no notifications will be sent to the laboratory's accrediting agencies; changes to the organizational chart will be updated during or prior to the annual review process. Changes or additions in these key personnel will also be noted by the additional signatures on the QAM Local Approval page. In any case, the QAM will remain in effect until the next scheduled revision.

1.8 Laboratory Job Descriptions

1.8.1 General Manager

1. Oversees all functions of the operations.
2. Authorizes personnel development including staffing, recruiting, training, workload scheduling, employee retention and motivation.
3. Prepares budgets and staffing plans.
4. Monitors the Quality Systems of the laboratory and advises the Quality Manager accordingly.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.2 Quality Manager

1. Oversees the laboratory Quality Systems while functioning independently from laboratory operations. Reports directly to the General Manager.
2. Monitors Quality Assurance policies and Quality Control procedures to ensure that the laboratory achieves established standards of quality.
3. Maintains records of quality control data and evaluates data quality.
4. Conducts periodic internal audits and coordinates external audits performed by regulatory agencies or customer representatives.
5. Reviews and maintains records of proficiency testing results.
6. Maintains the document control system
7. Assists in development and implementation of appropriate training programs.
8. Provides technical support to laboratory operations regarding methodology and project QA/QC requirements.
9. Maintains certifications from federal and state programs.
10. Ensures compliance with all applicable state, federal and industry standards.

11. Maintains the laboratory training records, including those in the Learning Management System (LMS).

1.8.3 Technical Director

1. Monitors the standards of performance in quality assurance and quality control data
2. Monitors the validity of analyses performed and data generated.
3. Reviews tenders, contracts and QAPPs to ensure the laboratory can meet the data quality objectives for any given project
4. Serves as the general manager of the laboratory in the absence of the GM, AGM and QM.
5. Provides technical guidance in the review, development and validation of new methodologies.

1.8.4 Administrative Business Manager

1. Responsible for financial and administrative management for the entire facility.
2. Provides input relative to tactical and strategic planning activities.
3. Organizes financial information so that the facility is run as a fiscally responsible business.
4. Works with staff to confirm that appropriate processes are put in place to track revenues and expenses.
5. Provide ongoing financial information to the General Manager and the management team so they can better manage their business.
6. Utilizes historical information and trends to accurately forecast future financial positions.
7. Works with management to ensure that key measurements (mileposts) are put in place to be utilized for tread analysis—this will include personnel and supply expenses, and key revenue and expense ratios.
8. Works with General Manager to develop accurate budget and track on an ongoing basis.
9. Works with entire management team to submit complete and justified capital budget requests and to balance requests across departments.
10. Works with project management team and administrative support staff to ensure timely and accurate invoicing.

1.8.5 Client Services Manager

1. Oversees all the day to day activities of the Client Services Department which includes Project Management and, possibly, Sample Control.
2. Responsible for staffing and all personnel management related issues for Client Services.
3. Serves as the primary senior consultant to customers on all project related issues such as set up, initiation, execution and closure.
4. Performs or is capable of performing all duties listed for that of Project Manager.

1.8.6 Project Manager

1. Coordinates daily activities including taking orders, reporting data and analytical results.
2. Serves as the primary technical and administrative liaison between customers and PASI.
3. Communicates with operations staff to update and set project priorities.
4. Provides results to customers in the requested format (verbal, hardcopy, electronic, etc.).
5. Works with customers, laboratory staff, and other appropriate PASI staff to develop project statements of work or resolve problems of data quality.
3. Responsible for solicitation of work requests, assisting with proposal preparation and project initiation with customers and maintain customer records.
4. Mediation of project schedules and scope of work through communication with internal resources and management.
5. Responsible for preparing routine and non-routine quotations, reports and technical papers.
6. Interfaces between customers and management personnel to achieve customer satisfaction.
7. Manages large-scale complex projects.
8. Supervises less experienced project managers and provide guidance on management of complex projects.
6. Arranges bottle orders and shipment of sample kits to customers.
7. Verifies login information relative to project requirements and field sample Chains-of-Custody.

1.8.7 Project Coordinator

1. Responsible for preparation of project specifications and provides technical/project support.
2. Coordinates project needs with other department sections and assists with proposal preparation.
3. Prepares routine proposals and invoicing.
4. Responsible for scanning, copying, assembling and binding final reports.
5. Other duties include filing, maintaining forms, process outgoing mail, maintaining training database and data entry.

1.8.8 Department Manager/Supervisor

1. Oversees the day-to-day production and quality activities of their assign department.
2. Ensures that quality assurance and quality control criteria of analytical methods and projects are satisfied.
3. Assesses data quality and takes corrective action when necessary.
4. Approves and releases technical and data management reports.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.9 Group Leader/Supervisor

1. Trains analysts in laboratory operations and analytical procedures.
1. Organizes and schedules analyses with consideration for sample holding times.
2. Implements data verification procedures by assigning data verification duties to appropriate personnel.
3. Evaluates instrument performance and supervises instrument calibration and preventive maintenance programs.
4. Reports non-compliance situations to laboratory management including the Quality Manager.

1.8.10 Laboratory Analyst

1. Performs detailed preparation and analysis of samples according to published methods and laboratory procedures.

2. Processes and evaluates raw data obtained from preparation and analysis steps.
3. Generates final results from raw data, performing primary review against method criteria.
4. Monitors quality control data associated with analysis and preparation. This includes examination of raw data such as chromatograms as well as an inspection of reduced data, calibration curves, and laboratory notebooks.
5. Reports data in LIMS, authorizing for release pending secondary approval.
6. Conducts routine and non-routine maintenance of equipment as required.
7. Performs or is capable of performing all duties associated with that of Laboratory Technician.

1.8.11 Laboratory Technician

1. Prepares standards and reagents according to published methods or in house procedures.
2. Performs preparation and analytical steps for basic laboratory methods.
3. Works under the direction of a Laboratory Analyst on complex methodologies.
4. Assists Laboratory Analysts on preparation, analytical or data reduction steps for complex methodologies.
5. Monitors quality control data as required or directed. This includes examination of raw data such as chromatograms as well as an inspection of reduced data, calibration curves, and laboratory notebooks.

1.8.12 Sample Management Personnel

1. Signs for incoming samples and verifies the data entered on the Chain-of-Custody forms.
2. Enters the sample information into the Laboratory Information Management System (LIMS) for tracking and reporting.
3. Stages samples according to EPA requirements.
4. Assists Project Managers and Coordinators in filling bottle orders and sample shipments.

1.8.13 Systems Administrator or Systems Manager

1. Assists with the creation and maintenance of electronic data deliverables (EDDs).
2. Coordinates the installation and use of all hardware, software and operating systems.
3. Performs troubleshooting on all aforementioned systems.
4. Trains new and existing users on systems and system upgrades.
5. Maintains all system security passwords.
6. Maintains the electronic backups of all computer systems.

1.8.14 Safety/Chemical Hygiene Officer

1. Maintains the laboratory Chemical Hygiene Plan.
2. Plans and implements safety policies and procedures.
3. Maintains safety records.
4. Organizes and/or performs safety training.
5. Performs safety inspections and provides corrective/preventative actions.
6. Assists personnel with safety issues (e.g. personal protective equipment).

1.8.15 Program Director/Hazardous Waste Coordinator

1. Evaluates waste streams and helps to select appropriate waste transportation and disposal companies.
2. Maintains complete records of waste disposal including waste manifests and state reports.
3. Assists in training personnel on waste-related issues such as waste handling and storage, waste container labeling, proper satellite accumulation, secondary containment, etc.
4. Conducts a weekly inspection of the waste storage areas of the lab.

1.9 Training and Orientation

Each new employee receives a five part orientation: human resources, ethics and data integrity, safety, Quality Systems, and departmental.

The human resources orientation includes benefits, salary, and company policies. All records are stored with Human Resources.

The ethics and data integrity training covers the obligations of each employee to ensure the defensibility of laboratory data. Employees are provided with general policies related to ethics in the laboratory and specific examples of improper practices that are unacceptable in any PASI facility. The employee is trained to make the right decisions with regards to laboratory practices and where to go for answers in circumstances where they may be unclear as to the correct protocol.

The safety orientation includes an in-depth review of the PASI Chemical Hygiene Plan/Safety Plan, which are consistent with the requirements of OSHA's Hazard Communication Program (29 CFR 1910.1200) and other pertinent regulations.

The Quality Systems orientation provides the new employee with information through an introduction to the Quality Assurance Manual and SOPs, acceptable record keeping practices, and the individual's responsibility to data quality. Quality Systems training is reinforced with the new employee as specific topics are covered during the departmental or analytical method training. Quality Systems training will address policies and practices that ensure the quality and defensibility of the analytical data. These topics include but are not limited to traceability of measurements, method calibration, calibration verification, accuracy, precision and uncertainty of measurements, corrective actions, documentation and root cause analysis.

The new employee's Department Supervisor provides the employee with a basic understanding of the role of the laboratory within the structure of PASI and the basic elements of that individual's position.

Supervised training uses the following techniques:

- Hands-on training
- Training checklists
- Lectures and training sessions
- Method-specific training
- Conferences and seminars
- Short courses
- Specialized training by instrument manufacturers
- Proficiency testing programs.

Group Supervisors/Leaders are responsible for providing documentation of training and proficiency for each employee under their supervision. The employee's training file indicates what procedures an analyst or a technician is capable of performing, either independently or with supervision. The files also include documentation of continuing capability (see Section 3.4 for details on Demonstration of Capability requirements). Training documentation files for each person are maintained by the Quality Office either in hardcopy format or within the Learning Management System (LMS).

All procedures and training records are maintained and available for review during laboratory audits. These procedures are reviewed/updated periodically by lab management. Additional information can be found in SOP S-ALL-Q-020 Orientation and Training Procedures or its equivalent revision or replacement.

1.10 Laboratory Safety

It is the policy of PASI to make safety and health an integral part of daily operations and to ensure that all employees are provided with safe working conditions, personal protective equipment, and requisite training to do their work without injury. Each employee is responsible for his/her own safety by complying with established company rules and procedures. These rules and procedures as well as a more detailed description of the employees' responsibilities are contained in the corporate Safety Manual and Chemical Hygiene Plan.

1.11 Security and Confidentiality

Security is maintained by controlled access to laboratory buildings. Exterior doors to laboratory buildings remain either locked or continuously monitored by PASI staff. Keyless door-lock combinations (and computer access codes/logins) are changed on periodically. Posted signs direct visitors to the reception office and mark all other areas as off limits to unauthorized personnel. All visitors to the facility must sign the Visitor's Logbook maintained by the receptionist. A staff member will accompany them during the duration of their stay on the premises unless the GM, QM or TD specify otherwise. In this instance, the staff member will escort the visitor back to the reception area at the end of his/her visit where he/she signs out. The last staff member to leave their department for the day should ensure that all outside access points to that area are secure.

Additional security is provided where necessary, e.g., specific secure areas for sample, data and customer report storage, as requested by customers or cases where national security is of concern. These areas are lockable within the facilities, or are in secure offsite storage. Access is limited to specific individuals or their designees. Security of sample storage areas is the responsibility of the Sample Custodian. Security of samples and data during analysis and data reduction is the responsibility of Group Supervisors. Security of customer report archives is the responsibility of the Client Services Manager. These secure areas are locked whenever these individuals or their designees are not present in the facility.

Access to designated laboratory sample storage locations is limited to authorized personnel only. Provisions for lock and key access are provided. No samples are to be removed without proper authorization. If requested by customer or contract, samples are not to be removed from secure storage areas without filling out the associated internal Chain-of-Custody records.

Standard business practices of confidentiality are applied to all documents and information regarding customer analyses. Specific protocols for handling confidential documents are described in PASI SOPs. Additional protocols for internal identification of samples and data by number only are implemented as required under contract specific Quality Assurance Project Plans (QAPPs).

All information pertaining to a particular customer, including national security concerns will remain confidential. Data will be released to outside agencies only with written authorization from the customer or where federal or state law requires the company to do so (i.e. federal or state subpoena).

2.0 SAMPLE CUSTODY

2.1 Sampling Support

Each individual PASI laboratory provides shipping containers, sample containers (including applicable chemical preservatives), custody documents, and field quality control samples (e.g., trip blanks) to support field-sampling events. Guidelines for sample container types, preservatives, and holding times for a variety of methods are listed in Attachment VIII. Note that all analyses listed are not necessarily performed at all PASI and there may be additional laboratory analyses performed that are not included in these tables. PASI - Minnesota may provide pick-up and delivery services to their customers when needed.

2.2 Field Services Division

Pace Analytical has a large Field Services Division which is based in their Minneapolis facility as well as limited field service capabilities in some of the other facilities. Field Services provides comprehensive nationwide service offerings including:

- Stack Testing
- Ambient Air
- CEM Certification Testing
- Air Quality Monitoring
- Onsite Analytical Services- FTIR and GC
- Real-time Process Diagnostic/Optimization Testing
- Wastewater, Groundwater and Drinking Water Monitoring
- Storm water and Surface Water Monitoring
- Soil and Waste Sampling
- Mobile Laboratory Services

The Field Services Division operates under the PASI Corporate Quality System, with applicable and necessary provisions to address the activities, methods, and goals specific to Field Services for a unit specific Quality Program. All procedures and methods used by Field Services are documented in Standard Operating Procedures and Procedure Manuals.

2.3 Project Initiation

Prior to accepting new work, the laboratory reviews performance capability. The laboratory establishes that sufficient resources (personnel, equipment capacity, analytical method capability, etc.) are available to complete the required work. The customer needs and data quality objectives are defined and appropriate environmental test methods are assured to meet customer's requirements by project managers or sales representative. Project Managers review laboratory certifications. Members of the management staff review current instrument capacity, personnel availability and training, analytical procedures capability and projected sample load. Management then informs the sales and client services personnel whether or not the laboratory can accept the new project via written correspondence, email, and/or daily operations meetings.

The laboratory maintains records of all such reviews, including discussions with customers. Routine analytical project documentation of quotes, notes, dates, initials and/or recordings is maintained in a project folder by project management. Conditions for new and more complex contracts are determined by the General Managers and sales representatives. Quality Manager and/or Technical Director(s) is consulted on technical requirements and operations staff provides input on volume capacities. Evidence

of these reviews is maintained in the form of awarded Request for Proposals (RFPs), signed quotes or contracts, and a Customer Relationship Management (CRM) database. If a review identifies a potential mismatch between customer requirements and laboratory capabilities and/or capacities, Pace will specify its level of commitment by listing these exceptions to the requirements within the RFP, quote or contract.

Additional information regarding specific procedures for reviewing new work requests can be found in SOP S-ALL-C-006 Review of Analytical Requests, or its equivalent revision or replacement.

2.4 Chain-Of-Custody

A chain-of-custody (COC) (see Attachment VII) document provides the legal documentation of samples from time of collection to completion of analysis. Importance is stressed on completeness of COCs. PASI has implemented Standard Operating Procedures to ensure that sample custody traceability and responsibility objectives are achieved for every project.

Field personnel or client representatives complete a chain-of-custody form for all samples. Samples are received by the laboratory accompanied by these forms.

If sample shipments are not accompanied by the correct documentation, the Sample Receiving department notifies a Project Manager. The Project Manager then obtains the correct documentation/information from the customer in order for analysis of samples to proceed.

The sampler is responsible for providing the following information on the chain-of-custody form:

- Customer project name
- Project location or number
- Field sample number/identification
- Date and time sampled
- Sample type (matrix)
- Preservative
- Requested analyses
- Sampler signature
- Relinquishing signature
- Date and time relinquished
- Sampler remarks (if applicable)
- Custody Seal Number (if applicable)
- Regulatory Program Designation
- The state where the samples were collected to ensure all applicable state requirements are met
- Turnaround time requested
- Purchase order number

The record is filled out completely and legibly with indelible ink. Errors are corrected by drawing a single line through the initial entry and initialing and dating the change. All transfers of samples are recorded on the chain-of-custody in the “relinquished” and “received by” sections. All information except signatures is printed.

Additional information can be found in SOP S-ALL-C-001 Sample Management or its equivalent revision or replacement.

2.5 Sample Acceptance Policy

In accordance with regulatory guidelines, PASI complies with the following sample acceptance policy for all samples received.

If the samples do not meet the sample receipt acceptance criteria outlined below, the laboratory is required to document all non-compliances, contact the customer, and either reject the samples or fully document any decisions to proceed with analyses of samples which do not meet the criteria. Any results reported from samples not meeting these criteria are appropriately qualified on the final report.

All samples must:

- Have unique customer identification that are clearly marked with durable waterproof labels on the sample containers and that match the chain of custody.
- Have clear documentation on the chain of custody related to the location of the sampling site with the time and date of sample collection.
- Have the sampler's name and signature
- Have the requested analyses clearly marked
- Have clear documentation of any special analysis requirements (data deliverables, etc.);
- Be in appropriate sample containers with clear documentation of the preservatives used.
- Be correctly preserved unless method allows for laboratory preservation.
- Be received within holding time. Any samples with hold times that are exceeded will not be processed without prior customer permission.
- Have sufficient sample volume to proceed with the analytical testing. If insufficient sample volume is received, analysis will not proceed without customer approval.
- Be received within appropriate temperature ranges - not frozen but ≤6°C (See Note 1), unless program requirements or customer contractual obligations mandate otherwise (see Note 2). The cooler temperature is recorded directly on the COC and the SCUR. Samples that are delivered to the lab immediately after collection are considered acceptable if there is evidence that the chilling process has been started, for example by the arrival of the samples on ice. If samples arrive that are not compliant with these temperature requirements, the customer will be notified. The analysis will NOT proceed unless otherwise directed by the customer. If less than 72 hours remain in the hold time for the analysis, the analysis may be started while the customer is contacted to avoid missing the hold time. Data will be appropriately qualified on the final report.

  Note 1: Temperature will be read and recorded based on the precision of the measuring device. For example, temperatures obtained from a thermometer graduated to 0.1°C will be read and recorded to ±0.1°C. Measurements obtained from a thermometer graduated to 0.5°C will be read to ±0.5°C. Measurements read at the specified precision are not to be rounded down to meet the ≤6°C limit (i.e. 6.2°C rounded and recorded as 6°C).

  Note 2: Some microbiology methods allow sample receipt temperatures of up to 10°C. Consult the specific method for microbiology samples received above 6°C prior to initiating corrective action for out of temperature preservation conditions.

Upon sample receipt, the following items are also checked and recorded:

- Presence of custody seals or tapes on the shipping containers
- Sample condition: Intact, broken/leaking
- Sample holding time
- Sample pH when required
- Appropriate containers

Samples for drinking water analysis that are improperly preserved, or are received past holding time, are rejected at the time of receipt, with the exception of VOA samples that are tested for pH at the time of analysis.

Additional information can be found in SOP S-ALL-C-001 Sample Management or its equivalent revision or replacement.

2.6 Sample Log-in

After sample inspection, all sample information on the chain-of-custody is entered into the Laboratory Information Management System (LIMS).

This permanent record documents receipt of all sample containers including:

- Customer name and contact
- Customer number
- Pace Analytical project number
- Pace Analytical Project Manager
- Sample descriptions
- Due dates
- List of analyses requested
- Date and time of lab receipt
- Field ID code
- Date and time of collection
- Any comments resulting from inspection for sample rejection

All samples received are logged into the LIMS system within one working day of receipt. Sample login may be delayed due to customer clarification of analysis needed, corrective actions for sample receipt non-conformance, or other unusual circumstances. If the time collected for any sample is unspecified and Pace is unable to obtain this information from the customer, the laboratory will use *00:00* as the time sampled. All hold times will be based on this sampling time and qualified accordingly if exceeded.

The Laboratory Information Management System (EPIC Pro) automatically generates a unique identification number for each sample created in the system. The LIMS sample number follows the general convention of BB-XXXXX-YYY. The BB represents the laboratory identification within Pace's laboratory network. The 5 digit "X" number represents the project number followed by a 3 digit sample number. The project number is a sequential number that is assigned as a new project is created. The sample number corresponds to the number of samples submitted by the client. In addition to the unique sample ID, there is a sample container ID that consists of the sample number, the container type (ex. BP1U), and bottle 1 of Y, where Y represent the total number of containers of that particular type. Together the sample LIMs number and sample container ID number create a unique barcode encryption that can be linked to the sample analysis requested by the client. This unique identification number is placed on the sample container as a durable label and becomes the link between the laboratory's sample management system and the client's field identification; it will be a permanent reference number for all future interactions.

Sample labels are printed from the LIMS system and affixed to each sample container.

Samples with hold times that are near expiration date/time may be sent directly to the laboratory for analysis at the discretion of the Project Manager and/or General Manager.

Additional information can be found in SOP S-ALL-C-001 Sample Management or its equivalent revision or replacement.

2.7 Sample Storage

2.7.1 Storage Conditions

Samples are stored away from all standards, reagents, or other potential sources of contamination. Samples are stored in a manner that prevents cross-contamination (e.g. volatile samples are stored separate from other samples). All sample fractions, extracts, leachates and other sample preparation products are stored in the same manner as actual samples or as specified by the analytical method.

2.7.2 Temperature Monitoring

Samples are taken to the appropriate storage location (ambient, refrigerator, freezer) immediately after sample receipt and check-in procedures are completed. All sample storage areas are located in limited access areas and are monitored to ensure sample integrity.

The temperature of each refrigerated storage area is maintained at $\leq 6^{\circ}C$ unless state or program requirements differ. The temperature of each freezer storage area is maintained at $< -10^{\circ}C$ unless state or program requirements differ. The temperature of each storage area is monitored and recorded each workday. If the temperature falls outside the acceptable limits, the following corrective actions are taken and appropriately documented:

- The temperature is rechecked after two hours to verify temperature exceedance. Corrective action is initiated if necessary.
- The Quality Manager and/or laboratory management are notified if the problem persists.
- The samples are relocated to a proper environment if the temperature cannot be maintained after corrective actions are implemented.
- The affected customers are notified.
- Documentation is provided on analytical report.

2.7.3 Hazardous Materials

Pure product or potentially heavily contaminated samples are tagged as "hazardous" or "lab pack" and are stored separately from other samples.

2.7.4 Foreign/Quarantined Soils

Depending on the soil disposal practices of the laboratory, foreign soils and soils from USDA regulated areas are segregated. The USDA requires these samples to be incinerated or sterilized by an approved treatment procedure.

Additional information can be found in SOP MN-Q-253 Procedure for Handling of USDA Regulated Soils or its equivalent revision or replacement.

2.8 Sample Protection

PASI laboratory facilities are operated under controlled access to ensure sample and data integrity. Visitors must register at the front desk and be properly escorted.

Samples are removed from storage areas by designated personnel and returned to the storage areas, if necessary, immediately after the required sample quantity has been taken.

Upon customer request, additional and more rigorous chain of custody protocols for samples and data can be implemented. For example, some projects may require complete documentation of sample custody within the secure laboratory.

Additional information can be found in SOP S-ALL-C-001 Sample Management or its equivalent revision or replacement.

2.9 Subcontracting Analytical Services

Every effort is made to perform chemical analyses for PASI customers within the laboratory that receives the samples. When subcontracting to a laboratory other than the receiving laboratory (inside or outside the PASI network) becomes necessary, a preliminary verbal communication with an appropriate laboratory is undertaken. Customers are notified in writing of the lab's intention to subcontract any portion of the testing to another laboratory. Work performed under specific protocols may involve special considerations.

Prior to subcontracting samples to a laboratory outside Pace Analytical, the potential sub-contract laboratory will be pre-qualified by verifying that the subcontractor meets the following criteria:

- All certifications required for the proposed subcontract are in effect,
- Sufficient professional liability and other required insurance coverage is in effect, and
- Is not involved in legal action by any federal, state, or local government agency for data integrity issues and has not been convicted in such investigation at any time during the past 5 years.

Additional information can be found in SOP S-MN-Q-259 ***Evaluation & Qualification of Vendors*** or its equivalent revision or replacement. The contact and preliminary arrangements are made between the PASI Project Manager and the appropriate subcontract laboratory personnel. The specific terms of the subcontract laboratory agreement include:

- Method of analysis
- Number and type of samples expected
- Project specific QA/QC requirements
- Deliverables required
- Laboratory certification requirement
- Price per analysis
- Turnaround time requirements

Chain-of-custody forms are generated for samples requiring subcontracting to other laboratories. Sample receiving personnel re-package the samples for shipment, create a transfer chain-of-custody form and record the following information:

- Pace Analytical Laboratory Number
- Matrix
- Requested analysis
- Special instructions (quick turn-around, required detection or reporting limits, unusual information known about the samples or analytical procedure).
- Signature in "Relinquished By"

All subcontracted sample data reports are sent to the PASI Project Manager.

Any Pace Analytical work sent to other labs within the PASI network is handled as subcontracted work (also known as inter-regional) and all final reports are labeled clearly with the name of the laboratory performing the work. Any non-NELAC work is clearly identified. PASI will not be responsible for analytical data if the subcontract laboratory was designated by the customer.

Additional information can be found in SOP S-MN-C-004 Subcontracting Samples, or its equivalent revision or replacement.

2.10 Sample Retention and Disposal

Samples (and sample by-products) must be retained by the laboratory for a period of time necessary to protect the integrity of the sample or sample by-product (e.g. method holding time) and to protect the interests of the laboratory and the customer.

Unused portions of samples are retained by each laboratory based on program or customer requirements for sample retention and storage. The sample retention time is a minimum of 45 days from receipt of the samples. Samples requiring storage beyond this time due to special requests or contractual obligations will not be stored under temperature controlled conditions unless the laboratory has sufficient capacity and their presence does not compromise the integrity of other samples.

After this period expires, non-hazardous samples are properly disposed of as non-hazardous waste. The preferred method for disposition of hazardous samples is to return the excess sample to the customer. If it is not feasible to return samples, or the customer requires PASI to dispose of excess samples, PASI will arrange for proper disposal by an approved contractor.

Additional information can be found in SOP S-ALL-S-002 Waste Handling and S-MN-C-001 Sample Management or their equivalent revisions or replacements.

3.0 ANALYTICAL CAPABILITIES

3.1 Analytical Method Sources

PASI laboratories are capable of analyzing a full range of environmental samples from a variety of matrices, including air, surface water, wastewater, groundwater, soil, sediment, biota, and other waste products. The latest valid editions of methodologies are applied from regulatory and professional sources including EPA, ASTM, USGS, NIOSH, and State Agencies. Section 11 of this manual is a representative listing of general analytical protocol references. PASI discloses in writing to its customers and regulatory agencies any instances in which modified methods are being used in the analysis of samples.

In the event of a customer-specific need, instrumentation constraint or regulatory requirement, PASI laboratories reserve the right to use valid versions of methods that may not be the most recent edition available.

3.2 Analytical Method Documentation

The primary form of documentation of analytical methods is the Standard Operating Procedure (SOP). SOPs contain pertinent information as to what steps are required by an analyst to successfully perform a procedure. The required contents for the SOPs are specified in the company-wide SOP for Preparation of SOPs (S-ALL-Q-001).

The SOPs may be supplemented by other training materials that further detail how methods are specifically performed. This training material will undergo periodic, documented review along with the other Quality System documentation.

3.3 Analytical Method Validation

In some situations, PASI develops and validates methodologies that may be more applicable to a specific problem or objective. When non-standard methods (e.g. methods other than EPA, NIOSH, ASTM, AOAC, etc.) are required for specific projects or analytes of interest, or when the laboratory develops a method, or modifies a standard method, the laboratory validates the method prior to applying it to customer samples. Method validity is established by meeting criteria for precision and accuracy as established by the data quality objectives specified by the end user of the data. The laboratory records the validation procedure, the results obtained and a statement as to the usability of the method. The minimum requirements for method validation include determination of the limit of detection and limit of quantitation, evaluation of precision and bias, and evaluation of selectivity of each analyte of interest.

Additional information can be found in SOP MN-Q-252 Methods Validation and Modification Studies, or equivalent revisions or replacement.

3.4 Demonstration of Capability (DOC)

Analysts complete an initial demonstration of capability (IDOC) study prior to performing a method or when there is a change in instrument type, personnel or test method (when a defined ‘work cell’ is in operation, the entire work cell must meet the criteria). The mean recovery and standard deviation of each analyte, taken from 4 replicates of a quality control standard is calculated and compared to method criteria (if available) or established lab criteria for evaluation of acceptance. Each laboratory maintains copies of all demonstrations of capability and corresponding raw data for future reference and must document the acceptance criteria prior to the analysis of the DOC. Demonstrations of capability are verified on an annual basis.

Alternative demonstration of capability procedures may be used for IDOC for methods that don’t lend themselves to the “4 replicate” approach. For methods that only measure precision, the precision of four

laboratory duplicate pairs will be assessed. The relative percent differences must be within the method acceptance limits. For procedures like TCLP or SPLP, the analyst will demonstrate making the buffered solution and performing the tumbling process. The trainer or supervisor will sign-off on demonstration of capability of the tumbling process. Additional demonstration of capability options will be specified in the Method Performance section of the applicable method SOP.

For Continuing Demonstrations of Capability, the laboratories may use Performance Testing (PT) samples or any of the approaches utilized for IDOCs. For methods or procedures that do not lend themselves to the "4 replicate" approach, the demonstration of capability requirements will be specified in Section 14 – Method Performance of the applicable SOP.

Addition information can be found in SOP S-ALL-Q-020 Orientation and training Procedures.

3.5 Regulatory and Method Compliance

PASI understands that expectations of our customers commonly include the assumption that laboratory data will satisfy specific regulatory requirements. Therefore PASI attempts to ascertain, prior to beginning a project, what applicable regulatory jurisdiction, agency, or protocols apply to that project. This information is also required on the Chain-of-Custody submitted with samples.

PASI makes every effort to detect regulatory or project plan inconsistencies, based upon information from the customer, and communicate them immediately to the customer in order to aid in the decision-making process. PASI will not be liable if the customer chooses not to follow PASI recommendations.

It is PASI policy to disclose in a forthright manner any detected noncompliance affecting the usability of data produced by our laboratories. The laboratory will notify customers within 30 days of fully characterizing the nature of the nonconformance, the scope of the nonconformance and the impact it may have on data usability.

4.0 QUALITY CONTROL PROCEDURES

4.1 Data Integrity System

The data integrity system at PASI provides assurances to management that a highly ethical approach is being applied to all planning, training and implementation of methods. Data integrity is crucial to the success of our company and Pace Analytical is committed to providing a culture of quality throughout the organization. To accomplish this goal, PASI has implemented a data integrity system that encompasses the following four requirements:

1. A data integrity training program: Standardized training is given to each new employee and a yearly refresher is presented to all employees. Key topics within this training include:
   - Need for honesty in analytical reporting
   - Process for reporting data integrity issues
   - Specific examples of unethical behavior and improper practices
   - Documentation of non-conforming data that is still useful to the data user
   - Consequences and punishments for unethical behavior
   - Examples of monitoring devices used by management to review data and systems
2. Signed data integrity documentation for all employees: This includes a quiz following the Ethics training session and written agreement to abide by the Code of Ethics and Standards of Conduct explained in the employee manual The quiz along with the employee's electronic signature of agreement are maintained within the Learning Management System.
3. In-depth, periodic monitoring of data integrity: Including peer data review and validation, internal data audits, proficiency testing studies, etc.
4. Documentation of any review or investigation into possible data integrity infractions. This documentation, including any disciplinary actions involved, corrective actions taken, and notifications to customers must be available for review for lab assessors and must be retained for a minimum of five years.

PASI management makes every effort to ensure that personnel are free from any undue pressures that affect the quality of their work including commercial, financial, over-scheduling, and working condition pressures.

Corporate management also provides all PASI facilities a mechanism for confidential reporting of data integrity issues that ensures confidentiality and a receptive environment in which all employees are comfortable discussing items of ethical concern. The anonymous message line is monitored by the Corporate Director of Quality, Safety and Training who will ensure that all concerns are evaluated and, where necessary, brought to the attention of executive management and investigated. **The message line voice mail box is available at 612-607-6427.**

4.2 Method Blank

A method blank is used to evaluate contamination in the preparation/analysis system. The method blank is processed through all preparation and analytical steps with its associated samples.

A method blank is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (e.g. volatiles), a method blank is processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The method blank consists of a matrix similar to the associated samples that is known to be free of the analytes of interest. Laboratories will characterize a representative matrix as "clean" if the matrix contains contaminants at less than ½ the laboratory's reporting limit.

Each method blank is evaluated for contamination. The source of any contamination is investigated and documented corrective action is taken when the concentration of any target analyte is detected above the

reporting limit and is greater than 1/10 of the amount of that analyte found in any associated sample. Corrective actions include the re-preparation and re-analysis of all the samples (where possible) along with the full set of required quality control samples. Data qualifiers must be applied to any result reported that is associated with a contaminated method blank.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

For Ohio VAP projects, the lab must minimize the use of qualified data. In the case of method blank contamination, the lab is required to reanalyze the associated samples with an acceptable blank (no reportable contamination) if there is sufficient sample remaining. The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding method blanks for Ohio VAP projects.

4.3 Laboratory Control Sample

The Laboratory Control Sample (LCS) is used to evaluate the performance of the entire analytical system including preparation and analysis.

An LCS is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (e.g. volatiles), an LCS will be processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The LCS consists of a matrix similar to the associated samples that is known to be free of the analytes of interest that is then spiked with known concentrations of target analytes.

The LCS contains **all** analytes specified by a specific method or by the customer or regulatory agency (which may include full list of target compounds, with certain exceptions. These exceptions may include analyzing only specific Aroclors when PCB analysis is requested or not spiking with all EPA Appendix compounds when a full Appendix list of compounds is requested). In the absence of specified components, the lab will spike with the following compounds:

- For multi-peak analytes (e.g. PCBs, technical chlordane, toxaphene), a representative standard will be processed.
- For methods with long lists of analytes, a representative number of target analytes may be chosen. The following criteria is used to determine the number of LCS compounds used:
    - For methods with 1-10 target compounds, the lab will spike with all compounds
    - For methods with 11-20 target compounds, the lab will spike with at least 10 compounds or 80%, whichever is greater
    - For methods with greater than 20 compounds, the lab will spike with at least 16 compounds.

The LCS is evaluated against the method default or laboratory-derived acceptance criteria. Method default control limits will be used until the laboratory has a minimum of 20 (preferably greater than 30) data points from which to derive internal criteria. Any compound that is outside of these limits is considered to be ‘out of control’ and must be qualified appropriately. Any associated sample containing an ‘out-of-control’ compound must either be re-analyzed with a successful LCS or reported with the appropriate data qualifier.

For LCSs containing a large number of analytes, it is statistically likely that a few recoveries will be outside of control limits. This does not necessarily mean that the system is out of control, and therefore no corrective action would be necessary (except for proper documentation). NELAC has allowed for a minimum number of marginal exceedances, defined as recoveries that are beyond the LCS control limits (3X the standard deviation) but less than the marginal exceedance limits (4X the standard deviation). The number of allowable exceedances depends on the number of compounds in the LCS. If more analyte

recoveries exceed the LCS control limits than is allowed (see below) or if any one analyte exceeds the marginal exceedance limits, then the LCS is considered non-compliant and corrective actions are necessary. The number of allowable exceedances is as follows:

- >90 analytes in the LCS- 5 analytes
- 71-90 analytes in the LCS- 4 analytes
- 51-70 analytes in the LCS- 3 analytes
- 31-50 analytes in the LCS- 2 analytes
- 11-30 analytes in the LCS- 1 analyte
- <11 analytes in the LCS- no analytes allowed out)

A matrix spike (MS) can be used in place of a LCS in a batch as long as the MS passes the LCS acceptance criteria (this is a NELAC allowance). When this happens, full documentation must be made available to the data user. If this is not allowed by a customer or regulatory body, the associated samples must be rerun with a compliant LCS (if possible) or reported with appropriate data qualifiers.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

For Ohio VAP projects, the lab must minimize the use of qualified data. In the case of LCS failures, the lab is required to reanalyze the associated samples with an acceptable LCS (all applicable recoveries within acceptable limits) if there is sufficient sample remaining. The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding LCSs for Ohio VAP projects.

For Department of Defense projects, the lab is not allowed to have any target analytes that exceed its LCS control limits. In the case of LCS failures, the lab is required to reanalyze the associated samples with an acceptable LCS (all applicable recoveries within acceptable limits) if there is sufficient sample remaining. The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding LCSs for Department of Defense projects. See applicable method SOPs for further corrective action.

4.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is used to determine the effect of the sample matrix on compound recovery for a particular method. The information from these spikes is sample or matrix specific and is not used to determine the acceptance of an entire batch (see LCS).

A **Matrix Spike/Matrix Spike Duplicate** (MS/MSD) set is processed at a frequency specified in a particular method or as determined by a specific customer. This frequency will be specified in the applicable method SOP or customer QAPP. In the absence of such requirements, an MS/MSD set is routinely analyzed once per every 20 samples per general matrix (i.e. soil, water, biota, etc.) per method.

The MS and MSD consist of the sample matrix that is then spiked with known concentrations of target analytes. Lab personnel spike customer samples that are specifically designated as MS/MSD samples or, when no designated samples are present in a batch, randomly select samples to spike that have adequate sample volume or weight. Spiked samples are prepared and analyzed in the same manner as the original samples and are selected from different customers if possible.

The MS and MSD contain all analytes specified by a specific method or by the customer or regulatory agency. In the absence of specified components, the lab will spike with the same number of compounds as previously discussed in the LCS section.

The MS and MSD are evaluated against the method or laboratory-derived criteria. Any compound that is outside of these limits is considered to be ‘out of control’ and must be qualified appropriately. Batch acceptance, however, is based on method blank and LCS performance, not on MS/MSD recoveries. The

spike recoveries give the data user a better understanding of the final results based on their site-specific information.

A matrix spike and sample duplicate will be performed instead of a matrix spike and matrix spike duplicate when specified by the customer or method.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

For Ohio VAP projects, the lab must minimize the use of qualified data. In the case of MS/MSD failures, the lab is required to reanalyze the associated samples only when the associated LCS also fails acceptance criteria and if there is sufficient sample remaining. When an LCS is acceptable and the MS results are outside of criteria, and no system anomaly is detected, the samples will be reported with appropriate data qualifiers indicating matrix interference. The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding LCSs for Ohio VAP projects.

4.5 Surrogates

Surrogates are compounds that reflect the chemistry of target analytes and are typically added to samples for organic analyses to monitor the effect of the sample matrix on compound recovery.

Surrogates are added to each customer sample (for organics), method blank, LCS and MS prior to extraction or analysis. The surrogates are evaluated against the method or laboratory-derived acceptance criteria. Any surrogate compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Samples with surrogate failures are typically re-extracted and/or re-analyzed to confirm that the out-of-control value was caused by the matrix of the sample and not by some other systematic error. An exception to this would be samples that have high surrogate values but no reportable hits for target compounds. These samples would be reported, with a qualifier, because the implied high bias would not affect the final results.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

4.6 Sample Duplicate

A sample duplicate is a second portion of sample that is prepared and analyzed in the laboratory along with the first portion. It is used to measure the precision associated with preparation and analysis. A sample duplicate is processed at a frequency specified by the particular method or as determined by a specific customer.

The sample and duplicate are evaluated against the method or laboratory-derived criteria for relative percent difference (RPD). Any duplicate that is outside of these limits is considered to be 'out of control' and must be qualified appropriately.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

For Ohio VAP projects, the lab must minimize the use of qualified data. In the case of duplicate samples exceeding the RPD criteria found in applicable analytical SOPs, the lab is required to reanalyze the associated sample and duplicate as long as no sampling error was detected (if there is sufficient sample remaining). If the sample and duplicate still do not agree, a comment would be made stating there is a sample anomaly (i.e. non-homogeneous). The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding sample duplicates for Ohio VAP projects.

4.7 Internal Standards

Internal Standards are method-specific analytes added to every standard, method blank, laboratory control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes. At a minimum, the laboratory will follow method specific guidelines for the treatment of internal standard recoveries as they are related to the reporting of data.

Deviations made from this policy must be approved by the Quality Manager prior to release of the data.

For Ohio VAP projects, samples with internal standard failures, outside of method criteria, must be reanalyzed to confirm sample matrix effect. The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding internal standards for Ohio VAP projects.

4.8 Field Blanks

Field blanks are blanks prepared at the sampling site in order to monitor for contamination that may be present in the environment where samples are collected. These field quality control samples are often referenced as field blanks, rinseate blanks, or equipment blanks. The lab analyzes these field blanks as normal samples and informs the customer if there are any target compounds detected above the reporting limit.

4.9 Trip Blanks

Trip blanks are blanks that originate from the laboratory as part of the sampling event and are used to monitor for contamination of samples during transport. These blanks accompany the empty sample containers to the field and then accompany the collected samples back to the lab. These blanks are routinely analyzed for volatile methods where ambient background contamination is likely to occur.

4.10 Limit of Detection (LOD)

PASI laboratories are required to use a documented procedure to determine a limit of detection (LOD) for each analyte of concern in each matrix reported. All sample-processing steps of the preparation and analytical methods are included in this determination. For any test that does not have a valid LOD, sample results below the limit of quantitation (LOQ) cannot be reported.

The LOD is initially established for the compounds of interest for each method in a clean matrix with no target analytes present and no interferences at a concentration that would impact the results. The LOD is then determined every time there is a change in the test method that affects how the test is performed or when there has been a change in the instrument that affects the sensitivity. If required by customer, method or accreditation body, the LOD will be re-established annually for all applicable methods.

Unless otherwise noted, the method used by PASI laboratories to determine LODs is based on the Method Detection Limit (MDL) procedure outlined in 40 CFR Part 136, Appendix B. Where required by regulatory program or customer, the above referenced procedure will be followed.

Where specifically stated in the published method, LODs (or MDLs) will be performed at the listed frequency.

The validity of the LOD must be verified by detection (a value greater than zero) of the analytes in a QC sample in each quality system matrix. The QC sample must contain the analyte at no more than 3X the LOD for a single analyte test and 4X the LOD for multiple analyte tests. This verification must be performed on each instrument used for sample analysis and reporting of data. The validity of the LOD must be verified as part of the LOD determination process. This verification must be done prior to the use of the LOD for sample analysis.

An LOD study is not required for any analyte for which spiking solutions or quality control samples are not available (e.g. temperature).

The LOD, if required, shall be verified annually for each quality system matrix, technology and analyte. In lieu of performing full LOD (MDL) studies annually, the lab can verify the LOD (MDL) on an annual basis, providing this verification is fully documented and does not contradict other customer or program requirements that the lab must follow. The requirements of this verification are:

- The spike concentration of the verification must be no more than 3X times the LOD for single analyte tests and 4X the LOD for multiple analyte tests.
- The lab must verify the LOD on each instrument used for the reporting of sample data.
- The lab must be able to qualitatively identify all target analytes in the verification standard (distinguishable from noise).

For Ohio VAP projects, a valid MDL must be in place prior to sample analysis. MDLs must be spiked at or below the reporting limit. The MDL will not be accepted if it was spike higher than the reporting limit.

Additional information can be found in SOP S-ALL-Q-004 Method Detection Limit Studies or its equivalent revision or replacement.

4.11 Limit of Quantitation (LOQ)

A limit of quantitation (LOQ) for every analyte of concern must be determined. For PASI laboratories, this LOQ is referred to as the RL, or Reporting Limit. This RL is based on the lowest calibration standard concentration that is used in each initial calibration. Results below this level are not allowed to be reported without qualification since the results would not be substantiated by a calibration standard. For methods with a determined LOD, results can be reported out below the LOQ but above the LOD if they are properly qualified (e.g. J flag).

There must be a sufficient buffer between the LOD and the limit of quantitation (LOQ). The LOQ must be higher than the LOD.

The LOQ, if required, shall be verified annually for each quality system matrix, technology and analyte. To verify the LOQ, the laboratory will prepare a sample in the same matrix used for the LCS. The sample will be spiked with target analytes at the concentration(s) equivalent to or less than the RL(s). This sample must undergo the routine sample preparation procedure including any routine sample cleanup steps. The sample is then analyzed and the recovery of each target analyte determined. The recovery for each target analyte must meet the laboratories current control limits.

For DoD approved methods, the LOQ and LOD shall be verified quarterly and valid LOQ must be in place prior to sample analysis.

Additional information can be found in SOP S-ALL-Q-004 Method Detection Limit Studies or its equivalent revision or replacement.

4.12 Estimate of Uncertainty

PASI laboratories can provide an estimation of uncertainty for results generated by the laboratory. The estimate quantifies the error associated with any given result at a 95% confidence interval. This estimate does not include bias that may be associated with sampling. The laboratory has a procedure in place for making this estimation. In the absence of a regulatory or customer-specific procedure, PASI laboratories base this estimation on the recovery data obtained from the Laboratory Control Spikes. The uncertainty is a function of the standard deviation of the recoveries multiplied by the appropriate Student's t Factor at 95% confidence. Additional information pertaining to the estimation of uncertainty and the exact manner

in which it is derived are contained in the SOP S- MN-Q-255 Estimation of Measurement Uncertainty, or its equivalent revision or replacement.

The measurement of uncertainty is provided only on request by the customer, as required by specification or regulation and when the result is used to determine conformance within a specification limit.

4.13 Proficiency Testing (PT) Studies

PASI laboratories participate in the NELAC-defined proficiency testing program. PT samples are obtained from approved providers and analyzed and reported at a minimum of two times per year for the relevant fields of testing per matrix.

The lab initiates an investigation whenever PT results are deemed 'unacceptable' by the PT provider. All findings and corrective actions taken are reported to the Quality Manager. A corrective action plan (including re-analysis of similar samples) is initiated and this report is sent to the appropriate state accreditation agencies for their review.

PT samples are treated as typical customer samples, utilizing the same staff, methods, equipment, facilities, and frequency of analysis. PT samples are included in the laboratory's normal analytical processes and do not receive extraordinary attention due to their nature.

Comparison of analytical results with anyone participating in the same PT study is prohibited prior to the close of the study.

Additional information can be found in SOP S-ALL-Q-010 PE/PT Program or its equivalent revision or replacement.

4.14 Rounding and Significant Figures

In general, the PASI laboratories report data to no more than three significant digits. Therefore, all measurements made in the analytical process must reflect this level of precision. In the event that a parameter that contributes to the final result has less than three significant figures of precision, the final result must be reported with no more significant figures than that of the parameter in question. The rounding rules listed below are descriptive of the LIMS and not necessarily of any supporting program (Excel, etc.).

Rounding

PASI-Minnesota follows the odd / even guidelines for rounding numbers:

- If the figure following the one to be retained is less than five, that figure is dropped and the retained ones are not changed (with three significant figures, 2.544 is rounded to 2.54).
- If the figure following the ones to be retained is greater than five, that figure is dropped and the last retained one is rounded up (with three significant figures, 2.546 is rounded to 2.55).
- If the figure following the ones to be retained is five and if there are no figures other than zeros beyond that five, then the five is dropped and the last figure retained is unchanged if it is even and rounded up if it is odd (with three significant figures, 2.525 is rounded to 2.52 and 2.535 is rounded to 2.54).

Significant Digits

Unless specified by federal, state or local requirements or on specific request by a customer, PASI-Minnesota reports all analytical results to 3 significant digits, regardless of the magnitude of the value reported.

PASI- Minnesota follows the following convention for reporting to a specified number of significant figures. Unless specified by federal, state or local requirements or on specific request by a customer, the laboratory reports:

- Values > 10 – Reported to 3 significant digits
- Values ≤ 10 – Reported to 2 significant digits

5.0 DOCUMENT MANAGEMENT AND CHANGE CONTROL

5.1 Document Management

Additional information can be found in SOP S-ALL-Q-002 Document Management.

Pace Analytical Services, Inc. has an established procedure for managing documents that are part of the quality system. The list of managed documents includes, but is not limited to, Standard Operating Procedures, Quality Assurance Manuals, quality policy statements, training documents, work-processing documents, charts, posters, memoranda, notices, forms, software, and any other procedures, tables, plans, etc. that have a direct bearing on the quality system.

A master list of all managed documents is maintained at each facility identifying the current revision status and distribution of the controlled documents. This establishes that there are no invalid or obsolete documents in use in the facility. All documents are reviewed periodically and revised if necessary. Obsolete documents are systematically discarded or archived for audit or knowledge preservation purposes.

Each managed document is uniquely identified to include the date of issue, the revision identification, page numbers, the total number of pages and the issuing authorities. For complete information on document numbering, refer to SOP S-ALL-Q-003 Document Numbering.

As an alternative to the hard copy system of controlled documents, secured electronic copies of controlled documents may be maintained on the local or wide-area network (LAN or WAN). These document files must be read-only for all personnel except the Quality Department and system administrator. Other requirements for this system are as follows:

- Electronic documents must be readily accessible to all facility employees.
- Electronic documents (i.e. pdf's) must be locked from printing. All hardcopy SOPs must be obtained from the Quality Department.

5.1.1 Quality Assurance Manual (QAM)

The Quality Assurance Manual is the company-wide document that describes all aspects of the quality system for PASI. The base QAM template is distributed by the Corporate Quality Department to each of the regional Quality Managers. The regional management personnel modify the necessary and permissible sections of the base template and submit those modifications to the Corporate Director of Quality for review. Once approved and signed by both the CEO and the Director of Quality, the General Manager, Quality Manager and Technical Director(s) sign the Quality Assurance Manual. Each regional Quality Manager is then in charge of distribution to employees, external customers or regulatory agencies and maintaining a distribution list of controlled document copies. The Quality Assurance Manual template is reviewed on an annual basis by all of the PASI Quality Managers and revised accordingly by the Director of Quality, Safety and Training.

5.1.2 Standard Operating Procedures (SOPs)

SOPs fall into two categories: company-wide documents (starting with the prefix S-ALL-) and facility-specific documents (starting with the individual facility prefix).

The purpose of the company-wide SOPs is to establish policies and procedure that are common and applicable to all PASI facilities. Company-wide SOPs are document-controlled by the corporate quality office and signed copies are distributed to all of the regional Quality Managers. The regional management personnel sign the company-wide SOPs. The regional Quality

Manager is then in charge of distribution to employees, external customers or regulatory agencies and maintaining a distribution list of controlled document copies.

Regional PASI facilities are responsible for developing facility-specific SOPs applicable to their respective facility. The regional facility develops these facility-specific SOPs based on the corporate-wide SOP template. This template is written to incorporate a set of minimum method requirements and PASI best practice requirements. The regional facilities may add to or modify the corporate-wide SOP template provided there are no contradictions to the minimum method or best practice requirements. Facility-specific SOPs are controlled by the regional Quality Manager according to the corporate document management policies.

SOPs are reviewed every two years at a minimum (a more frequent review may be required by state or federal agencies or customers). A review of the document does not necessarily constitute a re-issue of a new revision. Documentation of this review and any applicable revisions are made in the last section of each SOP. This provides a historical record of all revisions.

All copies of superseded SOPs are removed from general use and the original copy of each SOP is archived for audit or knowledge preservation purposes. This ensures that all PASI employees use the most current version of each SOP and provides the Quality Manager with a historical record of each SOP.

Additional information can be found in SOP S-ALL-Q-001 Preparation of SOPs or its equivalent revision or replacement.

For Ohio VAP certification, it is required by the Ohio Administrative Code that the lab must seek Ohio VAP review and approval of all SOPs and Quality Manual subsequent modifications prior to implementation.

For DoD approval, SOPs are reviewed annually.

5.1.3 Other Documentation

Additional documents such as Forms and Spreadsheets are controlled through the document management system.

5.2 Document Change Control

Changes to managed documents are reviewed and approved in the same manner as the original review. Any revision to a document requires the approval of the applicable signatories. After revisions are approved, a revision number is assigned and the previous version of the document is officially retired. Copies may be kept for audit or knowledge preservation purposes.

All controlled copies of the previous document are replaced with controlled copies of the revised document and the superseded copies are destroyed or archived. All affected personnel are advised that there has been a revision and any necessary training is scheduled.

6.0 EQUIPMENT AND MEASUREMENT TRACEABILITY

Each PASI facility is equipped with sufficient instrumentation and support equipment to perform the relevant analytical testing or field procedures performed by each facility. Support equipment includes chemical standards, thermometers, balances, disposable and mechanical pipettes, etc. This section details some of the procedures necessary to maintain traceability and perform proper calibration of instrumentation and support equipment. See Attachment III for a list of equipment currently used at the Minnesota PASI facility.

6.1 Standards and Traceability

Each PASI facility retains all pertinent information for standards, reagents and chemicals to assure traceability to a national standard. This includes documentation of purchase, receipt, preparation and use.

Upon receipt, all purchased standard reference materials are recorded into a standard logbook or database and assigned a unique identification number. The entries include the facility's unique identification number, the chemical name, manufacturer name, manufacturer's identification numbers, receipt date and expiration date. Vendor's certificates of analysis for all standards, reagents, or chemicals are retained for future reference.

Subsequent preparations of intermediate or working solutions are also documented in a standard logbook or database. These entries include the stock standard name and lot number, the manufacturer name, the solvents used for preparation, the solvent lot number and manufacturer, the preparation steps, preparation date, expiration dates, preparer's initials, and a unique PASI identification number. This number is used in any applicable sample preparation or analysis logbook so the standard can be traced back to the standard preparation record. This process ensures traceability back to the national standard.

All prepared standard or reagent containers include the PASI identification number, the standard or chemical name, the date of preparation, the date of expiration, the concentration with units, and the preparer's initials. This ensures traceability back to the standard preparation logbook.

If a second source standard is required to verify an existing calibration or spiking standard, this standard is purchased from a different supplier. If no second source is available, a second standard from a different lot may be purchased from the same supplier if the lot can be demonstrated as prepared independently from other lots.

Additional information concerning standards and reagent traceability can be found in the SOP S-ALL-Q-025 Standard and Reagent Preparation and Traceability or its equivalent revision or replacement.

6.2 General Analytical Instrument Calibration Procedures

All types of support equipment and instrumentation are calibrated or checked before use to ensure proper functioning and verify that the laboratory's requirements are met. All calibrations are performed by, or under the supervision of, an experienced analyst at scheduled intervals against either certified standards traceable to recognized national standards or reference standards whose values have been statistically validated.

Calibration standards for each parameter are chosen to establish the linear range of the instrument and must bracket the concentrations of those parameters measured in the samples. The lowest calibration standard is the lowest concentration for which quantitative data may be reported. Data reported below this level is considered to have less certainty and must be reported using appropriate data qualifiers (e.g. J flag) or explained in a narrative. The highest calibration standard is the highest concentration for which quantitative data may be reported. Data reported above this level is considered to have less certainty and must be reported using appropriate data qualifiers (e.g. E flag) or explained in the narrative. Any specific method requirement for number and type of calibration standards supersedes the general requirement. Instrument and method specific calibration criteria are explained within the specific analytical standard operating procedures for each facility.

Instrumentation or support equipment that cannot be calibrated to specification or is otherwise defective is clearly labeled as out-of-service until it has been repaired and tested to demonstrate it meets the laboratory's specifications. All repair and maintenance activities including service calls are documented in the maintenance log. Equipment sent off-site for calibration testing is packed and transported to prevent breakage and is in accordance with the calibration laboratory's recommendations.

In the event that recalibration of a piece of test equipment indicates the equipment may have been malfunctioning during the course of sample analysis, an investigation is performed. The results of the investigation along with a summary of the information reviewed are documented and maintained by the Quality Manager. If the investigation indicates sample results have been impacted, the customer is notified within 30 days. This allows for sufficient investigation and review of documentation to determine the impact on the analytical results. Instrumentation found to be consistently out of calibration is either repaired and positively verified or replaced.

Raw data records are retained to document equipment performance. Sufficient raw data is retained to reconstruct the instrument calibration and explicitly connect the continuing calibration verification to the initial calibration.

6.2.1 General Organic Calibration Procedures

Calibration standards are prepared at a minimum of five concentrations for organic analyses. Results from all calibration standards must be included in constructing the calibration curve with the following exceptions:

- The lowest level calibration standard may be removed from the calibration as long as the remaining number of concentration levels meets the minimum established by the method and standard operating procedure. For multi-parameter methods, this may be done on an individual analyte basis. The reporting limit must be adjusted to the lowest concentration included in the calibration curve.
- The highest level calibration standard may be removed from the calibration as long as the remaining number of concentration levels meets the minimum established by the method and standard operating procedure. For multi-parameter methods, this may be done an individual analyte basis. The upper limit of quantitation must be adjusted to the highest concentration included in the calibration curve.
- Multiple points from either the high end or the low end of the calibration curve may be excluded as long as the remaining points are contiguous in nature and the minimum number of levels remain as established by method or standard operating procedure. The reporting limit or quantitation range, which is appropriate, must be adjusted accordingly.
- Results from a concentration level between the lowest and highest calibration levels can be excluded from the calibration curve for an acceptable cause with approval from the responsible department supervisor if the results for all analytes are excluded and the point is replaced by re-analysis. Re-analysis must occur within the same 12 hour tune time period for GC/MS methodologies and within 8 hours of the initial analysis for non-GC/MS methodologies. All samples analyzed prior to the re-analyzed calibration curve point must be re-analyzed after the calibration curve is completed.

Initial calibration curves are evaluated against appropriate statistical models as required by the analytical methods. Curves that do not meet the appropriate criteria require corrective action that may include re-running the initial calibration curve. All initial calibrations are verified with a standard obtained from a second manufacturer or second lot from the same manufacturer if the lot can be demonstrated as prepared independently from other lots prior to the analysis of samples. Sample results are quantitated from the initial calibration unless otherwise required by regulation, method, or program.

The calibration curve is periodically verified by the analysis of a mid-level continuing calibration verification (CCV) standard during the course of sample analysis. Calibration verification is performed at the beginning and end of each analytical batch (except if an internal standard is used only one verification at the beginning of the batch is needed), whenever it is expected that the analytical system may be out of calibration, if the time period for calibration has expired, or for analytical systems that contain a calibration verification requirement. This verification standard must meet acceptance criteria in order for sample analysis to proceed.

In the event that the CCV does not meet the acceptance criteria, a second CCV may be injected as part of the diagnostic evaluation and corrective action investigation. If the second CCV is acceptable, the analytical sequence is continued. If both CCVs fail, the analytical sequence is terminated. All samples analyzed since the last compliant CCV are re-analyzed for methodologies utilizing external calibration.

When instruments are operating unattended, the autosamplers may be programmed to inject consecutive CCVs as a preventative measure against CCV failure with no corrective action. In this case, both CCVs must be evaluated to determine potential impact to the results. A summary of the decision tree and necessary documentation are listed below:

- If both CCVs meet the acceptance criteria, the analytical sequence is allowed to continue without corrective action. (The 12 hour clock begins with the injection of the second CCV.)
- If the first CCV does not meet the acceptance criteria and the second CCV is acceptable, the analytical sequence is continued and the results are reported.
- If the first CCV meets the acceptance criteria and the second CCV is out of control, the samples following the out of control CCV must be re-analyzed in a compliant analytical sequence.
- If both CCVs are out of control, all samples since the last acceptable CCV must be re-analyzed in a compliant analytical sequence.

Some analytical methods require that samples be bracketed by passing CCVs analyzed both before and after the samples. This is specific to each method but, as a general rule, all external calibration methods require bracketing CCVs. Most internal standard calibrations do not require bracketing CCVs.

Some analytical methods require verification based on a time interval; some methods require a frequency based on an injection interval. The type and frequency of the calibration verifications is dependent on both the analytical method and possibly on the quality program associated with the samples. The type and frequency of calibration verification will be documented in the method specific SOP employed by each laboratory.

For Ohio VAP projects, the lab must minimize the use of qualifed data. In the case of calibration verification standard failures, the lab is required to reanalyze the CCV and the associated samples so as not to report qualified data (sample data may only be reported if the failure produces a high bias and the samples are non-detect). Where possible, the second attempt should be made using the original aliquot of the standard unless there is reason to suspect that the standard is the cause of failure. The lab must make every effort to take the appropriate corrective actions and resolve any anomalies regarding calibration verification standard failures for Ohio VAP projects.

6.2.2 General Inorganic Calibration Procedures

The instrument is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. A calibration blank is also included. Initial calibration curves are evaluated against appropriate statistical models as required by the analytical methods. The number of calibration standards used depends on the specific method criteria or customer project requirements, although normally a minimum of three standards is used.

The ICP and ICP/MS can be standardized with a zero point and a single point calibration if:

- Prior to analysis, the zero point and the single point calibration are analyzed and a linear range is established,
- Zero point and single point calibration standards are analyzed with each batch
- A standard corresponding to the LOQ is analyzed with the batch and meets the established acceptance criteria
- The linearity is verified at the frequency established by the method or manufacturer.

All initial calibrations are verified with a standard obtained from a second manufacturer or second lot from the same manufacturer if the lot can be demonstrated as prepared independently from other lots prior to the analysis of samples. Sample results are quantitated from the initial calibration unless otherwise required by regulation, method, or program.

During the course of analysis, the calibration curve is periodically verified by the analysis of calibration verification standards. A calibration verification standard is analyzed within each analytical batch at method/program specific intervals to verify that the initial calibration is still valid. The CCV is also analyzed at the end of the analytical batch.

A calibration blank is also run with each calibration verification standard to verify the cleanliness of the system. All reported results must be bracketed by acceptable CCVs. Instrument and method specific calibration acceptance criteria are explained within the specific analytical standard operating procedures for each facility.

Interference check standards are also analyzed per method requirements and must meet acceptance criteria for metals analyses.

6.3 Support Equipment Calibration Procedures

All support equipment is calibrated or verified at least annually using NIST traceable references over the entire range of use. The results of calibrations or verifications must be within the specifications required or the equipment will be removed from service until repaired. The laboratory maintains records to demonstrate the correction factors applied to working thermometers.

Prior to use on each working day, balances, ovens, refrigerators, freezers, and water baths are checked in the expected use range with NIST traceable references in order to ensure the equipment meets laboratory specifications.

6.3.1 Analytical Balances

Each analytical balance is checked and (if necessary) calibrated annually by a qualified service technician. The calibration of each balance is checked each day of use with weights traceable to NIST. Calibration weights are ASTM Class 1 (or other class weights that have been calibrated against a NIST standard weight) and are re-certified annually against a NIST traceable reference. Some accrediting agencies may require more frequent checks. If balances are calibrated by an external agency, verification of their weights must be provided. All information pertaining to balance maintenance and calibration is recorded in the individual balance logbook and/or is maintained on file in the Quality department.

6.3.2 Thermometers

Certified, or reference, thermometers are maintained for checking calibration of working thermometers. Reference thermometers are provided with NIST traceability for initial calibration and are re-certified, at a minimum, yearly with equipment directly traceable to NIST.

Working thermometers are compared with the reference thermometers annually according to corporate metrology procedures. Each thermometer is individually numbered and assigned a correction factor based on the NIST reference source. In addition, working thermometers are visually inspected by laboratory personnel prior to use and temperatures are documented.

Laboratory thermometer inventory and calibration data are maintained in the Quality department.

6.3.3 pH/Electrometers

The meter is calibrated before use each day, and once after each four hours of continuous use, using fresh buffer solutions. Please see S-MN-I-526 or equivalent for details.

6.3.4 Spectrophotometers

During use, spectrophotometer performance is checked at established frequencies in analysis sequences against initial calibration verification (ICV) and continuing calibration verification (CCV) standards.

6.3.5 Mechanical Volumetric Dispensing Devices

Mechanical volumetric dispensing devices including bottle top dispensers, pipettes, and burettes, excluding Class A volumetric glassware, are checked for accuracy on a quarterly basis. The accuracy of glass microliter syringes is verified and documented prior to use.

Additional information regarding calibration and maintenance of laboratory support equipment can be found in SOP S-ALL-Q-013 Support Equipment or its equivalent revision or replacement.

6.4 Instrument/ Equipment Maintenance

The objectives of the Pace Analytical maintenance program are twofold: to establish a system of instrument care that maintains instrumentation and equipment at required levels of calibration and sensitivity, and to minimize loss of productivity due to repairs.

The Laboratory Operations Manager and department manager/supervisors are responsible for providing technical leadership to evaluate new equipment, solve equipment problems and coordinate instrument repair and maintenance. The analysts have a primary responsibility to perform routine maintenance.

To minimize downtime and interruption of analytical work, preventative maintenance is routinely performed on each analytical instrument. Up-to-date instructions on the use and maintenance of equipment are available to staff in the department where the equipment is used.

Department manager/supervisors are responsible for maintaining an adequate inventory of spare parts required to minimize equipment downtime. This inventory includes parts and supplies that are subject to frequent failure, have limited lifetimes, or cannot be obtained in a timely manner should a failure occur.

All major equipment and instrumentation items are uniquely identified to allow for traceability. Equipment/instrumentation are, unless otherwise stated, identified as a system and not as individual pieces. The laboratory maintains equipment records that include the following:

- The name of the equipment and its software
- The manufacturer's name, type, and serial number
- Approximate date received and date placed into service
- Current location in the laboratory

- Condition when received (new, used, etc.)
- Copy of any manufacturer's manuals or instructions
- Dates and results of calibrations and next scheduled calibration (if known)
- Details of past maintenance activities, both routine and non-routine
- Details of any damage, modification or major repairs

All instrument maintenance is documented in maintenance logbooks that are assigned to each particular instrument or system.

When maintenance is performed to repair an instrument problem, depending on the initial problem, demonstration of return to control may be satisfied by the successful analysis of a reagent blank or continuing calibration standard. The entry must include a summary of the results of that analysis and verification by the analyst that the instrument has been returned to an in-control status. In addition, each entry must include the initials of the analyst making the entry, the dates the maintenance actions were performed, and the date the entry was made in the maintenance logbook, if different from the date(s) of the maintenance.

Any equipment that has been subjected to overloading or mishandling, or that gives suspect results, or has been shown to be defective, is taken out of service and clearly identified. The equipment shall not be used to analyze customer samples until it has been repaired and shown to perform satisfactorily.

7.0 CONTROL OF DATA

Analytical results processing, verification and reporting are procedures employed that result in the delivery of defensible data. These processes include, but are not limited to, calculation of raw data into final concentration values, review of results for accuracy, evaluation of quality control criteria and assembly of technical reports for delivery to the data user.

All analytical data undergo a well-defined, well-documented multi-tier review process prior to being reported to the customer. This section describes procedures used by PASI for translating raw analytical data into accurate, final sample reports and PASI data storage policies.

7.1 Analytical Results Processing

When analytical, field, or product testing data is generated, it is either recorded in a bound laboratory logbook (e.g. Run log or Instrument log) or copies of computer-generated printouts are appropriately labeled and filed. These logbooks and other laboratory records are kept in accordance with each facility's Standard Operating Procedure for documentation storage and archival. If the lab chooses to minimize paper usage, these records can be kept as electronic records. In this case, the laboratory must ensure that there are sufficient redundant electronic copies so no data is lost due to unforeseen computer issues.

The primary analyst is responsible for initial data reduction and review. This includes confirming compliance with required methodology, verifying calculations, evaluating quality control data, noting discrepancies in logbooks and as footnotes or narratives, and uploading analytical results into the LIMS.

The primary analyst or project manager then compiles the initial data package for verification. This compilation must include sufficient documentation for data review. It may include standard calibrations, chromatograms, manual integration documentation, electronic printouts, chain-of-custody forms, and logbook copies.

Some agencies or customers require different levels of data reporting. For these special levels, the primary analyst may need to compile additional project information, such as initial calibration data or extensive spectral data, before the data package proceeds to the verification step.

7.2 Data Verification

Data verification is the process of examining data and accepting or rejecting it based on pre-defined criteria. This review step is designed to ensure that reported data are free from calculation and transcription errors, that quality control parameters are evaluated and that any discrepancies are properly documented.

Analysts performing the analysis and subsequent data reduction have primary responsibility for quality of the data produced. The primary analyst initiates the data verification process by reviewing and accepting the data, provided QC criteria have been met for the samples being reported. Data review checklists, either hardcopy or electronic, are used to document the data review process. The primary analyst is responsible for the initial input of the data into the LIMS.

The completed data package is then sent to a designated qualified reviewer (this cannot be the primary analyst). The following criteria have been established to qualify someone as a data reviewer. To perform secondary data reviewer, the reviewer must:

1. Have a current Demonstration of Capability (DOC) study on file and have an SOP acknowledgement form on file for the method/procedure being reviewed; or, See Note
2. Have a DOC on file for a similar method/technology (i.e. GC/MS) and have an SOP acknowledgment form on file for the method/procedure being reviewed; or, See Note

3. Supervise or manage a Department and have an SOP acknowledgment form on file for the method/procedure being reviewed; or,
4. Have significant background in the department/methods being reviewed through education or experience and have an SOP acknowledgment form on file for the method/procedure being reviewed.

Note: Secondary reviewer status must be approved personally by the Quality Manager or General Manager in the event that this person has no prior experience on the specific method or general technology (i.e. GC/MS).

This reviewer provides an independent technical assessment of the data package and technical review for accuracy according to methods employed and laboratory protocols. This assessment involves a quality control review for use of the proper methodology and detection limits, compliance to quality control protocol and criteria, presence and completeness of required deliverables, and accuracy of calculations and data quantitation. The reviewer also validates the data entered into the LIMS.

Once the data have been technically reviewed and approved, authorization for release of the data from the analytical section is indicated by initialing and dating the data review checklist or otherwise initialing and dating the data (or designating the review of data electronically). The Operations or Project Manager examines the report for method appropriateness, detection limits and QC acceptability. Any deviations from the referenced methods are checked for documentation and validity, and QC corrective actions are reviewed for successful resolution.

7.3 Data Reporting

All data segments pertaining to a particular PASI project number are delivered to the Client Services Department (Project Manager) for assembly into the final report. All points mentioned during technical and QC reviews are included in a case narrative if there is potential for data to be impacted.

Final reports are prepared according to the level of reporting required by the customer and can be transmitted to the customer via hardcopy or electronic deliverable. A standard PASI final report consists of the following components:

1. A title which designates the report as “Final Report”, “Laboratory Results”, “Certificate of Results”, etc.
2. Name and address of laboratory (or subcontracted laboratories, if used).
3. Phone number and name of laboratory contact where questions can be referred.
4. A unique number for the report (project number). The pages of the report shall be numbered and a total number of pages shall be indicated (usually in the cover letter).
5. Name and address of customer and name of project (if applicable).
6. Unique identification of samples analyzed (including customer sample numbers).
7. Identification of any sample that did not meet acceptable sampling requirements (from NELAC or other governing agency), such as improper sample containers, holding times missed, sample temperature, etc.
8. Date and time of collection of samples, date of sample receipt by the laboratory, dates of sample preparation and analysis, and times of sample preparation and analysis when the holding time for either is 72 hours or less and for Department of Defense projects.
9. Identification of the test methods used.
10. Identification of sampling procedures if sampling was conducted by the laboratory.
11. Deviations from, additions to, or exclusions from the test methods. These can include failed quality control parameters, deviations caused by the matrix of the sample, etc., and can be shown as a case narrative or as defined footnotes to the analytical data.
12. Identification of whether calculations were performed on a dry or wet-weight basis.
13. Reporting limits used.
14. Final results or measurements, supported by appropriate chromatograms, charts, tables, spectra, etc.
15. A signature and title of person accepting responsibility for the content of the report (can be an equivalent electronic identification) and date report was issued.

16. A statement clarifying that the results of the report relate only to the samples tested or to the samples as they were received by the laboratory.
17. If necessary, a statement indicating that the report must not be reproduced except in full, without the written approval of the laboratory.
18. Identification of all test results provided by a subcontracted laboratory or other outside source.
19. Identification of results obtained outside of quantitation levels.
20. Additional items may be required per Client QAPPs or different state regulations, i.e. Affidavit for Ohio VAP reports.

Any changes made to a final report shall be designated as "Revised" or equivalent wording. The laboratory must keep sufficient archived records of all lab reports and revisions. For higher levels of data deliverables, a copy of all applicable raw data is sent to the customer along with a final report of results. When possible, the PASI facility will provide electronic data deliverables (EDD) as required by contracts or upon customer request.

Customer data that requires transmission by telephone, telex, facsimile or other electronic means undergoes appropriate steps to preserve confidentiality. Additional information on data reduction and validation can be found in SOP MN-L-132 Data Reduction, Validation and Reporting, or equivalent replacement.

The following positions are the only approved signatories for PASI final reports:

- Senior General Manager
- General Manager
- Quality Manager
- Client Services Manager
- Project Manager
- Project Coordinator

7.4 Data Security

All data including electronic files, logbooks, extraction/digestion/distillation worksheets, calculations, project files and reports, and other information used to produce the technical report are maintained secured and retrievable by the PASI facility.

7.5 Data Archiving

All records compiled by PASI are maintained legible and retrievable and stored secured in a suitable environment to prevent loss, damage, or deterioration by fire, flood, vermin, theft, and/or environmental deterioration. Records are retained for a minimum of five years unless superseded by federal, state, contractual, and/or accreditation requirements. These records may include, but are not limited to, customer data reports, calibration and maintenance of equipment, raw data from instrumentation, quality control documents, observations, calculations and logbooks. These records are retained in order to provide for possible historical reconstruction including sampling, receipt, preparation, analysis and personnel involved. NELAP-related records will be made readily available to accrediting authorities. Access to archived data is documented and controlled by the Quality Manager or a designated Data Archivist.

Records that are computer-generated have either a hard copy or electronic write-protected backup copy. Hardware and software necessary for the retrieval of electronic data is maintained with the applicable records. Archived electronic records are stored protected against electronic and/or magnetic sources.

In the event of a change in ownership, accountability or liability, reports of analyses performed pertaining to accreditation will be maintained by the acquiring entity for a minimum of five years. In the event of

bankruptcy, laboratory reports and/or records will be transferred to the customer and/or the appropriate regulatory entity upon request.

7.6 Data Disposal

Data that has been archived for the facility's required storage time may be disposed of in a secure manner by shredding, returning to customer, or utilizing some other means that does not jeopardize data confidentiality. Records of data disposal will be archived for a minimum of five years unless superseded by federal, contractual, and/or accreditation requirements.

8.0 QUALITY SYSTEM AUDITS AND REVIEWS

8.1 Internal Audits

8.1.1 Responsibilities

The Quality Manager is responsible for designing and/or conducting internal audits in accordance with a predetermined schedule and procedure. Since internal audits represent an independent assessment of laboratory functions, the auditor must be functionally independent from laboratory operations to ensure objectivity. The auditor must be trained, qualified and familiar enough with the objectives, principles, and procedures of laboratory operations to be able to perform a thorough and effective evaluation. The Quality Manger evaluates audit observations and verifies the completion of corrective actions. In addition, a periodic corporate audit will be conducted by the Director of Quality, Safety and Training and/or designee. The corporate audits will focus on the execution of the Quality System as outlined in this manual but may also include other quality programs applicable to each laboratory.

8.1.2 Scope and Frequency of Internal Audits

Internal systems audits are conducted yearly at a minimum. The scope of these audits includes evaluation of specific analytical departments or a specific quality-related system as applied throughout the laboratory.

Examples of system-wide elements that can be audited include:

- Quality Systems documents, such as Standard Operating Procedures, training documents, Quality Assurance Manual and all applicable addenda
- Personnel and training files.
- General laboratory safety protocols.
- Chemical handling practices, such as labeling of reagents, solutions, standards, and associated documentation.
- Documentation concerning equipment and instrumentation, calibration/maintenance records, operating manuals.
- Sample receipt and management practices.
- Analytical documentation, including any discrepancies and corrective actions.
- General procedures for data security, review, documentation, reporting and archiving.
- Data integrity issues such as proper manual integrations.

When the operations of a specific department are evaluated, a number of additional functions are reviewed including:

- Detection limit studies
- Internal chain-of-custody documentation
- Documentation of standard preparations
- Quality Control limits and Control charts

Certain projects may require an internal audit to ensure laboratory conformance to site work plans, sampling and analysis plans, QAPPs, etc.

A representative number of data audits are completed annually. The report format of any discrepancy is similar to that of other internal audits.

The laboratory, as part of their overall internal audit program, ensures that a review is conducted with respect to any evidence of inappropriate actions or vulnerabilities related to data integrity. Discovery and reporting of potential data integrity issues are handled in a confidential manner until such time as a follow up evaluation, full investigation, or other appropriate actions are completed and the issues clarified. All investigations that result in findings of inappropriate activity are fully documented, including the source of the problem, the samples and customers affected, the impact on the data, the corrective actions taken by the lab and which final reports had to be re-issued. Customers are notified within 30 days when the investigation indicates analytical results are affected.

8.1.3 Internal Audit Reports and Corrective Action Plans

Additional information can be found in SOP S-ALL-Q-011 Audits and Inspections or its equivalent revision or replacement.

A full description of the audit, including the identification of the operation audited, the date(s) on which the audit was conducted, the specific systems examined, and the observations noted are summarized in an internal audit report. Although other personnel may assist with the performance of the audit, the Quality Manager writes and issues the internal audit report identifying which audit observations are deficiencies that require corrective action.

When audit findings cast doubt on the effectiveness of the operations or on the correctness of validity of the laboratory's environmental test results, the laboratory will take timely corrective action and notify the customer in writing within 30 days, if investigations show that the laboratory results may have been affected.

Once completed, the internal audit report is issued jointly to the Laboratory General Manager and the manager(s)/supervisor(s) of the audited operation at a minimum. The responsible manager(s)/supervisor(s) responds within 14 days with a proposed plan to correct all of the deficiencies cited in the audit report. The Quality Manager may grant additional time for responses to large or complex deficiencies (not to exceed 30 days). Each response must include timetables for completion of all proposed corrective actions.

The Quality Manager reviews the audit responses. If the response is accepted, the Quality Manager uses the action plan and timetable as a guideline for verifying completion of the corrective action(s). If the Quality Manager determines that the audit response does not adequately address the correction of cited deficiencies, the response will be returned for modification.

To complete the audit process, the Quality Manager performs a re-examination of the areas where deficiencies were found to verify that all proposed corrective actions have been implemented. An audit deficiency is considered closed once implementation of the necessary corrective action has been verified. If corrective action cannot be verified, the associated deficiency remains open until that action is completed.

8.2 External Audits

PASI laboratories are audited regularly by regulatory agencies to maintain laboratory certifications, and by customers to maintain appropriate specific protocols.

Audit teams external to the company review the laboratory to assess the existence of systems and degree of technical expertise. The Quality Manager and other QA staff host the audit team and assist in facilitation of the audit process. Generally, the auditors will prepare a formalized audit report listing deficiencies observed and follow-up requirements for the laboratory. In some cases, items of concern are discussed during a debriefing convened at the end of the on-site review process.

The laboratory staff and supervisors develop corrective action plans to address any deficiencies with the guidance of the Quality Manager. The Laboratory General Manager provides the necessary resources for staff to develop and implement the corrective action plans. The Quality Manager collates this information and provides a written report to the audit team. The report contains the corrective action plan and expected completion dates for each element of the plan. The Quality Manager follows-up with the laboratory staff to ensure corrective actions are implemented.

8.3 Quarterly Quality Reports

The Quality Manager is responsible for preparing a quarterly report to management summarizing the effectiveness of the laboratory Quality Systems. This status report will include:

- Results of internal systems or performance audits
- Corrective action activities
- Discussion of QA issues raised by customers
- Results of third party or external audits
- Status of laboratory certifications
- Proficiency Testing Study Results
- Results of internal laboratory review activities
- Summary of holding time violations
- Method detection limit study status
- Training activity summary
- SOP revision summary
- 3P Implementation summary (internal program)
- Other significant Quality System items

The Corporate Director of Quality, Safety & Technology utilizes the information from each laboratory to make decisions impacting the Quality Systems of the company as a whole. Each General Manager utilizes the quarterly report information to make decisions impacting Quality Systems and operational systems at a local level.

Additional information can be found in SOP S-ALL-Q-014 Quality System Review or its equivalent revision or replacement.

8.4 Annual Managerial Review

A managerial review of Quality Systems is performed on an annual basis at a minimum. This allows for assessing program effectiveness and introducing changes and/or improvements.

The managerial review must include the following topics of discussion:

- Policy and procedure suitability
- Manager/Supervisor reports
- Internal audit results
- Corrective and preventative actions
- External assessment results
- Proficiency testing studies
- Sample capacity and scope of work changes
- Customer feedback, including complaints

This managerial review must be documented for future reference by the Quality Manager and copies of the report are distributed to laboratory staff. The laboratory shall ensure that any actions identified during the review are carried out within an appropriate and agreed timescale.

8.5 Customer Service Reviews

As part of the annual managerial review listed previously, the sales staff is responsible for reporting on customer feedback, including complaints. The acquisition of this information is completed by performing surveys.

The sales staff continually receives customer feedback, both positive and negative, and reports this feedback to the lab management in order for them to evaluate and improve their management system, testing activities and customer service.

In addition, the labs must be willing to cooperate with customers or their representatives to clarify customer requests and to monitor the lab's performance in relation to the work being performed for the customers.

9.0 CORRECTIVE ACTION

Additional information can be found in SOP S-ALL-Q-012 Corrective Action/Preventive Action **Process** or its equivalent revision or replacement.

During the process of sample handling, preparation and analysis, certain occurrences may warrant the necessity of corrective actions. These occurrences may take the form of analyst errors, deficiencies in quality control, method deviations, or other unusual circumstances. The Quality System of PASI provides systematic procedures for documentation, monitoring and completion of corrective actions. This can be done using PASI's LabTrack system that lists among other things, the deficiency by issue number, the deficiency source, responsible party, root cause, resolution, due date, and date resolved.

9.1 Corrective Action Documentation

The following items are examples of laboratory deviations or non-conformances that warrant some form of documented corrective action:

- Quality Control data outside of acceptance criteria
- Sample Acceptance Policy deviations
- Missed holding times
- Instrument failures (including calibration failure)
- Sample preparation or analysis errors
- Sample contamination
- Errors in customer reports
- Audit findings (internal and external)
- Proficiency Testing (PT) sample failures
- Customer complaints or inquiries

Documentation of corrective actions may be in the form of a comment or footnote on the final report that explains the deficiency (e.g. matrix spike recoveries outside of acceptance criteria) or it may be a more formal documentation (either paper system or computerized spreadsheet). This depends on the extent of the deficiency, the impact on the data, and the method or customer requirements for documentation.

The person who discovers the deficiency or non-conformance initiates the corrective action documentation on the Non-Conformance Corrective/ Preventative Action report and/or LabTrack. The documentation must include the affected projects and sample numbers, the name of the applicable Project Manager, the customer name and the sample matrix involved. The person initiating the corrective action documentation must also list the known causes of the deficiency or non-conformance as well as any corrective/preventative actions that they have taken. Preventive actions must be taken in order to prevent or minimize the occurrence of the situation.

In the event that the laboratory is unable to determine the cause, laboratory personnel and management staff will start a root cause analysis by going through an investigative process. During this process, the following general steps must be taken into account: defining the non-conformance problem, assigning responsibilities, determining if the condition is significant, and investigating the root cause of the nonconformance problem. General non-conformance investigative techniques follow the path of the sample through the process looking at each individual step in detail. The root cause must be documented within Lab Track or on the Corrective/Preventative Action Report.

After all the documentation is completed, the routing of the Corrective/Preventative Action Report and /or Lab Track will continue from the person initiating the corrective action, to their immediate supervisor or the Project Manager and finally to the Quality Manager, who is responsible for final review and signoff of all formal corrective/preventative actions.

9.2 Corrective Action Completion

9.2.1 Quality Control outside of acceptance criteria

The analyst that is generating or validating Analytical data is responsible for checking the results against established acceptance criteria (quality control limits). The analyst must immediately address any deficiencies discovered. Method blank, LCS or matrix spike failures are evaluated against method, program, and customer requirements and appropriate footnotes are entered into the LIMS system. Some deficiencies may be caused by matrix interferences. Where possible, matrix interferences are confirmed by re-analysis.

Quality control deficiencies must be made known to the customer on the final report for their review of the data for usability. If appropriate, the supervisor is alerted to the QC failure and if necessary a formal corrective action can be initiated. This may involve the input of the Quality Manager or the General Manager.

The department supervisor and/or Operations Manager are responsible for evaluating the source of the deficiency and for returning the analytical system to control. This may involve instrument maintenance, analytical standard or reagent evaluation, or an internal audit of the analytical procedure.

See applicable analytical SOPs for further guidance on QC acceptance criteria.

9.2.2 Sample Acceptance Policy deviations

Any deviation from the Sample Acceptance Policy listed in this Manual must be documented on the Chain-of-Custody or other applicable form by the sample receiving personnel or by the Project Manager. Analysts or supervisors that discover such deviations must contact the sample receiving personnel or appropriate Project Manager so they can initiate the proper documentation and customer contact. If a more formalized corrective action must be documented, the Quality Manager is made aware of the situation.

The customer is notified of these deviations as soon as possible so they can make decisions on whether to continue with the sample analysis or re-sample. Copies of this documentation are included in the project file.

9.2.3 Missed holding times

In the event that a holding time requirement has been missed, the analyst or supervisor must complete a formal corrective action form. The Project Manager and the Quality Manager must be made aware of these hold time exceedances.

The Project Manager must contact the customer for appropriate decisions to be made with the resolution documented and included in the customer project file. The Quality Manager includes a list of all missed holding times in their Quarterly Report to the corporate office.

9.2.4 Instrument Failures

In the event of an instrument failure that either causes the necessity for re-analysis or questions the validity of generated results, a formal corrective action must be initiated. The analyst and supervisor evaluate any completed data for validity and usability. They are also responsible for returning the instrument to valid operating condition and for documenting that the system is in control (e.g. acceptable calibration verification).

9.2.5 Sample Preparation or Analysis errors

When there is an error in the preparation or analysis of samples, the analyst evaluates the impact on the usability of the analytical data with the assistance of the supervisor or manager. The affected samples will be re-processed or re-analyzed under acceptable conditions. In the event that no additional sample is available for re-analysis, the customer must be contacted for their decision on how to proceed. Documentation may take the form of footnotes or a formal corrective action form.

9.2.6 Errors in customer reports

When an error on the customer report is discovered, the Project Manager is responsible for initiating a formal corrective action form that describes the failure (e.g. incorrect analysis reported, reporting units are incorrect, reporting limits do not meet objectives). The Project Manager is also responsible for revising the final report if necessary and submitting it to the customer.

9.2.7 Audit findings

The Quality Manager is responsible for documenting all audit findings and their corrective actions. This documentation must include the initial finding, the persons responsible for the corrective action, the due date for reporting back to the auditing body, the root cause of the issue, and the corrective action taken to resolve the findings. The Quality Manager is also responsible for providing any back-up documentation used to prove that a corrective action has been completed.

9.2.8 Proficiency Testing failures

Any PT result returned to the Quality Manager as "not acceptable" requires an investigation and applicable corrective actions. The operational staff is made aware of the PT failures and they are responsible for reviewing the applicable raw data and calibrations and list possible causes for error. The Quality Manager reviews their findings and initiates another external PT sample or an internal PT sample to try and correct the previous failure. Replacement PT results must be monitored by the Quality Manager and reported to the applicable regulatory authorities.

9.2.9 Customer Complaints

Project Managers are responsible for issuing corrective action forms for customer complaints. As with other corrective actions, the possible causes of the problem are listed and the form is passed to the appropriate analyst or supervisor. After the corrective actions have been listed, the Project Manager reviews the corrective action to determine if the customer needs or concerns are being addressed.

Additional information can be found in SOP S-ALL-Q-012 Corrective Action/Preventative Action Process.

9.3. Preventive Action Documentation

Pace laboratories can take advantage of several available information sources in order to identify needed improvements in all of their systems (technical, managerial, quality, etc.). These sources may include:

- Management Continuous Improvement Plan (CIP) metrics which are used by all production departments within Pace. When groups compare performance across the company, ways to improve systems are discovered. These improvements can be made within a department or lab-wide.

- Annual managerial reviews- part of this NELAC-required review is to look at all processes and procedures used by the lab over the past year and to determine ways to improve these processes in the future.
- Quality systems reviews- any frequent checks of quality systems (monthly logbook reviews, etc.) can uncover issues that can be corrected or adjusted before they become a larger issue.

When improvement opportunities are identified or if preventive action is required, the lab can develop, implement, and monitor preventive action plans.

10.0 GLOSSARY

3P Program	The Pace Analytical continuous improvement program that focuses on Process, Productivity and Performance. Best Practices are identified that can be used by all PASI labs.
Accuracy	The agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator.
Aliquot	A portion of a sample taken for analysis.
Analyte	The specific chemical species or parameter an analysis seeks to determine.
Batch	Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.
Blank	A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.
Blind Sample	A sample for submitted for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test analyst or laboratory proficiency in the execution of the measurement process.
Calibration	To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard must bracket the range of planned or expected sample measurements.
Calibration Curve	The graphic representation of known values, such as concentrations for a series of calibration standards and their instrument response.
Chain-of-Custody (COC)	A record that documents the possession of samples from the time of collection to receipt in the laboratory. This record generally includes the number and type of containers, mode of collection, collector, time of collection, preservation, and requested analyses.
Confirmation	Verification of the identity of a component through the use of an alternate scientific approach from the original method. These may include, but are not limited to: • second-column confirmation • alternate wavelength • derivatization derivative • mass spectral interpretation • additional cleanup procedures
Contract Required Detection Limit (CRDL)	Detection limit that is required for EPA Contract Laboratory Program (CLP) contracts.
Contract Required Quantitation Limit (CRQL)	Quantitation limit (reporting limit) that is required for EPA Contract Laboratory Program (CLP) contracts.
Comparability	An assessment of the confidence with which one data set can be compared to another. Comparable data are produced through the use of standardized procedures and techniques.

Completeness	The percent of valid data obtained from a measurement system compared to the amount of valid data expected under normal conditions. The equation for completeness is: % Completeness = (Valid Data Points/Expected Data Points)*100
Calibration Verification	The process of verifying a calibration by analysis of standards and comparing the results with the known amount.
Control Chart	A graphic representation of a series of test results, together with limits within which results are expected when the system is in a state of statistical control (see definition for Control Limit)
Control Limit	A range within which specified measurement results must fall to verify that the analytical system is in control. Control limit exceedances may require corrective action or require investigation and flagging of nonconforming data.
Corrective Action	The action taken to eliminate the causes of a nonconformity, defect, or other undesirable situation in order to prevent recurrence.
Corrective and Preventative Action (CAPA)	The primary management tools for bringing improvements to the quality system, to the management of the quality system's collective processes, and to the products or services delivered which are an output of established systems and processes.
Data Quality Objective (DOQ)	Systematic strategic planning tool based on the scientific method that identifies and defines the type, quality, and quantity of data needed to satisfy a specified use or end user.
Data Reduction	The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more usable form.
Demonstration of Capability	A procedure to establish the ability of the analyst to generate acceptable accuracy.
Detection Limit (DL)	General term for the lowest concentration or amount of the target analyte that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value. See definitions for Method Detection Limit and Limit of Detection.
Document Control (Management)	Procedures to ensure that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled (managed) to ensure use of the correct version at the location where the prescribed activity is performed.
Dry Weight	The weight after drying in an oven at a specified temperature.
Duplicate or Replicate Analysis	The identically performed measurement on two or more sub-samples of the same sample within a short interval of time
Environmental Sample	A representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. Environmental samples can generally be classified as follows: • Non Potable Water (Includes surface water, ground water, effluents, water treatment chemicals, and TCLP leachates or other extracts) • Drinking Water - Delivered (treated or untreated) water designated as potable water • Water/Wastewater - Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents • Sludge - Municipal sludges and industrial sludges. • Soil - Predominately inorganic matter ranging in classification from sands to clays. • Waste - Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes
Equipment Blank	A sample of analyte-free media used to rinse common sampling equipment to check effectiveness of decontamination procedures.
Field Blank	A blank sample prepared in the field by filling a clean container with reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken.

Field Measurement	Determination of physical, biological, or radiological properties, or chemical constituents that are measured on-site, close in time and space to the matrices being sampled/measured, following accepted test methods. This testing is performed in the field outside of a fixed-laboratory or outside of an enclosed structure that meets the requirements of a mobile laboratory.
Holding Time	The maximum time that samples may be held prior to preparation and/or analysis as defined by the method.
Homogeneity	The degree to which a property or substance is uniformly distributed throughout a sample.
Initial Calibration (ICAL)	The process of analyzing standards, prepared at specified concentrations, to define the quantitative response relationship of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a calibration verification standard do not conform to the requirements of the method in use or at a frequency specified in the method.
Internal Standards	A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.
Intermediate Standard Solution	Reference solutions prepared by dilution of the stock solutions with an appropriate solvent.
Laboratory Control Sample (LCS)	A blank sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. Sometimes referred to as Laboratory Fortified Blank, Spiked Blank or QC Check Sample.
Limit of Detection (LOD)	An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte and matrix specific and may be laboratory-dependent.
Limit of Quantitation (LOQ) .	The minimum levels, concentrations or quantities of a target variable (e.g. target analyte) that can be reported with a specified degree of confidence
Laboratory Information Management System (LIMS)	A computer system that is used to maintain all sample information from sample receipt, through preparation and analysis and including sample report generation.
Learning Management System (LMS)	A web-based database used by the laboratories to track and document training activities. The system is administered by the corporate training department and each lab's learn centers are maintained by a local administrator.
Lot	A quantity of bulk material of similar composition processed or manufactured at the same time.

Matrix	The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions are used: • **Aqueous or Non-Potable Water**: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts. • **Drinking Water**: any aqueous sample that has been designated a potable or potentially potable water source. • **Saline/Estuarine**: any aqueous sample from an ocean or estuary, or other saltwater source. • **Non-aqueous liquid**: any organic liquid with <15% settleable solids. • **Biological Tissue**: any sample of a biological origin such as fish tissue, shellfish or plant material. Such sample can be grouped according to origin. • **Solid**: includes soils, sediments, sludges, and other matrices with >15% settleable solids. • **Chemical Waste**: a product or by-product or an industrial process that results in a matrix not previously defined • **Air and Emissions**: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas vapor that are collected with a sorbent tube, impinger solution, filter, or other device.
Matrix Spike (MS)	A sample prepared by adding a known quantity of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the matrix on a method's recovery efficiency. (sometimes referred to as Spiked Sample or Fortified Sample)
Matrix Spike Duplicate (MSD)	A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of precision of the recovery of each analyte. (sometimes referred to as Spiked Sample Duplicate or Fortified Sample Duplicate)
Method Blank	A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures: and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Method Detection Limit (MDL)	One way to establish a Limit of Detection (LOD); defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.
Performance Based Measurement System (PBMS)	An analytical system wherein the data quality needs, mandates or limitations of a program or project are specified and serve as criteria for selecting appropriate test methods to meet those needs in a cost-effective manner.
Precision	The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.
Preservation	Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.
Proficiency Testing	A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.
Protocol	A detailed written procedure for field and/or laboratory operation that must be strictly followed.
Quality Assurance Project Plan (QAPP)	A formal document describing the detailed quality control procedures required by a specific project.
Quality Assurance (QA)	An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Control (QC)	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.
Quality Control Sample	A sample used to assess the performance of all or a portion of the measurement system. QC samples may be Certified Reference Materials, a quality system matrix fortified by spiking, or actual samples fortified by spiking.
Quality Assurance Manual	A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users.
Quality System	A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.
Random Error	The EPA has established that there is a 5% probability that the results obtained for any one analyte will exceed the control limits established for the test due to random error. As the number of compounds measured increases in a given sample, the probability for statistical error also increases.
Raw Data	Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g. tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.
Reagent Grade	Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.
Reference Standard	A standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived.
Reporting Limit (RL)	The level at which method, permit, regulatory and customer-specific objectives are met. The reporting limit may never be lower than the Limit of Detection (i.e. statistically determined MDL). Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified. There must be a sufficient buffer between the Reporting Limit and the MDL.
Representativeness	A quality element related to the ability to collect a sample reflecting the characteristics of the part of the environment to be assessed. Sample representativeness is dependent on the sampling techniques specified in the project work plan.
Sample Delivery Group (SDG)	A unit within a single project that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days. Data from all samples in an SDG are reported concurrently.
Sample Tracking	Procedures employed to record the possession of the samples from the time of sampling until analysis, reporting and archiving. These procedures include the use of a Chain-of-Custody Form that documents the collection, transport, and receipt of compliance samples to the laboratory. In addition, access to the laboratory is limited and controlled to protect the integrity of the samples.
Sensitivity	The capability of a method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.
Standard	A substance or material with properties known with sufficient accuracy to permit its use to evaluate the same property in a sample.

Standard Blank	A calibration standard consisting of the same solvent/reagent matrix used to prepare the calibration standards without the analytes. It is used to construct the calibration curve by establishing instrument background.
Standard Operating Procedure (SOP)	A written document which details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks
Stock Standard	A concentrated reference solution containing one or more analytes prepared in the laboratory using an assayed reference compound or purchased from a reputable commercial source.
Surrogate	A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.
Systems Audit	An on-site inspection or assessment of a laboratory's quality system.
Traceability	The property of a material or measurement result defining its relationship to recognized international or national standards through an unbroken chain of comparisons.
Training Document	A training resource that provides detailed instructions to execute a specific method or job function.
Trip Blank	This blank sample is used to detect sample contamination from the container and preservative during transport and storage of the sample. A cleaned sample container is filled with laboratory reagent water and the blank is stored, shipped, and analyzed with its associated samples.
Uncertainty Measurement	The parameter associated with the result of a measurement that characterized the dispersion of the values that could be reasonably attributed to the measurand (i.e. the concentration of an analyte).
WBT	Web based training
Work Cell	A well defined group of analysts that together perform the method analysis.

11.0 REFERENCES

- "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act." Federal Register, 40 CFR Part 136.
- "Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods." SW-846.
- "Methods for Chemical Analysis of Water and Wastes", EPA 600-4-79-020, 1979 Revised 1983, U.S. EPA.
- U.S. EPA Contract Laboratory Program Statement of Work for Organic Analysis
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- "Standard Methods for the Examination of Water and Wastewater." Current Edition APHA-AWWA-WPCF
- "Annual Book of ASTM Standards", Section 4: Construction, Volume 04.04: Soil and Rock; Building Stones, American Society of Testing and Materials.
- "Annual Book of ASTM Standards", Section 11: Water and Environmental Technology, American Society of Testing and Materials.
- "NIOSH Manual of Analytical Methods", Third Edition, 1984, U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health.
- "Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water", U.S. EPA, Environmental Monitoring and Support Laboratory – Cincinnati (September 1986).
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- Methods for Non-conventional Pesticides Chemicals Analysis of Industrial and Municipal Wastewater, Test Methods, EPA-440/1-83/079C
- Environmental Measurements Laboratory (EML) Procedures Manual, HASL-300, US DOE, February, 1992.
- Requirements for Quality Control of Analytical Data, HAZWRAP, DOE/HWP-65/R1, July, 1990.
- Requirements for Quality Control of Analytical Data for the Environmental Restoration Program, Martin Marietta, ES/ER/TM-16, December, 1992.
- Quality Assurance Manual for Industrial Hygiene Chemistry, AIHA, 1988
- National Environmental Laboratory Accreditation Conference, Constitution, Bylaws, and Standards. Most recent
- ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories.

12.0 REVISIONS

The PASI Corporate Quality and Safety Manager files both a paper copy and electronic version of a Microsoft Word document with tracked changes detailing all revisions made to the previous version of the Quality Assurance Manual. This document is available upon request. All revisions are summarized in the table below.

Document Number	Reason for Change	Date
Quality Assurance Manual Revision 10.0	Throughout the document, Pace was replaced with PASI or in some cases with Pace Analytical. Also, corrections were made to wording, grammar, spelling, and formatting. SECTION 1: • Updated the PASI mission statement • Deleted Financial Responsibility, Drug-Free Workplace, Non-Harassment, Proper and Professional Conduct, Protection of Property, and Communication sections. • Added Assistant General Manager/ Operations Manager, Technical Director, Administrative Business Manager, Project Manager, Project Coordinator, Field Analyst, Laboratory Technician & Field Technician job descriptions • Added detailed Chain of Command to Laboratory Organization section • Updated the Training and Orientation section to reflect current practices • Deleted a portion of the Laboratory Safety section and added a reference to the Safety Manual and Chemical Hygiene Plan. SECTION 2: • Switched the order of Chain of Custody and Sample Acceptance Policy sections • Added details of project review documentation to Project Initiation section • Added steps to sample log in SECTION 3: • Deleted reference to local addenda for companywide SOPs • Rearranged sentences • Added “PASI will not be liable if the customer chooses not to follow PASI recommendations” to the Regulatory and Method Compliance section. SECTION 4: • Added details to the documentation of review or investigation of possible data integrity. • Corrected wording in Method Blank section • Deleted from LCS/LCSD section an out-of-control statement that said affected samples associated with a failing LCS must be re-analyzed SECTION 5: • Added “Electronic documents must be readily accessible to all facility employees” to Documents Management section • Updated the Standard Operating Procedure section to describe the new PASI corporate SOP Templates and distribution. SECTION 6: • Re-organized & re-named sections • Updated the interpretation of the Calibration Verification policy • Added clarification to the definition of the Second Source Standard • Revised Single Point Calibration procedure to address NELAC requirement • Incorporated Spare Parts into Instrument/ Equipment Maintenance SECTION 7:	20Jun2006

Document Number	Reason for Change	Date
	• Updated Analytical Results Processing section to clarify data documentation policy. • Deleted "All data that are manually entered into the LIMS is reviewed at a rate of 100%" and deleted the use of checklists statement from Data Verification section • Integrated paragraphs for better flow • Deleted item # 15, "If required, a statement of the estimated uncertainty of the test results." from the Data Reporting section • Added Data Security section to describe PASI data security practices • Added fire, flood, and vermin protection requirement to Data Archiving section • Added statement to Data Archiving section describing that NELAP related records are available to accrediting authorities. • Added Data Disposal section SECTION 8: • Deleted first paragraph stating that Pace labs are subject to internal and external audits and reviews. • Added description of PASI internal audit program and investigations • Added requirement that corrective action be taken and customer notified within 3 days if audit findings show that test results may have been affected • Updated requirement for manager(s)/supervisor(s) to respond to audit findings with a plan to correct all deficiencies within 14 days. Statement included that allows Quality Manager to grant additional time for response. • Added to Annual Managerial Review section that "The laboratory shall ensure that any actions identified during the review are carried out within an appropriate and agreed timescale." SECTION 9: • Added documentation requirement for reporting discovery of deficiency or non-conformance, must be documented "on the Non-Conformance Corrective/ Preventative Action report and/or QA Trak." • Added "Preventative actions must be taken in order to prevent or minimize the occurrence of the situation." • Added a paragraph to describe the new PASI Root Cause Analysis procedure. SECTION 10: • Added the following definitions: Contract Required Detection Limit (CRDL), Contract Required Quantitation Limit (CRQL), Corrective and Preventative Action (CAPA), Non Potable Water (to Environmental Sample definition), Intermediate Standard Solution, Quality Control Sample, Stock Standard, Uncertainty Measurement, Working Standard Solution, SECTION 11: • Added ISO/IEC 17025:2005 reference Appendix: • Added Appendix I: Quality Control Calculations	
Quality Assurance Manual Revision 11.0	Overall conversion to template format. Removed all references to Addenda. Changes required based on conversion are not explicitly noted unless change represents a significant policy change. SECTION 1: • Add comment to address continuous improvement to quality system. • Changed statement of purpose in Section header to "Mission Statement". • Added requirements for appointment when Technical Director absent.	17Sep2007

Document Number	Reason for Change	Date
	• Added requirements for notification to AA's and updates to organizational charts when management changes. • Added Client Services Manager job description. SECTION 2: • Changed temperature requirements to "Not Frozen but ≤6°C". • Added flexible section concerning default sampling time in absence of customer-specified time. • Added flexible section to address sample and container identification by the LIMS. • Changed sample retention requirement to 45 days from receipt of samples. Added comment allowing for storage outside of temperature controlled conditions. SECTION 3: • Inserted allowance for use of older methods. • Changed references to work processing and training documents to allow for use of LMS and other types of training media. • Inserted allowance for alternative DOCs where spiking not possible. SECTION 4: • Inserted reference to Anonymous Message line. • Inserted reference to the use of default control limits. • Inserted allowance for release of data without corrective action for obvious matrix interferences. • Inserted reference to the treatment of internal standards. • Inserted allowance for use of MDL annual MDL verification in lieu of full 40 CFR Part 136 annual MDL studies. • Inserted general procedure for LOQ verification SECTION 5: • Added general process for approval and use of QAM template. • Removed specific reference of Work Process Manuals. Left flexible section to include all other controlled documentation. SECTION 6: • No changes noted. SECTION 7: • Added qualifications for secondary reviewers. SECTION 8: • Changed frequency listing for Corporate Audits. SECTION 9: • Changed references from QA Track to Lab Track – left flexible to accommodate information still in QA Track. SECTION 10: • No changes noted. SECTION 11: • No changes noted. ATTACHMENTS: • Standardized format for Attachments.	
Quality Assurance Manual Revision 12.0	General: replaced the word 'client' with 'customer', where applicable. SECTION 1: • Section 1.6.4: added language for clarity	13Nov2008

Document Number	Reason for Change	Date
	• Added new section 1.8.1; responsibilities of General Managers. • Section 1.8.2: added reference to LMS. • Added new section 1.8.15: responsibilities of Waste Coordinators. • Section 1.9, last paragraph: changed 'annually' to 'periodically'. Next to last paragraph- added reference to LMS. SECTION 2: • Added new section 2.2 entitled Field Services. • Section 2.3: added reference to the new Review of Analytical Requests SOP. • Changed optional text in 2.6 to explain how EpicPro assigns unique ID # to projects and samples including the unique container ID • Section 2.7.2: changed freezer temp requirement to match SOP. SECTION 3: • Section 3.4: Included optional language for performing IDOCs for tests not amenable to spiking using the "4 replicate" approach. SECTION 4: • Section 4.1: expanded language to allow electronic signature and storing of integrity training documentation within the LMS • Section 4.10: revised and added language regarding LOD studies, initial verification and annual verification, where applicable. • Section 4.11: changed PRL to RL. • Section 4.13: added editable line regarding PT study information. Changed wording to say approved PT providers are utilized • Section 4.14: added sentence regarding rounding rules listed applying only to LIMS. SECTION 5: • Section 5.1, last bullet point: changed language to reflect that SOPs must be locked from printing if controlled electronically. SECTION 6: • Section 6.3.1: adjusted language about classes of weights potentially used. • Section 6.3.3: removed customer-specific requirement to re-calibrate every four hours but added space for this to be added back in where applicable. • Added reference to Attachment III in the introductory paragraph to this section. SECTION 7: • Sections 7.1-7.3: added language for those labs that are minimizing or eliminating the need for paper copies. • Section 7.2: clarified language in numbered items so that it does not appear that all 4 criteria must be applicable at one time. • Section 7.3: added list of approved signatories for final reports. SECTION 8: • Section 8.1.2, last paragraph: revised language regarding data integrity issues and added a timeframe to notify customers of affected data. • Added section 8.5 "Customer Service Reviews"- ISO requirement SECTION 9: • Added new section 9.3 regarding Preventive Action. SECTION 10: • No revisions. SECTION 11:	

Document Number	Reason for Change	Date
	• No revisions. Attachments: • Attachment IIb: updated corporate org chart • Attachment III: Added Montana equipment to list • Attachment IV: Added Montana Division floor plan • Attachment VI: Added Montana Division certification information • Attachment VIII: revised to match the current Analytical Guides.	
Quality Manual Revision 12.1	Local revisions made per A2LA Audit Clarified sample preservation chart, updated the Program Director/Hazardous Coordinator title in section 1; updated SOP references, updated B.Pike's extension. 2.6 Corrected the default sample collection time to 00:00 4.3 Added DoD LCS criteria 4.11 Added LOQ/LOD criteria 5.1.2 Added annual review criteria for SOPs 8.1.3 Corrected the notification period to 30 days Added the definition of Work Cell to the definitions section Added additional SOPs Added list of NELAC Accredited methods	08Jul2009

ATTACHMENT I

Quality Control Calculations

PERCENT RECOVERY (%REC)

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

NOTE: The SampleConc is zero (0) for theLCS and Surrogate Calculations

PERCENT DIFFERENCE (%D)

$$\%D = \frac{MeasuredValue - TrueValue}{TrueValue} * 100$$

where:
TrueValue = Amount spiked (can also be the $\overline{CF}$ or $\overline{RF}$ of the ICAL Standards)
Measured Value = Amount measured (can also be the CF or RF of the CCV)

PERCENT DRIFT

$$\%Drift = \frac{CalculatedConcentration - TheoreticalConcentration}{TheoreticalConcentrtion} * 100$$

RELATIVE PERCENT DIFFERENCE (RPD)

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

where:
R1 = Result Sample 1
R2 = Result Sample 2

CORRELATION COEFFICIENT (R)

$$CorrCoeff = \frac{\sum_{i=1}^{N} W_i * (X_i - \overline{X}) * (Y_i - \overline{Y})}{\sqrt{\left(\sum_{i=1}^{N} W_i * (X_i - \overline{X})^2\right) * \left(\sum_{i=1}^{N} W_i * (Y_i - \overline{Y})^2\right)}}$$

With:	N	Number of standard samples involved in the calibration
	i	Index for standard samples
	Wi	Weight factor of the standard sample no. i
	Xi	X-value of the standard sample no. i
	X(bar)	Average value of all x-values
	Yi	Y-value of the standard sample no. i
	Y(bar)	Average value of all y-values

ATTACHMENT I (CONTINUED)

Quality Control Calculations (continued)

STANDARD DEVIATION (S)

$$S = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{(n-1)}}$$

where:
n = number of data points
X_i = individual data point
$\overline{X}$ = average of all data points

AVERAGE ($\overline{X}$)

$$\overline{X} = \frac{\sum_{n=1}^{i} X_i}{n}$$

where:
n = number of data points
X_i = individual data point

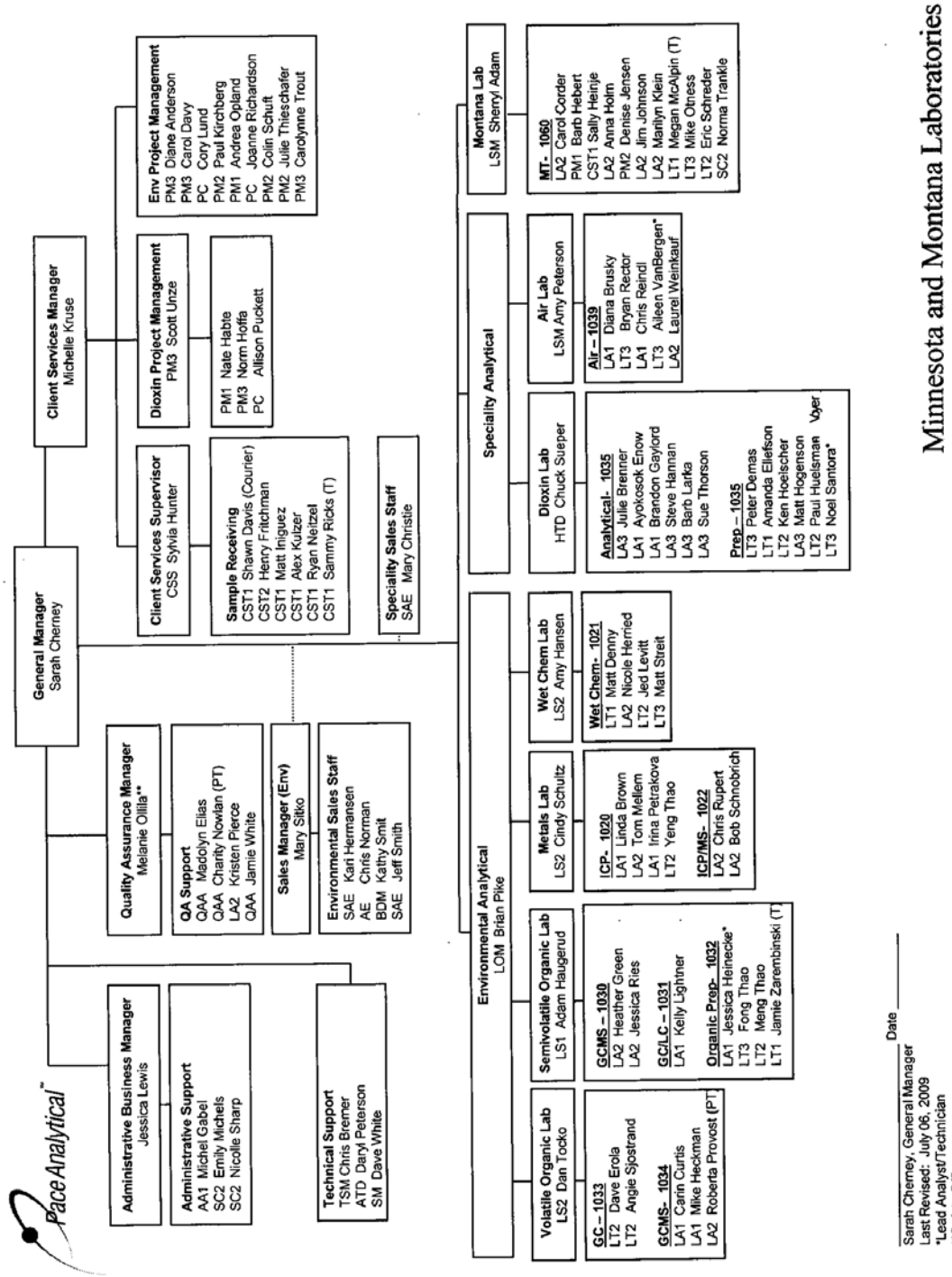
RELATIVE STANDARD DEVIATION (RSD)

$$RSD = \frac{S}{\overline{X}} * 100$$

where:
S = Standard Deviation of the data points
$\overline{X}$ = average of all data points

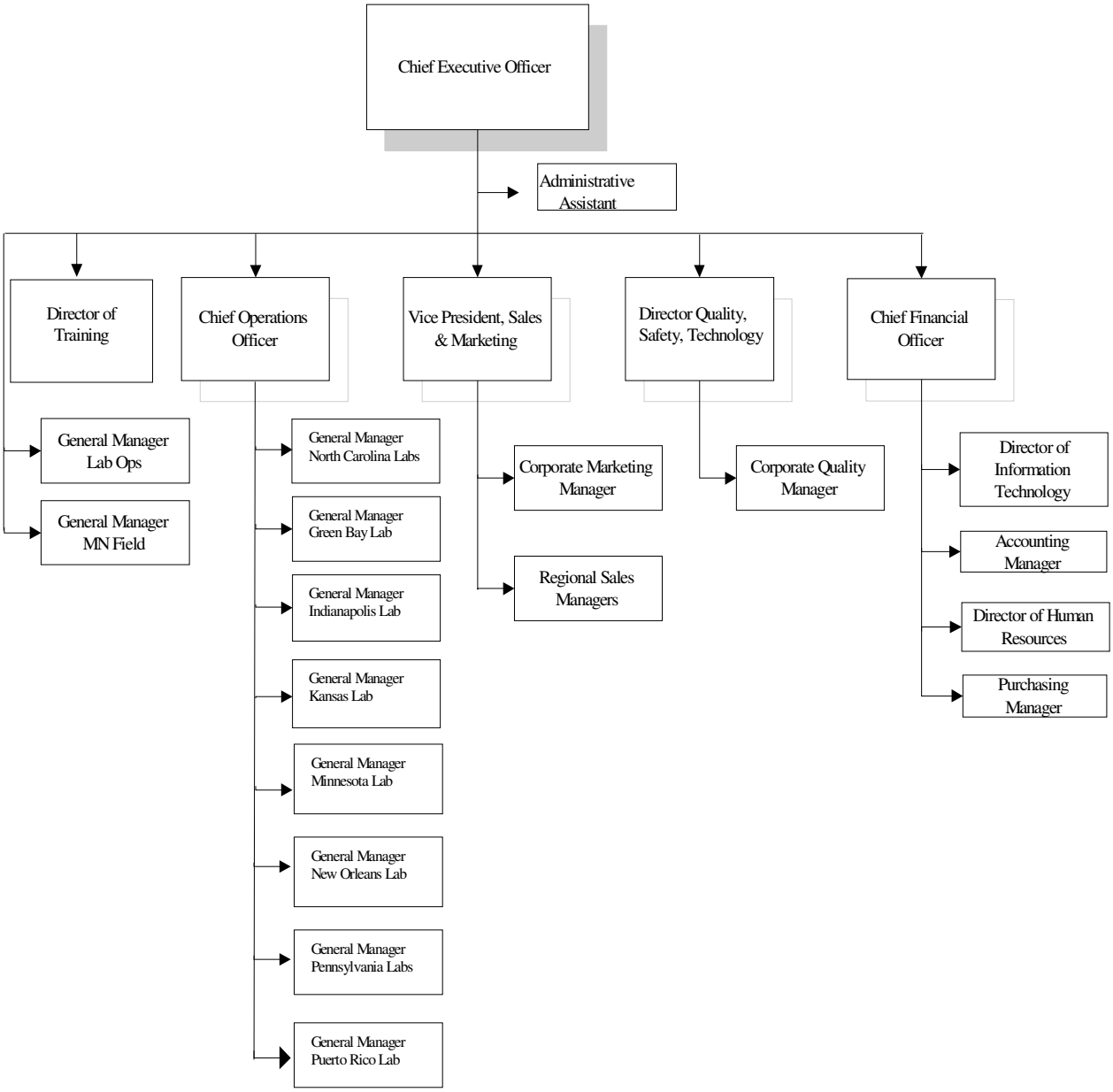
ATTACHMENT IIA

PASI – MINNESOTA ORGANIZATIONAL CHART



ATTACHMENT IIB

PASI – CORPORATE ORGANIZATIONAL CHART



ATTACHMENT III

PASI – MINNESOTA EQUIPMENT LIST

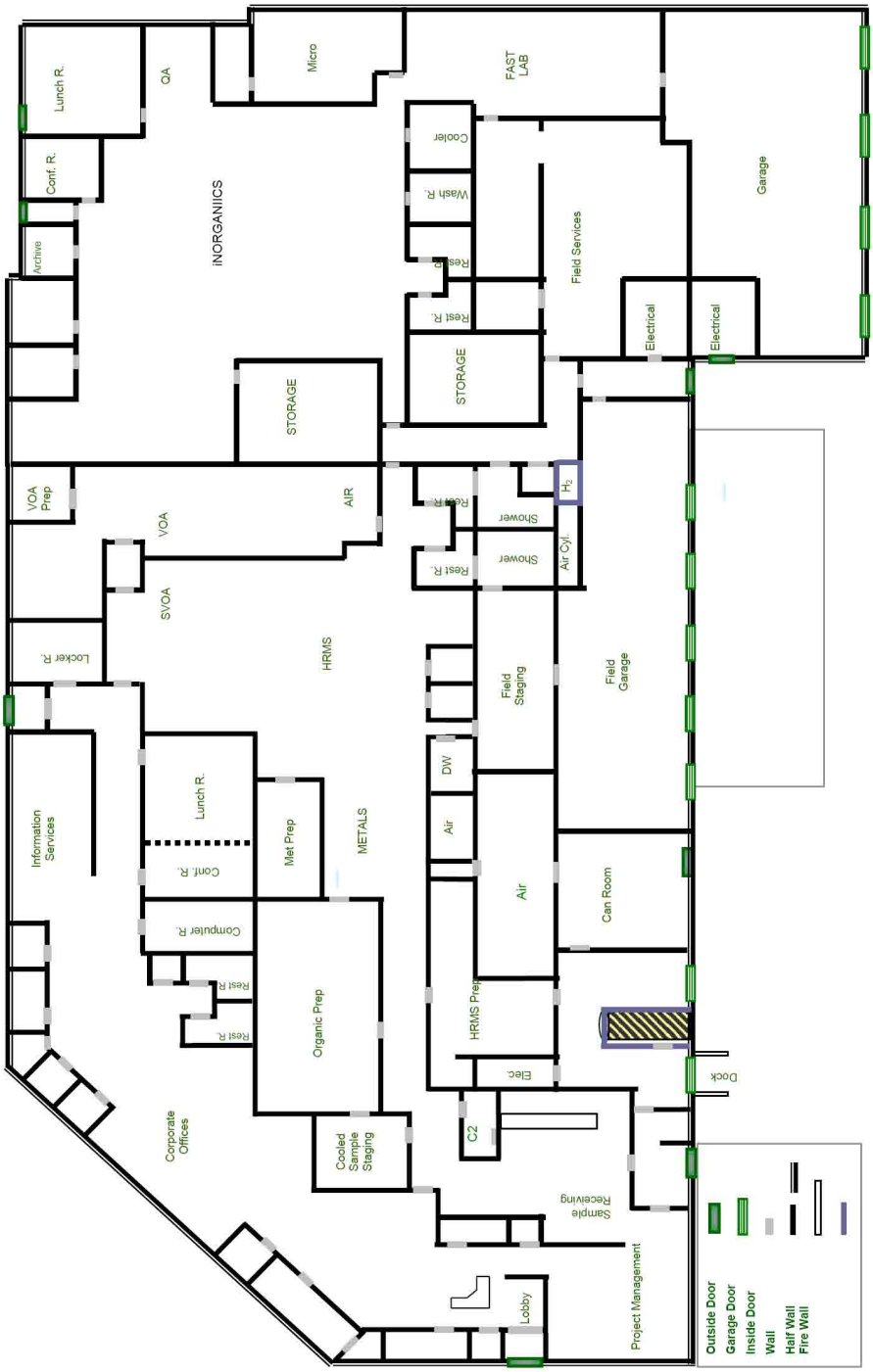
INSTRUMENT	MANUFACTURER	MODEL NUMBER	DETECTOR(S)	ANALYSIS
GC/MS/VOA	Hewlett-Packard	5890	PID/FID	TO3/AIR
GC/MS/VOA	Agilent	6890/5973	MS	TO14/TO15
GC/MS/VOA	Hewlett-Packard	5890/5972	MS	TO14/TO15
GC/MS/VOA	Hewlett-Packard	6890 / 5973	MS	SW8260
GC/MS/VOA	Hewlett-Packard	6890 / 5973	MS	SW8260
GC/MS/VOA	Hewlett-Packard	6890 / 5973	MS	SW8260
GC/MS/VOA	Agilent	6890 / 5973	`	SW8260
GC/MS/VOA	Hewlett-Packard	6890 / 5973	MS	SW8260
GC/MS/VOA	Agilent	6890/5973	MS	524.2
GC/MS/VOA	Agilent	6890/5973	MS	TO14/TO15
GC/MS/VOA	Hewlett-Packard	5890/5971	MS	SW8260
GC/MS/SMVOA	Hewlett-Packard	5890 / 5972	MS	BNA
GC/MS/SMVOA	Hewlett-Packard	6890/5973	MS	SIM,agList, cPAH
GC/MS/SMVOA	Hewlett-Packard	5890		8270 SIM
GC/MS/SMVOA	Agilent	6890/5973	MS	SIM,agList, cPAH
GC/MS/SMVOA	Agilent	6890/5973	MS	PCDD/PCDF
GC/MS/SMVOA	Agilent	6890/5973	MS	BNA
GC PETROLEUM RELATED VOLATILES	Hewlett-Packard	5890	PID/FID	BTEX
GC PETROLEUM RELATED VOLATILES	Hewlett-Packard	5890	PID/FID	BTEX
GC PETROLEUM RELATED VOLATILES	Hewlett-Packard	5890	PID/FID	TO3/AIR
GC PETROLEUM RELATED VOLATILES	Agilent	6890/1888	TCD/FID	Headspace
GC PETROLEUM RELATED VOLATILES	Hewlett-Packard	5890	TCD/FID	Fixed Gases
GC PETROLEUM RELATED VOLATILES	Hewlett-Packard	5890	PID/FID	VPH
GC PETROLEUM RELATED VOLATILES	Hewlett-Packard	5890	PID/FID	VPH
GC PETROLEUM RELATED SMVOA	Hewlett-Packard	5890	FID	DRO
GC PETROLEUM RELATED SMVOA	Hewlett-Packard	5890	FID	EPH
GC SMVOA	Hewlett-Packard	5890	DUAL ECD	PCB
GC SMVOA	Hewlett-Packard	6890	DUAL ECD	Pest/PCB
GC SMVOA	Hewlett-Packard	6890	FID	DRO

ICP	Perkin-Elmer	Optima 3300DV	SCCD	Metals
ICP	Perkin-Elmer	Optima 4300DV	SCCD	Metals
ICP/MS	Perkin-Elmer	ELAN9000	MS	Metals
MERCURY ANALYZER	Perkin-Elmer	FIMS 100	Spectrometer	Mercury
AUTO ANALYZER	Konelab	20	Spectrometer	Anions
ION CHROMATOGRAPH	Dionex	ICS-1000	NA	Anions
OVEN	Tempcon	N8620-10	NA	Preparation
OVEN	Lab Line	Imperial II	NA	Preparation
OVEN	Despatch	NA	NA	AIR
OVEN	VWR	1370F	NA	General
OVEN	Precision	STM135	NA	General
OVEN	Thelco	130DM	NA	General
OVEN	Baxter	DK63	NA	HRMS
OVEN	Fisher Scientific	650G	NA	% moisture
OVEN	Fisher Scientific	550-126	NA	General
OVEN	Fisher Isotemp Oven	255D	NA	General
OVEN	Precision	511135	NA	General
INCUBATOR	Fisher Scientific	307	NA	BOD
INCUBATOR	VWR	2020	NA	BOD
TURBIDITY	HF Scientific	Micro 100	NA	Turbidity
TURBIDITY	HF Scientific	Micro 100	NA	Turbidity
TURBIDITY	AF Scientific, In.	Micro 1000	NA	Turbidity
TURBIDITY	HF Instruments	PRT100	NA	Turbidity
AUTOCLAVE	Heinicke Co.	Sterilquick	NA	Autoclave
AUTOCLAVE	Market Forge	Sterilmatic	NA	Autoclave
CENTRIFUGE	Becton Dickenson	CompactII	NA	HRMS
HIGH RESOLUTION MASS SPECTROMETER	MicroMass	Ultimas	MS	PCDD/PCDF
HIGH RESOLUTION MASS SPECTROMETER	MicroMass	Ultimas	MS	PCDD/PCDF
HIGH RESOLUTION MASS SPECTROMETER	MicroMass	Premiere	MS	PCDD/PCDF
HIGH RESOLUTION MASS SPECTROMETER	ThermoScientific	Trace GC Ultra/DFS	MS	PCDD/PCDF
HIGH RESOLUTION MASS SPECTROMETER	ThermoScientific	Trace GC Ultra/DFS	MS	PCDD/PCDF
DISSOLVED OXYGEN METER	YSI	5000	NA	BOD
ION ANALYZER	Orion	EA 940	NA	pH
ION ANALYZER	Orion	EA 940	NA	fluoride, pH
pH METER	Orion	290A	NA	pH
pH METER	Accumer Research	AR50	NA	pH
pH METER	Orion	420A	NA	pH

CONDUCTIVITY METER	Oakton	RS232/CON 110	Probe - 1D7	specific conductivity
COD REACTOR	Bioscience		NA	COD
MICROWAVE EXTRACTION UNIT	Milestone	Ethos E	NA	Dioxin
MIDI DISTILLATION UNIT	Env. Express	Pace # 19582		CN, NH3, phenols
MIDI DISTILLATION UNIT	Env. Express	Pace # 19604		CN, NH3, phenols
METALS MICROWAVE DIGESTOR	CEM Corporation	MDS-2100	NA	Metals Dig
METALS HOT BLOCK	Env. Express	SC 154	NA	Metals Dig
METALS HOT BLOCK	Env. Express	SC 154	NA	Metals Dig
METALS HOT BLOCK	Env. Express	SC 154	NA	Metals Dig
SONICATOR	Misonix	XL 2020	NA	3550
SONICATOR	Misonix	XL 2015	NA	3550
SONICATOR	Misonix	3000		3550
SONICATOR	Misonix	3000		3550
DENVER MAXX BALANCE	Denver Instrumentation	MXX-212	NA	NA
A&D BALANCE	A&D	FX 3200		Soil Prep
BALANCE	A&D	FX 4000	NA	
BALANCE	Mettler	AJ100	NA	
BALANCE	A&D	FX-3200	NA	
BALANCE	Mettler	AE100	NA	
BALANCE	Fisher Scientific	A-200DS	NA	
BALANCE	OHAUS	Adventurer	NA	
BALANCE	Fisher Scientific	7224DA	NA	
BALANCE	OHAUS	Explorer Pro EP114C	NA	
BALANCE	Mehler	AE100	NA	
MilliQ Purification System	MilliQ	MilliQUV plus	NA	
MICROSCOPE	Olympus	BH-2	NA	Asbestos
MICROSCOPE	Olympus	BH-2	NA	Asbestos
MICROSCOPE	Olympus	BH-2	NA	Asbestos

ATTACHMENT IV

PASI – MINNESOTA



ATTACHMENT IV CONT.
PASI-MONTANA DIVISION

ATTACHMENT V

PASI – MINNESOTA SOP LIST

SOP Title	SOP Number
Determination of Methane, Ethane, and Ethene in Air Modified TO-3	S-MN-A-002
Analysis of Air Samples for Volatile Organic Compounds by Gas Chromatography/PID-FID method TO-3	S-MN-A-003
Cleaning, Certification, Leak Checking and Preparation for Shipment of SUMMA Passivated Canisters	S-MN-A-004
Determination of Fixed Gases in Air by Modified 3C	S-MN-A-005
Methane, Ethane, Ethene, and Propane in Water by GCFID mod. 3810 and RSK 175	S-MN-A-007
Sample Preparation and Analysis of Polychlorinated Biphenyls (PCBs) in Ambient Air using High Volume Polyurethane Foam	S-MN-A-010
Analysis of Whole Air Sample for Volatile Organic Compound by GC/MS EPA TO15/TO14	S-MN-A-013
Operation and Maintenance of the Perkin Elmer ELAN 6000 ICP-MS	S-MN-I-525
Sample Management	S-MN-C-001
Bottle Order Database	S-All-C-002
Bottle Preparation	S-MN-C-003
Internal Chain of Custody	S-MN-C-005
Subcontracting Samples	S-MN-C-004
Preparing Waste for Shipment	S-MN-C-703
Preparation and Analysis of Samples for the Determination of Dioxins and Furans by USEPA Method 8290	S-MN-H-001
Preparation and Analysis of Samples for the Determination of Dioxins and Furans using USEPA Method 1613B	S-MN-H-002
Preparation and Analysis of Samples for the Determination of 2,3,7,8-TCDD using USEPA Method 1613B, Drinking Water	S-MN-H-003
Percent Lipids Determination	S-MN-H-004
Preparation and Analysis of Samples for the Determination of PCDDs, PCDFs, and PCBs by modified USEPA Method 23, TO9, or NY State Guidelines	S-MN-H-005
Preparation and Analysis of Samples for the Determination of Dioxins and Furans by USEPA Method 8280	S-MN-H-007
Method 1668, PCB Congener (WHO List)	S-MN-H-009
Preparation and Analysis of Samples for the Determination of Chlorinated Biphenyl Congeners by USEPA Method 1668A	S-MN-H-014
Preparation and Analysis of Samples for the Determination of Polybrominated Diphenyl Ether Congeners	S-MN-H-016
RapidScreen Analysis of Samples for PCDDs and PCDFs	S-MN-H-017
Preparation and Analysis of Samples for the Determination of Dioxins and Furans by USEPA Method 8290A	S-MN-H-019
Preparation and Analysis of Samples for the Determination of Pesticides by USEPA Method 1699	S-MN-H-020
Preparation and Analysis of Samples for the Determination of Dioxin and Furans by USEPA Method DLM2.0	S-MN-H-021
TCLP/SPLP	S-MN-I-312
Inductively Coupled Plasma Atomic Emission Spectroscopy (RCRA)	S-MN-I-313
Water Extraction of Soil	S-MN-I-334
Hardness by Calculation	S-MN-I-338
Biochemical Oxygen Demand (BOD)	S-MN-I-348
COD-Titrimetric, Low Level	S-MN-I-351
Phenols	S-MN-I-354

SOP Title	SOP Number
Oil & Grease - 1664	S-MN-I-357
Hexavalent Chromium in Water, Wastewater, and Soil	S-MN-I-358
Mercury in Liquid and Solid/Semis-Solid Waste	S-MN-I-359
Alkalinity, Titrimetric	S-MN-I-365
Total Cyanide in Water	S-MN-I-366
Percent Solids (Moisture)	S-MN-I-367
Digest Procedure for Aqueous Samples to be Analyzed by Induct Coupled Plasma (SW-846)	S-MN-I-458
Metals Preparation for Solid samples, Wipes and Filters	S-MN-I-460
Fluoride in Water and Wastewater	S-MN-I-470
Chemical Oxygen Demand (COD) in Water, Wastewaters and Industrial Wastes	S-MN-I-472
Total Phosphorus in Water	S-MN-I-473
Specific Conductivity	S-MN-I-474
Total Cyanide in Soil	S-MN-I-476
Ortho Phosphorus	S-MN-I-477
Particulate Matter (PM10) (Method 5) in the Atmosphere	S-MN-I-484
Settleable Solids	S-MN-I-486
Analysis of Air Samples by EPA Method 29	S-MN-I-487
Metals Analysis by ICP/MS - Method 6020 and 200.8	S-MN-I-492
Standard Test Method for Screening Apparent Specific Gravity and Bulk Density Waste	S-MN-I-493
Determination of Total Recoverable Phenolics by Flow Injection Colorimetry	S-MN-I-494
Operation and Maintenance of the MDS-2100 Microwave	S-MN-I-499
Turbidity in Water	S-MN-I-501
Chlorine, Total Residual in Water	S-MN-I-502
Use and Maintenance of the Konelab	S-MN-I-507
Determination of Nitrate/Nitrite in surface and wastewaters by Flow Injection Analysis with the Konelab (Low Flow Method)	S-MN-I-508
Determination of Chloride by Konelab	S-MN-I-509
Determination of Sulfate by Konelab	S-MN-I-510
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Amenable Cyanide and Weak Dissociable Cyanide in Water	S-MN-I-515
Paint Filter Liquids Test	S-MN-I-516
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Gravimetric Determination of Oil and Grease by SPE	S-MN-I-520
Cyanide Extraction Procedure for Solids and Oils	S-MN-I-522
Preparation of Aqueous Samples for ICPMS Analysis by Method 3030C	S-MN-I-523
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Determination of TSP and PM 10	S-MN-I-527
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Total CN in Water - Macro Distillation	S-MN-I-529
Weak Acid Disociable Cyanide in Water - Macro Distillation	S-MN-I-530
Operation of the DEENA automated Prep System	S-MN-I-531
Determination of Inorganic Anions by Ion Chromatography	S-MN-I-532
Quality Control Recordkeeping for Bulk Asbestos Analysis	S-MN-I-533
Bulk Analysis Using Polarized Light Microscopy	S-MN-I-534

SOP Title	SOP Number
Microscope Adjustment – Phase Contrast	S-MN-I-535
Microscope Alignment	S-MN-I-536
Fiber Counts by NIOSH 7400 Using Excel Spreadsheet	S-MN-I-537
Permanent Mounting Fiber Count Reference & Quality Control Sample Preparation	S-MN-I-538
System Security and Integrity	S-ALL-IT-001
Back Up Policy	S-ALL-IT-002
Data Archiving	S-MN-L-106
Reagent Water Quality	S-MN-L-110
Generation of EDD	S-MN-L-112
Preventative, routine, and non-routine maintenance	S-MN-L-114
Receipt and Storage of Laboratory Supplies	S-MN-L-117
Common Laboratory Calculations and Statistical Evaluation of Data	S-MN-L-125
Data Reduction, Validation, and Reporting in the Env Lab	S-MN-L-132
Out of Specification Investigation	S-MN-L-133
Syringe Technique	S-MN-L-139
Procedure for Handling Aqueous Organic Extractable Samples Containing Sediment	S-MN-L-142
Purchasing Laboratory Supplies	S-MN-L-143
Total Coliform Bacteria	S-MN-MB-001
Fecal Coliform by MF	S-MN-MB-002
Heterotrophic Plate Count	S-MN-MB-003
Total Coliform Bacteria by MF	S-MN-MB-005
Sample Container Sterility Verification	S-MN-MB-006
Method For Sonicator Tuning	S-MN-O-414
The Determination of Specific Aromatic Compounds and Gasoline Range Organic in Water	S-MN-O-427
Analysis of Polychlorinated Biphenyls in Oil, Soil, Water, Wipe and Air Matrixes	S-MN-O-432
Extractable Base/Neutral and Acid Organic Compounds in Liquid, Solid, and TCLP Matrices by Gas Chromatography/Mass Spectrometry Capillary Column Technique	S-MN-O-436
Cleaning Glassware in the Organic Laboratory	S-MN-O-465
Determination of Diesel Range Organics in Water (Wisconsin modified DRO)	S-MN-O-466
Determination of Diesel Range Organics in Soil (Wisconsin modified DRO)	S-MN-O-467
The Determination of Specific Aromatic Compounds and Gasoline Range Organics in Soil	S-MN-O-487
Determination of Diesel Range Organics In Water & Soil SW8015 (Modified)	S-MN-O-489
Determination of Acid Cleanup of PCB Extracts	S-MN-O-494
Sonication Extraction Technique (SW3550) for Base/Neutral and Acid Compounds	S-MN-O-495
Continuous Liquid-Liquid Extraction (SW3520) for Base/Neutral and Acid Compounds	S-MN-O-496
Spike Verification in the Organic Prep Lab	S-MN-O-497
Preparation of Anhydrous Sodium Sulfate for Extraction Purposes	S-MN-O-500
Nitrogen Evaporation Technique	S-MN-O-503
Sample Concentration Technique	S-MN-O-504
Continuous Liquid-Liquid Extraction (SW3520) for Polyaromatic Hydrocarbons by 8270-SIM	S-MN-O-506
8270-L Extractable Base/Neutral and Acid Organic Compounds in Water and Liquid Matrices by GC/MS Capillary Column Technique w/Selective Ion Monitoring	S-MN-O-507
Solvent Exchange into Hexane	S-MN-O-509
Sample Conversion to Acetonitrile	S-MN-O-510
Analysis of Volatile Organic Compounds by GC/MS Method 8260	S-MN-O-521
Purgeable Total Petroleum Hydrocarbons in Water (8015 Mod / CA LUFT/ NWTPH/OA-1)	S-MN-O-525
Copper Cleanup Procedure for Pesticides and Polychlorinated Biphenyls	S-MN-O-527
Analysis of Volatile Organic Compounds by GC/MS Method 624	S-MN-O-529

SOP Title	SOP Number
Extractable Base/Neutral and Acid Organic Compounds in Liquid by EPA Method 625	S-MN-O-532
Ethylene glycol, Propylene Glycol, Triethylene Glycol by Modified 8015	S-MN-O-533
Analysis of Air samples by GC/MS - Method TO-13	S-MN-O-534
Continuous Liq/Liq extraction for Method 8270C (Dual pH) by SW 3520C	S-MN-O-539
Soxhlet Extraction for PAH Analysis by GC/MS:SIM	S-MN-O-540
Volatiles Sample Compositing Procedure	S-MN-O-541
Analysis of Volatile Organic Compounds in Water Method 524.2	S-MN-O-546
The Determination of Extractable Petroleum Hydrocarbons by Method NwTPH-Dx	S-MN-O-553
The Determination of Diesel Range Organics and Residual Range Organics by AK102-AK103	S-MN-O-554
Purgeable Total Petroleum Hydrocarbons in Water (NWTPH)	S-MN-O-555
Determination of Gasoline Range Organices by Method AK101	S-MN-O-556
DrieRite Regeneration Procedure	S-MN-O-557
Analysis of 1,4 Dioxane by Selective Ion Monitoring (SIM) GC/MS SW846 Method 8260B Modified	S-MN-O-558
The Determination of Volatile Petroleum Hydrocarbons by Method MA-VPH	S-MN-O-559
The Determination of Extractable Petroleum Hydrocarbons by Method MA-EPH	S-MN-O-560
Determination of Parent and Alkylated PAH Compounds in Solid and Liquid Matrices by GC/MS SIM	S-MN-O-561
Sample Management	S-MN-C-001
Bottle Preparation	S-MN-C-003
Internal Chain of Custody	S-MN-C-005
Subcontracting Samples	S-MN-C-004
Preparation of SOPs	S-ALL-Q-001
Document Management	S-ALL-Q-002
Document Numbering	S-ALL-Q-003
Method and Instrument Detection Limit Studies	S-ALL-Q-004
Laboratory Documentation	S-ALL-Q-009
Performance Evaluation (PE)/Proficiency Testing (PT) Program	S-ALL-Q-010
Audits and Inspection	S-ALL-Q-011
Corrective Action/ Preventative Action Process	S-ALL-Q-012
Support Equipment	S-ALL-Q-013
Quality System Review	S-ALL-Q-014
Manual Integrations	S-MN-Q-214
Subcontracting Samples	S-ALL-Q-017
Monitoring Storage Units	S-ALL-Q-018
Training Procedures	S-ALL-Q-020
Sub-Sampling (Sample Homogenization)	S-ALL-Q-021
3P Program: CIP	S-ALL-Q-022
Standard and Reagent Preparation and Traceability	S-ALL-Q-025
Software Validation	S-All-Q-026
Use and Operation of Lab Track System	S-ALL-Q-028
Mint Miner Data File Review	S-All-Q-029
Operation of Data Checker For Epic Pro	S-All-Q-030
MCL Violation Reporting	S-All-Q-033
Precision and Accuracy Measurement, Evaluation, and Trend Assessment	S-MN-Q-205
Control of Hazardous Energy Program - Lockout/Tagout	S-MN-Q-249
Method Validation and Modification Studies	S-MN-Q-252
Procedure for Handling of USDA regulated soils	S-MN-Q-253
Laboratory Spreadsheet Validation	S-MN-Q-254

SOP Title	SOP Number
Estimation of Measurement Uncertainty	S-MN-Q-255
Continuous Electronic Temperature Monitoring	S-MN-Q-256
Method of Change	S-MN-Q-257
Evaluation and Qualification of Vendors	S-MN-Q-259
Use of A2LA Terms and Symbols	S-MN-Q-260
Hazard Assessments	S-ALL-S-001
Waste Handling	S-ALL-S-002

ATTACHMENT VI

PASI – MINNESOTA NELAC ACCREDITED METHODS

Drinking Water Methods

EPA 524.2	SM 4500 Cl-E	SM 4500 F-C	EPA 180.1
EPA 1613B	SM 4500 CN-E	SM 4500 H+-B	EPA 120.1
ASTM D516-02	SM 4500 CN-G	SM 4500 NO2-B	SM 2340B
EPA 200.8	SM 2320B	SM 4500 P-E	

Non-Potable Water

CA-LUFT	EPA 120.1	SM 2320B	SM 3500 Cr-D
EPA 1613B	EPA 160.4	SM 2340B	SM 4500 Cl-E
EPA 1668	EPA 180.1	SM 2540 B	SM 4500 CN-E
EPA 624	EPA 350.1	SM 2540 C	SM 4500 CN-G
EPA 625	EPA 410.4	SM 2540 D	SM 4500 F-C
EPA 8015	EPA 420.1	SM 2540 E	SM 4500 H+-B
EPA 8021	EPA 420.4	SM 2540 F	SM 4500 NO2-B
EPA 8082	EPA 7196	SM 5220C	SM 4500 NO3-H
EPA 8260	EPA 1664A	SM 5220D	SM 4500 P-E
EPA 8270	EPA 9012	SM 5210B	ASTM D516-02
EPA 8280	EPA 200.7	EPA 6010	
EPA 8290	EPA 200.8	EPA 6020	
WiDRO	EPA 245.1	EPA 7470	
WiGRO			

Solid/Chemical Materials

EPA 8015	EPA 1613B	EPA 1311	EPA 9012
EPA 8021	EPA 1668	EPA 1312	EPA 9045
EPA 8082	WiDRO	EPA 6010	EPA 7196
EPA 8260	WiGRO	EPA 6020	EPA 9071
EPA 8270	CA-LUFT	EPA 7471	
EPA 8280			
EPA 8290			

Biological Tissues

EPA 8290	EPA 1613B	EPA 1668A

Air and Emissions

EPA TO3	EPA TO9A	EPA TO14A	RSK-175
EPA TO4A	EPA TO13A	EPA TO15	

ATTACHMENT VII

PASI – MINNESOTA CERTIFICATION LIST

State	Agency	Program	Cert #
Alabama	Dept of Environmental Mgmt	Dioxin-DW	40770
Alaska	Dept. of Environmental Conservation	Contaminated Sites (6010B, 6020, 8260B, PCBs, PAHs)	UST-078
Alaska	Dept. of Environmental Conservation	Dioxin-DW	MN64-07
Arizona	Dept of Health Services	Dioxin-DW, WW, HW	AZ0014
Arkansas	Dept of Environmental Quality	Dioxins	88-0680
California	Dept of Health Services	Dioxin-DW, WW, HW Envir-DW, WW, HW	01155CA
Colorado	Dept. of Public Health & Environment	Dioxin-DW	Pace Analytical
Connecticut	Dept of Public Health	Dioxins	PH-0256
Delaware	Health & Solical Services	Dioxin-DW	
EPA Region 5	Water Division	Dioxin-DW	WD-15J
EPA Region 8	Water Division	Dioxin-DW Enviro – DW *	8TMS-Q
Florida (NELAP)	Dept of Health Services	Diox-DW, WW, HW, Air Envir-DW, WW, HW, Air	E87605
Georgia	Environmental Protection Division	Dioxin-WW, HW via NELAP	E87605
Georgia	Dept of Natural Resources	Dioxin-DW	959
Guam	Guam EPA	Dioxin-DW	Pace Analytical
Idaho	Dept. of Health & Welfare	Dioxin-DW Enviro-DW	Pace Analytical MT00012*
Hawaii	Dept of Health	Dioxin-DW	SLD
Illinois	Illinois EPA	Dioxin-DW, HW, WW via NELAP	200011
Indiana	Dept of Health	Dioxin-DW via EPA Region 5	C-MN-01
Iowa	Dept.of Natural Resources	Envir.-DW, WW, UST	368
Kansas	Dept of Health and	Dioxin-DW	E-10167

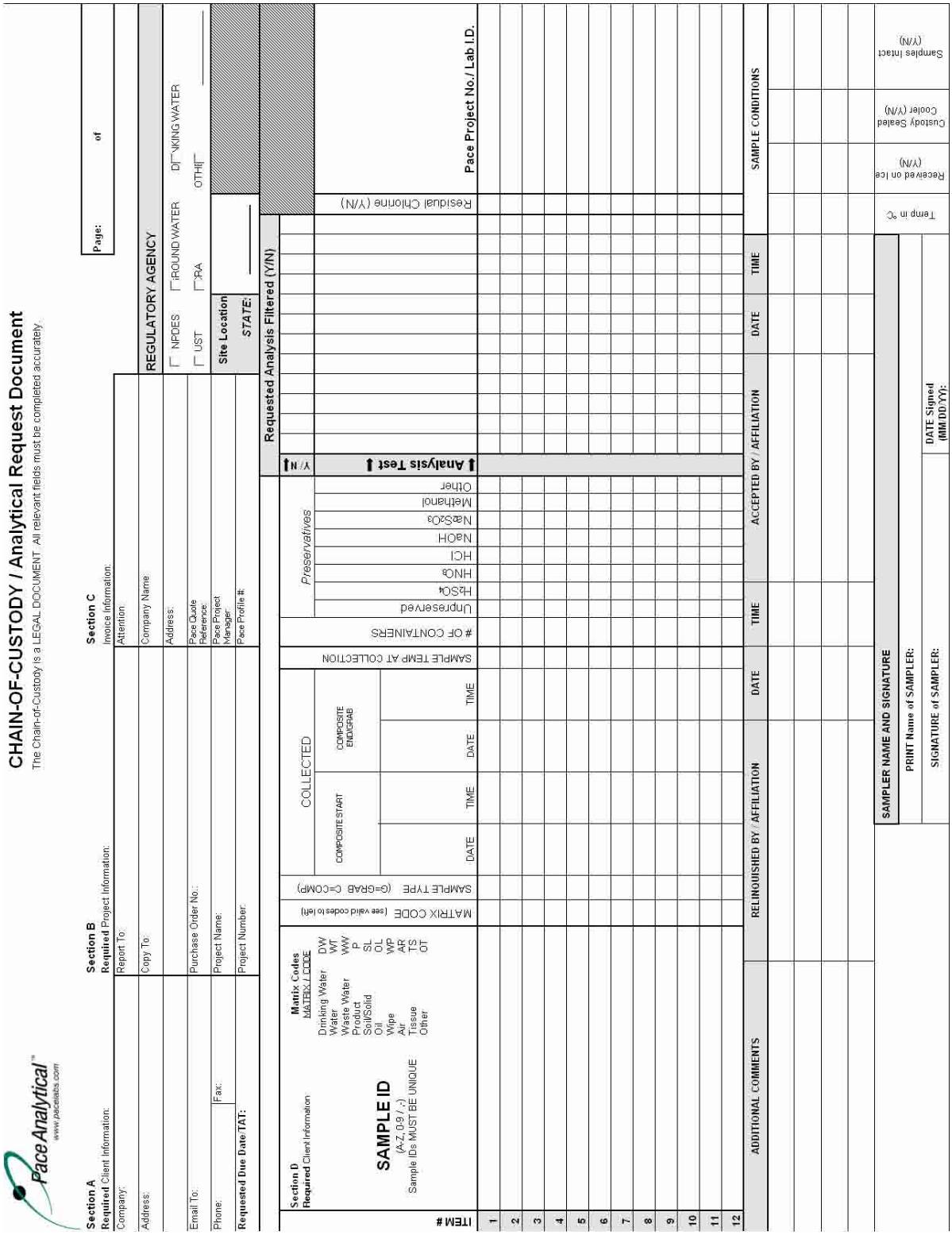
	Environment	Envir-DW, WW, HW	
Kentucky	Dept of Environmental Protection	Dioxin-DW	90062
Louisiana	Department of Environmental Quality	Dioxin-WW, HW, Air	3086
Louisiana	Department of Health and Hospitals	Dioxin-DW	LA050005
Maine	Dept of Human Services	Dioxin-DW via EPA Region 5	2007029
Maryland	Dept. of Heath and Mental Hygiene	Dioxin-DW	322
Michigan	Dept. of Public Health	Dioxin-DW	9909
Minnesota	Dept of Health	Envir-DW, WW, HW Dioxin-DW, WW, HW	027-053-137
Mississippi	Dept. of Health and Environmental Control	Dioxin-DW	Pace
Montana	Montana Dept. of Public Health and Human Services	Dioxin-DW, Envir-DW Envir-DW	CERT0092 CERT0040 *
Nebraska	Dept. of Health & Human Services.	Dioxin-DW	Pace
Nevada	Health Division	Dioxin-DW, WW	MN_00064_2000_72
New Jersey	Dept of Environmental Protection	Dioxin-DW, WW, HW Envir-WW, HW, Air	MN002
New Mexico	NM Environment Dept. Drinking Water Bureau	Dioxin-DW	Pace
New York	Dept of Health	Dioxin-DW, WW, Air Envir-Air	11647
North Carolina	Dept of Environment, Health and Natural Resources	Envir-WW, HW	530
North Carolina	State Public Health Laboratory	Dioxin-DW	27700
North Dakota	Dept of Health and Consolidated Labs	Envir-DW, WW, HW	R-036
NVLAP	NVLAP	Asbestos	101292-0 *
Ohio	Ohio EPA Ohio VAP	Dioxin-DW via EPA Region 5	4150 CL101
Oklahoma	Dept of Environmental Quality	Dioxin-DW Envir-HW	D9921 9507

Oregon	ELAP	Dioxin-DW, WW, HW, Air Enviro: Air	MN200001
Pennsylvania	Dept of Environmental Protection	Dioxin-DW, WW, HW Envir: DW, WW, HW	68-00563
Saipan (CNMI)	Div. Of Environmental Quality	Dioxin-DW	Pace Analytical
South Carolina	Dept. of Health and Environmental Control	Dioxin-DW, WW, HW	74003001
Texas	Department of Health	Dioxin-DW, WW, HW	T104704192-07-TX
Tennessee	Dept of Health	Dioxin-DW Envir-DW	2818
Utah	Department of Health	Dioxin-DW, WW, HW	ID# PAM Account# 6126071700
Virginia	Dept of General Services	Dioxin-DW	251
Washington	Dept of Ecology	Dioxin-DW, WW, HW Envir-DW, WW, HW	C754
Wisconsin	Dept of Natural Resources	Dioxin-DW, WW, HW Envir-DW, WW, HW	999407970
West Virginia	Dept of Health and Human Resources	Dioxin-DW	9952C

* CERTIFICATION HELD BY THE MONTANA DIVISION

ATTACHMENT VIII

PASI – CHAIN OF CUSTODY



ATTACHMENT IX
METHOD HOLD TIME, CONTAINER AND PRESERVATION GUIDE

PASI – MINNESOTA

Parameter	Matrix	Container	Preservative	Max Hold Time
2, 3, 7, 8-TCDD	Soil	8 oz Glass Jar		90/40 Days
2, 3, 7, 8-TCDD	Water	1 L glass		90/40 Days
Acidity	Water	250 mL Plastic		14 Days
Alaska 101 GRO	Water	40 mL glass	HCl	14 Days
Alaska 101 GRO	Soil	4 oz jar	surrogated MeOH	14 Days
Alaska 102 DRO	Water	1L amber glass	HCl	14 Days*
Alaska 102 DRO	Soil	4 or 8 oz. amber jar or core tube		14 Days*
Alaska 103 RRO	Soil	4 or 8 oz. amber jar or core tube		14 Days*
Alkalinity	Water	250 mL Plastic		14 Days
Alpha Emitting Radium Isotopes	Water	1L glass	HNO_3	180 days
Anions by IC, including Br, Cl, F, NO_2, NO_3, SO_4**	Water	250 mL plastic		Br, Cl, F, SO_4 (28 Days) NO_2, NO_3 (48 Hours)
Aromatic and Halogenated Volatiles	Soil	5035 vial kit		14 days
Aromatic and Halogenated Volatiles	Water	3 40 mL glass	HCl, $Na_2S_2O_3$	14 Days
Asbestos**		Clearly labeled container	Ambient storage	NA
Bacteria, Total Plate Count	Water	100 mL Plastic	$Na_2S_2O_3$	24 Hours
Base/Neutrals and Acids	Soil	8 oz Glass Jar		14/40 Days
Base/Neutrals and Acids	Water	1 L glass	if Res. Chlorine present, treat w/$Na_2S_2O_3$	7/40 Days
Base/Neutrals, Acids & Pesticides	Water	1 L glass	if Res. Chlorine present, treat w/$Na_2S_2O_3$	7/30 Days
BOD/cBOD	Water	500 mL Plastic		MN 24hrs otherwise 48 hours
BTEX/Total Hydrocarbons	Air	Summa Canister		14 Days
BTEX/Total Hydrocarbons	Air	Tedlar Bag		48 Hours
CARB 429 (HRMS PAH)	Water	1 Liter		1 Year to Extraction*
CARB 429 (HRMS PAH)	Solid	4 or 8 oz. Jar		1 Year to Extraction*
CARB 429 (HRMS PAH)	Tissue	4 or 8 oz. Jar		1 Year to Extraction*
Chloride	Water	250 mL Plastic		28 Days
Chlorinated Herbicides	Soil	8 oz Glass Jar		14/40 Days
Chlorinated Herbicides	Water	1 L glass	if Res. Chlorine present, treat w/$Na_2S_2O_3$	14/28 Days
Chorine, Residual	Water	500 mL plastic		Analyze within 15 minutes
COD	Water	250 mL plastic	H_2SO_4	28 Days
Color	Water	250 plastic		48 Hours
Condensable Particulate Emissions	Air	Solutions		6 Months
Cyanide, Reactive	Water	250 mL plastic		28 Days
Cyanide, Total and Amenable	Water	250 mL plastic	NaOH	14 Days, 24 Hours if Sulfide present
Diesel Range Organics	Soil	8 oz Glass Jar		14/40 Days
Diesel Range Organics	Water	1L glass	HCl	7/40 Days
Dioxins & Furans	Air	PUF		30/45 Days
EDB & DBCP	Water	1 L glass	HCl, $Na_2S_2O_3$	14 Days
Explosives	Water	1 L glass		7/40 Days
Explosives	Soil	8 oz Glass Jar		14/40 Days
Extractable Petroleum Hydrocarbons**	Water	1 L glass	HCl	14/40 Days
Extractable Petroleum Hydrocarbons**	Solid	4 oz jar		7/40 Days
Coliform, Fecal SM9222D	Water	100mL	10% sodium thiosulfate	6 hours for waste water, 30 hours for potable water
Coliform, Total SM9223B	Water	100mL	10% sodium thiosulfate	6 hours for waste water, 30 hours for potable water
Ferrous Iron	Water	250 mL plastic		Immediate
Flashpoint/Ignitability	Water	250 mL plastic		28 Days
Fluoride	Water	500 mL plastic		28 Days
Gamma Emitting Radionuclides	Water	1 L glass	HNO_3	180 days

Parameter	Matrix	Container	Preservative	Max Hold Time
Gas Range Organics	Water	40 mL glass	HCl	14 Days
Gasoline Range Organics	Soil	5035 vial kit		14 days
Gross Alpha (NJ 48Hr Method)	Water	1L glass	HNO_3	48 Hrs
Gross Alpha and Gross Beta	Water	1L glass	HNO_3	180 days
Haloacetic Acids	Water	40 mL glass	NH_4Cl	14/7 Days
Hardness, Total ($CaCO_3$)	Water	250 mL plastic	HNO_3	6 Months
Hexavalent Chromium	Water	250 mL plastic		24 Hours
Hydrogen Halide & Halogen Emissions	Air	Solutions		6 Months
Lead Emissions	Air	Filter/Solutions		6 Months
Low Level Mercury	Water	Glass	BrCl	90 days (if preserved and oxidized)
Mercury	Soil	8 oz Glass Jar		28 days
Mercury	Water	250 mL plastic	HNO_3	28 Days
Metals	Air	Filters		6 Months
Metals	Soil	8 oz Glass Jar		6 months
Metals (and other ICP elements)	Water	250 mL plastic	HNO_3	6 Months
Methane, Ethane, & Ethene	Water	20 mL glass	HCl	14 Days
Methane, Ethane, Ethene	Air	Summa Canister		14 Days
Methane, Ethane, Ethene	Air	Tedlar Bag		48 Hours
Method 23/TO9	Air	Sampling Head		30 Days to Extraction*
Method 1631E	Water	500mL Glass	Performed in the lab	Oxidized in bottle within 28 days.
Nitrogen, Ammonia	Water	500 mL plastic	H_2SO_4	28 Days
Nitrogen, Kjeldahl	Water	1 L plastic	H_2SO_4	28 Days
Nitrogen, Nitrate	Water	250 mL plastic		48 Hours
Nitrogen, Nitrate & Nitrite	Water	250 mL plastic	H_2SO_4	28 Days
Nitrogen, Nitrite	Water	250 mL plastic		48 Hours
Nitrogen, Organic	Water	250 mL plastic	H_2SO_4	28 Days
Non-Methane Organics	Air	Summa Canister		14 Days
Non-Methane Organics	Air	Tedlar Bag		48 Hours
Odor	Water	1 L glass		24 Hours
Oil and Grease/HEM	Water	1 L glass	H_2SO_4	28 Days
Organchlorine Pesticides and PCB's	Water	1 L glass	if Res. Chlorine present, treat w/$Na_2S_2O_3$	7/40 Days
Organochlorine Pesticides & PCBs	Air	PUF		7/40 Days
Organochlorine Pesticides and PCB's	Water	1 L glass	If Res. Chlorine present, treat w/ $Na_2S_2O_3$	7/40 Days
Organochlorine Pesticides and PCBs	Soil	8 oz Glass Jar		14/40 Days
Organophosphorous Pesticides	Soil	8 oz Glass Jar		14/40 Days
Organophosphorous Pesticides	Water	1 L glass	if Res. Chlorine present, treat w/ $Na_2S_2O_3$	7/40 Days
Oxygen, Dissolved (Probe)	Water	500 mL plastic		Analyze within 15 minutes
Paint Filter Liquid Test	Water	250 mL plastic		N/A
Particulates	Air	Filters		6 Months
Permanent Gases	Air	Summa Canister		14 Days
Permanent Gases	Air	Tedlar Bag		48 Hours
pH	Water	250 mL plastic		Analyze within 15 minutes
Phenol, Total	Water	1L glass	H_2SO_4	28 Days
Phosphorus, Orthophosphate	Water	250 mL plastic		Filter within 15 minutes, Analyze within 48 Hours
Phosphorus, Total	Water	250 mL plastic	H_2SO_4	28 Days
Polynuclear Aromatic Hydrocarbons	Air	PUF		7/40 Days
Polynuclear Aromatic Hydrocarbons	Soil	8 oz Glass Jar		14/40 Days
Polynuclear Aromatic Hydrocarbons	Water	1L glass	if Res. Chlorine present, treat w/ $Na_2S_2O_3$	7/40 Days
Radioactive Strontium	Water	1L glass	HNO_3	180 days
Radium-226 Radon Emanation Technique	Water	1L glass	HNO_3	180 days
Radium-228	Water	1L glass	HNO_3	180 days
Silica, Dissolved	Water	250 mL plastic		28 Days
Solids, Settleable	Water	1L plastic		48 Hours
Solids, Total	Water	1L plastic		7 Days
Solids, Total Dissolved	Water	1L plastic		7 Days

Parameter	Matrix	Container	Preservative	Max Hold Time
Solids, Total Suspended	Water	1L plastic		7 Days
Solids, Total Volatile	Water	1L plastic		7 Days
Specific Conductance	Water	250 mL plastic		28 Days
Stationary Source Dioxins & Furans	Air	XAD Trap		30/45 Days
Stationary Source Mercury	Air	Filters		6 Months, 28 Days for Hg
Stationary Source Metals	Air	Filters		6 Months, 28 Days for Hg
Stationary Source PM10	Air	Filters		6 Months
Stationary Source Particulates	Air	Filter/Solutions		6 Months
Sulfate	Water	250 mL plastic		28 Days
Sulfide, Reactive	Water	250 mL plastic		28 Days
Sulfide, Total	Water	500 mL plastic	NaOH,ZnOAc	7 Days
Sulfite	Water	500 mL plastic		Analyze within 15 minutes
Surfactants	Water	250 mL plastic		48 Hours
Total Organic Carbon (TOC)	Water	250 mL glass	H_2SO_4 or HCl	28 Days
Total Organic Halogen (TOX)	Water	500 mL glass		14 Days
Tritium	Water	1L glass	HNO_3	180 days
Turbidity	Water	250 mL plastic		48 Hours
Uranium Radiochemical Method	Water	1L glass	HNO_3	180 days
Volatiles	Air	Summa Canister		28 Days (14 Days for MN)
Volatiles	Air	Tedlar Bag		48 Hours
Volatiles	Soil	5035 vial kit		14 days
Volatiles	Water	3 40 mL glass	HCl, $Na_2S_2O_3$	14 Days
Volatiles	Water	3 40 mL glass		7 unpreserved
Volatile Petroleum Hydrocarbons**	Water	3 40 mL glass	HCl	14 days
Volatile Petroleum Hydrocarbons**	Solid	3 40 mL glass, or 8oz jar	MeOH or packed jar	7 days to extraction/ 28 days analysis
WIGRO	Water	3 40 ml vials	HCl	14 Days
WIGRO	Solid	5035 vial kit	See *Note*	14 Days
WIDRO	Water	1 Liter	HCl	7 Days to Extraction*
WIDRO	Solid	Tared 4 oz. Jar		10 Days to extraction***
1614	Water	1 Liter		1 Year to Extraction*
1614	Solid	4 or 8 oz. Jar		1 Year to Extraction*
1614	Tissue	4 or 8 oz. Jar		1 Year to Extraction*
1653	Water	2 L	pH<2 H_2SO_4	30 Days to Extraction; 30 days to analysis
1668	Water	1 Liter		1 Year to Extraction*
1668	Solid	4 or 8 oz. Jar		1 Year to Extraction*
1668	Tissue	4 or 8 oz. Jar		1 Year to Extraction*
8015 (MeOH, EtOH)	Water	3 40 ml vials	HCl	14 Days
8280	Water	1 Liter		30 Days to Extraction*
8280	Solid	4 or 8 oz. Jar		30 Days to Extraction*
8290	Solid	4 or 8 oz. Jar		30 Days to Extraction*
8290	Water	1 Liter		30 Days to Extraction*
8290	Waste	2 oz		30 Days to Extraction*

**40 Days from Extraction to Analysis. (EPA 1613)*
45 Days from Extraction to Analysis (SW8290, 1668, 8280 and Method 23/TO9)
***Analysis is only conducted in the Montana Division*
****WIDRO soil method requires that solvent be added within 10 days of collection. If solvent is added within 10 days of collection, extraction/analysis must occur within 47 days from collection.*
Note: 5035 kit contains 2 vials water, preserved by freezing or 2 vials aqueous $NaHSO_4$ preserved at 4^oC and 1 vial MeOH preserved at 4^oC and 1 vial unpreserved at 4^oC.

Pace Analytical®

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Page: of 924510

Section A Required Client Information:

Company	
Address	
Email To:	
Phone	Fax
Requested Due Date/TAT:	

Section B Required Project Information:

Report To:
Copy To:
Purchase Order No.:
Project Name:
Project Number:

Section C Invoice Information:

Attention:
Company Name:
Address:
Pace Quote Reference:
Pace Project Manager:
Pace Profile #:

REGULATORY AGENCY

☐ NPDES ☐ GROUND WATER ☐ DRINKING WATER
☐ UST ☐ RCRA ☐ Other_____

SITE LOCATION ☐GA ☐IL ☐IN ☐MI ☐MN ☐NC ☐OH ☐SC ☐WI ☐OTHER_____

Section D Required Client Information

SAMPLE ID

One Character per box.
(A-Z, 0-9 / .-)
Samples IDs MUST BE UNIQUE

Valid Matrix Codes

MATRIX	CODE
DRINKING WATER	DW
WATER	WT
WASTE WATER	WW
PRODUCT	P
SOIL/SOLID	SL
OIL	OL
WIPE	WP
AIR	AR
OTHER	OT
TISSUE	TS

ITEM #	MATRIX CODE	SAMPLE TYPE G=GRAB C=COMP	COLLECTED COMPOSITE START DATE	COLLECTED COMPOSITE START TIME	COLLECTED COMPOSITE END/GRAB DATE	COLLECTED COMPOSITE END/GRAB TIME	SAMPLE TEMP AT COLLECTION	# OF CONTAINERS	Preservatives: Unpreserved	H_2SO_4	HNO_3	HCl	NaOH	$Na_2S_2O_3$	Methanol	Other	Filtered (Y/N)	Requested Analysis:	Residual Chlorine (Y/N)	Pace Project Number / Lab I.D
1																				
2																				
3																				
4																				
5																				
6																				
7																				
8																				
9																				
10																				
11																				
12																				

Additional Comments:

RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME

SAMPLE CONDITION

	Y/N	Y/N	Y/N	Temp in °C
	Y/N	Y/N	Y/N	Received on Ice
	Y/N	Y/N	Y/N	Custody Sealed Cooler
	Y/N	Y/N	Y/N	Samples Intact

SAMPLER NAME AND SIGNATURE

PRINT Name of SAMPLER:

SIGNATURE of SAMPLER: DATE Signed (MM / DD / YY)

SEE REVERSE SIDE FOR INSTRUCTIONS

ORIGINAL

Pace Analytical®
www.pacelabs.com

Pace Analytical Services, Inc.
1241 Bellevue Street, Ste. 9
Green Bay, WI 54302
(920) 469-2436

Client: ____________________

Client Sample ID: ____________________

Date Collected: ____________ Time: ____________

Collected by: ____________________

Analysis: ____________________

Preservatives: ☐None ☐HNO_3 ☐H_2SO_4 ☐NaOH ☐HCl

☐$Na_2S_2O_3$ ☐MeOH ☐Zn Acetate ☐Other: ____________

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☐$Na_2S_2O_3$ ☐MeOH ☐Zn Acetate ☐Other: ____________

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Client: ____________________

Client Sample ID: ____________________

Date Collected: ____________ Time: ____________

Collected by: ____________________

Analysis: ____________________

Preservatives: ☐None ☐HNO_3 ☐H_2SO_4 ☐NaOH ☐HCl

☐$Na_2S_2O_3$ ☐MeOH ☐Zn Acetate ☐Other: ____________

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Client: ____________________

Client Sample ID: ____________________

Date Collected: ____________ Time: ____________

Collected by: ____________________

Analysis: ____________________

Preservatives: ☐None ☐HNO_3 ☐H_2SO_4 ☐NaOH ☐HCl

☐$Na_2S_2O_3$ ☐MeOH ☐Zn Acetate ☐Other: ____________

CUSTODY SEAL

DATE ____________________

SIGNATURE ____________________

QEC
Quality Environmental Containers
800-255-3950 • 304-255-3900

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www.pacelabs.com

Pace Analytical Services, Inc.
1241 Bellevue Street, Suite 9
Green Bay, WI 54302
Phone: 920.469.2436
Fax: 920.469.8827

STANDARD OPERATING PROCEDURE

Measurement of Volatile Solids and Solids in Waters

Reference Methods: Standard Methods 2540-B, -C, -D, -E, -G, ASTM D2974 and EPA 160.1, 160.2, 160.3, 160.4

SOP NUMBER:	S-ALL-GB-I-014-Rev.04
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-ALL-GB-I-014-Rev.3

APPROVAL

Nils K Melberg
Nils Melberg, Laboratory General Manager — Date: 5/29/09

Kate E. Grams
Kate Grams, Laboratory Quality Manager — Date: 5/29/09

Chad Rusch, Department Manager — Date: 5/29/09

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

This is **COPY#** 7 Distributed on **02/16/10** by **LAB** and is ___ **CONTROLLED or** X **UNCONTROLLED**

Table of Contents

1. Purpose

1.1 This Standard Operating Procedure (SOP) describes operations used to measure the parameters in the following table:

Test		Matrix	Method	Reports as
TS	Total Solids	Water	SM 2540B	mg/L
TS	Total Solids	Solid	SM 2540G	%
TSS	Total Suspended Solids	Water	SM 2540D	mg/L
TDS	Total Dissolved Solids	Water	SM 2540C	mg/L
TVS	Total Volatile Solids	Water	EPA 160.4	mg/L
TVS	Total Volatile Solids	Solid	EPA 160.4	%
TVSS	Total Volatile Suspended Solids	Water	EPA 160.4	mg/L
OM	Organic Matter	Solid	ASTM D2974-87(C)	%
FOC	Fractional Organic Carbon	Solid	ASTM D2974-87	%
ASH	Ash	Solid	ASTM D2974-87(C)	%

2. Scope and Application

2.1 This method is applicable to the determination of Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), and Total Volatile Solids (TVS) in water samples.

2.2 This method is applicable to the determination of Total Solids (TS) and its Volatile (TVS) and Fixed Solids (FS) fractions in soil and semisolid samples. The terms total or fixed solids apply to matter left after drying in an oven at 103-105º C and igniting in a muffle furnace at a 550ºC temperature and a defined time interval.

2.3 This method is applicable to the determination of Fractional Organic Carbon (FOC), ASH, and Organic Matter (OM) in soil and semisolid samples. The term fractional organic carbon (FOC) applies to the weight loss after ignition, multiplied by a 0.58 factor and reported as % Fractional Organic Carbon.

2.4 This procedure is restricted to use by, or under the supervision of, analysts experienced with the use of laboratory information systems, balances, desiccators, and ovens. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. Summary of Method

3.1 Total Solids (TS) – A well-mixed sample is evaporated to dryness and the residue solids are measured gravimetrically.

3.2 Total Suspended Solids (TSS) – A well-mixed sample is filtered. The residue collected by the filter is dried and measured gravimetrically.

3.3 Total Dissolved Solids (TDS) – A well-mixed sample is filtered. The filtrate passing through the filter is evaporated to dryness and the residue solids are measured gravimetrically.

3.4 Total Volatile Solids (TVS, TVSS) – Residue obtained from the determination of TS, or TSS is ignited at 550ºC in a muffle furnace. The loss of weight on ignition is reported as % Volatile Solids for solid samples and mg/L Volatile Solids for liquid samples.

3.5 Fixed Solids (FS) - Residue obtained from the determination of TS is ignited at 550ºC in a muffle furnace. The weight remaining after ignition is reported as % Fixed Solids.

3.6 Fractional Organic Carbon (FOC) - Residue obtained from the determination of TS is ignited at 440ºC in a muffle furnace. The weight loss after ignition is multiplied by a 0.58 factor and reported as % Fractional Organic Carbon.

3.7 Organic Matter (OM) - Residue obtained from the determination of TS is ignited at 440ºC in a muffle furnace. The weight loss after ignition is reported as % Organic Matter.

3.8 ASH - Residue obtained from the determination of TS is ignited at 440ºC in a muffle furnace. The weight remaining after ignition is used to calculate and report the % ASH.

4. Interferences

4.1 Non-representative materials, e.g., leaves and sticks should be removed from the sample prior to measurement unless it is determined that their inclusion is desired.

4.2 Measurements are subject to negative bias for samples containing significant quantities of ammonium carbonate, volatile organics, or other volatile materials that could be lost during drying.

4.3 The residue of samples for TS and TDS that are highly mineralized, especially containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require longer drying, desiccation, and rapid weighing.

4.4 Samples for TS and TDS containing high concentrations of bicarbonate will require careful, and possibly prolonged, drying to ensure that all bicarbonate is converted to carbonate.

4.5 The volumes of aliquots for TS and TDS should be selected to limit the total residue to 200 mg to prevent the residue from crusting over and trapping water during drying.

4.6 Samples for TSS with high TDS, such as saline waters, brines, and some wastes, may be subject to positive bias. Care must be taken to properly rinse the filter to minimize the bias.

5. Safety

5.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan are made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

5.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, Waste Handling.

5.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prévention.

6. Definitions

6.1 Batch – A grouping of 20, or less, environmental samples of similar matrix, which are prepared and/or analyzed together with the same method.

6.2 Blank Sample – A sample analyzed to determine potential contamination attributed to sample handling and analysis.

6.3 Duplicate Sample – A second aliquot of the same environmental sample analyzed in the same manner as the original sample in order to evaluate precision.

6.4 Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

6.5 Laboratory Control Sample (LCS) – A blank matrix sample spiked with a known concentration of analytes of interest. Laboratory accuracy is evaluated using the LCS.

6.6 Laboratory Information Management System (LIMS) – This is a system for transferring, processing, storing, and reporting analytical results.

6.7 Replicate Samples – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.8 Pace Reporting Limit (PRL) – The lowest level that will be reported by this method. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

6.9 Solid – matrix such as soils, sediments, sludge, organic liquids, oils or aqueous products and by-products of industrial processes, and aqueous samples with more than 10% settle able solids.

6.10 Total Solids Content (TSC) – Total Solids Content is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature of 103-105ºC.

6.11 Volatile Solids – Residue obtained from the determination of TS is ignited at 550ºC in a muffle furnace. The loss of weight on ignition is reported as % Volatile Solids.

6.12 Fixed Solids - Residue obtained from the determination of TS is ignited at 550ºC in a muffle furnace. The weight remaining after ignition is reported as % Fixed Solids.

6.13 Refer to Section 10 of the Pace Quality Manual for additional terms used in this SOP.

7. Sample Collection, Preservation and Handling

7.1 Samples are collected in plastic, glass, or any appropriate containers that prevents drying during storage.

7.2 Samples are stored at 4±2oC and analyzed as soon as possible to minimize microbiological decomposition of organic solids.

7.3 Samples should be analyzed as soon as possible and the holding time must not exceed **7 days** from time of collection. Samples analyzed after 7 days of collections must be qualified with the “H” qualifier.

8. Equipment and Supplies

8.1 Analytical balance – Electronic, capable of weighing to 0.1 mg.

8.2 Vacuum Filtration System – Includes filter holder, membrane filter funnel, vacuum flask and vacuum pump.

8.3 Glass Fiber Filters (for TDS) – Gelman type A/E, Whatman 934-H, or equivalent.

8.4 Glass Fiber Filters (for TSS) – Pre-weighed from Environmental Express, with matched aluminum evaporating dishes.

8.5 Graduated Cylinders – 50, 100, 250, 500 and 1000mL.

8.6 Disposable Aluminum Weighing Dish, Low Form, Fisherbrand p/n 08-732-100, or equivalent.

8.7 Wide bore serological pipettes and pipette helper.

8.8 Drying Ovens – capable of maintaining 103-105ºC and 178-182ºC.

8.9 Desiccator

8.10 Indicating Desiccant – Fisher p/n 07-578-3B, or equivalent.

8.11 Non-indicating Desiccant – Fisher p/n 07-577-3B, or equivalent

8.12 Laboratory Scoopulas

8.13 Muffle furnace (for volatile and fixed solids) – Capable of maintaining temperature of 440ºC and 550ºC.

8.14 Evaporating Beaker (TS/TDS) – 50 mL

8.15 Ceramic Evaporating Dishes (TVS)

9. Reagents and Standards

9.1 ERA DataPacK Total Volatile Solids Standard, Cat # 913 for TVS, OM, and FOC analysis.

9.2 APG Solids APGplus Standard, Cat #4033 for TS, TSS*, and TDS analyses.

9.3 Alpha-Trol Standard, Cat #NC9460010 for TS, TSS, and TDS* analysis.

9.4 Deionized Reagent Water (DI) – ASTM Type II, or equivalent.

* Not the preferred standard for this test.

10. Calibration

10.1 Balance Calibration – The only required calibration is the analytical balance.

10.2 The balance must be calibrated at least annually by an outside agency and checked **daily** across the range of use, using Class 1 or 2 weights as per the most current version of SOP ALL-Q-013 *Support Equipment* and associated addenda.

10.3 Each weighing of the batch is bracketed at the beginning and end with either a 1g or 50g verification.

10.3.1 1g for TSS and TVSS with a tolerance of +/-0.0100g

10.3.2 50g for TS, TDS, TVS, OM, and FOC with a tolerance of +/-0.5000g

11. Procedure

11.1 Create the analytical batch in Horizon.

11.2 Open LimsLink and create a new worksheet for the batch to be analyzed.

11.3 Pre-Weighed Dried Evaporating Dish or Beaker – Dry the beaker at 180ºC for 30-60min. Ignite the evaporating beaker at 550ºC for 1 hour in a muffle furnace. Cool in desiccator, and store there until ready to use. Record their weight prior to use.

11.4 Check that the oven temperature is recorded in the logbook each morning and is within required specifications before placing samples into oven as per the most current version of SOP ALL-Q-013 *Support Equipment* and associated addenda.

11.5 **Weighing Dry/Muffle Weights**

11.5.1 Oven temperatures are the same as those described for the test being conducted.

11.5.2 Place the samples back into the oven for 15 minutes and repeat desiccating , cooling, and weighing steps until weight change is $\leq$0.0005g.

11.5.3 If the first and second weights agree within 0.0005 g, or if the weight loss between the first and second weighing is less than 4%, the analysis is complete. If not, place them back into the oven for and additional 15 minutes. Cool in the desiccator, and weigh a third time.

11.5.4 If the third weigh is within 0.0005 g of either the first or second weight or if the weight loss between the second and the third weighing is less than 4%, the analysis is complete.

11.5.5 If the weight loss between the second and third weighing is more than 0.0005g and 4%, heat, cool, and weigh the sample a fourth time and use the fourth weight to calculate the result.

11.6 **Total Solids Determination (TS)**

11.6.1 For each sample and QC point place a pre-dried evaporating beaker on the balance and record the weight. The initial weights must be confirmed by obtaining a second weight. The weight change must be $\leq$0.0005g before use.

11.6.2 Method blank (MB) – Using a graduated cylinder, measure out 50mL of Nanopure (or equivalent) water and pour into a tared and dried evaporating beaker. Record the volume for TS-waters and weight for TS-solids analysis in LimsLink.

11.6.3 Laboratory Control Sample (LCS) – Using a graduated cylinder, measure out 50mL of Alpha-Trol (or equivalent) and pour into a tared and dried evaporating beaker. Record the volume for TS-waters and weight for TS-solids analysis in LimsLink.

11.6.4 Sample Duplicate (DUP) – At least one DUP must be analyzed per ten samples.

11.6.5 Sample

12.5.4.1 For Solids Samples – Weight out 1 to 1.5g of sample in a pre-dried evaporating beaker. Record the weight in LimsLink.

12.5.4.2 For Aqueous Samples - Shake the sample thoroughly and measure an aliquot (between 1mL and 50mL, typically 10mL) into a pre-dried evaporating beaker using a graduated cylinder. Record the volume in LimsLink.

11.6.6 Place the samples to dry in the oven overnight at 103-105^{O}C. (Overnight is a period of time $\geq$ 8 hours.)

11.6.7 After drying overnight, remove from oven and place into the desiccator to cool. After the samples have cooled, obtain the weight of the samples as per Section 12.5, and record in LimsLink.

11.6.8 If Total Volatile Solids (TVS) are also to be performed proceed to Section 12.9. Note: TVS utilizes a different LCS than the TS.

11.7 **Total Suspended Solids Determination (TSS)**

11.7.1 Record Filter IDs and weights in LimsLink for samples and batch QC.

11.7.2 Method blank (MB) – Using a graduated cylinder measure out 1000mL of Nanopure (or equivalent) water, record the volume in LimsLink, and start at 12.7.8.

11.7.3 Laboratory Control Sample (LCS) – Using a graduated cylinder measure out 50mL of Alpha-Trol (or equivalent), record the volume in LimsLink, and start at 12.7.8.

11.7.4 Sample Duplicate (DUP) – At least one DUP must be analyzed per ten samples.

11.7.5 For wastewater, the Pace Analytical Services, Inc. - Green Bay Laboratory uses 500mL in order to meet Wisconsin Reporting Limit requirement of 2.0 mg/L.

11.7.6 For South Carolina work a sample volume is chosen to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to 1 L.

11.7.7 Shake the sample thoroughly and measure the chosen aliquot using a graduated cylinder.

11.7.8 Prepare the filter system with a fresh pre-weighed filter. Handle the filter with forceps only. Wet the filter with a small volume of DI water to seat it. Discard the rinse water.

11.7.9 Filter the sample and wash the filter 3 times with approximately 10mL of DI water. Maintain the filter vacuum for about 1 minute after filtration is complete.

11.7.10 Remove the filter with forceps and place it back into the evaporating dish.

11.7.11 Place the samples (filters and residue) to dry in the oven a minimum of 3 hours at 103-105^{O}C.

11.7.12 After drying, remove from oven and place into the desiccator to cool. After the samples have cooled, record the weight of the samples as per Section 12.5.

11.7.13 If Total Volatile Suspended Solids (TVSS) are also to be performed proceed to Section 12.10.

11.8 **Total Dissolved Solids (TDS)**

11.8.1 For each sample and QC point place a pre-dried evaporating beaker on the balance and record the weight. The initial weights must be confirmed by obtaining a second weight. The weight change must be $\leq$0.0005g before use.

11.8.2 Method blank (MB) – Using a graduated cylinder measure out 50mL of Nanopure (or equivalent) water, record the volume in LimsLink, and start at step 12.8.6.

11.8.3 Laboratory Control Sample (LCS) – Using a graduated cylinder measure out 50mL of APG Solids APGplus Standard (or equivalent), record the volume in LimsLink, and start at step 12.8.6.

11.8.4 Sample Duplicate (DUP) – At least one DUP must be analyzed per ten samples.

11.8.5 Shake the sample thoroughly and measure a 50mL aliquot using a graduated cylinder.

11.8.6 Prepare the filter system with a fresh pre-weighed filter. Handle the filter with forceps only. Wet the filter with a small volume of DI water to seat it. Discard the rinse water.

11.8.7 Filter the sample and transfer the filtrate to a pre-weighed dried evaporating dish or beaker.

11.8.8 Place the samples to dry in the oven overnight at 178-182^{O}C (Overnight is a period of time $\geq$ 8 hours.)

11.8.9 After drying overnight, remove from oven and place into the desiccator to cool. After the samples have cooled, record the weight of the samples as per Section 12.5.

11.9 **Total Volatile Solids (TVS)**

11.9.1 For each sample and QC point place a pre-dried evaporating beaker on the balance and record the weight. The initial weights must be confirmed by obtaining a second weight. The weight change must be $\leq$0.0005g before use.

11.9.2 Method blank (MB) – Using a graduated cylinder, measure out 50mL of Nanopure (or equivalent) water, pore into a tared evaporating beaker. Record the weight in LimsLink.

11.9.3 Laboratory Control Sample (LCS) – Using a graduated cylinder, measure out 50mL of ERA DataPacK Total Volatile Solids Standard (or equivalent), pore into a tared evaporating beaker. Record the weight in LimsLink.

11.9.4 Sample Duplicate (DUP) – At least one DUP must be analyzed per ten samples.

11.9.5 Sample

12.5.4.3 For Solids Samples – Weight out 1 to 1.5g of sample in a pre-dried evaporating beaker. Record the weight in LimsLink.

12.5.4.4 For Aqueous Samples - Shake the sample thoroughly and measure an aliquot (between 1mL and 50mL, typically 10mL) into a pre-dried evaporating beaker using a graduated cylinder. Record the volume in LimsLink.

11.9.6 Follow TS Sections 12.6.6 to 12.6.7 to obtain a dried residue.

11.9.7 Place the evaporating beaker or filter and evaporating dish. into the muffle furnace at **550ºC** for 1 hour.

11.9.8 After 1 hour, remove from muffle furnace and place into the desiccator to cool. After the samples have cooled, record the weight of the samples as per Section 12.5.

11.10 **Total Volatile Suspended Solids (TVSS)**

11.10.1 Method blank (MB) – Using a graduated cylinder, measure out 1000mL of Nanopure (or equivalent) water, record the volume in LimsLink.

11.10.2 Sample Duplicate (DUP) – At least one DUP must be analyzed per ten samples.

11.10.3 Shake the sample thoroughly and measure the chosen aliquot (see sections 12.7.5 and 12.7.6) using a graduated cylinder. Record the volume in LimsLink.

11.10.4 Follow TSS Sections 12.7.8 to 12.7.12 to obtain a dried residue.

11.10.5 Place the filter and evaporating dish. into the muffle furnace at **550ºC** for 1 hour.

11.10.6 After 1 hour, remove from muffle furnace and place into the desiccator to cool. After the samples have cooled, record the weight of the samples as per Section 12.5 in LimsLink.

11.11 **Fractional Organic Carbon (FOC), ASH, and Organic Matter (OM)**

11.11.1 For each sample and QC point place a pre-dried evaporating beaker on the balance and record the weight. The initial weights must be confirmed by obtaining a second weight. The weight change must be $\leq$0.0005g before use.

11.11.2 Method blank (MB) – Using a graduated cylinder, measure out 50mL of Nanopure (or equivalent) water, pore into a tared evaporating beaker, record the weight in LimsLink.

11.11.3 Laboratory Control Sample (LCS) – Using a graduated cylinder, measure out 50mL of ERA DataPacK Total Volatile Solids Standard (or equivalent), pore into a tared evaporating beaker, record the weight in LimsLink.

11.11.4 Sample Duplicate (DUP) – At least one DUP must be analyzed per ten samples.

11.11.5 Samples – Into a tared evaporating beaker weigh out about 1-1.5g of sample. Record the weight in LimsLink.

11.11.6 Follow Sections 12.6.6 to 12.6.7 to obtain a dried residue.

11.11.7 Place the evaporating beakers into the muffle furnace at **440ºC** for 1 hour.

11.11.8 After 1 hour, remove from muffle furnace and place into the desiccator to cool. After the samples have cooled, record the weight of the samples as per Section 12.5 in LimsLink.

11.12 **Entering Results into Horizon**

11.12.1 Post samples and batch QC using LimsLink.

11.12.2 Evaluate batch QC in Horizon. Non-reported LCSs need to be evaluated in LimsLink.

11.13 **Calculations**

Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS) in mg/L

$$= \frac{(A - B) \times 1000 \times 1000}{V}$$

Where:

V = sample volume (mL)

Total Solids
A = final weight (dry weight of residue and dish, g)
B = dish weight (g)

Total Suspended Solids
A = final weight (dry weight of residue and filter, g)
B = filter weight (g)

Total Dissolved Solids
A = final weight (dry weight of residue and dish, g)
B = dish weight (g)

Volatile Solids (TVS and TVSS mg/L)

$$= \frac{(A - D) \times 1000 \times 1000}{V}$$

Volatile Solids (TVS %)

$$= \frac{(A - D) \times 100}{(A - B)}$$

% Fixed Solids

$$= \frac{(D - B) \times 100}{(A - B)}$$

% FOC

$$= ((1-((D-B) / (A - B))) \times 100) \times (0.58)$$

% OM

$$= ((1-((D-B) / (A-B))) \times 100)$$

Where:

A = dry weight (weight of dried residue and dish g)

B = dish weight (g)

C = weight of wet sample and dish (g)

D = muffled weight (weight of residue and dish after ignition, g)

V = volume (mL)

11.13.1 Precision - The relative percent difference (RPD) is calculated as:

$$\textbf{RPD} = \frac{|S - D|}{(S + D)/2} * 100$$

where: **S** = sample value
D = duplicate value

11.13.2 Constant Weight is calculated as:

$$\textbf{Constant Weight (\%)} = \frac{|FW - CW|}{(FW + CW)/2} * 100$$

where FW = First Weighing, mg

CW = Confirmation Weighing, mg

If FW – CW is 0.0005 g or less, then there is not a need to calculate as a percentage.

12. Quality Control

12.1 Refer to the most current version of the Pace Quality Manual Appendix I *Quality Control Calculations* and SOP GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

12.2 Method Blank (MB) – A MB is carried through all prep procedures and analyzed with a frequency of 5% or one per batch of up to 20 environmental samples.

12.2.1 TS, TDS, TVS, FOC, FS, and OM all use 50mL of deionized water for the method blank.

12.2.2 TSS and TVSS both use 1000mL of deionized water for the method blank.

12.2.3 For tests that are reported in %, the MB is evaluated in mg/Kg. The mg/kg result must be less than 20 mg/kg. Data can be reported if the sample mg/Kg result is 10x greater than the method blank. The value reported in Epic Pro will be adjusted to 0%.

12.2.4 For tests that are reported in mg/L the absolute value must be < PRL.

12.2.5 When measurements are above the PRL, terminate analysis, correct the problem, verify the calibration, and reanalyze all analytical samples analyzed since the last compliant calibration blank

12.2.6 If the analyte is detected in the method blank between the MDL and the PRL, then samples need to be qualified with a "B" when MDL reporting is required and sample results are greater than the MDL and less than 10 times the absolute value detected in the blank. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

12.3 Laboratory Control Sample (LCS) – The LCS is carried through all preparation procedures with frequency of 5% or one per batch of up to 20 environmental samples. The only test without an LCS is TVSS.

12.3.1 ERA DataPacK Total Volatile Solids Standard, Cat. # 913 is used for TVS, FOC, and OM analysis. Equivalent can be used.

12.3.2 APG Solids APGPlus standard, Cat #4033 is used for TDS analysis. Equivalent can be used.

12.3.3 Alpha-Trol Standard, CAT#NC9460010 is used for TS and TSS analysis. Equivalent can be used.

12.3.4 A Laboratory Control Spike Duplicate (LCSD) must be analyzed if the client requests one.

12.3.5 The LCS recovered concentration must be within calculated in house limits or default limits of $\pm$ 20%.

12.3.6 For tests that are reported in %, the LCS is evaluated in mg/Kg in LimsLink and not reported in Epic Pro.

12.3.7 When measurements are outside the control limits, check for errors in calculations, standards preparation, and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.3.8 If no errors are found, sufficient sample is available, it is within hold, re-prepare the LCS (and/or LCSD) and all associated samples. If the recovery is within the limits in the analysis, accept the second set of data. If the recovery is still out side the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant LCS.

12.3.9 If sufficient sample volume is not available or the samples are now outside of hold, report the sample data with a qualifier flag (&) on each of the samples associated with the non-compliant LCS (and/or LCSD). Contact the project manager regarding the occurrence.

12.3.10 When an LCSD is performed, the precision between the LCS and LCSD must a be $\leq$20% RPD.

12.3.11 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.3.12 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with an "R1" data qualifier.

12.4 Duplicate - Analyze one sample in duplicate per 10 samples or less. The sample used for the duplicate is selected at random, unless specified by the client. The relative percent different (RPD) between duplicates must be $\leq$10%.

12.4.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.4.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with an "R1" data qualifier

12.5 Constant Weight - Place the samples back into the 103-105ºC oven, and/or 440/550ºC muffle furnace for 15 minutes and repeat cooling, weighing, and desiccating steps until weight change is $\leq$0.0005g or the weight loss between the two weights is less than 4%.

12.6 Balance - The balance must be verified daily across the range of use, before use, as per the most current version of SOP ALL-Q-013 *Support Equipment* and associated addenda.

12.6.1 Each weighing of the batch is bracketed at the beginning and end with either a 1g or 50g verification.

12.6.2 1g for TSS and TVSS with a tolerance of +/-0.0100g

12.6.3 50g for TS, TDS, TVS, OM, and FOC with a tolerance of +/-0.5000g

12.7 Oven - The oven temperature is recorded in the logbook each morning and must be within required specifications before placing samples into oven as per the most current version of SOP ALL-Q-013 *Support Equipment* and associated addenda.

12.8 Hold - When preparation of a sample exceeds 7 days past the time of collection, notify the project manager before proceeding. If a sample is run past 7 days after collection, flag the result with an "H" data qualifier.

12.9 See attachments Table A and Table B for a summary of QC

13. Method Performance

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.1.2 Demonstration of Capability (DOC) – Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC). DOC's must be repeated annually. Analyze 4 replicate environmental sample aliquots. Calculate the mean and standard deviations of the results. The relative percent different (RPD) between replicates must be $\leq$ 5% or the study must be repeated.

14. Pollution Prevention and Waste Management

14.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

14.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

14.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. References

15.1 Method 2540-G, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

15.2 ASTM D2974-87, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, May 29, 1987

15.3 VA30007.00.004, Recommendations Regarding the Sampling and Analysis of Fractional Organic Carbon (FOC) in Soils, Technical Decision Compendium, Rule OAC 3745-300-07, March 2000

16. Tables, Diagrams, Flowcharts, Appendices, Addenda, etc.

16.1 Table A: **QUALITY CONTROL**

16.2 Table B: **ANALYST/TECHNICIAN DATA ASSESSMENT**

16.3 Flow charts – Attachment I.

17. Revisions

Document Number	Reason for Change	Date
S-ALL-GB-I-014-Rev.1	Consolidated SOPs ALL-I-014-rev.1, ALL-GB-I-014-rev.1, and GB-I-050-Rev.0. Section 12.6.2 - added South Carolina minimum residue requirements.	24Aug2007
S-ALL-GB-I-014-Rev.2	Corrected FOC and OM calculations and definitions	05Oct2007
S-ALL-GB-I-014-Rev.3	Clarified analysis steps for each test. Changed qualifiers to match Epic Pro.	28Apr2008
S-ALL-GB-I-014-Rev.4	Included notations on how to evaluate MB and LCS for tests reporting in %. Updated Signature Page to Periodic Review.	29May2009

Table A. QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**SM 2540G – ASTM D2974-87**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples, whichever is more frequent. None performed on TVSS.
Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.

Table B. ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**SM2540G – ASTM 2974-87 If these conditions are not achieved ⇒**
Method Blank	• 1
Precision Duplicate Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the "A" data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used If the PS and PSD fails precision control limits flag the parent with the "*" (precision) data qualifier.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the "&" (accuracy) and "*" (precision) qualifier to reflect the deficiencies.

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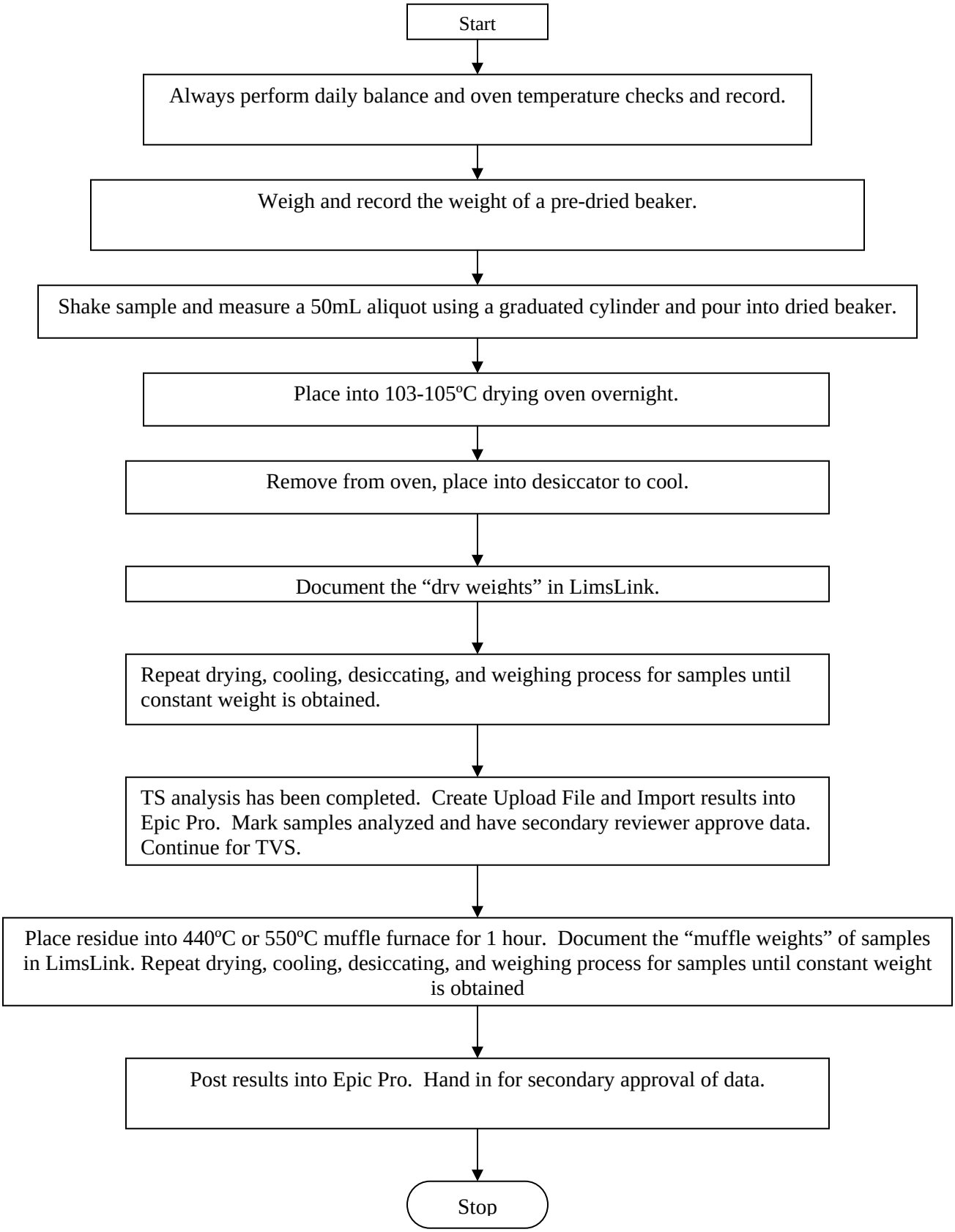
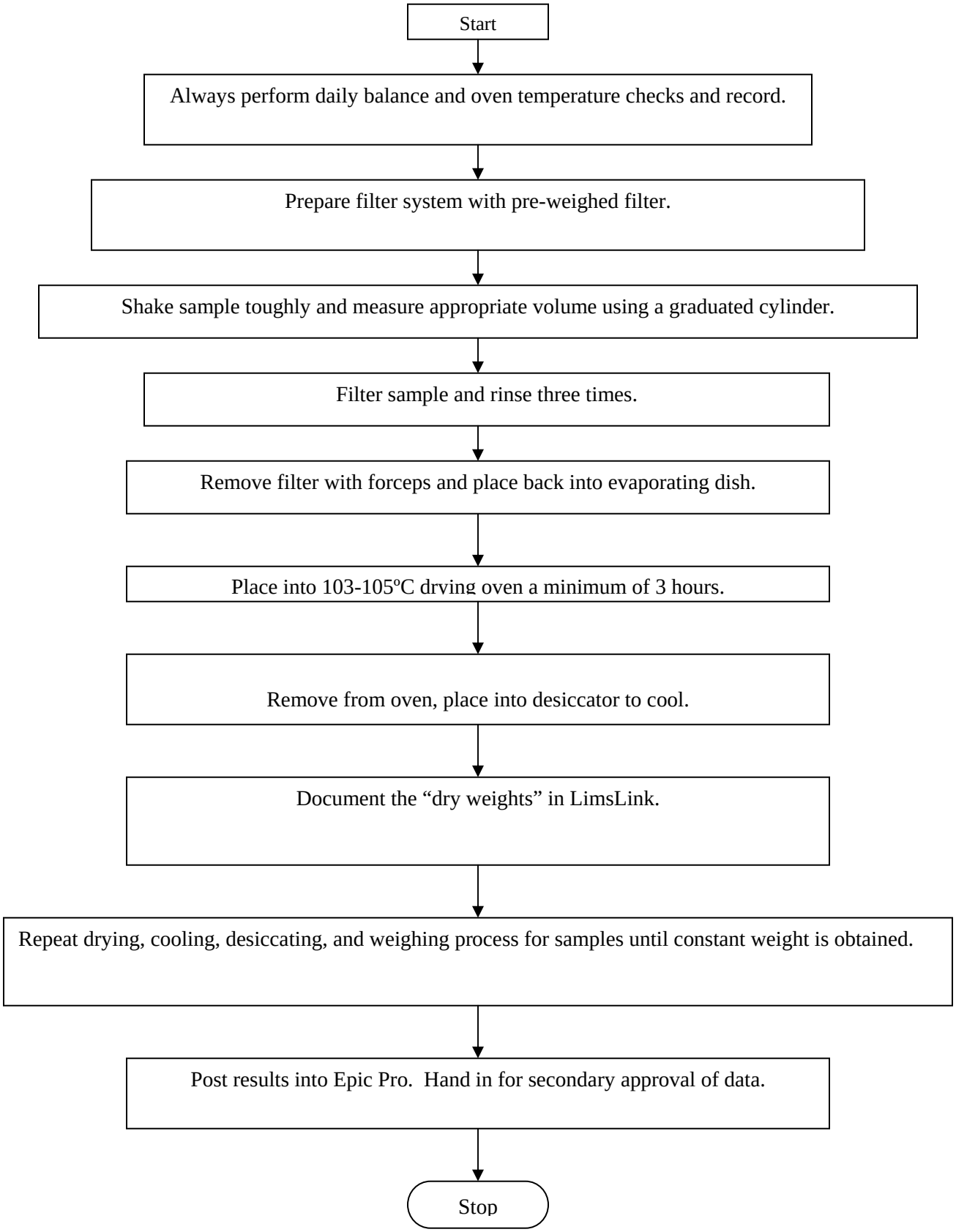
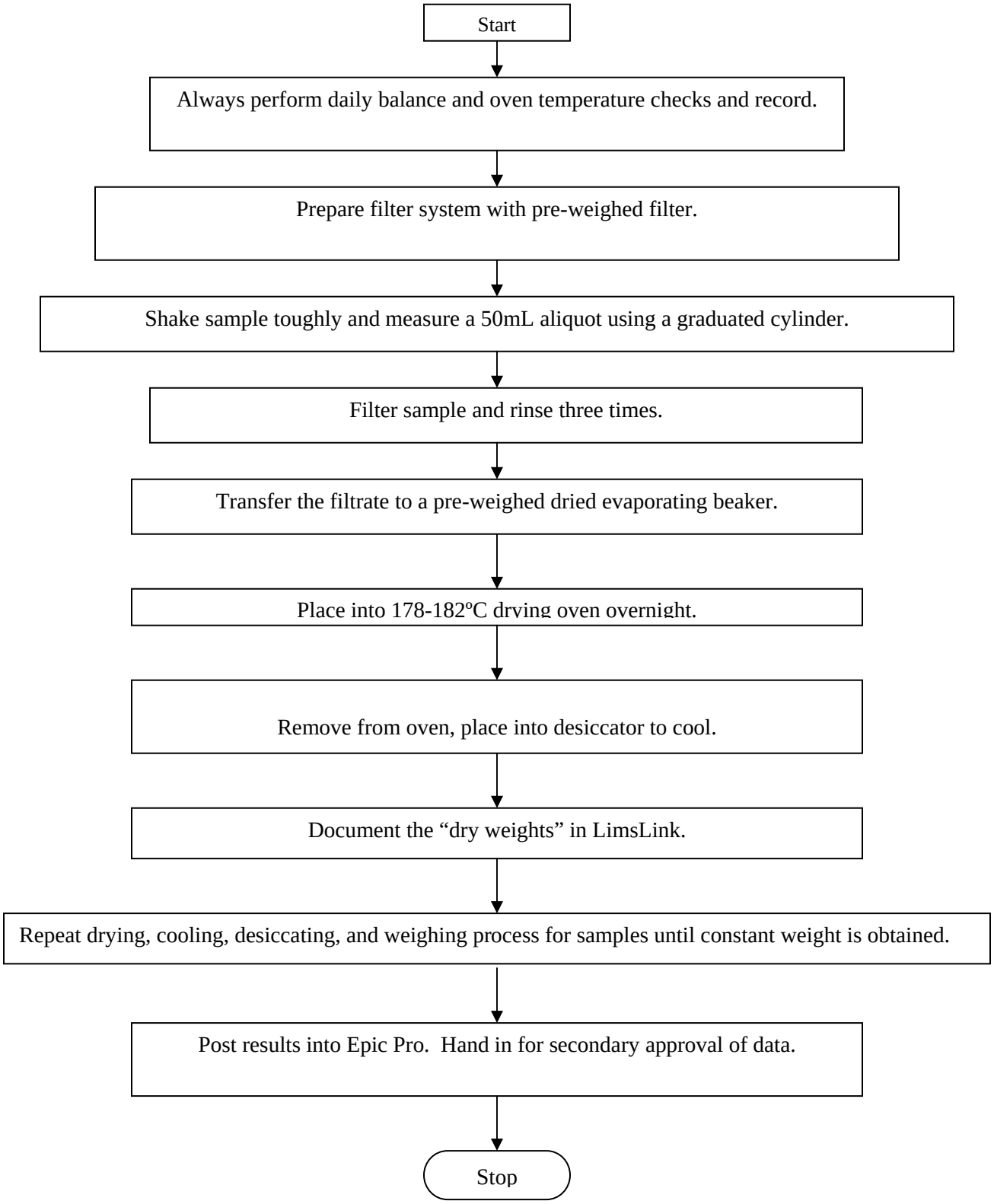
Attachment I – TS and TVS FLOWCHART



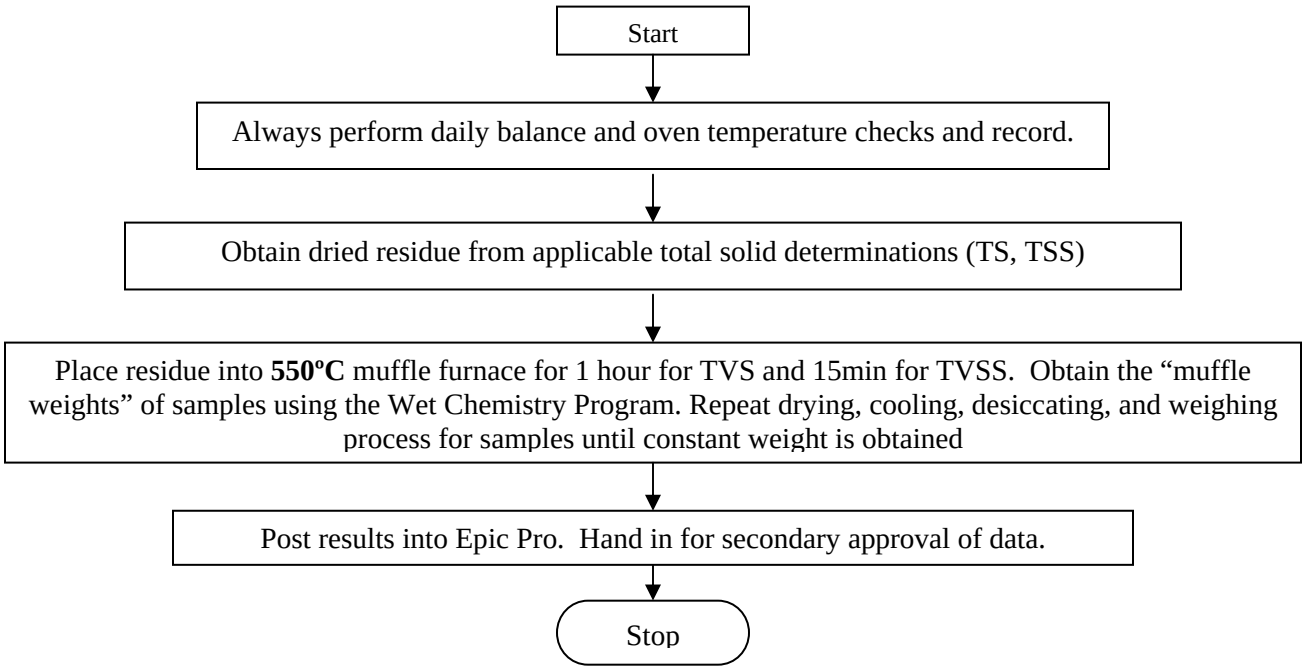
Attachment I – TSS FLOWCHART



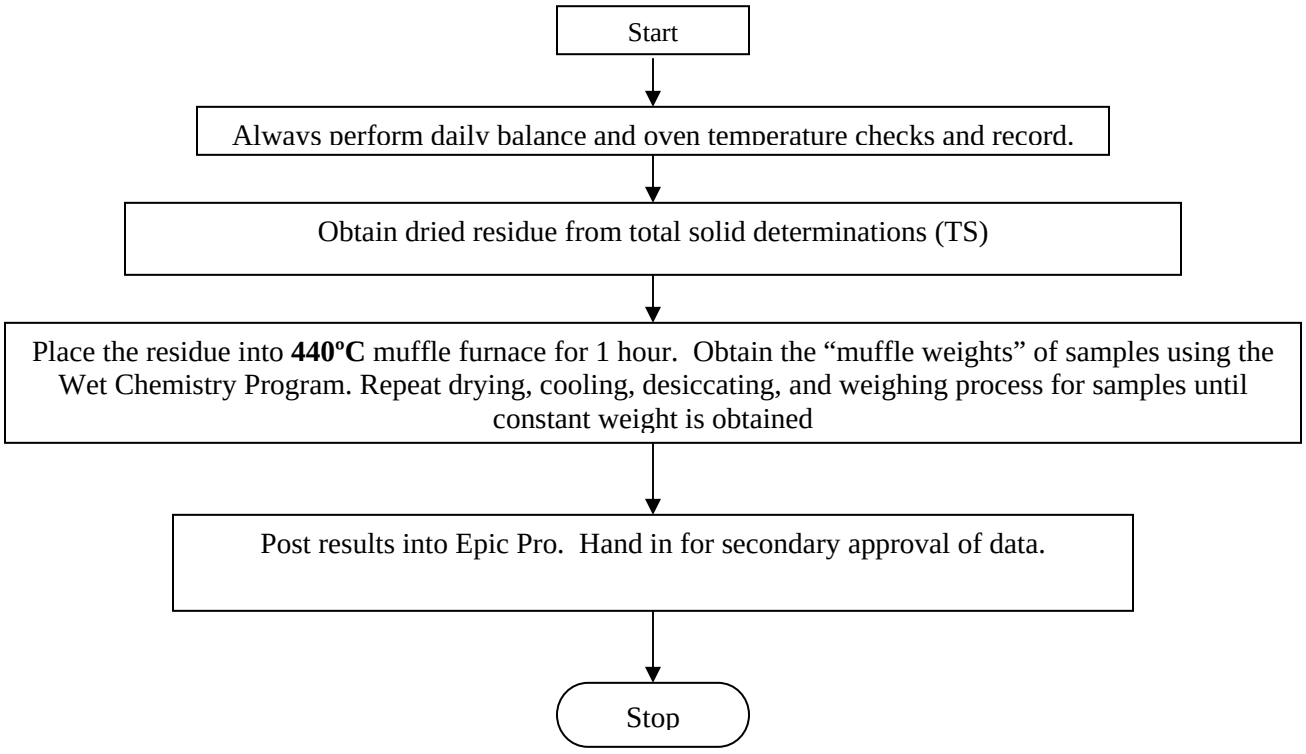
Attachment I – TDS FLOWCHART



Attachment I – TVS and TVSS FLOWCHART



Attachment I – OM and FOC FLOWCHART



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STANDARD OPERATING PROCEDURE

The Determination of Total Organic Carbon Using the Teledyne Tekmar Fusion

Reference Methods: SM 5310 C and SW846 9060A

SOP NUMBER:	S-GB-I-063-Rev.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	First Issue

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 12/29/09

Kate Grams, Laboratory Quality Manager — Date: 12/29/09

Chad Rusch, Department Manager — Date: 12/29/2009

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

This is **COPY#** **4** Distributed on **02/16/10** by **LAB** and is ____ **CONTROLLED or** **X** **UNCONTROLLED**

Table of Contents

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1. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the procedures used to determine the concentration of Total Organic Carbon (TOC), Total Carbon (TC), and Total Inorganic Carbon (TIC) in aqueous samples using the Teledyne Tekmar Fusion Instrument. This SOP follows analytical methods SM 5310C and SW 846-9060.

2. SCOPE AND APPLICATION

This SOP pertains to drinking waters, ground waters, surface waters, domestic and industrial waste samples. This SOP includes analysis using quadruplicate repetitions for SW 846-9060 and duplicate repetitions for SM 5310C.

3. SUMMARY OF METHOD

When running water samples, the sample is injected into a reactor filled with a persulfate solution where it is oxidized by means of ultra-violet light. The product of the reaction is CO_2 gas, which is then blown into the non-dispersive infrared detector (NDIR). The NDIR uses infrared energy to measure the CO_2. This measurement is proportional to the carbon in the sample. In order to analyze for TOC the water sample must first have the Inorganic Carbon (IC) removed by the addition of acid and being purged with nitrogen. TC analysis is done with out the acid addition and nitrogen purge.

4. INTERFERENCES

4.1 Carbonate and bicarbonate carbon represent interferences under the terms of this test and must be removed or accounted for in the final calculation.

4.2 When dealing with a water matrix, this SOP is applicable only to homogenous samples that can be injected into the apparatus reproducibly by means of an auto-sampler syringe.

5. SAFETY

5.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan are made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

5.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

5.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

6. DEFINITIONS

6.1 Total Carbon (TC): The measurement of all the carbon in the sample, both inorganic and organic.

6.2 Total Organic Carbon (TOC): All carbon atoms covalently bonded in organic molecules. To measure TOC, all the inorganic carbon is removed by addition of acid and purging: The result is that only organic carbon is left.

6.3 Total Inorganic Carbon (TIC): The measurement of the total inorganic carbon is found by subtracting the Total Organic Carbon from the Total Carbon. TIC = TC – TOC.

6.4 Additional definitions can be found in Section 10 of the Pace Analytical Services, Inc. Quality Manual.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Water samples are collected in amber glass 40mL VOA vials or 4oz amber glass jars, which are acidified with H_2SO_4 to a pH of <2. Samples are shipped to the lab on ice and stored at 4^{o}C until time of analysis. Analysis must occur within 28 days of sample collection. Samples to be analyzed for Total Carbon must be received unpreserved in amber glass 40mL VOA vials or 4 oz amber glass jars.

8. REAGENTS AND STANDARDS

8.1 Reagents

8.1.1 Phosphoric Acid (H_3PO_4) – 85%

8.1.2 Phosphoric Acid (H_3PO_4) – 21%

To make: Fill 1000mL volumetric flask with 500mL of DI Water. Pour 250mL phosphoric acid into the volumetric. Transfer to 1000mL bottle and label. Shelf life = 1 year.

8.1.3 Deionized water (DI water)

8.1.4 Purified Compressed Nitrogen

8.1.5 Sodium Persulfate – Neat

8.1.6 Sodium Persulfate Solution, 10.0% w/v – Dissolve 100 g of sodium persulfate in a one liter volumetric flask, add 500 ml DI water followed by 25 ml 85% phosphoric acid. Dilute to volume with deionized water.

8.2 Standards

8.2.1 Two sources of neat Potassium hydrogen phthalate (KHP)

8.2.1.1 A **Primary Source** to be used for C**alibration**, **CCV**s and **RLVS** standards. Expiration date – 5 years from date of receipt, not to exceed manufacturers expiration date.

8.2.1.2 A **Secondary Source** to be used for **ICV, LCS**, and **MS/MSD** standards and spikes. Expiration Date – 5 years from date of receipt, not to exceed manufacturers expiration date.

8.2.2 See Table A for Stock, Intermediate, and Working Standards, instructions and concentrations. **Shelf Life = 1 Month**

9. EQUIPMENT AND SUPPLIES

9.1 **Equipment**

9.1.1 Teledyne Tekmar Fusion TOC analyzer with NDIR detector

9.1.2 Calibrated Mechanical Pipettes –Assorted adjustable air displacement pipettes with disposable tips - Eppendorf or equivalent.

9.1.3 Volumetric flasks

10. CALIBRATION AND STANDARDIZATION

10.1 Turn on the Teledyne Tekmar Fusion TOC analyzer power and the Compressed Nitrogen.

10.2 Enter Teledyne Tekmar Fusion software through the Fusion icon. Double click on the instrument in the dialog box, this will open the full screen instrument control.

10.3 **Activating the instrument**. Go to the Instrument dropdown and select Ready Mode. This will turn on the UV lamp and ready the instrument for use.

10.4 **Setting up a new curve**. Go to NEW dropdown and select Calibration then TOC. This is where the new calibration curve is named. Through the Edit drop down rows can be

10.5 **Activating the New Curve**. Set the new curve as the active curve by going to the Setup dropdown and selecting Calibration, then Set Active, and TOC Curves. From the popup set the Aux to the calibration curve just set up. Leave all the other fields set to Default. OK will close the popup.

10.6 **Running the New Curve**. Click Run then Sample Setup and change the sample type to TOC Standard. In the popup select Aux and then click OK. In the new popup select the level that is to be run by highlighting it. Number of Repeats should be 1, Method ID is based on ppm range and date made, Mode is TOC, and the Calibration Curve should reflect the new curve. Click Save/Use. Click Start and enter sample weight (40uL for standards and blanks) and follow the prompts to inject the boat. After a calibration point is run a calibration popup will appear showing each point that has been analyzed. From this popup different points can be selected, the curve calculated, and the calibration report printed. This popup is closed by clicking OK.

10.7 Rest of Calibration Points. Repeat 10.4.6 for the rest of the calibration points. For each point TOC Standard will need to be selected even though it is already showing. This is done to initiate the next popup.

10.8 When four standards have been read click on menu command Results, Calibration. Select the calibration curve ID. This is the same as the popup that shows after each calibration point. Locate and check the calibration points just performed, all others should not be checked. This will create a calibration curve. The curve will be 1st order linear. The r-squared value must be greater than 0.995, if not, recalibrate.

10.9 Initial Calibration QC. Change the Sample Type to Sample and analyze the applicable QC: ICV, ICB, RLVS, CCV, and CCB.

10.10 The calibration report and all analyses should be printed out with all standards traced back to COA and scanned to a file on the desktop labeled the same as the calibration ID.

11. PROCEDURE

11.1 There are two different methods by which to analyze TOC: SW846 9060A and SM 5310C.

11.1.1 When referencing Method SW846 9060A, quadruplicate analysis is required for all samples. Each sample will be composed of 4 individual injections. Report all four individual injection readings and the average of the four readings.

11.1.2 When referencing Method SM 5310C, two injections of the sample within 10% RPD is a valid analysis. The first injection reading that is within 10% RPD of the next injection reading is reported. If the first two injection readings are at or below the PQL, precision is NOT calculated and the first injection reading is reported. If no injection reading is within 10% RPD of the next injection reading and the injection readings are above the PQL, the sample must be rerun. This is used for water matrix only.

11.1.3 No injections can be used if they are above the curve. The sample must be diluted and rerun.

11.2 Water Sample Preparation

11.2.1 Prepare the water sample as follows:

11.8.4.1 Shake sample vigorously to suspend the sediment.

11.8.4.2 Pipette 1.00mL of sample into a clean 40mL auto-sampler vial and dilute to 20mL with 19.0mL of lab water.

11.8.4.3 The Teledyne Tekmar Fusion will add 1mL of 21% Phosphoric Acid to all samples and QC including MB, LCS, and MS/MSD and purge with Nitrogen. For TC analysis the Teledyne Tekmar Fusion will not add 1mL of 21% Phosphoric Acid and not purge with Nitrogen.

11.8.4.4 Prepare Method Blank (MB) by pipetting 20.0mLs DI water into clean 40mL auto-sampler vial.

11.8.4.5 Prepare the Laboratory Control Spike (LCS) by pipetting 1.0mL of 100mg/L Secondary Intermediate Standard into clean 40mL auto-sampler vial and dilute to 20mL with 19.0mL of lab water.

11.8.4.6 Prepare the Matrix Spike (MS), Matrix Spike Duplicate (MSD) by pipetting 1.0mL of 100mg/L Secondary Intermediate Standard and 1.00mL of sample into clean 40mL auto-sampler vial and dilute to 20mL with 18.0mL of lab water.

11.3 Water Sample Analysis.

11.3.1 Turn on the compressed nitrogen tank then turn on the Teledyne Tekmar Fusion power switch on the instrument.

11.3.2 Log onto Fusion icon on desktop

11.3.3 Once Fusion window is open click on Ready icon on top toolbar to turn on instrument lamp.

11.3.4 Build sample schedule by selecting New and then Schedule.

11.3.5 Schedule begins with line 1 clean, line 2 blank, followed by the batch samples with appropriate CCV, CCB, and RLVS samples included. Run a CCV/CCB every 10 samples and at the end of the run.

11.3.6 Sample ID follows the following format “sample number_Batch number_X dilution”. Click on Method ID cell and then select the appropriate method being used in the batch, method will attach its calibration automatically. This is where TC and TOC is differentiated.

11.3.7 Select number of reps to be run, CCV, CCB, RLVS run via single reps, samples are 4 reps for 9060 and 2 reps for 5310C.

11.3.8 Once all samples have been added to schedule click “save and start” on upper toolbar. Save schedule as “WETA Batch # HBN # TOC Date”

11.3.9 Schedule will shut off automatically once the end of the schedule has been reached.

11.4 Shutdown

11.4.1 Turn off the Teledyne Tekmar Fusion power switch, upper right front of instrument.

11.4.2 Turn off the compressed nitrogen at the cylinder valve.

11.5 Epic Pro/LimsLink

11.5.1 Samples are batched in Epic Pro.

11.5.2 Samples are pulled into a new LimsLink file created for the batches in the analysis.

11.5.3 The sample dilutions are recorded in LimsLink.

11.5.4 When the analytical run has been completed, acceptable data is then posted to Epic Pro.

11.6 Calculations:

11.6.1 The instrument provides raw data results in ppm (mg/L) for aqueous samples. Add data produced by the Teledyne Tekmar Fusion must be processed through the appropriate curve.

11.6.2 SW846 9060A Sample Calculations:

Injection 1:

Raw Data Value mg/L X Dilution = TOC (mg/L) (TOC1)

Injection 2:

Raw Data Value mg/L X Dilution = TOC (mg/L) (TOC2)

Injection 3 (Quad Only):

Raw Data Value mg/L X Dilution = TOC (mg/L) (TOC3)

Injection 4 (Quad Only):

Raw Data Value mg/L X Dilution = TOC (mg/L) (TOC4)

11.6.3 SW846 9060A average Sample result (quadruplicate)

$$\text{Quad Average Result} = \frac{(TOC1) + (TOC2) + (TOC3) + (TOC4)}{4 \{\text{number of injections}\}}$$

11.6.4 For samples analyzed in Quadruplicate (SW846 9060A) each injection is calculated using the appropriate injection equation according to 11.6.2. The average final result is acquired using 11.6.3. The final average result from 11.6.4 is reported as well as each individual injection's final result.

11.6.5 SW846 9060A : The accuracy is calculated based on the average and not the individual injections.

11.6.6 SM 5310C: Repetition acceptance criteria

Relative percent difference (RPD) must be less than 10%

$$\%\ RPD = \frac{I\ Rep.\ 1 - Rep.\ 2I}{(Rep.\ 1 + Rep.\ 2)/2} \times 100$$

Rep. 1 = raw amount of first replicate
Rep. 2 = raw amount of second replicate

11.6.7 SM 5310C : The first rep that is within the acceptance criteria stated in 11.6.6 is reported as follows:

Raw Data Value mg/L X Dilution = TOC (mg/L)

11.6.8 MS/MSD calculation for both SW846 9060A and SM 5310C:

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result
SR = Sample result
SA = Spike added

For SW846 9060A: recovery is only calculated on the final average – not each injection.

11.6.9 Precision (for QC samples) for both SW846 9060A and SM 5310C:

The precision is calculated based on the % recovery of the matrix spike / matrix spike duplicate (MS/MSD) result.

Relative percent difference (RPD) calculation:

$$\% \text{ RPD} = \frac{|MS-MSD|}{(MS+MSD)/2} \times 100$$

For SW846 9060A: precision is only calculated on the final average – not each injection.

12. QUALITY CONTROL

12.1 Refer to the most current version of the Pace Quality Manual Appendix I Quality Control Calculations and SOP GB-Q-009 Common Laboratory Calculations and Statistical Evaluation of Data for equations and calculation details.

12.2 Initial Calibration Verification (ICV) must be run immediately following the instrument calibration. The ICV must be prepared from stock standard obtained from a different source than the stock standard used to prepare the initial calibration and must be prepared at a level at or near the mid range of the calibration curve. The result of the ICV must fall within the range of 90%-110% - if not rerun or recalibrate.

12.3 Initial Calibration Blank (ICB) – An ICB is analyzed after the ICV and must meet the acceptance criteria before samples are analyzed. The absolute value of the ICB result must be less than the laboratory PQL – if not rerun or recalibrate.

12.4 Continuing Calibration Verification (CCV) - Each analytical run must begin and end with a CCV and a CCV must be run every 10 samples. The CCV must be prepared from the same solution as the mid-point calibration standard and the result must fall within the range of 90%-110%. If outside the range, rerun 1X. If still outside the range, the problem must be corrected before continuing and the affected samples reanalyzed.

12.5 The Continuing Calibration Blank (CCB) – A CCB is analyzed after the CCV and must meet the acceptance criteria before samples are analyzed. The absolute value of the CCB result must be less than the laboratory PQL. If outside the range, rerun 1 time. If still outside the range, correct the problem and rerun all samples back to the last passing CCB.

12.6 Method Blank - A Method Blank (MB) must be prepared and analyzed with every sample batch or every 10 samples whichever is more frequent. The data obtained is used to assess contamination from the laboratory environment. Values that exceed the PQL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis. Values that are between the MDL and PQL are evaluated based on the concentration in the samples compared to the concentration in the blank.

12.7 Laboratory Control Sample (LCS) - A LCS prepared from an independent source must be performed with every batch. The LCS must be evaluated for accuracy and must meet the laboratory generated control limits before samples are analyzed. If no in-house limits are in use, then a range of 80 - 120% will be used. If the LCS recovery does not meet the acceptance criteria corrective action must be taken and the LCS recovery must be acceptable before proceeding with sample analysis. A LCSD is performed when requested by the client or when there is insufficient sample volume to perform a matrix spike / matrix spike duplicate. The LCS/LCSD must be evaluated for precision and must meet the laboratory generated control criteria.

12.8 Matrix spike/Matrix spike duplicate - A MS/MSD pair must be prepared and analyzed every 10 samples. The MS must be a duplicate of the aliquot used for sample analysis. Calculate the percent recovery, corrected for concentration measured in the parent sample, and compare to the in-house generated limits. If no in-house limits are in used then a range of 80 - 120% will be used. Calculate the precision between the MS and MSD and compare to the in-house generated limits. If no in-house limits are in use, then an upper limit of 20% will be used.

12.9 Reporting Limit Verification Standard (RLVS) – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

12.10 When preparation of a sample exceeds 28 days past the time of collection, notify the project manager before proceeding. If a sample is run past 28 days after collection, flag the result with appropriate data qualifier.

12.11 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with appropriate data qualifier.

12.12 See attachments Table B and Table C for a summary of QC.

13. METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, Orientation and Training Procedures. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.1.2.1 Analysis of four (4) replicates of reagent water spiked with 5.00mL of 100 mg/L Secondary Intermediate Standard to 20 mL final volume with DI Water. The recovery is to be within the current water LCS QC limits for the known concentrations and 20% RSD for all replicates.

13.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, Method Detection Limit Studies, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.1.4 Linear Calibration Range - The linear calibration range must be determined initially and verified whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. If any verification data exceeds the initial values by $\pm$ 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

13.1.5 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, PE/PT Program, to demonstrate continuing competence. All results are stored in the QA office.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

14.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, Waste Handling.

14.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. REFERENCES

15.1 40CFR Part 136 National Institute of Standards and Technology (NIST)

15.2 Standard Methods for the Examination of Water and Wastes, on-line Edition – Method 5310 C -00.

15.3 USEPA Test Methods for Evaluating Solid Wastes, SW 846, 3rd Edition, Methods 9060A.

15.4 PASI Quality Manual, current revision

15.5 Teledyne Tekmar Fusion TOC analyzer User Manual

16. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

16.1 Table A**: STANDARD**S

16.2 Table B: **QUALITY CONTROL**

16.3 Table C: **ANALYST/TECHNICIAN DATA ASSESSMENT**

17. REVISIONS

Revision Number	Reason for Change	Date
S-GB-I-063-Rev.00	First Issue	28Dec2009

Table A: STANDARDS:

Standard Name	Final Conc. (mg/L)	Amount of Std Added	Conc. of Std	Name of Std Used	Reagent Used	Final Volume (mL)
Stock and Intermediate Standards						
4000mg/L Primary Stock Standard	4000	4250 mg	Neat	Primary KHP Neat	DI Water	500
4000mg/L Secondary Stock Standard	4000	4250 mg	Neat	Secondary KHP Neat	DI Water	500
100mg/L Primary Intermediate Standard	100	5.0 mL	4000 mg/L	4000mg/L Primary Stock Standard	DI Water	200
100mg/L Secondary Intermediate Standard	100	5.0 mL	4000 mg/L	4000mg/L Secondary Stock Standard	DI Water	200
Calibration and QC Standards						
Calibration Std 1	0.00	0.00 mL	-	-	DI Water	100
Calibration Std 2	0.10	0.10 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
Calibration Std 3	0.25	0.25 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
Calibration Std 4	0.50	0.50 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
Calibration Std 5	1.00	1.00 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
Calibration Std 6	2.00	2.00 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
Calibration Std 7	5.00	5.00 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
Calibration Std 8	10.0	10.0 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
ICV	5.00	1.00 mL	100 mg/L	100mg/L Secondary Intermediate Standard	DI Water	20
CCV	5.00	5.00 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
ICB/CCB	0.00	0.00 mL	-	-	DI Water	100
RLVS	0.10	0.10 mL	100 mg/L	100mg/L Primary Intermediate Std.	DI Water	100
MB	0.00	0.00 mL	-	-	DI Water	20
LCS	5.00	1.00 mL	100 mg/L	100mg/L Secondary Intermediate Standard	DI Water	20
MS/MSD	5.00	1.00 mL	100 mg/L	100mg/L Secondary Intermediate Standard	Analytical Sample	20

Table B. QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**TOC**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples. A LCSD is required if MS/MSD is not performed.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.
Initial Calibration	Minimum of 5 standards plus blank. Must be performed every time before samples are analyzed.
RLVS	After the calibration and monthly at minimum.
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. CCV – analyzed after every 10 samples.
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. CCB – analyzed after every CCV pair.

Table C. ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**TOC If these conditions are not achieved ⇒**
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
RLVS standard	• 5
Initial / Continuing Calibration Verification	• 6
Initial / Continuing Calibration Blank	• 7

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the appropriate data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the concentration of the spike is less than 25% of the concentration of the parent, dilute parent to a level that the subsequent spike concentration will be greater than 25% the parent and so the parent concentration is above the PQL. Rerun the parent, MS, and MSD at this new dilution. If the MS and/or MSD fails at the diluted concentration, appropriately flag the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately flag the parent sample if either the MS and/or MSD fails. If the MS and MSD fails precision control limits flag the parent with the appropriate precision data qualifier.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the appropriate accuracy and appropriate precision qualifier to reflect the deficiencies.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

6. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. If the ICV/CCV recovers greater than the control limit and the samples bracketing the out of control ICV/CCV are non-detects, the results may be reported without a flag.

7. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

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STANDARD OPERATING PROCEDURE

The Determination of Total Organic Carbon Using the Apollo 9000 Instrument

Reference Method: EPA 9060A

SOP NUMBER:	S-GB-I-059-REV.01
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-I-059-REV.00

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 5/21/09

Kate Grams, Laboratory Quality Manager — Date: 5/21/09

Chad Rusch, Department Manager — Date: 5/21/09

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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Table of Contents

Section **Page**

1. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the procedures used to determine the concentration of Total Organic Carbon (TOC) in solid and soil samples using the Apollo 9000 Instrument.

2. SCOPE AND APPLICATION

This SOP is applicable the analysis of Total Organic Carbon (TOC) in soils and solids. The applicable range is MDL to the top standard in the curve. The current Pace Reporting Limit is 250 mg/kg. The current MDL can be found in Epic Pro.

3. SUMMARY OF METHOD

The sample is placed in a combustion furnace where it heats up and reacts with the catalyst that is contained in the furnace. The product of the reaction is CO_2 gas, which is then blown into the non-dispersive infrared detector (NDIR). The NDIR uses electromagnetic radiation or infrared energy to measure the CO_2. This measurement is proportional to the carbon in the sample. In order to analyze for TOC the sample must first have the Inorganic Carbon (IC) removed during the preparation process utilizing acid and heat.

4. INTERFERENCES

4.1 Carbonate and bicarbonate carbon represent interferences under the terms of this test and must be removed or accounted for in the final calculation.

4.2 This SOP is applicable only to those samples that can be adequately ground with mortar and pestle to result in a fairly homogenous sample.

5. SAFETY

5.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan are made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

5.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

5.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

6. DEFINITIONS

6.1 Total Carbon (TC): The measurement of all the carbon in the sample, both inorganic and organic.

6.2 Total Organic Carbon (TOC): All carbon atoms covalently bonded in organic molecules. To measure TOC, all the inorganic carbon is removed by addition of acid and purging: The result is that only organic carbon is left.

6.3 Total Inorganic Carbon (TIC): The measurement of the total inorganic carbon is found by subtracting the Total Organic Carbon from the Total Carbon. TIC = TC – TOC.

6.4 Additional definitions can be found in Section 10 of the Pace Analytical Services, Inc. Quality Manual.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Table 1. SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Matrix	Method	Container(s)	Preservation	Shipment Conditions	Lab Storage Conditions
Solid	9060A	4 oz Clean glass containers	None 28 days	On ice 4+/- 2^{o} Celsius	4^{0}C

8. REAGENTS AND STANDARDS

8.1 Reagents

8.1.1 Sulfuric Acid (H_2SO_4) – concentrated

8.1.2 Sulfuric Acid (H_2SO_4) – 10%

To make: Fill 2000mL volumetric flask with 1000mL of DI Water. Measure out 200mL of concentrated Sulfuric Acid and add to volumetric flask. Dilute to volume. Shelf life = 6 months.

8.1.3 Deionized water (DI Water)

8.1.4 Purified Compressed Air

8.2 Standards

8.2.1 Potassium hydrogen phthalate (KHP) – 4000 mg/L calibration stock solution

To make: Fill a 100mL volumetric flask with approximately 50mL of DI water. Dissolve 850 mg of KHP in the DI water. Dilute to volume. Shelf life = 1 month.

8.2.2 Soil 1 Point Calibration Standard – 2000 mg/Kg

Fill a 10mL volumetric flask with approximately 5mL of DI water. Pipette 5.0mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

8.2.3 Soil Calibration Standard 1 – 0 mg/Kg

10mL DI water.

8.2.4 Soil Calibration Standard 3 – 1000 mg/Kg

Fill a 10mL volumetric flask with approximately 5mL of DI water. Pipette 2.5mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

8.2.5 Soil Calibration Standard 2 and Reporting Limit Verification Standard (RLVS) – 250 mg/Kg

Fill a 10mL volumetric flask with approximately 5mL of DI water. Pipette 2.5mL of Soil Calibration Standard 3 (1000mg/Kg) into the flask. Dilute to volume. Shelf life = 1 month.

8.2.6 Soil Calibration Standard 4 – 2000 mg/Kg

Fill a 10mL volumetric flask with approximately 5mL of DI water. Pipette 5.0mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

8.2.7 Potassium hydrogen phthalate (KHP) – 4000 mg/L ICV stock solution

Fill a 100mL volumetric flask with approximately 50mL of DI water. Dissolve 850 mg of KHP in the DI water. Dilute to volume. Shelf life = 1 month.

Note: The KHP used to prepare the ICV stock solution must be from another source than the KHP used to prepare the calibration stock solution.

8.2.8 Soil Initial Calibration Verification (ICV) –1000 mg/Kg

Fill a 10mL volumetric flask with approximately 5mL of DI water. Pipette 2.5mL of ICV stock solution into the flask. Dilute to volume. Shelf life = 1 month.

8.2.9 Laboratory Control Spike (LCS) – An independently prepared certified solution of Potassium hydrogen phthalate (KHP) at a concentration equal to the mid-range calibration standard. Shelf life = 1 month from solution being made in the lab.

8.2.10 Soil Continuing Calibration Verification (CCV) –1000 mg/Kg

Fill a 10mL volumetric flask with approximately 5mL of DI water. Pipette 2.5mL of calibration stock solution into the flask. Dilute to volume. Shelf life = 1 month.

9. EQUIPMENT AND SUPPLIES

9.1 **Equipment**

9.1.1 Tekmar / Dohrmann Apollo 9000 TOC analyzer with NDIR detector

9.1.2 TOC Boat Analyzer – Rosemount/Dohrmann

9.1.3 Calibrated Mechanical Pipettes –Assorted adjustable air displacement pipettes with disposable tips - Eppendorf or equivalent

9.1.4 Analytical syringe – 500uL

9.1.5 Analytical syringe – 50uL

9.1.6 Hot Block

9.1.7 Analytical balance – accurate to 0.0001 gram

9.1.8 Mortar & Pestle

9.1.9 Spatula

9.1.10 Volumetric flasks

9.1.11 Oven

9.2 **Supplies**

9.2.1 Aluminum dishes

9.2.2 40 mL VOA vials

9.2.3 Digestion Tubes

9.2.4 Data printout paper

10. CALIBRATION AND STANDARDIZATION

10.1 Turn on the **TOC Boat Sampler** power (oven) and the **Compressed Air**.

10.2 Enter **TOC/Apollo 9000** software through the **Talk 4.2 Boat** icon.

10.3 *Activating the instrument.* Go to the **Setup** dropdown and select **Instrument**. Go to the **System** portion and select **Ready**. A bubbling sound will be made, signaling the instrument is not hibernating.

10.4 *Setting up a new curve.* Go to **Setup** dropdown and select **Calibration** then **Standards**. This is where the new calibration and the calibration points are set. Through the **Edit** drop down rows can be added, deleted, or copied and pasted. Create the following curve:

Table 2. Calibration Information

Standard ID	Concentration (ppmC)	Method ID	ugC	Comments
0ppmC	0	Boat Sampler	0.0000	
250ppmC	250	Boat Sampler	10.0000	
500ppmC	500	Boat Sampler	20.0000	
1000ppmC	1000	Boat Sampler	40.0000	
2000ppmC	2000	Boat Sampler	80.0000	

The **Cal. Curve ID** will be filled in when **File, Save As** is done. Save the file as the date that the calibration will be done. Click **OK** to exit.

10.5 *Activating the New Curve*. Set the new curve as the active curve by going to the **Setup** dropdown and selecting **Calibration,** then **Set Active,** and **TOC Curves**. From the popup set the **Aux** to the calibration curve just set up. Leave all the other fields set to **Default**. **OK** will close the popup.

10.6 *Running the New Curve*. Click **Run** then **Sample Setup** and change the sample type to **TOC Standard**. In the popup select **Aux** and then click **OK**. In the new popup select the level that is to be run by highlighting it. Number of Repeats should be 1, Method ID is Boat Sampler, Mode is TOC, and the Calibration Curve should reflect the new curve. Click Save/Use. **Click Start** and enter sample weight (40uL for standards and blanks) and follow the prompts to inject the boat. After a calibration point is run a calibration popup will appear showing each point that has been analyzed. From this popup different points can be selected, the curve calculated, and the calibration report printed. This popup is closed by clicking **OK**.

10.7 *Rest of Calibration Points*. Repeat 10.4.6 for the rest of the calibration points. For each point **TOC Standard** will need to be selected even though it is already showing. This is done to initiate the next popup.

10.8 When four standards have been read click on menu command **Results**, **Calibration**. Select the calibration curve ID. This is the same as the popup that shows after each calibration point. Locate and check the calibration points just performed, all others should not be checked. Click "**Recalc**" button. This will create a calibration curve. The curve will be 1st order linear. The r-sqr value must be greater than 0.995, if not, recalibrate.

10.9 *Initial Calibration QC*. Change the **Sample Type** to **Sample** and analyze the applicable QC: ICV, ICB, RLVS, CCV, and CCB.

10.10 The calibration report and all analyses should be printed out with all standards traced back to COA and scanned to a file on the desktop labeled the same as the calibration ID.

11. PROCEDURE

11.1 Two methods are used for soil samples, 9060A Quads and 9060A Mods. For 9060A Quads four replicates analyses of the sample are performed with each replicate and the average being reported. For 9060A Mods two replicate analyses of the sample are preformed with each replicate and the average being reported.

11.2 No injections can be used if they are above the curve. A smaller amount of sample must be used and rerun.

11.3 Soil Sample Preparation

11.3.1 Weigh 10 g of soil, add 10% Sulfuric Acid and place in a digestion block at 70°C. After sample does not react with acid. It is filtered and then baked in an oven at 103°C for a minimum of 18 hours.

11.3.2 Crush and grind the sample with a mortar and pestle to form a homogenous sample.

11.4 Epic Pro/LimsLink.

11.4.1 Samples are batched in Epic Pro.

11.4.2 Samples are pulled into a new LimsLink file created for that batches analysis by use of the batches WLD file.

11.4.3 The sample weights are recorded in LimsLink by the **Get Weight** button as the samples are weighed out.

11.4.4 When the analytical run has been completed and the data moved (see section 11.5.13), the instrument data is blended with the weights in LimsLink.

11.4.5 Acceptable data is then posted to EPIC Pro.

11.5 Sample Analysis.

11.5.1 Turn on the **TOC Boat Sampler** power (oven) and the **Compressed Air**.

11.5.2 Enter **TOC/Apollo 9000** software through the **Talk 4.2 Boat** icon.

11.5.3 *Activating the instrument.* Go to the **Setup** dropdown and select **Instrument**. Go to the **System** portion and select **Ready**. A bubbling sound will be made, signaling the instrument is not hibernating.

11.5.4 *Each analysis is performed as follows:* Click **Run** then **Sample Setup** and change the **Sample ID** to what is being analyzed. Sample Type should be **Sample**. Number of Repeats should be 1, Method ID is Boat Sampler, Mode is TOC, and the Calibration Curve should reflect the curve being used. Click Save/Use. **Click Start** and enter sample weight (40uL for standards and blanks) and follow the prompts to inject the boat. Once the instrument beeps and prints out the result from the injection, slide the boat out of the oven and wait at least one minute for the boat to cool down.

11.5.5 *CCV Analysis:* Inject 40 µL of the 1000 mg/Kg Soil Continuing Calibration Verification (CCV) standard into the boat through the septa using a 50-µL syringe.

11.5.6 *CCB Analysis:* Inject 40 µL of DI H_2O (CCB).

11.5.7 *Batch QC:* When running a Method Blank (MB), 40uL of DI water is injected into the boat. A Laboratory Control Spike (LCS) is run by injecting 40uL of the prepared LCS standard. Matrix Spike / Matrix Spike Duplicate (MS/MSD) are run by injecting 20uL of the 4000 mg/L calibration stock standard along with a variable weight of the parent sample for each the MS and MSD.

11.5.8 *Samples:* For each field sample in an analytical batch, weigh 0.04g or less into the boat. Run a CCV/CCB every 10 samples and at the end of the run.

11.5.9 While running samples, no injections can be used if they are above the curve. If an injection is above the curve, weigh out a smaller amount of the sample and rerun that injection.

11.5.10 To determine that the sample concentration is less than the reporting limit, at least 0.04 grams must be utilized.

11.5.11 *Continuing Analytical QC:* Run a CCV/CCB every 10 samples and at the end of the run.

11.5.12 *Printing data:* After the run has completed go to the **Results** drop down and select **Samples**. From here select the **File** dropdown and **Clear**. Then select the **File** drop down and Open **Results From Day**. Type in the year, month and day the samples were analyzed and then click **OK**. The samples will then appear. From the **File** dropdown select both **Print Summary Report** and **Print Detail Report**. Click **Exit** and **No** to Save Changes.

11.5.13 *Moving Data:* Click on the **Shortcut to Samples Folder** and copy the samples and QC analyzed. Paste into the **TemportTransfer Folder**. In this folder the icons are arranged by Type and the RAW Files are deleted. The remaining PRN Files are copied to the **Apollo 9000 Folder**. This is where LimsLink will access them.

11.6 Shutdown

11.6.1 Slide boat into oven.

11.6.2 Turn off the **TOC Boat Sampler** power (oven) and the **Compressed Air**.

11.7 Calculations:

11.7.1 All data produced by the Apollo 9000 must be processed through the appropriate curve.

Injection 1:
Soil:

$$\text{Raw Data Value (mg/L)} \times \frac{0.04\ (\text{ml})}{\text{Injection weight (g)}} \times \frac{1000\ (\text{g})}{1\ (\text{Kg})} \times \frac{1(\text{L})}{1000\ (\text{ml})} = \text{TOC (mg/Kg) (TOC1)}$$

Injection 2:
Soil:

$$\text{Raw Data Value (mg/L)} \times \frac{0.04\ (\text{ml})}{\text{Injection weight (g)}} \times \frac{1000\ (\text{g})}{1\ (\text{Kg})} \times \frac{1\ (\text{L})}{1000\ (\text{ml})} = \text{TOC (mg/Kg) (TOC2)}$$

11.7.2 Average sample result (mg/kg)

$$\text{Quad Average result} = \frac{(\text{TOC1}) + (\text{TOC2})}{2}$$

Note that soils are dried to 100% dry weight before analysis – therefore dry weight correction is not needed.

11.7.3 The result in mg/kg is divided by 10,000 to express the result as a percentage (%).

11.7.4 MS/MSD calculation

$$\%\ \text{Recovery} = \frac{\text{SSR - SR}}{\text{SA}} \times 100$$

SSR = Spike sample result
SR = Sample result
SA = Spike added

11.7.5 Precision (for QC samples):

The precision is calculated based on the % recovery of the matrix spike / matrix spike duplicate (MS/MSD) result.

Relative percent difference (RPD) calculation:

$$\% \text{ RPD} = \frac{|MS-MSD|}{(MS+MSD)/2} \times 100$$

12. QUALITY CONTROL

12.1 Refer to the most current version of the Pace Quality Manual Appendix I *Quality Control Calculations* and SOP GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

12.2 **Initial Calibration Verification (ICV)** must be run immediately following the instrument calibration. The ICV must be prepared from stock standard obtained from a different source than the stock standard used to prepare the initial calibration and must be prepared at a level at or near the mid range of the calibration curve. The result of the ICV must fall within the range of 90%-110% - if not rerun or recalibrate.

12.3 **Initial Calibration Blank (ICB**) – An ICB is analyzed after the ICV and must meet the acceptance criteria before samples are analyzed. The absolute value of the ICB result must be less than the laboratory EQL – if not rerun or recalibrate.

12.4 **Continuing Calibration Verification (CCV)** - Each analytical run must begin and end with a CCV and a CCV must be run every 10 samples. The CCV must be prepared from the same solution as the mid-point calibration standard and the result must fall within the range of 90%-110%. If outside the range, rerun 1X. If still outside the range, the problem must be corrected before continuing and the affected samples reanalyzed.

12.5 **The Continuing Calibration Blank (CCB**) – A CCB is analyzed after the CCV and must meet the acceptance criteria before samples are analyzed. The absolute value of the CCB result must be less than the laboratory EQL. If outside the range, rerun 1 time. If still outside the range, correct the problem and rerun all samples back to the last passing CCB.

12.6 **Method Blank** - A Method Blank (MB) must be prepared and analyzed with every sample batch or every 15 samples whichever is more frequent. The data obtained is used to assess contamination from the laboratory environment. Values that exceed the EQL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis. Values that are between the MDL and EQL are evaluated based on the concentration in the samples compared to the concentration in the blank.

12.7 **Laboratory Control Sample (LCS**) - A LCS prepared from an independent source must be performed with every batch or every 15 environmental samples, which ever is more frequent. The LCS must be evaluated for accuracy and must meet the laboratory generated control limits before samples are analyzed. If no in-house limits are in use, then a range of 80 - 120% will be used. If the LCS recovery does not meet the acceptance criteria corrective action must be taken and the LCS recovery must be acceptable before proceeding with sample analysis. A LCSD is performed when requested by the client or when there is insufficient sample volume to perform a matrix spike / matrix spike duplicate. The LCS/LCSD must be evaluated for precision and must meet the laboratory generated control criteria.

12.8 **Matrix spike/Matrix spike duplicate** - A MS/MSD pair must be prepared and analyzed every 10 samples. The MS must be a duplicate of the aliquot used for sample analysis. Calculate the percent recovery, corrected for concentration measured in the parent sample, and compare to the in-house generated limits. If no in-house limits are in used then a range of 80 - 120% will be used. Calculate the precision between the MS and MSD and compare to the in-house generated limits. If no in-house limits are in use, then an upper limit of 20% will be used.

12.9 **Reporting Limit Verification Standard (RLVS)** – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

12.10 When preparation of a sample exceeds 28 days past the time of collection, notify the project manager before proceeding. If a sample is run past 28 days after collection, flag the result with appropriate data qualifier.

12.11 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with appropriate data qualifier.

12.12 See attachments Table A and Table B for a summary of QC.

13. METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.1.4 Linear Calibration Range - The linear calibration range must be determined initially and verified whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

13.1.5 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

14.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

14.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. REFERENCES

15.1 PASI Quality Manual, current revision

15.2 USEPA Test Methods for Evaluating Solid Wastes, SW 846, 3rd Edition, Methods 9060A.

15.3 Apollo 9000 TOC Combustion Analyzer User Manual

16. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

16.1 Table A: **QUALITY CONTROL**

16.2 Table B: **ANALYST/TECHNICIAN DATA ASSESSMENT**

17. REVISIONS

Revision Number	Reason for Change	Date
S-GB-I-059-Rev.00	First Issue.	09Jan2009
S-GB-I-059-Rev.01	Updated Method Reference to SW846-9060A throughout document.	20May2009

Table A. QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**TOC**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples, whichever is more frequent. A LCSD is required if MS/MSD is not performed.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.
Initial Calibration	Minimum of 5 standards plus blank. Must be performed every time before samples are analyzed.
RLVS	After the calibration and monthly at minimum.
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. CCV – analyzed after every 10 samples.
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. CCB – analyzed after every CCV pair.

Table B. ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**TOC If these conditions are not achieved ⇒**
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
RLVS standard	• 5
Initial / Continuing Calibration Verification	• 6
Initial / Continuing Calibration Blank	• 7

1. In the absence of project specific requirements, sample detects less than 10 times the method blank contamination level is reported with the appropriate data qualifier. Sample detects greater than 10 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the concentration of the spike is less than 25% of the concentration of the parent, dilute parent to a level that the subsequent spike concentration will be greater than 25% the parent and so the parent concentration is above the EQL. Rerun the parent, MS, and MSD at this new dilution. If the MS and/or MSD fails at the diluted concentration, appropriately flag the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately flag the parent sample if either the MS and/or MSD fails. If the MS and MSD fails precision control limits flag the parent with the appropriate precision data qualifier.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the appropriate accuracy and appropriate precision qualifier to reflect the deficiencies.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

6. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. If the ICV/CCV recovers greater than the control limit and the samples bracketing the out of control ICV/CCV are non-detects, the results may be reported without a flag.

7. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

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STANDARD OPERATING PROCEDURE

Biological Tissue and Plant Preparation

Reference Methods: N/A

SOP NUMBER:	S-GB-L-001-REV.03
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-L-001-REV.02

LOCAL APPROVAL

Nils Melberg, Laboratory General Manager	08/07/09 Date
Kate Grams, Laboratory Quality Manager	8/7/09 Date
Glen Coder, Department Manager	8/7/09 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
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Section **Page**

1. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the processes utilized to grind plant and biological tissue samples into a homogenous sample suitable for use by the organic extraction and inorganic preparation staff.

2. SCOPE AND APPLICATION

The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of plant and biological tissue samples.

3. SUMMARY OF METHODS

3.1 Necropsy and/or filleting of whole body animals may be performed to isolate the individual organs or portions of the specimen to be homogenized and utilized for analysis.

3.2 This SOP involves instruction to chop, grind, and blend plant materials and biological tissue into a homogenized sample compatible with analysis of volatile organic compounds, semivolatile organic compounds, and metals.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the analytical results. All of these materials must be free from interferences under the conditions of the analysis by performing method blanks.

5. SAFETY

5.1 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan is made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

5.2 Protective eyeware, gloves, and a lab coat must be worn at all times. Hearing protection should be worn when the blender is in operation.

6. DEFINITIONS

Refer to glossary of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 Unprocessed samples must be kept frozen in their original sample containers.

7.2 Small rodents must undergo a special procedure to destroy any Hantavirus, which may be present. Refer to the most recent version of SOP S-GB-L-002 Small Rodent Handling and Homogenization for details.

7.3 After processing, the homogenate must be kept frozen in glass jars. Individual jars of samples are grouped together as appropriate and stored in a labeled cardboard box within the freezer.

8. EQUIPMENT AND SUPPLIES

8.1 Stainless steel spatula

8.2 HDPE or stainless steel cutting boards

8.3 Heavy bladed knives and/or meat cleavers

8.4 Mallets, plastic faces, 2-3 pounds

8.5 Hobart stainless steel meat grinder

8.6 Blender, stainless steel blade with glass or stainless steel containers (plastic containers not suitable)

8.7 Vial: 40 mL with Teflon-lined septum caps

8.8 Wide mouth 4-16 ounce glass jars with Teflon-lined septum caps

8.9 Catfish, Tilapia, or Canned tuna fish

8.10 Tekmar Tissumizer

8.11 Liquid Nitrogen or dry ice

8.12 Balance, 3 place

8.13 Aluminum foil

8.14 Forceps

8.15 Scaler, stainless steel spoons

8.16 Pliers

9. REAGENTS AND STANDARDS

9.1 Deionized Water

10. CALIBRATION

Refer to the current revision of S-ALL-Q-013 *Support Equipment* for how to calibrate a balance.

11. PROCEDURE

11.1 Clean the work area by wiping the surfaces with a damp cloth. Wash utensils and grinders with hot water and Liquinox. Rinse with tap water. Rinse with DI water. Allow the utensils and grinders to air dry. Cover with aluminum foil as needed to prevent contamination.

11.2 Depending on the sample matrix and specific instructions provided by the customer, the method for ensuring homogeneity may vary. Necropsy and/or filleting of whole body animals may be performed to isolate the individual organs or portions of the specimen to be homogenized and utilized for analysis. The project manager must be contacted for clarification prior to thawing the samples if there are any questions.

11.3 Select a set of samples for processing. Depending on the size of the specimen, remove the samples from the freezer to allow the specimen to partially thaw. Large specimen typically need to thaw overnight at room temperature. Small specimen require a shorter amount of time and may be placed in a refrigerator overnight or thawed at room temperature for 2-3 hours during the day of processing. It is important to make sure that each specimen is not touching another specimen during the thawing process.

11.4 Record the date and time that the specimen are taken out to thaw in the notebook.

11.5 Pre-label sample jars with the LIMS numbers. Transport the clean, dry utensils and pre-labeled jars to the countertop work area.

11.6 Once the specimen is adequately thawed, processing may begin. Compare the label on the specimen with the pre-labeled jar to make sure errors have not occurred.

11.7 Small fish, such as minnows, are usually collected as composites and will represent a single composite sample. Large whole fish that require compositing are chopped into cubes and put through the meat grinder together (refer to 11.10) and aliquots of the ground tissue are blended with liquid nitrogen (refer to 11.11).

11.8 If the specimen requires filleting prior to homogenization, thaw the fish to the point that it can be cut into with a sharp clean knife. Skinning or scaling may be necessary prior to filleting the fish.

11.8.1 **Skinning**: Catfish, bullheads, and other fish may need to be skinned prior to removing fillets. With a sharp knife slice the skin front to back along the dorsal side of fish. Make another incision from top to bottom just behind the gills. Hold the fish head with one hand and grasp an edge of the skin just behind the gill with pliers. Peel the skin back toward the tail.

11.8.2 **Scaling:** If scales are to be removed prior to filleting, lay the fish flat on a cutting board. Grasp the fish with one hand and with the other hand use a scaler to scrape the scales off the fish. Work the scaler from the tail toward the head. Rinse the scales and slime from fish prior to filleting.

11.8.3 **Filleting:** Begin with an incision just behind the gills, cutting through the fish from back to belly. Next, make a clean cut along the dorsal ridge towards the tail. Be careful not to cut into the gut cavity. After cutting through to the tail, separate the fillet from the rib cage, peeling the fillet from the carcass with the non-cutting hand. Pick out any bones with forceps.

11.9 Chop large whole body specimens, plant material, or fillets into 2-3 inch cubes using a sharp knife and mallet. Smaller samples of limited quantity must be finely ground using the blender in step 11.11.

11.10 Grind the cubes in a large commercial meat grinder to coarse texture. Repeat the procedure a minimum of two times to ensure proper texture.

11.11 Transfer the course ground sample to a stainless steel bowl containing liquid nitrogen. Place the frozen sample in a blender cup and blend the frozen tissue to a powder consistency.

11.12 Samples such as eggs, insects, and small individual organs (liver, brain) may be prepped with the tissumizer in a jar to avoid loss of sample. The technician documents that the sample was prepared in the jar on the prep worksheet or notebook.

11.13 Transfer the blended sample into the pre-labeled jars.

11.14 Clean the work area and the utensils in accordance with step 11.1 between samples.

11.15 Periodically, canned tuna or other fish is homogenized using this procedure for use as a quality control matrix in the laboratory.

12. QUALITY CONTROL

Not Applicable.

13. METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.2 The analyst must read and understand this procedure with written documentation maintained in the training file.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

14.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. REFERENCES

15.1 USEPA National Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume I: Fish Sampling and Analysis-Third Edition.

15.2 SOP S-GB-L-002 Small Rodent Handling and Homogenization.

16. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ETC.

16.2 Appendix I : Biota Homogenization Log.

Green Bay
Biota Homegenization Log

Pace Analytical

Project:
Date/Time Removed to Thaw: Location: 40FRG21/Room Temperature (circle one)
Date/Time Prepped:
Prepped by:
Nitrogen Fill Date/Lot#:

Logbook: 2695

Sample ID	Sample Type (Fish, Eggs, etc.)	Gender (Optional) M/F/J[1]	Scales/Skin Removed (Y/N)	Whole Body/Fillet (WB/F)	Whole Clams/Shucked (WC/S)	Composite Sample (> 1 per Sample ID) (Y/N)	Nitrogen (Y/N)	Resection Performed (Y/N)[2]	Sample Comments

(1) M = Male, F = Female, J = Juvenille or Unknown Gender
(2) See Resection Worksheet#

Reviewed By _____ Date _____

F-GB-O-083-REV.01 (10Jul2009) Biota Prep Logbook
Green Bay Laboratory

Page_____

17. REVISIONS

Document Number	Reason for Change	Date
KM-L-001.Rev.0	Converted LAB 27 Rev 0 to new format. Incorporated how to fillet a fish .	20Jan2005
KM-L-001 Rev.1	Incorporated how to skin and scale a fish. Added scaler and pliers to the equipment section.	20Dec2005
GB-L-001 Rev.0	Converted to Green Bay SOP Changed the General and Quality Managers	08Feb2007
S-GB-L-001-Rev.1	Updated Signature Page to new format. Section 7.2 – Changed Assistant General Manager to General Manager Section 7.5 – Changed review cycle to annually. Sections 8.2 and 11.1 – Updated SOP number Section 16.2 – added reference	20Mar2008
S-GB-L-001-Rev.2	Updated Signature page to Periodic Review Removed Section 7 Renumbered Document	29May2009
S-GB-L-001-Rev.3	Section 9 - Removed Methanol Section 11.1 – Removed to clean surface area with Methanol Section 11.0 – Clarified number of times to process through commercial meat grinder. Section 11 – Updated references. Added Appendix I: Biota Homogenization Log	07Aug2009

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STANDARD OPERATING PROCEDURE

The Determination of Lipids in Tissues, Fats, and Plants

Reference Methods: N/A

SOP NUMBER:	S-GB-L-003-REV.02
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-L-003-Rev.01

LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 05/26/09

Kate Grams, Laboratory Quality Manager — Date: 5/26/09

Glen Coder, Department Manager — Date: 5/26/09

PEROIDIC REVIEW

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Signature	Title	Date

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Section **Page**

1. PURPOSE

The purpose of this SOP is to describe the process utilized to determine the percentage of lipid present in biological tissues, fats and plants.

2. SCOPE AND APPLICATION

The policies and procedures contained in this SOP are applicable to all personnel involved in the determination of the percent lipid in biological tissues, fats and plants.

3. SUMMARY OF METHOD

An aliquot of a sample extract is placed into a pre-weighed aluminum weighing pan and the solvent is allowed to evaporate. The percentage of lipid present in the sample is then determined gravimetrically.

4. INTERFERENCES

Foreign material that falls into the weighing pans while the solvent is evaporating will bias the percent lipid result; therefore it is recommended to loosely cover the weighing pans with aluminum foil during the solvent evaporation step.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

6. DEFINITIONS

Refer to the glossary of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

After the extraction process is complete, sample extracts must be stored in the appropriate location until the time of percent lipid determination.

8. EQUIPMENT AND SUPPLIES

8.1 Equipment and Supplies

Instrumentation

Equipment	Vendor	Model / Version	Laboratory Identification	Description / Comments
Analytical Balance	Mettler	AE 200	40BALC	Electronic with RS-232 output, capable of weighing 0.0001g
Computer for LimsLink™				Automated sample weight upload into LIMS
LimsLink™ Software				

Supplies

Supplies	Vendor	Model / Version	Description / Comments
Disposable Aluminum Weighing Dishes	Fisher	Fisher p/n 08-732	
Pipet, Glass Serological	Fisher	Fisher p/n 007212011100	
Trays, plastic or metal	NA	NA	
Aluminum Foil	NA	NA	

9. REAGENTS AND STANDARDS

Not Applicable.

10. CALIBRATION

10.1 Analytical Balance Calibration

10.1.1 Annual Calibration - The balance must be calibrated at least annually by an outside agency and checked daily before each use using Class 1 or 2 weights. Refer to Pace SOP S-ALL-Q-013 *Support Equipment.*

10.2 Daily Calibration Check

10.2.1 Clean the balance and surrounding area prior to starting the daily calibration check.

10.2.2 Check the sight level on the balance. If it needs adjusting, level the balance.

10.2.3 The weight set ID indicated in the logbook is used as the primary set. If an alternate weight set ID is used, that ID must be recorded in the comment section of the balance calibration logbook for that day.

10.2.4 Tare the balance before weighing the NIST certified weights.

10.2.5 Use forceps or other means to lift each weight (Do not touch the weights with fingertips as the residue may artificially adjust the true value of the weights). Record the date of the calibration check, the true value of the weight, and the actual measured weight in the logbook. Repeat this procedure for the other certified weights. If calibration weights differ from the certified weights by more than specified in the balance calibration logbook, corrective action must be taken (see 11.3).

10.3 Corrective Action

10.3.1 Clean the balance and balance pan. Check the sight level on the balance and adjust if necessary. Re-tare and reweigh all the certified weights.

10.3.2 The internal calibration function (if available) of the balance may be used as a means of corrective action.

10.3.3 Utilize the internal calibration function and diagnostics. Refer to instrument manual.

10.3.4 Contact the QA office for assistance if the balance does not meet the calibration tolerances.

10.3.5 If the above action does not correct the problem, the balance should be taken out of service and appropriately labeled to avoid improper usage. A service technician should be contacted.

10.3.6 Record any corrective action. Initial and date all entries in the logbook.

11. PROCEDURE

11.1 Locate the samples to be analyzed, place on a cart and allow samples to warm to ambient temperature prior to processing.

11.2 Determine the number of aluminum weighing pans required for the number of samples to be analyzed, plus one for a blank and one for a duplicate.

11.3 The samples scheduled for analysis are batched in the **OEXT** QUE in groups of 20. The QC batch will also include a duplicate for one of the project biota samples.

11.4 After batching samples in EPIC Pro, print the work list. This creates an xxx.wld for LimsLink™ to recognize.

11.5 Open LimsLink™ to start a new worksheet, click on the running man icon. Select New. Name the worksheet by the QC batch number (Batch #). Click **OK** to initialize the method. To start the EPIC Pro upload, click on the ▶ green triangle (Play, Start) icon. Select sample info from Epic. Click **OK**.

11.6 Next, click on the worksheet header and select get file data. Scroll down and highlight the xxx.wld file that will be transferred. It will be designated the same number as the batch number. Click **OK**.

11.7 After file data has been loaded, click on the ■ red square icon to reset instrument list.

11.8 Verify balance calibration - refer to section 11.2 for balance check procedures and corrective actions. Refer to the balance logbook for the acceptance criteria for the designated balance.

11.9 For each sample, label and record the tare weight (to the nearest 0.0001 g) for an aluminum-weighing dish in the LimsLink™ worksheet (see **attachment I** – Acquiring weights and Auto posting).

11.10 Enter the sample weight extracted, the final volume of the sample extract, and the aliquot volume used for the lipid determination into the the LimsLink™ worksheet.

11.11 Using a clean serological pipette, place a 1.0mL aliquot of sample extract into the weighing pan. If there is not sufficient sample extract volume, a lesser volume may be used. Enter the volume of sample extract aliquot placed into the appropriate calculation sheet.

11.12 Weigh the sample and dish, recording to the nearest 0.01 g (**see attachment I** for recording the weight in LimsLink™).

11.13 Place the weighing pan onto a drying rack at room temperature or into a fume-hood for a minimum of 12 hours to allow for the extraction solvent to evaporate. The weighing pans may be lightly covered with aluminum foil to prevent foreign matter from falling into the pans during the solvent evaporation process.

11.14 After all the solvent has evaporated, weigh the dried residue to the nearest 0.0001g (see **Attachment I** for LimsLink™ posting procedures). This value is "gross dry weight".

11.15 Determine the Net Dry Weight for each sample by subtracting the pan weight value from the gross dry weight value.

11.16 Determine the percent lipid for each extract using the following calculation

$$\% \text{ Lipid} = \{(NDW * V)/ (W*A)\} *100$$

Where:

NDW = Net Dry Weight (g)

V = Volume of extract (mL)

W = Weight of sample extracted (g)

A = Volume of extract aliquot used for lipid determination

11.17 Report the final percent lipid as a percentage with three significant figures or two decimal places.

12. QUALITY CONTROL

12.1 The percent lipid determination must be performed on all method blanks, laboratory control spike/laboratory control spike duplicates, matrix spike/matrix spike duplicates and sample duplicates associated to an extraction batch.

12.2 The percent lipid results for all matrix spike/matrix spike duplicates and sample duplicates should be compared to the parent sample result to determine if there are any obvious irregularities with the determined results. The RPD between duplicates needs to ≤20%. If this requirement is not met, the sample must be qualified with the "R1" qualifier.

12.3 The method blank result must be ≤0.1%. If the method blank result is >0.1% then the analytical batch needs to be re-prepped and re-analyzed. If there is insufficient sample to re-prep, then the data need to be appropriately qualified with the "B" qualifier.

12.4 Calculations performed as part of this procedure by one analyst must be reviewed by another analyst that is familiar with the method.

13. METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in the training file.

13.1.2 Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) described in S-ALL-Q-020, *Orientation and Training Procedures.* All results must be ± 20% of the mean to qualify the analyst for reporting sample results. Results of DOC studies for each analyst shall be retained in the lab quality assurance office. Each analyst must successfully repeat this study annually to maintain qualification.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

14.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. REFERENCES

Randall, R.C., Lee, H., Ozretich, R.J., Lake, J.L., and Pruell, Pruell, R.J. "Evaluation of Selected Lipid Methods for Normalizing Pollutant Bioaccumulation". Environmental Toxicology and Chemistry, Vol 10, p. 1431-1436, (1991)

16. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

Attachment I
Acquiring Weights and Auto-posting Through LimsLink™

1. Acquiring the Weights and Auto-posting

1.1 In LimsLink™, click on the ▶ green triangle (Play, Start) icon and highlight **Tare Mass**. Click **OK.**

1.2 Number the weigh pans in the order of the work list and place them on a tray. Tare scale. Weigh the empty pans in order of the work list, pressing the button between each sample. Press red button to transfer weights in LimsLink™ worksheet.

1.3 Click on the ■ red square icon to reset instrument list.

1.4 Click on the ▶ green triangle (Play, Start) icon and highlight **Wet** M**ass**. Click **OK**.

1.5 Tare scale. Weigh the wet sample into the pans in order of the work list, pressing the button between each sample. Press red button to transfer weights in LimsLink™ worksheet

1.6 Click on the ■ red square icon to reset instrument list.

1.7 Close work sheet.

1.8 After the samples are dry, return to LimsLink™, click on the running man icon. Highlight the batch # and return to the worksheet.

1.9 ▶ green triangle (Play, Start) icon and highlight **Dry Mass**. Click **OK**.

1.10 Tare scale. Weigh the dry samples in order of the work list, pressing the button between each sample. Finally, press red button to transfer weights in LimsLink™ worksheet.

1.11 Tare scale. Weigh the constant weight dry samples in order of the work list, pressing the button between each sample. Finally, press red button to transfer weights in LimsLink™ worksheet.

1.12 % Lipids is calculated by the LimsLink worksheet using the following equation. Select a few samples randomly and verify that the answer is being calculated correctly:

$$\% \text{ Lipid} = \{(NDW * V)/ (W*A)\} *100$$

Where:

NDW = Net Dry Weight (g)

V = Volume of extract (mL)

W = Weight of sample extracted (g)

A = Volume of extract aliquot used for lipid determination

1.13 Highlight data that is going to be reported.

1.14 Select **Options** header and click on **Report 1**.

1.15 Wait for the **parser** and **auto-posting** programs to run. Wait for **parser 2** and **auto-posting** programs to run. **Auto-posting** is run 5 minutes after the **parser 2** runs. **Note**: It normally requires about 10 minutes to complete the data transfer.

1.16 Generate the validation list. Perform the final review.

2. Creating the Runlog

2.1 In LimsLink™, highlight data that will go into the Runlog.

2.2 In LimsLink™, click on **Printer** button. Select **Runlog** and click on **Report**.

2.3 Default path: G:\metals\prep\runlog\%moist.txt. Click on **OK**. Click on **Yes** to overwrite the system files.

2.4 After a **%lipid.txt** file has been created by LimsLink™, the data will be ready to be transferred to the **Runlog**.

2.5 Open the prep logbook.

2.6 Click on the **percent lipids** icon.

2.7 The **Runlog** sheet will come up:

- **Date**: This is the date on which the **Runlog** page is created. It should be the same as the date the samples are run.
- Click on **Import Samples** button. Data will transfer to the large box in the middle of the screen.
- Edit data and add comments as needed.
- **Signature**: Pick initials from the drop down box.

2.8 If you don't enter your initials, and then **exit** the screen, the data may still be edited. To do this, re-click on **instrument icon** and the data will be there for editing.

2.9 Once you have entered your initials, you will be able to review data by clicking on the **Review** icon. You can see your data, but it cannot be edited. If errors were made, see the QAO.

17. REVISIONS

Revision Number	Reason for Change	Date
KM-L-003-Rev.0	Converted SVO 59 Rev 0 to new format.	20Jan2005
GB-L-003-Rev.0	Converted to Green Bay SOP Changed the General and Quality Managers Section 13.2 Added RPD quality control requirement between duplicates. Section 13.3 Added Method Blank quality control requirement.	08Feb2007
S-GB-L-003-Rev.1	Updated Signature Page to new format. Section 7.2 – Changed Assistant General Manager to General Manager Section 7.5 – Changed review cycle to annually. Sections 11.2 and 11.3 were added to SOP Section 12 was revised to include EpicPro information. Section 13.2 – Updated to EpicPro qualifier. Section 14.1.2 – Update SOP reference. Revised Attachment 1	21Mar2008
S-GB-L-003-Rev.02	Update Signature Page Removed Section 7 – Responsibilities and Distribution.	26May2009

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STANDARD OPERATING PROCEDURE

Extraction of Biological Samples for Organochlorine Pesticides/PCBs

Reference Methods: SW-846 Method 3540C

SOP NUMBER:	S-GB-O-031-REV.01
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-031-Rev.0

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 02/29/08

Kate Grams, Laboratory Quality Manager — Date: 02/25/08

Glen Coder, Department Manager — Date: 02/07/08

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

This is **COPY#** **11** Distributed on **02/16/10** by **LAB** and is ____ **CONTROLLED or** **X** **UNCONTROLLED**

Table of Contents

1. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the extraction of homogenized biological tissue and plant samples compliant with SW-846 Method 3540C for analysis by SW-846 8081A and SW-846 8082.

2. SCOPE AND APPLICATION

2.1 This procedure is applicable to extraction and concentration of Organochlorine pesticides and PCBs from homogenized biological tissue and plant samples. Extracts may be prepared by this method for analysis by several chromatographic methods including, but not limited to, SW-846 Methods 8081A and 8082 following SOPs Pace Analytical Services, Inc. – Green Bay, S-GB-O-026, Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography; and Pace Analytical Services, Inc – Green Bay, S-GB-O-027, Analysis of Organochlorinated Pesticides by Gas Chromatography.

2.2 The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of extracts for chromatographic analysis.

3. SUMMARY OF METHODS

Approximately 20 grams of homogenized tissue or plant sample is mixed with sodium sulfate and extracted with methylene chloride for a minimum of 16 hours in a soxhlet extractor. The methylene chloride extracts are then concentrated, exchanged to hexane (dependent upon further extract cleanup) and concentrated to a volume of 10 mL.

4. INTERFERENCES

4.1 Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

4.2 Interferences co-extracted from samples will vary considerably depending on the source of the material. Contaminants that may interfere with the analysis may be removed from the extracts using any combination of cleanups including, but not limited to Gel Permeation Chromatography (GPC), Florisil column cleanup, Florisil cartridge cleanup, and Silica Gel Separation. These cleanup procedures are described in separate SOPs.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous material.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.3 The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

6. DEFINITIONS

6.1 Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

6.2 Duplicate Sample – A second aliquot of the same environmental sample analyzed in the same manner as the original sample in order to evaluate precision.

6.3 Laboratory Control Sample (LCS) – A blank matrix sample spiked with a known concentration of analytes of interest. The material is from a second source (not from same as calibration material). Laboratory accuracy is evaluated using the LCS. Refer to the determinative SOP for corrective action and contingencies for handling out of control data.

6.4 Laboratory Information Management System (LIMS) – A system for transferring, processing, storing, and reporting analysis results.

6.5 Lot – A quantity of bulk material of similar composition processed or manufactured at the same time.

6.6 Matrix Spike (MS) – An aliquot of an environmental sample spiked with known quantities of specified target compounds and subjected to the entire sample preparation and analysis procedure. The analysis results from a matrix spike sample are compared to results from an unspiked aliquot of the same sample to determine recovery of the spike from the sample matrix. Refer to the determinative SOP for corrective action and contingencies for handling out of control data. The sample used for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows.

6.7 Matrix Spike Duplicate (MSD) – A second aliquot of the sample that is treated the same as the original matrix spike sample. The relative percent difference between the matrix spike and matrix spike duplicate is calculated and used to assess method precision. Refer to the determinative SOP for corrective action and contingencies for handling out of control data.

6.8 Method Blank (MB) – A blank sample prepared in the laboratory containing all reagents and internal standards and is carried through the entire analytical procedure. The method blank is used to evaluate laboratory background and contamination. Refer to the determinative SOP for corrective action and contingencies for handling out of control data.

6.9 Method Detection Limit (MDL) – The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are determined by analyzing replicate spike samples prepared by the lab and taken through all preparation and analysis steps of the method. The method detection limit is calculated using the appropriate Student's t-parameter times the standard deviation of a series of spiked samples. MDL study information is located in the quality assurance office.

7. RESPONSIBILITIES AND DISTRIBUTION

7.1 Analyst – Any analyst using this procedure is responsible for reading, understanding, and following this SOP. Any deviation from this SOP must be reported to the appropriate

supervisor. The analyst must make their recommendations for changing the SOP to their supervisor or the QM in writing.

7.2 General Manager – The General Manager has overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory. The General Manager must ensure that all analysts are properly trained and qualified to use this procedure. The General Manager is also responsible to ensure that the SOP is followed. The General Manager is responsible for reviewing the SOP and communicating recommended changes to the QM. The General Manager shall review and approve all SOPs.

7.3 Quality Manager (QM) – The QM is responsible for monitoring the implementation of the SOPs. The QM shall participate in the revision of the SOP and make sure it is current. The QM shall review and approve all SOPs.

7.4 Distribution – The official version of this SOP is the signed hardcopy version found in the laboratory. A copy of the SOP shall be kept in the department for reference.

7.5 Revision – This SOP shall be reviewed every two years at a minimum. Independent of the minimum review frequency, revisions shall be incorporated as needed if procedures or methods change.

8. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 The homogenized samples must be kept frozen in glass jars.

8.2 Extracts should be stored at 4°±2ºC in the dark in Teflon-sealed containers until analysis is complete. The sample extracts must be analyzed within 40 days from extraction.

9. EQUIPMENT AND SUPPLIES

9.1 Soxhlet extractors: 55 mm inner diameter X 340 mm length holding cell with heaters and cold water condensers

9.2 Concentrator tubes: Kuderna-Danish, 10 ml, graduated (Kontes K-570050-1025 or equivalent)

9.3 Evaporation flasks: Kuderna-Danish 500 ml (Reliance G-9601-001 or equivalent)

9.4 Snyder columns: Kuderna-Danish, three-ball macro (Kontes K-503000-0121 or equivalent)

9.5 Culture tubes: 15 ml and 9 ml with Teflon-lined screw cap

9.6 Boiling chips: Teflon or pre-rinsed silicone carbide

9.7 Sodium Sulfate (Na_2SO_4): Preheated at 400°C for 4 hours in a crucible to remove contaminants

9.8 Water bath: Heated, with concentric ring cover, capable of temperature control within $\pm$5°C. The bath should be used in a hood.

9.9 Syringes: 250-1000µL Gastight syringes (Hamilton 1000 series or equivalent)

9.10 Beakers: 250 mL

9.11 Erlenmeyer flasks: 500 mL

9.12 Glass wool

9.13 Stainless steel spatulas

9.14 Analytical balance: Capable of weighing 300g $\pm$ 0.01g

9.15 Disposable Pasteur pipettes

10. REAGENTS AND STANDARDS

10.1 Methylene chloride, pesticide grade

10.2 Acetone, pesticide grade

10.3 Hexane, pesticide grade

10.4 Surrogate spiking solution: See Table 1 for standard preparation.

10.5 Matrix spiking solution: Dependent upon analysis requested. See Table 1 for standard preparation.

Table 1

Standard	Stock Standard	Conc.	Amount Used	Final Volume	Solvent Used	Final Conc.
Surrogate spiking solution	TMX (Tetrachloro-m-xylene) and DCB (Decachlorobiphenyl)	200µg/mL	10 mL	1000 mL	Acetone	2.0µg/mL
PCB Matrix Spike	One of either Aroclor 1016, 1242, 1248, 1254, or 1260	1000 µg/ml	1000 µL	200 mL	Acetone	5.0µg/mL
Pesticide Matrix Spike	Custom Pesticide Mix A and Custom Pesticide Mix B	5.0 - 50 µg/ml	2000 µL each of Mix A and Mix B	25 mL	Acetone	0.4 - 4.0µg/mL
Toxaphene Matrix Spike	Toxaphene Mix	1000 µg/ml	2500 µL	50 mL	Acetone	50.0µg/mL

Historical data or requirements of specific projects may determine the analytes and concentrations added to the sample spikes.

Custom Pesticide Mix A contains alpha-BHC, gamma-BHC, Heptachlor, Endosulfan I, Dieldrin, Endrin, 4,4'-DDD, 4,4'-DDT, and Methoxychlor.

Custom Pesticide Mix B contains beta-BHC, delta-BHC, Aldrin, Heptachlor epoxide, alpha-chlordane, gamma-chlordane, 4,4'-DDE, Endosulfan II, Endrin aldehyde, Endosulfan sulfate, and Endrin ketone.

11. CALIBRATION

The analytical balance used during this procedure must be calibrated prior to use each day. Refer to the current revision of *Support Equipment* (ALL-Q-013) for how to calibrate a balance.

12. PROCEDURE

12.1 Extraction

12.1.1 Attach Soxhlet extractors (55 mm i.d. X 340 mm length) to 500-mL Erlenmeyer flasks with ground glass joints.

12.1.2 Add two plugs of glass wool to each extractor, one to cover the bottom to prevent sample from entering the solvent return arm and the other to cover the top of the sample.

12.1.3 Add 300 mL of glass-distilled Methylene chloride to the Erlenmeyer flask, along with about five boiling chips. Attach the Erlenmeyer to the Soxhlet extractor.

12.1.4 Attach the extractors to the condensers in the fume hood.

12.1.5 Adjust the temperature so the extractors cycle at a rate of 12 to 15 cycles/hour.

12.1.6 Allow the extractors to rinse for 4 hours, then shut off the heaters and allow them to cool.

12.1.7 Remove the condensers and drain all the solvent remaining in the extractors into the Erlenmeyer flask.

12.1.8 Discard the solvent and add new boiling chips to Erlenmeyer flask.

12.1.9 The extractors are now ready for the samples.

12.1.10 Weigh 20g of sodium sulfate into a 250-mL beaker; this will represent the method blank. Weigh 20g of the control matrix into a second 250-mL breaker; this will be used for the control spike. Weigh 20g samples into separate 250-mL beakers. Record the actual weight in the extraction logbook.

12.1.11 Add 40g of anhydrous sodium sulfate to each beaker and mix. More sodium sulfate may be necessary: when a sufficient amount has been added, the sample will appear granular.

12.1.12 Place the beakers in a fume hood and let them dry, stirring occasionally.

12.1.13 Remove the top glass wool plug from the Soxhlet extractors that have been pre-rinsed.

12.1.14 Transfer the entire sample from the beaker to the extractor and place the glass wool plug on top. The sample level in the extractor should not exceed the top of the solvent return arm; this will keep the entire sample immersed in solvent during the extraction process. Rinse the sample beaker with $MeCl_2$ and add to the top of the Soxhlet extractor.

12.1.15 Add 500 µL of the 2.0 µg/mL surrogate spiking solution to all samples, laboratory control spikes, matrix spikes, and method blanks. (The amount of surrogate spiking solution added may need to be adjusted for the final volume of the sample extract.)

12.1.16 Add the appropriate amount of Matrix Spike solution(s) to the laboratory control spikes and matrix spikes. This will depend upon the analytes of interest and

project specific requirements. (The amount of matrix spike solution added may need to be adjusted for the final volume of the sample extract.)

12.1.16.1 For pesticide analysis add 1000 µL of the 0.4 - 4.0 µg/mL Pesticide Matrix Spike solution.

12.1.16.2 For PCB analysis add 1000 µL of the 5.0 µg/mL PCB Matrix Spike solution.

12.1.16.3 For Toxaphene analysis add 800 µL of the 50 µg/mL Toxaphene Matrix Spike solution.

12.1.16.4 Additional compounds which may be added include 2,4-DDT, 2,4-DDD, 2,4-DDE, Hexachlorobenzene, Pentachloroanisole, Oxychlordane, Trans-nonachlor, Cis-nonachlor, and Mirex.

12.1.17 Add 350 mL of glass-distilled methylene chloride to each Soxhlet extractor.

12.1.18 Attach the condensers and set the temperature so that the extractors cycle at a rate of 12 to 15 cycles per hour.

12.1.19 Let the extractors cycle for 16 hours.

12.1.20 After 16 hours shut off the heating elements and allow the samples to cool.

12.1.21 Rinse the extractor with about 50 mL of Methylene chloride and drain it into the collection Erlenmeyer flask.

12.1.22 Drain all solvent remaining in the extractor into the Erlenmeyer flask.

12.2 Concentration

12.2.1 Assemble a K-D concentrator by attaching a 10-mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all analytes of interest.

12.2.2 Pour the extracts into the K-D concentrators. Rinse the Erlenmeyer flasks with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

12.2.3 Add one or two clean boiling chips to the evaporative flasks and attach a three-ball Snyder column. Place the K-D apparatus on a hot water bath (100°C to 105°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatuses and the water temperature as required to complete the concentration in 10 to 15 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 5 to 10 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes.

12.2.4 Adjust the volume to 10 mL using methylene chloride.

12.2.5 Samples that are to be analyzed for PCBs only will require the extracts to be exchanged to hexane. For these extracts, add approximately 50 mL of hexane to the K-D apparatus and continue concentration to a volume of 4-6 mL. Remove the K-D apparatus from the water bath and allow it to drain and cool for at least

10 minutes or until extracts have cooled to air temperature. Adjust the final volume to 10 mL using hexane.

12.3 Extract Cleanups

12.3.1 Lipid Determination: One milliliter of the extract is used to determine the percent lipids using SOP GB-L-003-Rev.3, *The Determination of Lipids in Tissues, Fats, and Plants*. The remaining nine milliliters should go through the following cleanups necessary for the required analysis.

12.3.2 GPC Cleanup of Extracts: Sample extracts requiring pesticide and PCB analysis should have contaminants removed using gel permeation chromatography. This cleanup is not necessary for samples requiring only PCB analysis because the Florisil column cleanup procedure is validated specifically to remove contaminants from the PCBs. See Section 16 for SOP Reference.

12.3.3 Florisil Column Cleanup of Extracts for PCBs: Extracts requiring only PCB analysis should be cleaned using column chromatography with Florisil. See Section 16 for SOP Reference.

12.3.4 Florisil Cartridge Cleanup for pesticides: Extracts requiring pesticide analysis may be cleaned using Florisil cartridge cleanup. See Section 16 for SOP Reference.

12.3.5 Silica Gel Separation of Pesticides and PCBs: Extracts which are to be analyzed for both pesticides and PCBs may have the PCBs separated from the majority of the pesticides using column chromatography with silica gel. Extracts may be screened prior to this cleanup to determine if PCBs will cause a problem with the identification of pesticides in the extract. If PCBs are not present, or present at levels which will not interfere with pesticide analysis, this cleanup is not necessary. See Section 16 for SOP Reference.

13. QUALITY CONTROL

13.1 One method blank is extracted per 20 samples OR per extraction batch, whichever is more frequent. The method blank should be blank sodium sulfate or an analyte-free biota matrix such as tuna fish for animal extractions or alfalfa for plant analyses.

13.2 A laboratory control spike is extracted per 20 samples OR per extraction batch whichever is more frequent. Control spikes are usually prepared using analyte-free tuna fish for animal analysis or alfalfa for plant analyses. The control spike is fortified with a representative list of the analytes of interest.

13.3 **A** matrix spike and a matrix spike duplicate must be performed for every 20 samples when appropriate sample volume is present, otherwise a laboratory control spike duplicate will be performed. Matrix spikes are used to indicate matrix effects on the analysis of the analytes of interest. The sample used for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows.

13.4 Surrogate standards must be added to all samples, laboratory control spikes, matrix spikes, and method blanks prior to extraction. Surrogates are used to monitor the efficiency of the method on each sample and possible matrix related effects.

13.5 All quality control samples (MB, LCS, MS, MSD, and duplicate samples) must be analyzed by the same determinative methods as the samples in the batch. The acceptance criteria and corrective actions are described in the determinative method SOPs.

14. METHOD PERFORMANCE

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.3 An initial demonstration of capability (IDC) must be performed per S-All-Q-020, *Orientation and Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.4 14.4 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.5 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, Waste Handling.

15.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

16. REFERENCES

16.1 USEPA, SW-846, Method 3540C, “Soxhlet Extraction”, December 1996.

16.2 *Pace Analytical Services, Inc – Green Bay, S-GB-O-026,* Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography.

16.3 Pace Analytical Services, Inc – Green Bay, S-GB-O-027, Analysis of Organochlorinated Pesticides by Gas Chromatography.

16.4 Pace Analytical Services, Inc – Green Bay, GB-L-003, The Determination of Lipids in Tissues, Fats, and Plants.

16.5 Pace Analytical Services, Inc – Green Bay, S-GB-O-032, Gel Permeation Chromatography.

16.6 Pace Analytical Services, Inc – Green Bay, S-GB-O-036, Florisil Cleanup for PCBs.

16.7 Pace Analytical Services, Inc – Green Bay, S-GB-O-037, Florisil Cartridge Cleanup.

16.8 Pace Analytical Services, Inc – Green Bay, S-GB-O-038, Silica Gel Cleanup for Organic Analysis.

17. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ETC.

Not Applicable.

18. REVISIONS

Document Number	Reason for Change	Date
KM-O-001-rev.0	Converted SVO 60 Rev 1 to new format. Incorporated associated cleanup method references.	January 20, 2005
GB-O-031-rev.0	Converted to Green Bay SOP Update General Manager and Quality Manager Added correct SOPs to Sections 11, 14, 15 Section 13.3 Added procedure for selecting MS/MSD	February 08, 2007
GB-O-031-rev.1	Update Section 1.1 and 2.1 to include analytical methods and SOPs Updated Signature Page Updated Section 12.3 with references Updated Section 14 Updated Section 16 References	January 23, 2008

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STANDARD OPERATING PROCEDURE

Extraction of PCBs in Tissue Using the Automated Soxhlet

Reference Methods: SW-846 Method 3541

SOP NUMBER:	S-GB-O-052-REV.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	First Issue

APPROVAL

Nils K Melberg
Nils Melberg, Laboratory General Manager — Date: 11/20/09

Kate E. Grams
Kate Grams, Laboratory Quality Manager — Date: 11/11/09

Glen A. Coder
Glen Coder, Department Manager — Date: 11/18/09

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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Table of Contents

1. PURPOSE

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the extraction of biota/tissue samples compliant with SW-846 Method 3541 prior to PCB analysis.

2. SCOPE AND APPLICATION

2.1 This procedure is applicable to extraction and concentration of PCBs from tissue samples. Extracts may be prepared by this method for analysis by SW-846 Method 8082 as per the latest revision of Pace Analytical Services, Inc.'s SOP S-GB-O-026 *Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography* and SOP S-GB-O-041 *Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography by 8082A.*

2.2 The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of extracts for chromatographic analysis.

3. SUMMARY OF METHODS

3.1 A measured mass of sample, typically 10 grams, is mixed with sodium sulfate until it is free flowing. The beakers are loaded into the automated soxhlet unit. The samples are subjected to a pre-programmed heat and pressure extraction cycle, which isolates the organic components from the sample mixture by contact with the solvent. The extract is concentrated to a final volume and subjected to necessary cleanups prior to analysis, as needed.

4. INTERFERENCES

4.1 Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

4.2 Interferences co-extracted from samples will vary considerably depending on the source of the material. Contaminants that may interfere with the analysis may be removed from the extracts using any combination of cleanups including, but not limited to Florisil column cleanup (SOP: S-GB-O-036 *Florisil Clean-up of PCBs*), and Sulfuric Acid cleanup (SOP: S-GB-O-034 *Sulfuric Acid Clean-up.*

5. SAFETY

5.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent.

5.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

5.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution.

6. DEFINITIONS

6.1 Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 The homogenized samples must be kept frozen in glass jars.

7.2 Extracts should be stored at 4°±2ºC in the dark in Teflon-sealed containers until analysis is complete. The sample extracts must be analyzed within 40 days from extraction.

8. EQUIPMENT AND SUPPLIES

8.1 Soxtherm extractors with controllers

8.2 Extraction Beakers 54x130

8.3 KD concentration tubes

8.4 250 mL KD concentration flasks

8.5 Inert Rack for extraction beakers

8.6 Culture tubes: 9 ml with Teflon-lined screw cap

8.7 Boiling chips: Teflon or pre-rinsed silicone carbide

8.8 Syringes: 250-1000µL Gastight syringes (Hamilton 1000 series or equivalent)

8.9 Stainless steel spatulas

8.10 Analytical balance: Capable of weighing 300g $\pm$ 0.01g

8.11 Disposable Pasteur pipettes

8.12 Funnels

8.13 Fiberglass wool

9. REAGENTS AND STANDARDS

9.1 Dichloromethane, pesticide grade

9.2 Sodium Sulfate (Na_2SO_4): Preheated at 400°C for 4 hours in a crucible to remove contaminants

9.3 Surrogate spiking solution: See Table 1 for standard preparation.

9.4 Matrix spiking solution: Dependent upon analysis requested. See Table 1 for standard preparation.

Table 1

Standard	Stock Standard	Conc.	Amount Used	Final Volume	Solvent Used	Final Conc.
Surrogate spiking solution	TMX (Tetrachloro-m-xylene) and DCB (Decachlorobiphenyl)	200µg/mL	10 mL	1000 mL	Acetone	2.0µg/mL
PCB Matrix Spike	One of either Aroclor 1016, 1242, 1248, 1254, or 1260 or any combination*	1000 µg/ml	1000 µL	200 mL	Acetone	5.0µg/mL

Historical data or requirements of specific projects may determine the analytes and concentrations added to the sample spikes.
*South Carolina State Requirement – Both 1016 and 1260 must be spiked in all LCS, MS and MSD samples.

10. CALIBRATION

10.1 Refer to the most current version of S-ALL-Q-013 *Support Equipment* for the proper procedure to calibrate the analytical balance.

11. PROCEDURE

11.1 Extraction

11.1.1 Rinse the soxhlet extraction beakers with dichloromethane. Label with sample identification.

11.1.2 Weigh approximately 10g of sample into a soxtherm extraction beaker. Record the mass of the sample in the extraction log to the nearest tenth of a gram. Repeat the process for all samples and quality control samples. Tuna is used as the matrix for the limit control samples and sodium sulfate for the method blank.

11.1.3 Add and stir enough anhydrous sodium sulfate in each beaker to create a dry, free flowing mixture. The sample should appear granular.

11.1.4 Spike beaker with 250 µL of 2.0 µg/mL surrogate spiking solution. Apply directly to dried sample in extraction beaker.

11.1.5 Spike each laboratory control spike (LCS) and matrix spike (MS/MSD) with 500 µL of 5.0 µg/mL PCB Matrix Spike solution. The volume and concentration of the matrix spiking solution may vary depending on the project requirements**.**

11.1.6 Pour approximately 140 mL of dichloromethane into the extraction beaker.

11.1.7 Mix the sample and solvent with a stainless steel spatula to prevent air pockets from developing between the sample and bottom of the extraction beaker.

11.1.8 Verify the automated soxhlet extraction settings (program 05) as summarized.

Extraction temperature	180°C
Boil Time	2 hours
Solvent Reduction	0
Extraction Time	0
Cycle Time	2 hours
Solvent	Dichloromethane

11.1.9 Rotate the extraction beakers slightly to ensure seal of top o-ring and start the extraction procedure. The process will produce approximately 100 mL of extract.

11.1.10 Once samples have completed the extraction process, turn on the concentration bath to a setting of high. The temperature should be approximately 100°C.

11.1.11 Prepare filtering funnels by adding a small plug of fiber glass wool into the neck of the funnel. A small wooden stick may need to be used to properly place the glass wool plug. Place funnel on the concentration flask and rinse with dichloromethane

11.1.12 After extraction is complete, transfer extract to the concentration flask through the funnel to separate any free flowing sample.

11.1.13 Once the extract has completely passed through the funnel, take a spatula and transfer the sample from the extraction beaker to the funnel and rinse the beaker with dichloromethane.

11.1.14 When the funnel goes dry, add enough dichloromethane to completely saturate the sample in the funnel. Let the solvent drain until the funnel is dry.

11.1.15 Add a Teflon boiling stone to the concentration flask and concentrate sample to approximately 7 mL on a heated water bath with a temperature of approximately 100°C. Remove sample from the water bath, allow to cool and drain. Once cooled, concentrate sample to less than 5 mL using nitrogen as a sparge gas on a water bath set at 32°C $\pm$ 4°C .

11.1.16 Quantitatively transfer the extracts to labeled vials. Adjust the final volume to 5 mL using dichloromethane.

11.2 Extract Cleanups

11.2.1 Extracts are to be florisil cleaned following SOP: S-GB-O-036 *Florisil Clean-up of PCBs* and Sulfuric Acid cleaned following SOP: S-GB-O-034 *Sulfuric Acid Clean-up* before delivery.

11.3 Lipid analysis

11.3.1 Lipid analysis is to be determined following the SOP: S-GB-L-003 *The Determination of Lipid in Tissues, Fats, and Plants.*

12. QUALITY CONTROL

12.1 One method blank is extracted with each extraction batch of 20 or fewer samples of the same matrix. .

12.2 A laboratory control spike is extracted with each extraction batch of 20 or fewer samples of the same matrix.

12.3 A matrix spike and a matrix spike duplicate must be performed with each extraction batch when appropriate sample volume is present, otherwise a laboratory control spike duplicate will be performed. Matrix spikes are used to indicate matrix effects on the analysis of the analytes of interest. The sample used for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows.

12.4 Surrogate standards must be added to all samples, laboratory control spikes, matrix spikes, and method blanks prior to extraction. Surrogates are used to monitor the efficiency of the method on each sample and possible matrix related effects.

12.5 All quality control samples (MB, LCS, MS, MSD, and duplicate samples) must undergo the same preparation and cleanup methods as the samples in the batch. The acceptance criteria and corrective actions are described in the determinative method SOPs.

13. METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Quality Manual.

13.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.3 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.4 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.5 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the quality assurance office.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

14.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. REFERENCES

15.1 USEPA, SW-846, Method 3541, "Automated Soxhlet Extraction", September 1994.

15.2 SOP S-GB-O-026, Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography

15.3 SOP S-GB-O-036

16. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ETC.

Not Applicable

17. REVISIONS

Document Number	Reason for Change	Date
S-GB-O-	New Document	11Nov2009

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STANDARD OPERATING PROCEDURE

Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography by SW846-8082A

Reference Methods: SW-846 Method 8082A

SOP NUMBER:	S-GB-O-047-REV.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	First Issue

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 09/22/08

Kate Grams, Laboratory Quality Manager — Date: 09/22/08

Glen Coder, Department Manager — Date: 9/16/2008

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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Table of Contents

1. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to determine the concentration of PCBs in water, soil, sediment, waste, and biological samples in accordance with SW846 Method 8082A. Samples for analysis are prepared by SW846 Method 3510C, 3540C, 3541, and 3580A. See Section 15 for list of reference SOPs.

2. SCOPE AND APPLICATION

2.1 This method is used to determine the concentration of PCBs in extracts prepared from water, soil, sediment, waste, and biological samples. A list of the Aroclors routinely analyzed, their CAS numbers and Pace Reporting Levels (PRLs) are shown in Section 16, Table A. PRLs are subject to change based on current analytical system performance and actual sample matrices.

2.2 This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/electron capture detection (GC/ECD) systems and interpretation of complex chromatograms. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results

3. SUMMARY OF METHOD

3.1 Sample extracts are prepared for analysis by the appropriate sample preparation method. The procedures for extract preparation are described in separate SOPs. A volume of sample extract is injected into a GC and compounds in the effluent are detected by an ECD based on an operating program set up to achieve optimum separation and quantitation of target analytes.

3.2 Retention time windows, in combination with characteristic elution patterns from a dual-column analysis, are used in the identification of PCBs as Aroclors.

3.3 PCBs are quantified as Aroclor mixtures by comparison of their ECD response on a single column with a calibration curve(s) constructed from the response(s) of authentic standards.

3.4 Results are reported in parts per billion (µg/kg or µg/L). Soil and sediment sample results are corrected for moisture and reported on a dry weight basis. Biological results are reported based on wet weight, or “as is” basis.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants (primarily phthalate esters) in solvents, reagents, glassware and other sample processing hardware that leads to discrete artifacts and/or elevated baselines. Phthalate esters are common contaminants that result from contact with flexible plastics. Contact with common plastics or rubber products must be avoided. Lab ware should be constructed of glass, stainless steel, or PTFE, must be thoroughly cleaned and dried prior to use, and should be rinsed with the appropriate solvent immediately before use.

4.2 Elemental sulfur is a common environmental contaminant in many soil, sediment and leachate samples, producing a broad peak that will confound analysis of early eluting analytes. Sulfur may be removed from extracts by treatment with elemental mercury, copper powder, or similar procedure described in a separate SOP.

4.3 Waxes, lipids, and other similar high molecular weight materials may be co-extracted from samples typically resulting in baseline elevation during GC analysis. These interferences may be removed by sulfuric acid clean up and/or column chromatography cleanup using Florisil or gel permeation chromatography (GPC), all of which are described in separate SOPs. Other halogenated pesticides and similar industrial chemicals, which can interfere with analytes of interest, may be removed by these procedures as well.

4.4 All solvents, reagents, glassware, and sample processing hardware must be routinely demonstrated to be free from interferences under the conditions of the analysis by monitoring method blanks and taking corrective action as required.

5. SAFETY

5.1 The toxicity, or carcinogenicity, of many chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each analyst is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel.

5.2 Take precautions when handling samples. Samples should always be treated as potentially hazardous. The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

5.3 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.4 PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds should be prepared in a hood.

6. DEFINITIONS

6.1 All applicable definitions can be found in Section 10.0 of the PASI Quality Manual.

6.2 **Extract** – A solution of contaminants extracted and concentrated from a sample.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 **General Procedures** – Procedures for sample collection, preservation, and handling are described in the separate sample preparation SOPs.

7.2 **Holding Times**

7.2.1 **Water Samples** – Samples must be extracted within 7 days of collection.

7.2.2 **Soil, Solid, and Other Waste Samples** – Samples must be extracted within 14 days of collection.

7.2.3 **Biological Samples** – Samples remain frozen for up to one year or longer per client request prior to extraction; typical extraction hold times do not apply.

7.2.4 **Extracts** – Extracts must be analyzed within 40 days of preparation.

7.3 **Sample Storage** – Store all samples and extracts in the dark at 4 ± 2°C. Biological samples must be stored at or below 0°C until extracted.

8. REAGENTS AND STANDARDS

8.1 **Solvents** – Hexane and acetone, pesticide grade (Section 16, Table B). All solvents are stored at room temperature and environmental conditions.

8.2 **Analytical Standards** – Prepared from stock standard solutions and are required for initial calibration and continuing calibration checks (Section 16, Table C). The following describes the contents of each type of solution:

8.2.1 **Calibration and Calibration Check Standards** – Five concentration levels of calibration solutions are prepared containing equal amounts of Aroclors 1016 and 1260 (combined in the same solution named AR1660 throughout this document), as well as the surrogates decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX). A single point calibration standard is required for the other Aroclor mixtures preferably at the mid-point level of the AR1016/1260 curve. A calibration check solution (ICV) is also prepared at the mid-level concentration of AR1016/1260 from second source materials.

8.2.2 **Surrogate Standard Spiking Solution** – contains decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TMX) and is spiked into all samples prior to extraction.

8.2.3 **Matrix Spiking Solutions** – contain an Aroclor mixture that is spiked into all appropriate QC samples (LCS, MS, and MSD) prior to extraction. The Aroclor(s) spiked and/or spike amounts may be adjusted when prior knowledge of the type or concentration of Aroclor(s) present in the sample matrix is known, or to comply with project requirements.

8.3 **Preparation of Analytical Standard Solutions** – Standards are prepared from commercially available stock solutions. The sources of the stock solutions, recipes for preparing dilutions and working standards, and concentrations in all solutions are shown in Section 16, Table D. All standards are prepared in hexane and stored in amber vials with PTFE-lined screw caps at 4 ºC or colder.

8.4 **Stability of Analytical Standards** – Stock solutions of Aroclor mixtures must be replaced within 1 year of preparation. All dilutions and working standard solutions must be replaced within 6 months of preparation or sooner if the standards show signs of degradation. As each standard from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook

9. EQUIPMENT AND SUPPLIES

9.1 Instrumentation

9.1.1 **GC** – Hewlett Packard (HP) 5890 equipped with dual ECDs or HP 6890 equipped with dual µECDs.

9.1.2 **GC Autosampler** – HP 7673A (5890) or HP 7863 (6890).

9.1.3 **GC Columns** – Two of the following capillary columns may be used:

9.1.3.1 RTX CLPesticides I, 30m x 0.32mm I.D. (Restek)

9.1.3.2 RTX CLPesticides II, 30m x 0.32mm I.D. (Restek)

9.1.3.3 DB-1701, 30m x 0.32mm I.D. (J&W Scientific)

9.1.3.4 DB-5, 30m x 0.32mm I.D. (J&W Scientific)

9.1.4 **Data Processor** – TurboChrom IV or HP ChemStation.

9.1.5 **Printer** – HP LaserJet 5Si or equivalent.

9.2 Glassware and Materials

9.2.1 **Gastight Syringes** – any size ranging from 10µL to 1000µL (Hamilton series 1000 or equivalent)

9.2.2 **Autosampler Vials** – 1.8mL with crimp caps

10. CALIBRATION

10.1 Initial Calibration (ICAL)

10.1.1 Analysis of Standards

10.1.1.1 The initial calibration includes analysis of a five-point calibration curve of AR1660 at concentrations of 0.1, 0.3, 0.5, 0.8, and 1.0µg/mL, which includes TMX and DCB at concentrations of 0.01, 0.02, 0.05, 0.1, and 0.15µg/mL respectively. Inject a single point standard of Aroclors 1221, 1232, 1242, 1248, 1254, 1262 and 1268 at 0.5µg/mL.

10.1.1.2 Other calibration ranges may be substituted to meet expected concentrations of samples to be analyzed. If historical data indicates a specific Aroclor is present, a five point initial calibration may be performed for the Aroclor of concern instead of using the AR1660 mixture.

10.1.1.3 A minimum of five (preferably seven) peaks must be selected for each Aroclor. The peaks chosen for quantitation should be at least 25% of the height of the largest peak in each Aroclor and should have minimal co-elution with the peaks of other Aroclors.

10.1.2 **Retention Time (RT)** – Retention time windows are used for compound identifications in samples. The RT for all components in all standards must be within the windows specified for both columns.

10.1.2.1 Make at least three injections of all analytes of interest over a 72-hour period.

10.1.2.2 Record the retention time for each selected peak for each Aroclor mixture, to three decimal places. Calculate the mean and standard deviation for each peak.

10.1.2.3 The width of the retention time window is defined as ± 3 standard deviations of the mean established. The minimum retention window will be ± 0.03 minutes.

10.1.2.4 Establish the center of the RT window for each Aroclor mixture and surrogate using the absolute RT from the calibration verification standard at the beginning of the analytical shift. Optionally, the Initial Calibration RT windows may continue to be used as long as method criteria are met. For samples run during the same shift as an initial calibration, use the RT of the mid-point standard in the Initial calibration as the center of the RT window.

10.1.3 **Response Factors (RF)** – Individually tabulate the area responses for each of the five or more peaks selected for each Aroclor versus concentration of the five-point calibration standards for each GC column. Calculate RF for each peak using the following equation:

$$RF = \frac{A_x}{C_x}$$

Where:
A_x = Total area of analyte response.
C_x = Concentration of the analyte in the solution (µg/mL).

10.1.4 Acceptance Criteria – The percent relative standard deviation (%RSD) of the five calibration factors for each peak of each Aroclor, (1016 and 1260) along with the surrogates must be ≤ 20%. If this is the case, linearity can be assumed, and the average RF can be used for quantitation. If the %RSD is >20%, a linear calibration curve may be used if the correlation coefficient is ≥ 0.99. **The results for both columns must meet calibration acceptance criteria.**

10.2 Calibration Verification

10.2.1 **Initial Calibration Verification (ICV)** – In order to consider the initial calibration acceptable, an ICV standard must be analyzed. The ICV standard must be from a second source stock and meet the same criteria as the continuing calibration verification standard before the initial calibration may be considered valid.

10.2.2 **Continuing Calibration Verification (CCV)** – A midpoint calibration check standard must be injected at the beginning and end of each 12-hour analysis period, and at intervals of not less than once every 20 samples, for calibration verification. If the response factor (area/concentration) of the check standard deviates by more than 20% from the initial average response factor, the calibration is considered out of control and analysis must be stopped.

10.2.3 **Acceptance Criteria** – The percent difference (%D) is determined for every analyte and must be within ±20% of the calibration curve. Calculate %D for each peak using the following equation:

$$\%D = \left(\frac{R_1 - R_2}{R_1} \right) x100$$

Where:
R_1 = Mean Response factor from the ICAL
R_2 = RF calculated from the CCV

10.2.3.1 First determine whether the average %D for all of the peaks for each specific Aroclor with a five-point calibration is $\leq$ 20%. Each individual Aroclor must be evaluated separately. For example, the average %D for all of the peaks used for quantitation of AR1016 must be $\leq$ 20%. If the Aroclors themselves are acceptable, evaluate the %RSD for each surrogate. If the %D is $\leq$ 20% for each individual Aroclor and surrogate, the continuing meets the acceptance criteria.

10.2.3.2 If the ending calibration verification standard exceeds 20%D criteria on the high side (i.e., an increase in sensitivity) samples that had no Aroclors detected do not need to be reanalyzed. If the continuing calibration standard criterion is exceeded on the low side (i.e., a drop in sensitivity), all samples analyzed since the last acceptable CCV must be re-analyzed.

10.2.4 **All samples must be bracketed by acceptable calibration verifications on both columns.** Perform corrective action such as injection port or column maintenance. Prior to the analysis of any subsequent samples acceptable calibration verification must be established. In the event that this cannot be achieved, a new initial calibration must be performed.

10.2.5 **Pace Reporting Limit Standard (PRLS)** – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration and monthly thereafter, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate. The AR1660 0.1µg/mL initial calibration standard is used as the PRLS.

11 PROCEDURE

11.1 Sample Preparation – All sample extracts and standard solutions must be allowed to warm to room temperature before analysis.

11.2 GC/ECD System Preparation – Verify instrument parameters as set up for current operating conditions.

11.2.1 GC Column Conditions

Carrier Gas	UHP Helium
Flow Rate	3.4 mL/min.
Make-up Gas	UHP Nitrogen
Flow Rate	35.0 mL/min.
Detector Temp.	300°C
Injector Temp.	205°C
Injection	Splitless

11.2.2 GC Temperature Program

Initial Temp.	110°C
Initial Time	1.5 min.
Rate 1	20.00°C/min.
Final Temp. 1	140°C
Final Time 1	0.00 min.
Rate 2	11.00°C/min.
Final Temp. 2	280°C
Final Time 2	5.00 min.
Rate 3	20.00°C/min.
Final Temp. 3	300°C
Final Time 3	3.00 min.

11.3 **Batch Sequence** – Generate a sequence to run a batch of samples and the associated quality control samples.

11.3.1 **Initial Calibration** – For example, the batch for initial calibration should include the following:

Series of 2-3 Primes
Solvent Blank (Hexane)
AR1660-1 (0.1µg/mL)
AR1660-2 (0.3µg/mL)
AR1660-3 (0.5µg/mL)
AR1660-4 (0.8µg/mL)
AR1660-5 (1.0µg/mL)
Solvent Blank (Hexane)
AR1660-3 ICV
AR1660-1 (0.1µg/mL) (PRLS)

11.3.2 **Sample Analysis** – For example, the typical batch for analysis of PCBs should include the following:

AR1660-301 CCV (0.5µg/mL)
(20 samples or 12-hour period)
Method Blank
Laboratory Control Spike
Samples
Matrix Spike/Matrix Spike Duplicate
Duplicate Sample(s)
AR1660-302 CCV (0.5µg/mL)

11.4 **Load Autosampler** – Load the autosampler with the appropriate primes, solvent blanks, standards and samples for the batch as it was created.

11.5 **Analyze Samples** – Analyze all standards, quality control samples, and environmental samples.

11.5.1 The method blank and LCS extracted along with the samples should be analyzed on the same instrument as the samples.

11.5.2 If the analyst determines that interferences could be removed by sulfuric acid cleanup and/or sulfur removal, then the analyst will perform the necessary cleanups and re-analyze the samples. The blank and LCS will also undergo the same cleanups and be re-analyzed.

11.6 Qualitative Analysis of Results

11.6.1 **Identification**

11.6.1.1 To be identified as an Aroclor, peaks present in a sample extract must fall within the established retention time window for a specific Aroclor. Once the Aroclor pattern has been tentatively identified, compare the responses of 3 to 10 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. Overlay comparison of sample chromatograms with standard chromatograms may be required to clearly identify patterns.

11.6.1.2 Since the chromatograms for many Aroclor mixtures overlap, the presence of multiple mixtures may complicate their quantitation. Also, environmental "weathering" of PCBs may complicate reliable identification and quantitation.

11.6.2 **Confirmation**

11.6.2.1 Confirmation is generally required using a second GC column of dissimilar stationary phase. When dual-column analysis is performed for confirmation, the same initial and continuing calibration criteria apply to both columns. If analyte concentrations are sufficient, identifications may be confirmed by GC/MS by analyzing the same extract by SW846 Method 8270.

11.6.2.2 Since Aroclors provide distinct multiple peak patterns which may be identified by an experienced analyst, confirmation on the second column may be based upon pattern recognition.

11.7 Calculate Results

11.7.1 The amount of Aroclor is calculated using the individual response factor (single point) for each of the 7 characteristic peaks chosen for quantitation of that specific Aroclor. If Aroclor 1016 and/or 1260 is being quantified use the average response factor from the AR1660 curve. Use the single point response factor from the initial calibration for all other Aroclors. Surrogates are quantified based on the average response factors for TMX and DCB analyzed with the AR1660 curve. A concentration is determined using each of the characteristic peaks and then those 7 concentrations are averaged to determine the on-column concentration of that Aroclor.

11.7.2 If the initial on-column result of a sample extract exceeds the calibration range, the extract must be diluted and re-analyzed. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve. The GC data system will calculate concentration of each parameter as µg/mL on-column in the extract. Concentrations in samples are then calculated based on sample size, total volume of the final extract, any dilution factor, and any correction factor.

11.7.2.1 Water and Water-Miscible Waste Samples

$$\text{Final Concentration } (\mu\text{g/L}) = \frac{(C_x)(DF)(U_f)(V_t)}{(V_i)(V_o)}$$

Where:
C_x = On-column concentration in extract (µg/mL).
DF = Dilution factor.
U_f = Correction factor.
V_t = Volume of final extract (µL).
V_i = Volume injected (µL).
V_o = Volume of water sample extracted (mL).

11.7.2.2 Soil/Solid, Waste and Biological Samples

$$\text{Final Concentration } (\mu\text{g/Kg}) = \frac{(C_x)(DF)(U_f)(V_t)}{(V_i)(W_s)(S)}$$

Where:
C_x = On-column concentration in extract (µg/mL).
DF = Dilution factor.
U_f = Correction factor.
V_t = Volume of final extract (µL).
V_i = Volume injected (µL).
W_s = Weight of sample extracted (g).
S = Percent Solids (biological samples not corrected for percent solids).

11.8 **Quality Control Results** – Calculate recoveries for the surrogates in all samples; spiked analytes in LCS and MS/MSD samples; and Relative Percent Differences (RPD) for duplicate and MS/MSD samples.

12 QUALITY CONTROL

12.1 Calibration Checks

12.1.1 **ICAL** – If initial calibration criteria are not met, check standards preparation procedure for errors. Prepare new standards as required and re-run the calibration.

12.1.2 **Continuing Calibration Verification** – If the CCV criteria are not met, check system parameters, identify and correct likely causes, and re-run the check. An acceptable check is required to report sample results for the applicable batch.

12.1.3 **Pace Reporting Limit Standard (PRLS)** – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration and monthly thereafter, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate. The AR1660 0.1µg/mL initial calibration standard is used as the PRLS

12.2 **Surrogate Recoveries** – Surrogate compound(s) must be added to all samples, spikes, control samples and method blanks, prior to analysis as indicators of method accuracy. Laboratory-based accuracy limits should be used for acceptance criteria. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the samples.

12.2.1 If **both** surrogate recoveries fail this criterion, re-extraction of the sample may be necessary. If surrogate recoveries are higher than the acceptance criteria and target compounds are less than the reporting limit, the results may be reported with an appropriate footnote. If recoveries appear out of control due to sample matrix, report the results with an appropriate footnote.

12.2.2 One surrogate is allowed to be outside of the control limits. For instance, if an interfering peak obscures one surrogate, then that one surrogate may be excluded. The surrogate is considered diluted out and not evaluated when the dilution performed brings the theoretical on-column concentration below the concentration of the low standard in the initial calibration curve.

12.2.3 For samples run from the state of South Carolina, both surrogates must recover between 70-130%.

12.3 **Method Blank** –The method blank must not contain analyte responses at or above the reporting limit. If the results are not acceptable, re-analyze the method blank. If the problem persists, conduct maintenance to clean the analytical system. An acceptable method blank is required to report sample results for the applicable batch.

12.3.1 One surrogate is allowed to be outside of the control limits. For instance, if an interfering peak obscures one surrogate, then that one surrogate may be excluded. The surrogate is considered diluted out and not evaluated when the dilution performed brings the theoretical on-column concentration below the concentration of the low standard in the initial calibration curve.

12.3.2 If the blank contains any analyte of interest above the reporting limit, all of the associated samples, matrix spikes, and laboratory control spikes **must** be re-extracted unless the sample concentration is greater than 20X the amount found in the blank or the analyte is not detected in an associated sample. For Wisconsin projects this criteria will be “Above the LOD”.

12.4 **LCS Recoveries** – One LCS must be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. An acceptable LCS is required to report sample results for the applicable batch.

12.4.1 If the laboratory control spike does not meet the recovery criteria, the results of all QC performed with the batch will be evaluated by the analyst. Corrective actions include re-extraction of the samples or reanalysis of the extracts.

12.4.2 For samples run from the state of South Carolina, Ar1016 and 1260 must recover between 70-130%.

12.5 One LCSD must be analyzed with each batch of 20 samples if inadequate sample is available to perform a MS/MSD. Laboratory-based accuracy limits should be used to for acceptance criteria. An acceptable LCSD is required to report sample results for the applicable batch.

12.6 **MS/MSD Recoveries** – One MS/MSD pair should be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. The sample use for the MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows.

12.6.1 If a matrix spike recovery fails this criterion, the recovery of the other spiked sample in the MS/MSD pair should be evaluated. If recovery failures are duplicated then the sample matrix is suspected as the problem and the data should be flagged and the failures discussed in the sample narrative.

12.7 **Duplicate and MS/MSD RPDs** – Five percent of all environmental samples should be analyzed in duplicate. A MS/MSD pair is also an acceptable duplicate analysis. If results are not acceptable, check for possible sample preparation problems and re-analyze if needed. Report the results with an appropriate data qualifier.

13 METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

14 POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

14.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15 REFERENCES

15.1 USEPA, SW-846, Method 8082A, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography", February 2007.

15.2 USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

15.3 Pace Analytical Services, Inc – Green Bay, SOP S-ALL-GB-O-003, *"Separatory Funnel Extraction.*

15.4 Pace Analytical Services, Inc – Green Bay, SOP GB-O-031, "*Extraction of Biological Samples for Organochlorine Pesticides/PCBs*".

15.5 Pace Analytical Services, Inc – Green Bay, SOP GB-O-040, "*Extraction of Wipes and Oil for PCB Analysis"*.

15.6 Pace Analytical Services, Inc – Green Bay, SOP GB-O-041, "*Extraction of PCBs Using the Automated Soxhlet*".

15.7 Pace Analytical Services, Inc – Green Bay, SOP GB-O-032, "*Gel Permeation Chromatography*".

15.8 Pace Analytical Services, Inc – Green Bay, SOP GB-O-034 *Sulfuric Acid Cleanup"*.

15.9 Pace Analytical Services, Inc – Green Bay, SOP GB-O-035, "*Mercury Cleanup for the Removal of Sulfur from PCB Samples*".

15.10 Pace Analytical Services, Inc – Green Bay, SOP GB-O-036, "*Florisil Cleanup for PCBs*".

15.11 Pace Analytical Services, Inc – Green Bay, SOP GB-O-038, "*Silica Gel Cleanup of Organochlorine Pesticides and PCBs*".

15.12 Pace Analytical Services, Inc – Green Bay, SOP GB-O-039, "*Copper Cleanup for the Removal of Sulfur from PCB Samples*".

16 TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

16.1 Table A. Reporting Limits for PCBs.

Aroclor	CAS #	Water PRL (µg/L)	Soil PRL (µg/Kg)	Biota PRL (µg/Kg as is)
AR1016	12674-11-2	1.0	100	50
AR1221	11104-28-2	1.0	100	50
AR1232	11141-16-5	1.0	100	50
AR1242	53469-21-9	1.0	100	50
AR1248	12672-29-6	1.0	100	50
AR1254	11097-69-1	1.0	100	50
AR1260	11096-82-5	1.0	100	50
AR1262	37324-23-5	1.0	100	50
AR1268	11100-14-4	1.0	100	50

17.2 Table B. Solvents.

Reagent	Purity	Manufacturer	Vendor	Catalog #
Hexane	NS Grade	Burdick & Jackson	MG Scientific	B&J-217-4
Acetone	Pesticide Grade	Burdick & Jackson	MG Scientific	B&J-010-4

17.3 Table C. Standard Stock Solutions.

Standard	Concentration	Manufacturer	Catalog #
Pesticide Surrogate Mix	200µg/mL each in Acetone	Restek Corporation or equivalent	32000
Aroclor 1016 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32006
Aroclor 1221 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32007
Aroclor 1232 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32008
Aroclor 1242 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32009
Aroclor 1248 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32010
Aroclor 1254 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32011
Aroclor 1260 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32012
Aroclor 1262 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32409
Aroclor 1268 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32410
Aroclor 1016	1000µg/mL in Isooctane	Supelco or equivalent	4-8097
Aroclor 1260	1000µg/mL in Isooctane	Supelco or equivalent	4-4809

17.4 Table D. Preparation of Analytical Standard Solutions.

Analytical Standard	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Expiration Date
TMX/DCB Stock Solution	Pesticide Surrogate Mix	1000µL	20mL of Hexane	10µg/mL	1 year from date of preparation
AR1221 Stock Solution	Aroclor 1221 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1232 Stock Solution	Aroclor 1232 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1242 Stock Solution	Aroclor 1242 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1248 Stock Solution	Aroclor 1248 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1254 Stock Solution	Aroclor 1254 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1262 Stock Solution	Aroclor 1262 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1268 Stock Solution	Aroclor 1268 Mix	1000µL	10mL of Hexane	100µg/mL	1 year from date of preparation
AR1660 Stock Solution	Aroclor 1016 Mix Aroclor 1260 Mix	1000µL each	10mL of Hexane	100µg/mL each	1 year from date of preparation
AR1660 ICV Stock Solution	Aroclor 1016 Aroclor 1260	1000µL each	10mL of Hexane	100µg/mL each	1 year from date of preparation
AR1221-3 Calibration Standard	AR1221 Stock Solution TMX/DCB Stock Solution	AR1221 500µL TMX/DCB 500µL	100mL of Hexane	AR1221 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1232-3 Calibration Standard	AR1232 Stock Solution TMX/DCB Stock Solution	AR1232 500µL TMX/DCB 500µL	100mL of Hexane	AR1232 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1242-3 Calibration Standard	AR1242 Stock Solution TMX/DCB Stock Solution	AR1242 500µL TMX/DCB 500µL	100mL of Hexane	AR1242 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1248-3 Calibration Standard	AR1248 Stock Solution TMX/DCB Stock Solution	AR1248 500µL TMX/DCB 500µL	100mL of Hexane	AR1248 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1254-3 Calibration Standard	AR1254 Stock Solution TMX/DCB Stock Solution	AR1254 500µL TMX/DCB 500µL	100mL of Hexane	AR1254 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1262-3 Calibration Standard	AR1262 Stock Solution TMX/DCB Stock Solution	AR1262 500µL TMX/DCB 500µL	100mL of Hexane	AR1262 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1268-3 Calibration Standard	AR1268 Stock Solution TMX/DCB Stock Solution	AR1268 500µL TMX/DCB 500µL	100mL of Hexane	AR1268 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation
AR1660-1 Calibration Standard and PRLS	AR1660 Stock Solution TMX/DCB Stock Solution	AR1660 100µL TMX/DCB 100µL	100mL of Hexane	AR1660 0.1µg/mL TMX/DCB 0.01µg/mL	6 mo. from date of preparation
AR1660-2 Calibration Standard	AR1660 Stock Solution TMX/DCB Stock Solution	AR1660 300µL TMX/DCB 200µL	100mL of Hexane	AR1660 0.3µg/mL TMX/DCB 0.02µg/mL	6 mo. from date of preparation
AR1660-3 Calibration Standard	AR1660 Stock Solution TMX/DCB Stock Solution	AR1660 1000µL TMX/DCB 1000µL	200mL of Hexane	AR1660 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation

Analytical Standard	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Expiration Date
AR1660-4 Calibration Standard	AR1660 Stock Solution TMX/DCB Stock Solution	AR1660 800µL TMX/DCB 1000µL	100mL of Hexane	AR1660 0.8µg/mL TMX/DCB 0.10µg/mL	6 mo. from date of preparation
AR1660-5 Calibration Standard	AR1660 Stock Solution TMX/DCB Stock Solution	AR1660 1000µL TMX/DCB 1500µL	100mL of Hexane	AR1660 1.0µg/mL TMX/DCB 0.15µg/mL	6 mo. from date of preparation
AR1660-3 ICV Calibration Standard	AR1660 ICV Stock Solution TMX/DCB Stock Solution	AR1660 500µL TMX/DCB 500µL	100mL of Hexane	AR1660 0.5µg/mL TMX/DCB 0.05µg/mL	6 mo. from date of preparation

17 REVISIONS

Revision Number	Reason for Change	Date
S-GB-O-047-REV.00	First Issue.	11Sept2008

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Extraction of Polychlorinated Biphenyl (PCB) Isomers for Analysis by Isotope Dilution HRGC/HRMS

(SUPERSEDES: KNOX-ID-0013, Revision 8)

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1. Scope and Application

1.1 This procedure is used by TestAmerica Knoxville for the extraction of PCB isomers from a variety of environmental matrices. This procedure is based on EPA method 1668A and is designed to meet analytical program requirements where isotope dilution HRGC/HRMS analysis of polychlorinated biphenyl (PCB) isomers is specified.

1.2 This procedure is based on "performance-based" methods. These reference methods allow modifications to overcome interferences or lower the cost of measurements if all performance criteria in the methods are met and method equivalency is established. Deviations from the referenced methods have been incorporated into this procedure and are listed in section 17.1.

1.3 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCBs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 Screening and protocol assignment

2.1.1 All solid, sediment, waste and tissue samples are screened by GC/ECD prior to extraction. Aqueous samples may be screened if the potential for congener levels above 40 ng/L exists. Variations to sample size, spiking levels and final volume are established based on the screening result. Refer to Table 4.

2.2 Extraction

2.2.1 Aqueous samples (samples containing less than one percent solids): Stable isotopically labeled analogs of the toxic PCBs plus additional labeled PCBs (i.e., $^{13}C_{12}$ labeled internal standards) are spiked into a 1-L sample, and the sample is extracted with methylene chloride using separatory funnel techniques.

2.2.2 Solid, sediment and tissue samples: A 1.0 g sub-sample is screened to determine the greatest concentration for individual congeners. Based on the screen results, the sample is prepared by one of four protocols (refer to Table 4). Each protocol defines the sample amount to be extracted, the fraction of the extract to be used, and the final extract volume. Protocol 1 is for samples which can be processed without adjustments for high levels of PCB congeners. In this protocol, the internal standards are spiked into a sample containing 10 g of solids. The sample is extracted for 18-24 hours with 1:1 hexane/acetone using a Soxhlet extractor. The extract is

concentrated for cleanup.

NOTE: Sample sizes may be adjusted for dry weight or processed as received. The laboratory default for soil samples is to process as received. The laboratory default for sediment samples, is to adjust the sample amount extracted to a minimum dry weight.

2.2.3 Multi-phase samples: Samples containing multiple phases are separated and the phases are extracted following the procedures for the appropriate matrix. The extracts may be combined for cleanup and analysis or processed separately. Specific handling of multi-phase samples should be discussed and documented with the project manager prior to extraction of samples.

2.2.4 Tissue samples: A 1.0 g sub-sample is screened to determine the greatest concentration for individual congeners. Based on the screen results, the sample is prepared by one of four protocols (refer to Table 4). Each protocol defines the sample amount to be extracted, the fraction of the extract to be used, and the final extract volume. Protocol 1 is for samples which can be processed without adjustments for high levels of PCB congeners. In this protocol, a 10 g aliquot of homogenized tissue is blended with sodium sulfate, spiked with the internal standards, and extracted for 18-24 hours in a Soxhlet extractor using 1:1 hexane/acetone. If required, a portion of the extract is used to determine the lipid content. (Refer to SOP KNOX-OP-0020, “Gravimetric Percent Lipids Determination”, current revision.) The remaining extract is concentrated for cleanup.

2.2.5 Waste samples: Non-aqueous liquids such as oils and organic solvents are diluted or solvent exchanged in hexane.

2.3 After extraction, samples may be cleaned up using back-extraction with sulfuric acid, gel-permeation chromatography, silica gel chromatography, Florisil column chromatography, and/or TBA sulfur cleanup. Cleanup standards are added to each extract prior to initiating any cleanup steps.

2.4 After cleanup, the extract is concentrated to the appropriate final volume (refer to Table 4). Recovery standards are added to each extract and extracts are delivered to the HRMS lab for analysis. Refer to SOP KNOX-ID-0013, current revision.

3. Definitions

NOTE: Terminology differences existing in some isotope dilution reference methods regarding the functionality of the labeled analogs may lead to confusion. For example, EPA's Office of Solid Waste methods (8280, 8290) use the term "Internal Standards" to describe the labeled analogs which are added to the sample prior to extraction and used to quantitate the native targets. EPA's Office of Water methods (1613B, 1668, Revision A) use the term "Labeled Analogs" to describe these same compounds while using the term "Internal

Standards" to describe the labeled analogs which are added to the extract just prior to analysis and used to quantitate the recovery of the labeled analogs added before extraction. EPA's Office of Solid Waste methods (8280, 8290) uses the term "Recovery Standards" to describe these later labeled analogs.

The terminology conventions established by the EPA's Office of Solid Waste methods (8280, 8290) are used in the laboratory for all Standard Operating Procedures and internal communications as defined in this section.

3.1 Cleanup Standards: Isotopically labeled compounds that are added to samples, blanks, quality control samples, and calibration solutions. They are added to the samples after extraction but prior to extract cleanup, and are used to judge the efficiency of the cleanup procedures.

3.2 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.3 Recovery Standards: Isotopically labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

3.4 Additional definitions can be found in the Knoxville Quality Assurance Manual.

4. Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and solvents may be required. Where possible, reagents are cleaned by extraction or solvent rinse. The non-coplanar PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory at the minimum levels in this method, and baking of glassware in a kiln or furnace at 450 - 500°C may be necessary to remove these and other contaminants.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface. For specific glassware cleaning procedures, see SOP KNOX-QA-0002, “Glassware Cleaning”, current revision.

4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory method blanks (section 9.5) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The method blank consists of reagent water for water samples, sodium sulfate for solid samples and tissue samples, or reagent solvent for waste

samples.

4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCBs are measured by this method, the elimination of interferences is essential. The cleanup steps given in section 11.9 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCBs at the levels required by the method.

4.5 Cleanup of tissue - The natural lipid content of tissue can interfere in the analysis of tissue samples for PCBs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the sulfuric acid cleanup procedure in section 11.9.5, followed by GPC cleanup (section 11.9.6).

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile clean room gloves are worn. For operations using solvents that splash, silver shield gloves are recommended. Silver shield gloves protect against breakthrough for most of the solvents used in this procedure.

5.3 When using a scalpel, cut away from yourself. If you are holding something, cut away from your hand. Cut-resistant gloves must be worn when using a scalpel.

5.4 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid (1)	Corrosive, Oxidizer, Dehydradator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Methylene Chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation.
2-Propanol	Flammable	400 ppm -TWA	Flammable liquid and vapor. Harmful if swallowed or inhaled. Causes irritation to eyes and respiratory tract. Affects central nervous system. May be harmful if absorbed through the skin. May cause irritation to the skin.
Ethyl Ether	Flammable, Irritant, Peroxide Former	400 ppm-TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of within six months of opening the container. All unopened containers should be disposed of by the manufacturer's expiration date. See section 5.8.1.**

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations may have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim may experience tightness in the chest, breathlessness, and loss of consciousness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5 Chemicals that have been classified as **carcinogens**, **potential carcinogens**, or **mutagens include**: benzene, methylene chloride, polychlorinated biphenyls, and toluene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.6 Chemicals known to be **flammable** are: acetone, benzene, hexane, nonane, 2-propanol, ethyl ether, and toluene.

5.7 The following materials are known to be **corrosive**: sulfuric acid.

5.8 Peroxides are highly reactive and/or explosive compounds. Diethyl ether may form peroxides when stored or evaporated to dryness. Once peroxides are formed, they can be detonated by simply moving the container. Employees who handle these materials must be aware of this problem. They must know when to submit the materials for disposal, how to check for peroxides, and what to do if peroxides have formed. Rules for handling peroxide forming compounds are:

5.8.1 Write the date the container is received and first opened on the label. The materials in the container must be submitted for disposal within 6 months of when the container is opened or by the manufacturer's expiration date on the container, whichever comes first.

5.8.2 Whenever possible, purchase these materials in the smallest available containers and only open those containers that will be exhausted within 6 months.

5.8.3 Cap all containers tightly and store in a dark area away from heat sources. If possible purge the container with nitrogen before putting the cap on (suggestion: before replacing the cap).

5.8.4 Keep all materials that may form peroxides out of regular refrigerators. If they must be refrigerated, place them in explosion proof or flammable

refrigerators or freezers.

5.8.5 Perform monthly checks with peroxide test strips on all open containers.

5.8.6 Collect and preserve all waste that might form peroxides with alcohol or other anti-oxidizers.

5.8.7 Avoid evaporating these types of materials to dryness. If you have to evaporate the materials to near dryness, use a stream of nitrogen. If possible, contain the apparatus behind an explosion shield.

5.8.8 If the shelf life of a container of one of these materials is exceeded, a container has been open for more than 6 months, or there is evidence of peroxide formation, contact the Environmental Health and Safety Coordinator (EHSC) or Environmental Health and Safety Director (EHSD). DO NOT ATTEMPT TO OPEN OR MOVE THE CONTAINER. This could cause the peroxide to detonate. Visible evidence of potential peroxide formation includes formation of crystals around the cap, formation of a viscous layer at the bottom of the container, or rust around the surface of the can.

5.9 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.10 The preparation of all standards and reagents, as well as glassware cleaning procedures that involve solvents, will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.11 Equipment goggles or a face shield **must** be used when employees are using solvents to rinse or clean glassware

5.12 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.13 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Bench tops should be covered with plastic backed absorbent paper.

5.14 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.15 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.16 All work must be stopped in the event of a known or potential compromise to the health or safety of laboratory personnel. The situation must be reported immediately

to a laboratory supervisor.

6. Equipment and Supplies

NOTE: All glassware used in extraction and cleanup procedures is solvent rinsed 2-3 times before use with acetone, hexane and methylene chloride, at a minimum. Pre-extract Soxhlet apparatus with methylene chloride for at least 4 hours. Re-rinse the glassware with all solvents once. See SOP KNOX-QA-0002, “Glassware Cleaning”, current revision, for details.

NOTE: When extracting PCB samples, all of the reusable glassware used in the extraction and concentration process is identified with a "P" (for aqueous sample glassware), “L” or “LL” (for solid sample glassware) etch mark. Do note use any glassware that does not have a "P", “L” or “LL” etching.

6.1 Miscellaneous Laboratory Equipment

- 6.1.1 Laboratory fume hood of sufficient size to contain the equipment used for sample preparation.
- 6.1.2 Oven - Capable of maintaining a temperature of 105 ± 5°C.
- 6.1.3 Balance: >100 g capacity, accurate to $\pm$0.1 g.
- 6.1.4 Syringes, various sizes.
- 6.1.5 Teflon® squirt bottles, 500 mL.

6.2 Tissue Homogenization Equipment:

- 6.2.1 Laboratory blender with glass body and stainless steel blades.
- 6.2.2 Industrial meat grinder, Intedge Industries, Model C2H, or equivalent.
- 6.2.3 Laboratory homogenizer, OMNI GLH-01, Model LR060902, or equivalent.
- 6.2.4 Scalpel or knife.
- 6.2.5 Cut-resistant gloves.

6.3 Aqueous Sample Extraction Equipment

- 6.3.1 Separatory funnels, 250, 500, and 2000 mL, with Teflon® stopcocks.
- 6.3.2 500 mL round bottom flasks.
- 6.3.3 Separatory funnel rotator.
- 6.3.4 Graduated cylinder, 1-L capacity.

6.4 Solid/Tissue Sample Extraction Equipment

6.4.1 Soxhlet - 50-mm ID, 200-mL capacity with 500 mL flat bottom flask.

6.4.2 Glass condenser, capable of fitting top of Soxhlet apparatus.

6.4.3 Extraction thimble - Whatman high purity glass fiber thimbles

6.4.4 Heating mantles with temperature control.

6.4.5 Ultra-Pure PTFE boiling stones.

6.4.6 Flasks, Erlenmeyer, 500 mL.

6.4.7 Beakers, 500 mL.

6.4.8 Spatulas - Stainless steel.

6.5 Filtration Equipment

6.5.1 Glass wool – solvent rinsed.

6.5.2 Glass or stainless steel funnels.

6.5.3 Phase Separation Paper, Whatman 41 or equivalent.

6.5.4 Buchner funnel – 15 cm.

6.5.5 Glass-fiber filter paper for Buchner funnel above.

6.5.6 Filtration flasks - 1.5 to 2.0 L, with side arm.

6.6 Cleanup Equipment

6.6.1 Glass pipet, 1 mL, Class A.

6.6.2 Disposable pipets, 150 mm long x 5 mm ID.

6.6.3 Disposable pipets, 230 mm long x 5 mm ID.

6.6.4 Pipet bulbs, rubber, disposable.

6.6.5 250 mL and 500 mL round or flat bottom flasks.

6.6.6 20 mm x 240 mm glass column with support ring and tapered tip, for silica gel and Florisil cleanup.

6.6.7 Glass wool – solvent rinsed.

6.6.8 Graduated cylinder, 100 mL.

6.6.9 Oven - For baking and storage of absorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.6.10 Vortex mixer.

6.7 GPC Equipment

6.7.1 Gel permeation chromatography system, J2 Scientific Accu Prep, or equivalent.

6.7.2 Bio Beads - (S-X3) 200-400 mesh, 70 gm, Bio-Rad Laboratories, Richmond, CA, Catalog No. 152-2750, or equivalent.

6.7.3 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward.

6.7.4 Ultraviolet detector - Fixed wavelength (254 nm) and a semi-prep flow-through cell.

6.7.5 Laboratory data system.

6.7.6 Syringe - 10 mL with Luerlok fitting.

6.7.7 Syringe filter assembly, with disposable 5 µm filter discs, Millipore No. LSWP 01300, or equivalent.

6.8 Concentration Equipment

6.8.1 Nitrogen blowdown apparatus - N-Evap (Organomation Associates, Inc., South Berlin, MA), installed in a fume hood.

6.8.2 Kuderna-Danish (K-D) Apparatus - 500 mL.

6.8.3 Concentrator Tube - 10 mL, attached to K-D with clips.

6.8.4 Snyder Column - Three-ball macro.

6.8.5 Water Bath - Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.

6.8.6 Heating mantles with temperature control.

6.9 Sample Vials

6.9.1 Borosilicate glass, 12 mL and 40 mL disposable with Teflon® cap

6.9.2 Mini vials, 1.1 mL capacity with a tapered bottom, with Teflon®-faced, rubber septa and screw caps.

6.9.3 Amber glass vials with Teflon®-lined screw caps.

6.10 Screening Equipment

6.10.1 Shaker table.

6.10.2 An analytical system complete with a gas chromatograph and a ^{63}Ni electron capture detector and a data system capable of measuring peak height.

7. Reagents and Standards

CAUTION: Refer to Material Safety Data Sheets (MSDS) for specific safety information on chemicals and reagents prior to use or as needed.

CAUTION: During preparation of reagents, associates shall wear a lab coat, gloves, safety glasses with side shields, and laboratory approved shoes as a minimum. Reagents shall be prepared in a fume hood.

7.1 Sulfuric acid, concentrated - Reagent grade (specific gravity 1.84).

7.2 Sodium chloride - Reagent grade, prepare a 5% (w/v) solution in reagent water.

7.3 Sodium sulfate, reagent grade, anhydrous, J.T Baker 3375, or equivalent.

7.3.1 Sodium sulfate may be cleaned by putting approximately 600 g of sodium sulfate in large amber-colored glass jars and completely covering with methylene chloride, stirring the mixture with a stirring rod and letting the sodium sulfate soak for 5 minutes. The methylene chloride is drained and this step is repeated. After the methylene chloride is drained the sodium sulfate is transferred to a Buchner funnel fitted onto a vacuum flask and is rinsed 2 times with methylene chloride while a vacuum is being applied to the apparatus. The sodium sulfate is then placed into shallow borosilicate glass dishes where it is allowed to dry. It is placed in an oven at 130°C for 1 hour to complete the drying process. After drying, the sodium sulfate is transferred into pre-cleaned glass jars with Teflon® lined screw caps. These are placed in a desiccator until needed.

7.3.2 Alternatively, sodium sulfate is cleaned by heating at 400°C for a minimum of four hours.

7.4 Purified nitrogen.

7.5 Solvents - Acetone, toluene, n-hexane, 2-propanol, methanol, methylene chloride, ethyl ether, benzene and nonane; pesticide quality.

7.6 Prepare 6% diethyl ether in hexane (v/v) by combining 940 mL of hexane and 60 mL of diethyl ether in a 4000 mL amber glass bottle. Shake well to mix. Label the container and store in the solvent cabinet.

7.7 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 mega ohm resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.8 Florisil, pesticide residue (PR) grade (60/100) mesh; purchased activated at 1250°C (677°F), stored in a clear glass container with a ground glasstop. Place in an oven at 125-135 °C for a minimum of 4 hours. Remove from oven and allow to cool before use. Store in the oven while not in use.

7.9 Silica gel, F679-212, Fisher Chromatographic Silica Gel, 100-200 mesh or

equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Transfer to a shallow, borosilicate glass dish and air dry. After drying, cover with aluminum foil and activate in an oven at 130°C for a minimum of 4 hours. Store in labeled glass jars in a desiccator until use.

7.10 3.3% Deactivated silica gel – To prepare add 6.6 mL of reagent water to 200 g of pre-cleaned silica gel (section 7.9) in a 500 mL amber glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar. Store in a desiccator. Shake well again before each use.

7.11 Acidic silica gel - To prepare, add 57 mL of concentrated sulfuric acid to 180 g of pre-cleaned silica gel (section 7.9) in a 250 mL amber glass jar with a Teflon® lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel is free flowing and no longer sticks to the side of the jar. Store in a desiccator. Shake well again before each use.

7.12 Tetrabutylammonium hydrogen sulfate, Sigma Aldrich Cat. No 155837-100g, or equivalent, 97% purity.

7.12.1 Tetrabutylammonium (TBA) sulfite reagent - Prepare the reagent by dissolving 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL of reagent water in a wide mouth clear jar with a Teflon® lined screw cap. To remove impurities extract this solution three times with 20 mL portions of hexane, taking the hexane portion off the top and discarding. After discarding the last hexane wash, pour the TBA into a 250 mL amber glass jar and slowly add 25 g of sodium sulfite (in increments) to the solution. Shake the bottle until the sodium sulfite dissolves. Record the date prepared, initials of the preparer and expiration date on the bottle label. This solution can be stored for 1 month at room temperature in an amber bottle with a Teflon® lined lid.

7.13 Sodium sulfite, Sigma Aldrich Cat. No. 54872-1KG, or equivalent, 98+% purity.

7.14 8082 Surrogate Mix: A surrogate spiking solution which contains 0.2 mg/L tetrachloro-m-xylene and decachlorobiphenyl. This mix is spiked into samples that are being prepared for PCB screening.

7.15 $^{13}C_{12}$ Labeled PCB Congener Standards: Obtained as individual Certified Reference Standards from Cambridge Isotope Laboratories (CIL, Andover Massachusetts) and Wellington Laboratories (Guelph, Ontario, Canada). (Refer to Table 2 for a list of individual standards.) These standards are purchased at 40 µg/mL or 50 µg/mL in nonane. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. Once a standard ampoule has been vortexed and opened, the solution is transferred to an amber glass vial with a Teflon®-lined screw cap. When not being used, standards are stored in the dark in a refrigerator. These purchased standards are used to prepare the following mixed stock solutions and spiking solutions:

7.15.1 Internal Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled internal standards listed in Table 2, to a concentration of 1000 ng/mL in nonane.

7.15.2 Internal Standard Spiking Solution: Prepared by diluting the 1000 ng/mL internal standard stock solution to a concentration of 10 ng/mL in acetone. The concentration is verified by GC/MS before use. 1.0 to 4.0 mL of this solution is added to each solid/tissue sample prior to extraction. (Refer to Table 4, "Assignment of Sample Preparation Protocols" to determine the exact volume to add.) 0.20 mL of the internal standard spiking solution is added to each aqueous sample prior to extraction.

7.15.3 Recovery Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled recovery standards listed in Table 2 to a concentration of 1000 ng/mL in nonane.

7.15.4 Recovery Standard Spiking Solution: Prepared by diluting the 1000 ng/mL recovery standard stock solution to a concentration of 100 ng/mL in nonane. The concentration is verified by GC/MS before use. 100 µL of this spiking solution is added to each solid/tissue sample extract prior to analysis, whereas, 20 µL is added to each aqueous sample extract.

7.15.5 Cleanup Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled cleanup standards listed in Table 2, to a concentration of 5000 ng/mL in nonane.

7.15.6 Cleanup Standard Spiking Solution: Prepared by diluting the 5000 ng/mL cleanup standard stock solution to a concentration of 10 ng/mL in hexane. The concentration is verified by GC/MS before use. 1.0 mL of this solution is added to each solid/tissue sample extract prior to cleanup (refer to Table 4), whereas, 0.20 mL is added to each aqueous sample extract.

7.16 Native PCB Congener Standard Mix: Obtained as a Certified Reference Standard from Accustandard (New Haven, CT). This standard contains all 209 PCB congeners at 4000 ng/mL in nonane. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. Once a standard ampoule has been vortexed and opened, the solution is transferred to an amber glass vial with a Teflon®-lined screw cap. When not being used, the standard is stored in the dark in a refrigerator at 4 $\pm$ 2°C. This purchased standard is used to prepare the LCS spiking solution:

7.16.1 LCS Spiking Solution: Prepared by diluting the 4000 ng/mL native PCB congener standard to a concentration of 5.0 ng/mL in acetone. The concentration is verified by GC/MS before use. 1.0 mL of this solution is added to each solid/tissue LCS prior to extraction, whereas, 0.20 mL is added to each aqueous LCS.

7.17 QC Check Sample - A QC Check Sample should be obtained from a source

independent of the calibration standards. This check sample is a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has an SRM 1944 – New York/New Jersey Waterway Sediment, that the NYSDEC recommends for use.

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Login", current revision.

8.2 Sample Storage

8.2.1 Store aqueous samples in the dark at 0-4°C.

8.2.2 Store solid and tissue samples in the dark at <-10°C.

8.3 Holding Times

8.3.1 If stored according to the conditions specified in 8. 2, samples may be stored for up to one year.

8.3.2 Store sample extracts in the dark at room temperature until analyzed. If stored in the dark at room temperature, sample extracts may be stored for up to one year.

9. Quality Control

9.1 An initial demonstration of capability (IDOC) is performed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.1 For aqueous samples, extract, clean, concentrate, and analyze four 1-L aliquots of reagent water spiked with internal standards, cleanup standard, recovery standard and the LCS spiking solution, according to the procedures in section 11. For solid/tissue samples, extract, clean, concentrate, and analyze four aliquots of sodium sulfate/corn oil spiked with internal standards, cleanup standard, recovery standard and the LCS spiking solution, according to the procedures in section 11. All sample processing steps that are to be used for processing samples, including preparation, extraction and cleanup, shall be included in this test.

9.1.2 Using the results of the set of four analyses, compute the average percent recovery (%R) of the extracts and the relative standard deviation (RSD) of the concentration in ng/mL for each compound.

9.1.3 For each PCB and labeled compound, compare the RSD and %R with the corresponding limits for initial precision and recovery in Table 3. If the RSD and %R for all compounds meet the acceptance criteria, system

performance is acceptable and analysis of samples may begin. If, however, any individual RSD exceeds the precision limit or any individual %R falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 Internal Standards: Every sample, blank, and QC sample is spiked with $^{13}C_{12}$ labeled internal standards prior to extraction. Internal standards in samples, blanks, and QC samples are used to calculate the concentration of the target analytes or detection limits.

9.3 Cleanup Standards: Every sample, blank, and QC sample extract is spiked with $^{13}C_{12}$ labeled cleanup standards after extraction but prior to extract cleanup. They are used to assess the efficiency of the cleanup procedures.

9.4 Recovery Standards: Every sample, blank, and QC sample extract is spiked with $^{13}C_{12}$ labeled recovery standards prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

9.5 Method Blanks

9.5.1 A laboratory method blank must be run along with each batch of 20 or fewer samples. The method blank consists of reagent water for aqueous samples, sodium sulfate for solid and tissue samples, processed in the same manner and at the same time as the associated samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data..

9.6 Laboratory Control Sample - A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 samples. All analytes must be within established control limits specified in Table 3. The LCS is spiked with the compounds listed in Table 1.

9.7 QC Check Sample - Analyze the QC Check Sample (section7.17) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least annually.

9.8 Quality Control Batch - The batch is a set of up to 20 client samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank and a laboratory control sample.

10. Calibration and Standardization

10.1 Not applicable.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the

professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

11.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3 Samples are extracted by the following procedures depending upon sample matrix. Water samples are prepared by separatory funnel liquid/liquid extraction. Solid samples including soils, sediments, tissues and solid waste materials are prepared by Soxhlet extraction. Non-aqueous liquid wastes and organic solvents are prepared by waste dilution techniques.

NOTE: Samples should be removed from the refrigerator several hours before extraction and allowed to come to room temperature before measuring the volume or performing the extraction.

11.4 Aqueous Samples (samples containing 1% solids or less)

11.4.1 Refer to Knoxville SOP KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware.

11.4.2 For water samples, only use the glassware designated for those water samples.

11.4.3 Place separatory funnels, one for each sample, in the separatory rotator set up in the hood.

11.4.4 Place a 500 mL round bottom flask directly beneath the separatory funnel.

11.4.5 Plug a glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the methylene chloride stops dripping, place the funnel on top of the round bottom flask that is fitted with a paper clip to aid in filtering.

11.4.6 Inspect the sample for solids or biphasic sample characteristics. If either condition exists, consult the project manager for further instructions.

11.4.7 Mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. For the method blank and the LCS, use a 1000 mL graduated cylinder to measure 1000 mL of reagent water.

11.4.8 Verify the final volume of the extract. If the standard 20 µL is specified, add 0.20 mL of the 10 ng/mL internal standard spiking solutionto each sample, method blank and LCS. Additionally, add 0.20 mL of the 5.0

ng/mL LCS spiking solution to the LCS (and LCSD, MS/MSD, if required). Record the amount of spike used and the spike standard number on the extraction benchsheet.

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix II for the steps that must be taken.

11.4.9 Add 60 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel. Add 60 mL of methylene chloride to the method blank, LCS (and LCSD, if required).

11.4.10 Secure the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles may be worn when performing this procedure.

11.4.11 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.4.12 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the round bottom flask. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed. If at least 10 minutes has elapsed and other ways of breaking up or reducing the size of the emulsion have failed, the following steps may be tried to reduce the impact of the emulsion on the sodium sulfate.

11.4.12.1 Place a large piece of pre-cleaned glass wool in the funnel containing the sodium sulfate.

11.4.12.2 Spread the glass wool out, covering the entire surface of the sodium sulfate to about a depth of about 5 to 10 mm. If the emulsion is hard to break up and persistent, a small, additional layer of sodium sulfate may be added on top of the glass wool.

11.4.12.3 Drain the solvent and emulsion layer into the funnel, being careful to drain no more than 60 mL of volume if a clear phase layer cannot be determined.

11.4.12.4 If this procedure is used, the funnel should be rinsed with an extra 30 mL of methylene chloride to ensure all analytes are rinsed into the round bottom flask after the third portion of methylene chloride has drained through the sodium sulfate.

11.4.13 Repeat steps 11.4.9 through 11.4.12 two more times.

11.4.14 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.4.15 Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.4.16 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the sample volume on the extraction benchsheet.

11.4.17 Remove the glass funnel from the top of the round bottom flask.

11.4.18 Add a few boiling stones to the 500 mL flat-bottom boiling flask. Place a 3-ball Snyder column on the boiling flask. Pre-wet the Snyder column with 1 mL of hexane and concentrate the extract to approximately 10 mL. Add approximately 60 mL of hexane and concentrate to $\geq$ 10 mL.

NOTE: Over-concentration of heated extracts is known to cause the more volatile PCB congeners to vaporize and be lost. Therefore, do not concentrate to less than 10 mL.

11.4.19 Transfer the extract into a solvent-rinsed 40 mL vial, rinsing the 500 mL flask three times with approximately 3 mL of hexane. Add the rinses to the 40 mL vial.

11.4.20 Place the 40 mL vials into the N-EVAP concentration device and reduce the volume to approximately 0.5 mL. Do not allow the sample to go to dryness at any time. If an additional solvent exchange is needed, add 5 mL of hexane and swirl the vial. Reduce the volume of hexane to approximately 0.5 mL again to complete the solvent exchange. Adjust the final volume of the extract with hexane to 15 mL for acid cleanup or 2 mL for column cleanup. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene to aid in dissolving the sample. Proceed to section 11.9.

11.5 Solid/Tissue Sample Screening and Assignment of Sample Preparation Protocols

11.5.1 Because of the sensitivity of method 1668A, it is necessary to screen all solid/tissue samples and non-aqueous liquids before extraction to prevent instrument saturation and/or contamination.

11.5.2 Mark a 40 mL vial with the sample workorder number and tare the vial.

11.5.3 Add a 1 +/- 0.1 g subsample in accordance with KNOX-QA-0006, “Subsampling”, current revision.

11.5.4 Add 1.0 mL of 8082 surrogate mix. (Refer to section 7.14.)

11.5.5 Add 9 mL of hexane.

11.5.6 Cap tightly and secure on a platform shaker table.

11.5.7 Shake for 1 hour, minimum.

11.5.8 Filter aqueous extracts using a small funnel fitted with a GF filter paper and a small amount of sodium sulfate, into a 12 mL vial marked at 10.0 mL.

11.5.9 If the extract is colored in any way after filtering, transfer approximately 4 mL into a fresh 12 mL vial, add approximately 4 mL of sulfuric acid, cap tightly, and shake the vial for 30 seconds. If necessary, centrifuge the extract.

11.5.10 Deliver the extract to the GC analyst for screening.

11.5.11 Perform a single point initial calibration for each sequence on the screening instrument.

11.5.12 If no pattern and no prominent peaks are present, process the sample using protocol 1.

11.5.13 If an Aroclor-like pattern is observed, calculate the estimated concentration of the largest peak expected in the determinative analysis, and assign an extraction protocol using the “PCB Protocol Selection” spreadsheet on the local area network in the MSOffice\template\STL Knx SOG directory.

11.5.13.1 Determine the concentration of the most prominent technical mixture by comparison to Aroclor standards. Enter the Aroclor sample concentration (ppb) into the spreadsheet. Circle the amount entered on the GC hardcopy result.

11.5.13.2 For sediment samples, import the sample % moisture results.

11.5.13.3 Enter the average or selected surrogate recovery in the spreadsheet. The software will correct the PCB concentration for surrogate recovery.

11.5.13.4 The software will multiply the PCB concentration by 0.1 (the spreadsheet default) to correct for the weight percent of the largest single congener in an Aroclor mix. This value may be changed to represent special cases such as altered patterns or unusual technical mixtures, but documentation of the rationale must accompany the spreadsheet.

11.5.13.5 The software will then multiply the PCB concentration by 4 to account for single-peak coelutions.

11.5.13.6 The resulting concentration is used as the estimate of the largest peak expected in the determinative analysis and to assign an extraction protocol for each sample.

11.5.13.7 An independent analyst should review the data entry and protocol assignments. Initial and date the spreadsheet. Attach the spreadsheet and supporting GC data to the extraction benchsheet.

11.5.13.8 During sample preparation, adjust the sample extraction amount, spiking volumes, split ratio, final volume and bench dilution to reflect the selected protocol. (Refer to Table 4.)

11.6 Sample Pretreatment for Tissue Samples

11.6.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is homogenized prior to extraction using an industrial meat grinder, a laboratory blender, or a laboratory homogenizer. Select the equipment that is most appropriate for the size and type of tissue received.

11.7 Solid/Tissue Sample Extraction (samples containing more than 1% solids)

11.7.1 This section uses protocol 1 as an example. If another protocol has been assigned, the sample amount extracted, spike volumes and percent of extract used is modified based on Table 4.

11.7.2 Prepare and label the required number of Soxhlet systems. The Soxhlet is prepared by cleaning and rinsing per section 6, charging the boiling flask with solvent, assembling the components, and precleaning by refluxing for at least 4 hours before use.

11.7.3 For soil samples, transfer a well-mixed 10 g aliquot (+/- 0.1 g) of the sample into a glass microfiber extraction thimble. Record the sample weight on the extraction benchsheet.

11.7.4 For sediment samples, adjust the amount weighed to achieve 10 g dry weight. Determine the amount of sediment sample to extract using the “Sediment Extraction Amounts” spreadsheet on the local area network in the MSOffice\template\Knx OrgPrep directory. Transfer a well-mixed aliquot of the sample into a glass microfiber extraction thimble. Record the sample weight on the extraction benchsheet.

11.7.5 For tissue samples, weigh out 10 g (+/- 0.1 g) of homogenized tissue into a beaker or extraction thimble. Mix thoroughly with 20 g of sodium sulfate. Record the sample weight on the extraction benchsheet.

NOTE: If gravimetric lipids are to be determined using the tissue extracts, split the extract prior to the initiation of any cleanup steps and use 1 mL of

the 10 mL extract for lipids determination. (Refer to SOP KNOX-OP-0020, “Gravimetric Percent Lipids Determination”, current revision.)

11.7.6 For soil, sediment and tissue samples, sodium sulfate is used for the blank and LCS.

11.7.7 Spike each sample with 1 mL of the 10 ng/mL internal standard spiking solution (see section 7.15.2).

11.7.8 Spike the LCS (and LCSD, MS/MSD, if required) with 1 mL of the 5 ng/mL LCS spiking solution (see section 7.16.1).

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix II for the steps that must be taken.

11.7.9 If needed, add a small amount of glass wool to the top of the extraction thimble.

11.7.10 Pour approximately 350 mL of the 1:1 hexane/acetone into a 500 mL flat bottom flask. Place the flask in the heating mantle. Add several Teflon® boiling stones.

11.7.11 Place the extraction thimble in the glass Soxhlet extractor.

11.7.12 Assemble the Soxhlet system and secure to the lab supports.

11.7.13 Adjust the temperature of the heating mantle to bring the solvent in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour.

11.7.14 Soxhlet extract the sample in the above manner for 18-24 hours.

11.7.15 Turn off the heating mantle and allow the Soxhlet apparatus to cool.

11.7.16 Remove the condensers and allow the Soxhlet extractor chamber to empty, then remove the Soxhlet extractor from the 500 mL flat bottom flask.

NOTE: If the samples appear to have a water layer or moisture, dry the extract by filtering it through a sodium sulfate filled funnel.

11.7.17 Place a solvent-rinsed 3-ball Snyder column on the 500 mL flat bottom flask. Pre-wet the Snyder column with 1 mL of hexane and concentrate the extract to $\geq$ 10 mL.

NOTE: Over-concentration of heated extracts is known to cause the more volatile PCB congeners to vaporize and be lost. Therefore, do not concentrate to less than 10 mL.

11.7.18 Transfer the extract into a solvent-rinsed 40 mL vial, rinsing the 500 mL

flask three times with approximately 3 mL of hexane. Add the rinses to the 40 mL vial.

11.7.19 Place the 40 mL vial into the N-EVAP concentration device and reduce the volume to approximately 10 mL. Proceed to section 11.9 to perform acid cleanup.

11.8 Waste Sample Extraction

11.8.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.8.2 Add an appropriate amount of sample (based on screen results) to a solvent-rinsed 40 mL VOA vial.

11.8.3 10 mL of hexane is used for the blank and LCS.

11.8.4 Spike each sample with 1 mL of the 10 ng/mL internal standard spiking solution (see section 7.15.2).

11.8.5 Spike the LCS (and LCSD, MS/MSD, if required) with 1 mL of the 5 ng/mL LCS spiking solution (see section 7.16.1).

NOTE: Each time the samples are spiked, the spiking process should be witnessed by another analyst. Refer to Appendix II for the steps that must be taken.

11.8.6 Add hexane to bring the volume to 10 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene to the vial to aid in dissolving the sample. Proceed to section 11.9.5 to perform acid cleanup.

11.8.7 Record the weights and volumes used on the extraction benchsheets.

11.9 Extract Cleanup

11.9.1 Cleanup may not be necessary for relatively clean samples (e.g., treated effluents, groundwater, drinking water). If particular circumstances require the use of a cleanup procedure, the laboratory may use any or all of the procedures below or any other appropriate procedure. Before using a cleanup procedure, the laboratory must demonstrate that the requirements of Section 13.2 can be met using the cleanup procedure.

11.9.2 Soil, sediment and tissue sample extracts are typically taken through the following cleanup procedures: Acid cleanup, GPC and silica gel cleanup. Aqeous sample extracts are typically cleaned using silica gel and Florisil column cleanup procedures.

11.9.3 If the sample requires a split based on the protocols listed in Table 4, the split must be performed prior to the initiation of the first cleanup

procedure and prior to the addition of cleanup standards. For protocol 1 samples, use 5 mL of the 10 mL extract. Archive the remaining 5 mL aliquot of extract.

11.9.4 Spike each sample extract with an appropriate amount (i.e., 1.0 mL for solid, tissue and waste sample extracts; 0.20 mL for aqueous sample extracts) of the 10 ng/mL cleanup standard spiking solution (see section 7.15.6) prior to initiating any cleanup procedures..

11.9.5 Acid Cleanup

11.9.5.1 For protocol 1 samples, slowly add 4-5 mL of concentrated sulfuric acid to the 5 mL hexane extract in the 40 mL vial and shake for 30-60 seconds. For the other protocols listed in Table 4, adjust the acid proportionally to the extract volume. Vent the vial frequently while shaking. Let the vial stand for a minimum of 10 minutes or centrifuge to obtain well-defined separation of acid and solvent. Remove the acid layer with a glass pipet. (Optionally, the solvent layer can be removed.) Repeat the acid washing if the solvent layer is colored. (Perform a maximum of four acid washings.)

11.9.5.2 Add approximately 8 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 30 seconds. Vent the vial frequently while shaking. Let the vial stand for 10 minutes and remove the aqueous layer with a glass pipet. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.9.5.3 Place the 40 mL vial into the N-EVAP concentration device and reduce the volume to approximately 1 mL. Solvent exchange to methylene chloride and bring to a 10 mL volume. Proceed to section 11.9.6, GPC Cleanup.

11.9.6 GPC Cleanup

11.9.6.1 Gel permeation chromatography (GPC) removes high molecular weight interferences that cause GC column performance to degrade. It should be used for all soil, sediment, tissue and waste sample extracts. It may be used for water sample extracts that are expected to contain high molecular weight organic compounds (e.g., polymeric materials, humic acids).

11.9.6.2 Refer to SOP KNOX-OP-0022, current revision for detailed instructions re. GPC cleanup.

11.9.6.3 After GPC cleanup, concentrate the extract and solvent exchange to ~4 mL hexane using low-level K-D glassware.

Proceed to section 11.9.7, Silica Gel Column Cleanup.

11.9.7 Silica Gel Column Cleanup

11.9.7.1 Prepare 20 mm columns for each extract by placing a small amount of glass wool in the bottom of each column and then solvent rinsing with hexane. Shake out the excess hexane.

11.9.7.2 Mark the level to which the column packings will be added, starting at the top of the glass wool plug and proceeding from bottom to the top.

- Layer 1 – 12 mm (2 g) of 3.3% deactivated silica gel
- Layer 2 – 16 mm (4 g) of acidic silica gel
- Layer 3 – 12 mm (2 g) of 3.3% deactivated silica gel
- Layer 4 – 10 mm of sodium sulfate

11.9.7.3 Add the column packings to the 20 mm column in the order listed above, tapping the column to settle the contents to prevent channeling.

11.9.7.4 Add 30 mL of hexane to pre-elute the column. Do not collect the pre-eluted hexane.

11.9.7.5 When the hexane reaches the top of the sodium sulfate layer, place a solvent-rinsed 250 or 500 mL round or flat bottom flask under the column and transfer the sample extract into the column. Quickly rinse the extract vial with a small amount of hexane and add the rinse into the column. Repeat the rinse 2 more times.

11.9.7.6 As the solvent level from the last rinse reaches the top of the sodium sulfate layer, add 70 mL of hexane into the silica gel column to elute the PCB’s into the round bottom flask.

11.9.7.7 When the column stops dripping, add a solvent-rinsed Snyder column to the flask and concentrate the extract to $\geq$ 10 mL on a heating mantle.

NOTE: Over-concentration of heated extracts is known to cause the more volatile PCB congeners to vaporize and be lost. Therefore, do not concentrate to less than 10 mL.

11.9.7.8 Transfer the extract to a 40 mL vial, rinsing the flask with a small amount of hexane and add the rinse to the 40 mL vial. Repeat the rinse 2 more times.

11.9.7.9 Place the 40 mL vial into the N-EVAP concentration device and reduce the volume to approximately 10 mL. For aqueous samples, proceed to section 11.9.8, Florisil Column Cleanup. For soil, sediment, tissue and waste samples, proceed to section 11.9.10, Final Concentration.

11.9.8 Florisil Column Cleanup

11.9.8.1 Place a small ball of glass wool in the bottom of a 20 mm column. Rinse twice with hexane and shake out the excess hexane.

11.9.8.2 Attach the column to the lab support in the hood.

11.9.8.3 Pack the Florisil column with the following layers. Add the column packing while tapping the column to settle the contents to prevent channeling. The order of the layers is from bottom to top.

- Layer 1 - 8 cm (15 g) of Florisil
- Layer 2 - 2 cm (2 g) of sodium sulfate

11.9.8.4 Pour 80 mL of 6% diethyl ether in hexane (v/v) into a graduate cylinder (one graduate cylinder for each column) and set aside for later use in the procedure.

11.9.8.5 Pre-elute the column with 50 mL of 6% diethyl ether in hexane (v/v). This may be pushed through with a pipet bulb. Then pre-elute with 50 mL of hexane. Discard these pre-elutions.

11.9.8.6 Just before the level of hexane reaches the top of the sodium sulfate layer, place a solvent-rinsed 250 or 500 mL round or flat bottom flask under the column and transfer the sample extract into the top of the column. Quickly rinse the vial 3 times with a small amount of hexane and add these rinses to the column.

11.9.8.7 Just before the solvent level reaches the top of the sodium sulfate, pour the 80 mL of 6% diethyl ether in hexane (v/v) into the top of the column and allow this to drip through the column and into the round bottom flask.

11.9.8.8 When the column stops dripping, add a solvent-rinsed Snyder column to the round bottom flask and concentrate the extract to $\geq$ 10 mL on a heating mantle.

NOTE: Over-concentration of heated extracts is known to

cause the more volatile PCB congeners to vaporize and be lost. Therefore, do not concentrate to less than 10 mL.

11.9.8.9 Transfer the extract to a 40 mL vial, rinsing the round bottom flask with a small amount of hexane and add the rinse to the 40 mL vial. Repeat the rinse 2 more times.

11.9.8.10 If TBA cleanup is needed, place the 40 mL vial into the N-EVAP concentration device and reduce the volume to approximately 10 mL and proceed to section 11.9.9. Otherwise, proceed to section 11.9.10, Final Concentration.

11.9.9 Sulfur clean-up by Tetrabutylammonium (TBA)

11.9.9.1 Prepare sodium sulfate funnels by rinsing small funnels with acetone, methylene chloride and hexane, in that order. Add a small plug of glass wool and a small amount of sodium sulfate to each funnel. Rinse with hexane.

11.9.9.2 Add 1.0 mL of TBA sulfite reagent and 2.0 mL of 2-propanol to the vial containing the extract. Cap securely and vortex for 1 minute.

11.9.9.3 If the extract is colorless (or the initial color is unchanged) and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. However, if the precipitated sodium sulfite disappears, add more sodium sulfite in approximately 0.10 g portions and vortex until a solid residue remains.

11.9.9.4 Add 5 mL of reagent water and vortex the vial for 1 minute. Allow the layers to separate (at least 5 minutes). Pipet off the hexane layer (the top layer) and filter through the sodium sulfate funnel (prepared in 11.9.9.1 above) into a solvent-rinsed 40 mL vial.

11.9.9.5 Add 2 mL of fresh hexane to the sample extract vial. Vortex for 30 seconds and allow the layers to separate again. Pipet off the hexane portion and filter through the sodium sulfate funnel into the clean 40 mL vial. Repeat once.

11.9.9.6 Rinse the sodium sulfate funnel with approximately 2 mL of hexane. When the hexane stops dripping, remove the funnel and cap the vial.

11.9.9.7 Proceed to section 11.9.10 for final concentration.

11.9.10 Final Concentration

11.9.10.1 Place the 40 mL vial containing the extract in the N-EVAP

concentration apparatus and reduce the solvent volume to approximately 0.5 to 1.0 mL.

11.9.10.2 Label a 1.1 mL tapered mini vial with the sample ID. Cover with clear tape to prevent the ink from smearing and to help hold the mini-vial in the N-EVAP.

11.9.10.3 For aqueous samples, add 20 µL of the 100 ng/mL recovery standard spiking solution (see section 7.15.4) to the mini-vial and mark the level on the vial. Transfer the concentrated extract into the mini-vial, rinsing 2 times with small amounts of hexane. Then reduce the extract volume back down to 20 µL. Deliver the mini-vial to the HRMS lab for analysis.

11.9.10.4 For protocol 1 solid, sediment, tissue and waste samples, add 50 µL of the 100 ng/mL recovery standard spiking solution (see section 7.15.4) to the mini-vial and mark the level on the vial. Transfer the concentrated extract into the mini-vial, rinsing 2 times with small amounts of hexane. For protocol 1 samples, reduce the extract volume to 50 µL. Deliver the mini-vial to the HRMS lab for analysis.

11.9.10.5 For samples prepared according to protocols 2, 3 and 4, add 100 µL of the 100 ng/mL recovery standard spiking solution and dilute the extract with nonane to achieve the dilution factor shown in Table 4.Deliver the mini-vial to the HRMS lab for analysis.

12. Data Analysis and Calculations

12.1 Not applicable.

13. Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S006, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for

further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1 All attempts will be made to minimize the use of solvents and standard materials.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment, employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Waste methylene chloride, acetone, hexane and toluene shall be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container.
- Extracted solid/tissue samples, paper funnel filters, glass wool, etc., contaminated with solvents shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container.
- Contaminated sulfuric acid used during extract cleanup shall be placed in the acidic waste stream, contained in a poly satellite accumulation container.
- Extracted aqueous samples, contaminated with methylene chloride shall be placed in the organic water waste stream, contained in a poly satellite accumulation container.

16. References

16.1 Knoxville Laboratory Quality Assurance Manual (QAM), current revision.

16.2 Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, EPA-821-R-00-002, December 1999.

17. Miscellaneous

17.1 Deviations from EPA Method 1668, Revision A.

17.1.1 Additional recovery standards are used in this procedure. The additional standards are listed in Table 2.

17.1.2 A solvent mixture of 1:1 hexane/acetone is used for solids and tissues. Method 1668 uses toluene for extraction of solids and 1:1 methylene

chloride/hexane for tissues.

17.2 List of Tables and Appendices:

17.2.1 Table 1 - Concentration of Native PCB Congener Stock and Spiking Solutions

17.2.2 Table 2 - Concentration of $^{13}C_{12}$ Labeled PCB Congener Stock and Spiking Solutions

17.2.3 Table 3 - Acceptance Criteria for Performance Tests

17.2.4 Table 4 - Assignment of Sample Preparation Protocols

17.2.5 Appendix I – Example Extraction Benchsheet

17.2.6 Appendix II - Guidelines for the Spike Witnessing Process

Table 1 - Concentration of Native PCB Congener Stock and Spiking Solutions

Native PCB Congener	BZ/ IUPAC	Standard Source	Catalog Number	Vendor Conc (ng/mL)	LCS Spiking Solution Conc (ng/mL)
2-MoCB	1	AccuStd	S-99994-4x	4000	5.0
4-MoCB	3	AccuStd	S-99994-4x	4000	5.0
2,2'-DiCB	4	AccuStd	S-99994-4x	4000	5.0
4,4'-DiCB	15	AccuStd	S-99994-4x	4000	5.0
2,2',6-TrCB	19	AccuStd	S-99994-4x	4000	5.0
3,4,4'-TrCB	37	AccuStd	S-99994-4x	4000	5.0
2,2',6,6'-TeCB	54	AccuStd	S-99994-4x	4000	5.0
3,3',4,4'-TeCB	77	AccuStd	S-99994-4x	4000	5.0
3,4,4',5-TeCB	81	AccuStd	S-99994-4x	4000	5.0
2,2',4,6,6'-PeCB	104	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4'-PeCB	105	AccuStd	S-99994-4x	4000	5.0
2,3,4,4',5-PeCB	114	AccuStd	S-99994-4x	4000	5.0
2,3',4,4',5-PeCB	118	AccuStd	S-99994-4x	4000	5.0
2',3,4,4',5-PeCB	123	AccuStd	S-99994-4x	4000	5.0
3,3',4,4',5-PeCB	126	AccuStd	S-99994-4x	4000	5.0
2,2',4,4',6,6'-HxCB	155	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5-HxCB	156	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5'-HxCB	157	AccuStd	S-99994-4x	4000	5.0
2,3',4,4',5,5'-HxCB	167	AccuStd	S-99994-4x	4000	5.0
3,3',4,4',5,5'-HxCB	169	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4,4',5-HpCB	170	AccuStd	S-99994-4x	4000	5.0
2,2',3,4,4',5,5'-HpCB	180	AccuStd	S-99994-4x	4000	5.0
2,2',3,4',5,6,6'-HpCB	188	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5,5'-HpCB	189	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',5,5',6,6'-OcCB	202	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5,5',6-OcCB	205	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4,4',5,5',6-NoCB	206	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4',5,5',6,6'-NoCB	208	AccuStd	S-99994-4x	4000	5.0
DeCB	209	AccuStd	S-99994-4x	4000	5.0
All other CB congeners	NA	AccuStd	S-99994-4x	4000	5.0

Table 2 - Concentration of $^{13}C_{12}$ Labeled PCB Congener Stock and Spiking Solutions

Labeled PCB Congener	**BZ/ IUPAC**	**Standard Source**	**Catalog Number**	**Vendor Conc (ng/mL)**	Stock Conc (ng/mL)	Spiking Solution Conc (ng/mL)
Internal Standards						
$^{13}C_{12}$-2-chlorobiphenyl	1L	Cambridge	EC-4908	40,000	1000	10
$^{13}C_{12}$-4-chlorobiphenyl	3L	Cambridge	EC-4990	40,000	1000	10
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	Cambridge	EC-4911	40,000	1000	10
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	Cambridge	EC-1402	40,000	1000	10
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	Cambridge	EC-4909	40,000	1000	10
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	Cambridge	EC-4901	40,000	1000	10
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	Cambridge	EC-4912	40,000	1000	10
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	Cambridge	EC-1404	40,000	1000	10
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	Cambridge	EC-1412	40,000	1000	10
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	Cambridge	EC-4910	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	Cambridge	EC-1420	40,000	1000	10
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	Cambridge	EC-4902	40,000	1000	10
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	Cambridge	EC-1435	40,000	1000	10
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	Cambridge	EC-4904	40,000	1000	10
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	Cambridge	EC-1425	40,000	1000	10
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	Cambridge	EC-4167	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	Cambridge	EC-1422	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	Cambridge	EC-4051	40,000	1000	10
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	Cambridge	EC-4050	40,000	1000	10
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	Cambridge	EC-1416	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	Cambridge	EC-4905	40,000	1000	10
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	Cambridge	EC-4913	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	Cambridge	EC-1409	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	Cambridge	EC-1408	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	Cambridge	EC-4199	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	Cambridge	EC-4900	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	Cambridge	EC-1419	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	Cambridge	EC-1410	40,000	1000	10
Recovery Standards						
$^{13}C_{12}$-2,5-dichlorobiphenyl	9L	Cambridge	EC-4165	40,000	1000	100
$^{13}C_{12}$-2,4',5-trichlorobiphenyl	31L	Wellington	MBP-31	50,000	1000	100
$^{13}C_{12}$-2,4',6-trichlorobiphenyl	32L	Cambridge	EC-4163	40,000	1000	100
$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	52L	Cambridge	EC-1424	40,000	1000	100
$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	101L	Cambridge	EC-1405	40,000	1000	100
$^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl	127L	Cambridge	EC-1421	40,000	1000	100
$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	138L	Cambridge	EC-1436	40,000	1000	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	180L	Cambridge	EC-1407	40,000	1000	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	194L	Cambridge	EC-1418	40,000	1000	100
Cleanup Standards						
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	Cambridge	EC-1413	40,000	5000	10
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	Cambridge	EC-1415	40,000	5000	10
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	Cambridge	EC-1417	40,000	5000	10

Table 3 - Acceptance Criteria for Performance Tests

Toxic & LOC Congeners	IUPAC	Test Conc (ng/mL) [1]	IDOC %RSD	IDOC %R	LCS %R
2-chlorobiphenyl	1	50	40	60-140	50-150
4-chlorobiphenyl	3	50	40	60-140	50-150
2,2'-dichlorobiphenyl	4	50	40	60-140	50-150
4,4'-dichlorobiphenyl	15	50	40	60-140	50-150
2,2',6-trichlorobiphenyl	19	50	40	60-140	50-150
3,4,4'-trichlorobiphenyl	37	50	40	60-140	50-150
2,2',6,6'-tetrachlorobiphenyl	54	50	40	60-140	50-150
3,3',4,4'-tetrachlorobiphenyl	77	50	40	60-140	50-150
3,4,4',5-tetrachlorobiphenyl	81	50	40	60-140	50-150
2,2'4,6,6'-pentachlorobiphenyl	104	50	40	60-140	50-150
2,3,3',4,4'-pentachlorobiphenyl	105	50	40	60-140	50-150
2,3,4,4',5-pentachlorobiphenyl	114	50	40	60-140	50-150
2,3',4,4',5-pentachlorobiphenyl	118	50	40	60-140	50-150
2',3',4,4',5-pentachlorobiphenyl	123	50	40	60-140	50-150
3,3',4,4',5-pentachlorobiphenyl	126	50	40	60-140	50-150
2,2',4,4',6,6'-hexachlorobiphenyl	155	50	40	60-140	50-150
2,3,3',4,4',5-hexachlorobiphenyl	156	50	40	60-140	50-150
2,3',4,4',5,5'-hexachlorobiphenyl	157	50	40	60-140	50-150
2,3,3',4,4',5'-hexachlorobiphenyl	167	50	40	60-140	50-150
3,3',4,4',5,5'-hexachlorobiphenyl	169	50	40	60-140	50-150
2,2',3,4'5,6,6'-heptachlorobiphenyl	188	50	40	60-140	50-150
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	50	40	60-140	50-150
2,2',3,3',5,5',6,6'-octachlorobiphenyl	202	50	40	60-140	50-150
2,3,3',4,4',5,5',6-octachlorobiphenyl	205	50	40	60-140	50-150
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	50	40	60-140	50-150
2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208	50	40	60-140	50-150
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209	50	40	60-140	50-150
Internal Standards					
$^{13}C_{12}$-2-chlorobiphenyl	1L	100	50	35-135	30-140
$^{13}C_{12}$-4-chlorobiphenyl	3L	100	50	35-135	30-140
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	100	50	35-135	30-140
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	100	50	35-135	30-140
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	100	50	35-135	30-140
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	100	50	35-135	30-140
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	100	50	35-135	30-140
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	100	50	35-135	30-140
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	100	50	35-135	30-140
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	100	50	35-135	30-140
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	100	50	35-135	30-140
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	100	50	35-135	30-140
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	100	50	35-135	30-140

Table 3 - Acceptance Criteria for Performance Tests (continued)

Internal Standards	IUPAC	Test Conc (ng/mL) [1]	IDOC %RSD	IDOC %R	LCS %R
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	100	50	35-135	30-140
Cleanup Standards					
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	50	45	45-120	40-125
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	50	45	45-120	40-125
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	50	45	45-120	40-125

1 Test concentrations are based on ng/mL in the sample extract or standard solution.

Table 4 - Assignment of Sample Preparation Protocols

1668 Protocol	Protocol Name	Sample Amount Extracted (g)	Fraction of Extract Cleaned	IS Added (mL)	Cleanup Std Added (mL)	Recovery Std Added (µL)	Extract Delivery Volume (µL)	Prep Split Factor	QuantIMS Final Volume (µL)
P1	Clean	10	1/2	1	0.5 (added after split)	50	50	2	100
P2	Low	2	1	1	1	100	100	1	100
P3	Medium	1.25	1/2	2	1 (added after split)	100	250	2	200
P4	High	1	1/4	4	1 (added after split)	100	500	4	400

QuantIMS Final Volume (µL) = Extract Delivery Volume (µL) x Prep Split Factor x (nominal extract volume) / Extract Delivery Volume (µL)[(1]

[(1)] Nominal extract volume is 50 µL for protocol 1 and 100 µL for protocols 2, 3 and 4.

Appendix I – Example Extraction Benchsheet

TestAmerica Knoxville Extraction Sheet
1668 PCB Congener Sediment/Soil/Tissue by Soxhlet - KNOX-ID-0013

Batch Number: _____ Native Spike (5.0 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____ Delivered: _____ Initials/Date/Time

Soxhlet Start Date/Time: _____ Internal Std (10 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____

Soxhlet Stop Date/Time: _____ Cleanup Std (10 ng/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____ Received: _____ Initials/Date/Time

Tissue ☐ Soil ☐ Sediment ☐ Recovery Std (100 µg/mL) ID: _____ Spiked by: _____ Witness: _____ Date: _____

Lot Sample Number	Work Order Number	Suf	Protocol Number	Add sample to Soxhlet thimble. Record weight in g.	Water layer decanted? (Y,N,NA)	Add IS to all samples & QC. Record volume (mL).	Add native spike to LCS, LCSD, MS, MSD. Record volume (mL).	Extract 16 hr with 1:1 hexane/acetone.	Concentrate/solvent exchange to hexane to 10 mL.	Add cleanup std to all extracts. Record volume (mL).	Acid wash extracts.	Concentrate/solvent exchange to $MeCl_2$ to 10 mL.	Record volume extract taken through GPC cleanup (mL).	Concentrate/solvent exchange to hexane to ~4 mL.	Silica Gel Column Cleanup.	Concentrate to ~1 mL.	Add recovery std to mini-vial. Record volume added (µL). Transfer extract to vial.	Conc to delivery volume in nonane. Record del vol in µL.

1:1 Hexane/Acetone ID: _____ Na_2SO_4 Lot #: _____

Nonane Lot #: _____ H_2SO_4 Lot #: _____

MeCl2 Lot #: _____ 5% NaCl ID: _____

Balance ID: DI SI-0002

Comments: _____

Silica Gel Column Cleanup Reagents

Acid Silica Lot #: _____ Na_2SO_4 Lot #: _____

Deact.Silica Lot #: _____ Hexane Lot #: _____

Appendix II - Guidelines for the Spike Witnessing Process

- Make sure there are no distractions, for example, phone calls, checking samples on water bath, people coming in asking questions.
- The person spiking must tell the person who is witnessing what is being spiked and how much. Make sure the paperwork shows the spike amounts and spike IDs.
- The person witnessing should make sure they know and understand what is to be spiked and how much. Check the paperwork to verify.
- Check the syringe for air bubbles and also check the spike volume.
- It is a good idea to also check for cracks in the glassware.
- If client service requires spiking to occur when another analyst is not available, a witness is not required. In this case, the analyst will serve as his/her own witness, and must carefully double check the spike solutions and spike amounts added to the client samples and associated quality control samples. The analyst enters his/her initials as both the analyst and witness.

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Biphenyl (PCB) Isomers by Isotope Dilution HRGC/HRMS

(SUPERSEDES: KNOX-ID-0013, Revision 8)

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Laboratory Director

1 Scope and Application

1.1 This procedure is designed to meet analytical program requirements where HRGC/HRMS analysis of polychlorinated biphenyl (PCB) isomers is specified. The procedure is used by TestAmerica Knoxville for the detection and quantitative measurement of all 209 PCB isomers in a variety of environmental matrices at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. This procedure is based on EPA method 1668A.

1.2 The compounds listed in Table 1 may be determined by this procedure. The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The estimated minimum levels (EMLs) in Table 4 are the levels at which the PCBs can be determined with only common laboratory interferences present. The actual limits of detection and quantitation will vary depending on the complexity of the matrix.

1.3 The Low Calibration Levels (LCL's) of the method are listed in Table 3 for individual isomers. Analysis of a one-tenth aliquot of the sample permits measurements of concentrations up to 10 times the upper calibration range. Samples containing concentrations of PCB's that are greater than ten times the upper calibration are analyzed by protocols designed for such concentration levels.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in section 9.1.

1.5 This procedure is based on "performance-based" methods. These reference methods allow modifications to overcome interferences or lower the cost of measurements, if all performance criteria in the methods are met and method equivalency is established. Deviations from the referenced methods have been incorporated into this procedure and are listed in section 17.1. Deviations to this procedure are only allowed as specified in section 11.1.

1.6 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCBs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2 Summary of Method

2.1 All solid, semi-solid and fish tissue samples are screened by GC/ECD prior to extraction. Aqueous samples may be screened if the potential for congener levels above 40 ng/L exists. Variations to sample size, spiking levels and final volume are established based on the screening result.

2.2 After sample extraction, cleanup, and concentration, recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.3 An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's.

2.4 Quantitative analysis is performed using selected ion current profile (SICP) areas using the internal standard technique.

2.5 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3 Definitions

These definitions and purposes are specific to this method but conform to common usage as much as possible.

Note: Terminology differences existing in some isotope dilution reference methods regarding the functionality of the labeled analogs may lead to confusion. For example, EPA's Office of Solid Waste methods (8280, 8290) use the term "Internal Standards" to describe the labeled analogs which are added to the sample prior to extraction and used to quantitate the native targets. EPA's Office of Water methods (1613B, 1668) use the term "Labeled Analogs" to describe these same compounds while using the term "Internal Standards" to describe the labeled analogs which are added to the extract just prior to analysis and used to quantitate the recovery of the labeled analogs added before extraction. EPA's Office of Solid Waste methods (8280, 8290) uses the term "Recovery Standards" to describe these later labeled analogs.

The terminology conventions established by the EPA's Office of Solid Waste methods (8280, 8290) are used in the laboratory for all Standard Operating Procedures and internal communications as defined in this section.

3.1 Analyte – A PCB tested for by this method. The analytes are listed in Table 1.

3.2 Calibration standard (CAL) – A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration verification standard (VER) – The mid-point calibration standard (CS3) that is used to verify calibration. See Table 6a.

3.4 CB – Chlorinated biphenyl congener. One of the 209 individual chlorinated biphenyl congeners determined using this method. The 209 CBs are listed in Table 1.

3.5 Cleanup Standard – Isotopically labeled compounds that are added to samples, blanks, quality control samples, and calibration solutions. They are added to the samples after extraction but prior to extract cleanup, and are used to assess the efficiency of the cleanup procedures.

3.6 Congener – Any member of a particular homologous series, for example, 2,2'-DiCB.

3.7 CS0.5, CS1, CS2, CS3, CS4, CS5 – See Calibration standards and Table 6a.

3.8 Estimated Detection Limit (EDL) – The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.9 Estimated Maximum Possible Concentration (EMPC) – The calculated concentration of a signal having the same retention time as a PCB congener but which does not meet the other qualitative identification criteria defined in the method.

3.10 Estimated Minimum Detection Limit (EMDL) – The lowest concentration at which an analyte can be detected with common laboratory interferences present.

3.11 Estimated Minimum Level (EML) – The lowest concentration at which an analyte can be measured reliably with common laboratory interferences present.

3.12 Field blank – An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.13 GC – Gas chromatograph or gas chromatography.

3.14 Homologous Series – A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.15 HRGC – High resolution GC.

3.16 HRMS – High resolution MS.

3.17 ICV – Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the Initial calibration to verify the concentration of the initial calibration standards.

3.18 Internal Standards (IS) – Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate

the concentration of the target analytes or detection limits.

3.19 IPR (also known as IDOC)– Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

3.20 Isomer – Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 4-DiCB and 9-DiCB are structural isomers.

3.21 Laboratory blank – See Method blank.

3.22 Laboratory control sample (LCS) – See ongoing precision and recovery standard (OPR).

3.23 Laboratory reagent blank – See method blank.

3.24 Level of Chlorination (LOC) Congeners – The first and last eluting congeners in each homolog (or level of chlorination). (For the SPB-Octyl Column the LOC Congeners are 1, 3; 4,15; 19,37; 54, 77; 104, 126; 155, 169; 188, 189; 202, 205; 208, 206; 209)

3.25 Method blank – An aliquot of a clean test matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.26 Minimum Level (ML) – The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.27 MS – Mass spectrometer or mass spectrometry.

3.28 OPR (also know as ODOC) – Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.29 PAR – Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.30 PFK – Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.31 Primary dilution standard – A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare

calibration solutions and other solutions.

3.32 Quality control check sample (QCS) – A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.33 PCB – Polychlorinated biphenyl.

3.34 Reagent water – Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method minimum level for the analyte.

3.35 Recovery Standard (RS) – Isotopically labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

3.36 Relative Percent Difference (RPD) – A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.37 Relative standard deviation (RSD) – The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3.38 RF – Response factor. See Section 10.3.4.2.

3.39 RRF – Relative response factor. See Section 10.3.4.2.

3.40 SICP – Selected ion current profile; the line described by the signal at an exact m/z.

3.41 SPE – Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

3.42 Specificity – The ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.43 Stock solution - A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3.44 Surrogate Standards (SS) - Isotopically labeled compounds that are added to XAD samples and calibration solution. They are added to XAD sampling tubes before sampling and are used to measure sampling and recovery efficiency.

3.45 Toxic Congeners (or Toxic Isomers) – PCBs determined by the World Health Organization and USEPA to have dioxin-like toxicity. (PCBs 77, 81, 105, 114,

118, 123, 126, 156, 157, 167, 169, 189)

3.46 Toxic/LOC Congeners – PCBs belonging to either the Toxic Congeners list or the LOC Congeners list.

3.47 VER – See Calibration verification standard.

3.48 Additional definitions can be found in the TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents may be required. Where possible, reagents are cleaned by extraction or solvent rinse. The non-coplanar PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory at the minimum levels in this method, and baking of glassware in a kiln or furnace at 450 - 500°C may be necessary to remove these and other contaminants.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory method blanks (section 9.5) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCBs are measured by this method, the elimination of interferences is essential. Cleanup steps can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCBs at the levels shown in Table 3.

5 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.3 The effluents of sample splitters for the gas chromatograph and roughing pumps on

the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.5 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source may be removed from the vacuum manifold through a vacuum interlock.

5.6 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument may be left on.

5.7 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous memebranes and upper respiratory tract. Causes skin irritiation.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.8 Chemicals that have been classified as **carcinogens**, **potential carcinogens**, or **mutagens include**: methylene chloride, polychlorinated biphenyls, and toluene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.)

5.9 Chemicals known to be **flammable** are: acetone, hexane, nonane and toluene.

5.10 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.11 The preparation of all standards will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.12 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.13 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.14 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Bench tops should be covered with plastic backed absorbent paper.

5.15 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.16 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.17 All work must be stopped in the event of a known or potential compromise to the health or safety of laboratory personnel. The situation must be reported immediately to a laboratory supervisor.

6 Equipment and Supplies

6.1 Gas chromatograph - Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.1.1 Column #1 – 30±5-m long x 0.25±0.02-mm ID; 0.25-µm film SPB-Octyl (Supelco 2-4218, or equivalent).

6.1.2 Column #2 – 60-m x 0.32-mm ID x 0.25-µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062 or Restek No.10227, or equivalent).

6.2 Mass spectrometer - Electron impact ionization, shall be capable of repetitively selectively monitoring 20 exact m/z's minimum at high resolution (=10,000) during a period less than 1.0 second, and shall meet all of the performance specifications in Section 10.

6.3 GC/MS interface - The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.4 Data system - Capable of collecting, recording, and storing MS data.

7 Reagents and Standards

CAUTION: Refer to Material Safety Data Sheets (MSDS) for specific safety information on chemicals and reagents prior to use or as needed.

CAUTION: During preparation of reagents, associates shall wear lab coat, gloves, safety glasses with side shields, and laboratory approved shoes as a minimum. Reagents shall be prepared in a fume hood.

7.1 Solvents - Acetone, toluene, n-hexane, methanol, methylene chloride, and nonane; pesticide quality.

7.2 Perfluorokerosene (PFK) high boiling mass spectroscopy grade; bp 210-260°C; d^{20}_4 1.94; n^{20}_D 1.330; Fluka (Catalog No. - 77275).

7.3 $^{13}C_{12}$ Labeled PCB Congener Standards: Obtained as individual Certified Reference Standards from Cambridge Isotope Laboratories (CIL, Andover Massachusetts) and Wellington Laboratories (Guelph, Ontario, Canada). (Refer to Table 5b for a list of individual standards.) These standards are purchased at 40 µg/mL or 50 µg/mL in nonane. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. Once a standard ampoule has been vortexed and opened, the solution is transferred to an amber glass vial with a Teflon®-lined screw cap. When not being used, standards are stored in the dark in a refrigerator at 4 $\pm$ 2°C. These purchased standards are used to prepare the following mixed stock solutions and spiking solutions:

7.3.1 Internal Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled internal standards listed in Table 5b, to a concentration of 1000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.2 Internal Standard Spiking Solution: Prepared by diluting the 1000 ng/mL internal standard stock solution to a concentration of 10 ng/mL in acetone. 1.0 to 4.0 mL of this solution is added to each solid/tissue sample prior to extraction. (Refer to Table 12, "Assignment of Sample Preparation Protocols" to determine the exact volume to add.) 0.20 mL of the internal standard spiking solution is added to each aqueous sample prior to extraction.

7.3.3 Recovery Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled recovery standards listed in Table 5b to a concentration of 1000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.4 Recovery Standard Spiking Solution: Prepared by diluting the 1000 ng/mL recovery standard stock solution to a concentration of 100 ng/mL in nonane. 50 to 100 µL of this spiking solution is added to each solid/tissue sample extract prior to analysis (refer to Table 12), whereas, 20 µL is added to each aqueous sample extract.

7.3.5 Cleanup Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled cleanup standards listed in Table 5b, to a concentration of 5000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.6 Cleanup Standard Spiking Solution: Prepared by diluting the 5000 ng/mL cleanup standard stock solution to a concentration of 10 ng/mL in hexane. 0.5 to 1.0 mL of this solution is added to each solid/tissue sample extract prior to cleanup (refer to Table 12), whereas, 0.20 mL is added to each aqueous sample extract.

7.3.7 Sampling Surrogate Standard Stock Solution: Prepared by diluting the individual $^{13}C_{12}$ labeled sampling surrogate standards listed in Table 5b to a concentration of 5000 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.3.8 Sampling Surrogate Spiking Solution: Prepared by diluting the 5000 ng/mL sampling surrogate stock solution to a concentration of 50 ng/mL in nonane.

7.4 Native PCB Congener Standard Mix: Obtained as a Certified Reference Standard from Accustandard (New Haven, CT). This standard contains all 209 PCB congeners at 4000 ng/mL in nonane. If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the

standard. Once a standard ampoule has been vortexed and opened, the solution is transferred to an amber glass vial with a Teflon®-lined screw cap. When not being used, the standard is stored in the dark in a refrigerator at 4 ± 2°C. This purchased standard is used to prepare the following native stock solution and spiking solution:

7.4.1 Native PCB Congener Stock Solution: Prepared by diluting the 4000 ng/mL native PCB congener standard mix to a concentration of 40 ng/mL in nonane. The concentration is verified by GC/MS before use.

7.4.2 LCS Spiking Solution: Prepared by diluting the 4000 ng/mL native PCB congener standard to a concentration of 5.0 ng/mL in acetone. 1.0 mL of this solution is added to each solid/tissue LCS prior to extraction, whereas, 0.20 mL is added to each aqueous LCS.

7.5 Calibration Standard Solutions (CS 0.5 through CS 5) are prepared by dilution of the native PCB congener standards in section 7.4 and 7.4.1 and the labeled standards in section 7.3 in nonane. Table 6a shows the calibration solution analytes and final concentrations. Table 6b provides details for preparation of these calibration solutions.

7.5.1 This series of solutions is used to establish linearity and relative response factors for all compounds in the initial calibration solutions. These RRFs are used to quantify PCB congeners in the calibration verification (VER) and all samples. The CS3 standard is used for calibration verification. The VER solution is used to verify chromatographic performance and to update retention times and relative retention times.

7.6 PCB Congener Mix 1 through 5 standard solutions containing all 209 isomers are Certified Reference Standards (Accustandard Product No's. M-1668A-1, M-1668A-2, M-1668A-3, M-1668A-4, M-1668A-5). Stock solutions are purchased at 250-750 µg/mL in isooctane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with Teflon®-lined cap and is used as received. These five mixes are run in triplicate to determine the retention times for each of the congeners and which congeners will co-elute for each new SPB Octyl column used.

7.6.1 209 PCB ICAL Verification stock solution: Prepared by combining the five PCB Congener Mixes referred to in section 7.6 and diluting to a concentration of 5000-15000 ng/mL in nonane.

7.6.2 Initial Calibration Verification Standard. This is a single solution containing all 209 individual PCBs as well as internal standards and recovery standards at the following concentrations:

- mono, di, and tri CBs at 50 ng/mL
- tetra, penta, hexa and hepta CBs at 100 ng/mL

- octa, nona, and deca CBs at 150 ng/mL
- internal standards and recovery standards are at the same concentration as the calibration standards (CS 0.5 – CS 5).

This solution is always analyzed immediately after the initial calibration.

7.6.2.1 Combine 100 uL of 209 PCB ICAL verification stock solution (Section 7.6.1) (equivalent to 20 uL of each mix) with 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled internal standard stock solution, 100 uL of a 1/10 dilution of the 5000 ng/mL $^{13}C_{12}$ labeled cleanup standard stock solution, 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled recovery standard stock solution and 600 uL of nonane to produce the concentrations listed in section 7.6.2.

7.6.3 Retention Time Calibration Mixes: These are 5 solutions injected in triplicate to establish the retention time data referenced in section 10.2.3. Combine 20 uL of the Accustandard PCB Congener Mix 1 (Section 7.6) with 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled internal standard stock solution, 100 uL of a 1/10 dilution of the 5000 ng/mL $^{13}C_{12}$ labeled cleanup standard stock solution, 100 uL of the 1000 ng/mL $^{13}C_{12}$ labeled recovery standard stock solution and 600 uL of nonane to produce the concentrations listed in section 7.6.2. Repeat the process using the Accustandard PCB Congener Mixes 2 through 5.

7.7 QC Check Sample - A QC Check Sample should be obtained from a source independent of the calibration standards. This check sample is a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has an SRM 1944 – New York/New Jersey Waterway Sediment that the NYSDEC recommends for use.

8 Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, “Sample Receipt and Login”, current revision.

8.2 Holding Times

8.2.1 Store sample extracts in the dark at room temperature until analyzed. If stored in the dark at room temperature, sample extracts may be stored for up to one year.

9 Quality Control

9.1 Initial precision and recovery (IPR) or initial demonstration of capabilty (IDOC)

samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.1 For aqueous samples, extract, clean, concentrate, and analyze four 1-L aliquots of reagent water spiked with internal standards, cleanup standard, recovery standard and the LCS spiking solution, according to the procedures in section 11. For solid/tissue samples, extract, clean, concentrate, and analyze four aliquots of sodium sulfate/corn oil spiked with internal standards, cleanup standard, recovery standard and the LCS spiking solution, according to the procedures in section 11. All steps that are to be used for processing samples, including preparation, extraction and cleanup, shall be included in this test.

9.1.2 Using the results of the set of four analyses, compute the average percent recovery (%R) of the extracts and the relative standard deviation (RSD) of the concentration in ng/mL for each compound.

9.1.3 For each PCB and labeled compound, compare the RSD and %R with the corresponding limits for initial precision and recovery in Table 10. If the RSD and %R for all compounds meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, any individual RSD exceeds the precision limit or any individual %R falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 Internal Standards

9.2.1 Every sample, blank, and QC sample is spiked with internal standards. Internal standard recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. When properly applied, results from isotope dilution techniques are independent of recovery. The recovery of each internal standard should be within the limits in Table 10. If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than 25 percent, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDL's) are less than the estimated minimum levels (EML's), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated

detection limits (EDL's) are greater than the estimated minimum levels (EML's), re-extract and reanalyze the sample. If the ion chromatogram of the PFK lock mass m/z indicates ion suppression in the region where the internal standard elutes, reanalyzing the extract at up to a 1/10 dilution may improve the internal standard recovery. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional cleanups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.2.2 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.3 Cleanup Standards: Every sample, blank, and QC sample extract is spiked with $^{13}C_{12}$ labeled cleanup standards after extraction but prior to extract cleanup. They are used to assess the efficiency of the cleanup procedures.

9.4 Recovery Standards: Every sample, blank, and QC sample extract is spiked with $^{13}C_{12}$ labeled recovery standards prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

9.5 Method Blanks

9.5.1 A laboratory method blank must be run along with each analytical batch of 20 or fewer samples. The method blank consists of reagent water for aqueous samples, sodium sulfate for solid and tissue samples, processed in the same manner and at the same time as the associated samples. The method blank is used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive data. Analyze the blank immediately after analysis of the LCS to demonstrate freedom from contamination. The method blank should not contain any of the compounds of interest at a concentration above the estimated minimum level (EML) shown in Table 4.

9.5.2 Corrective action is required when compounds of interest are detected in the method blank above the EML. Corrective action may include reanalysis of the method blank. Contact the Project Manager to determine further corrective action. At a minimum, all associated results are qualified with a B flag. Re-extraction and reanalysis of all samples associated with a contaminated method blank is required if requested by the client or Project Manager. Investigation of the source of the method blank contamination will be initiated before further samples are extracted.

9.5.3 The method blank must have acceptable internal standard recoveries. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of

demonstrating that the analysis is free of contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.5.4 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.6 Instrument Blank

9.6.1 Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed.

9.6.2 An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.7 Laboratory Control Sample – A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 samples. All analytes must be within established control limits specified in Table 10. The LCS is spiked with the compounds listed in Table 5a.

9.7.1 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.
- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported and the failure is documented in the project narrative.

9.8 QC Check Sample - Analyze the QC Check Sample (section 7.7) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least annually.

10 Calibration and Standardization

10.1 Three types of calibration procedures are required. The first type establishes retention times, relative retention times and relative retention time windows to be used during the subsequent calibrations and analyses. The second type, initial calibration, is required to establish response factors and is required before any samples are analyzed. It may be required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The third type, continuing calibration, consists of analyzing the continuing calibration verification solution (VER). No samples are to be analyzed until acceptable

calibration as described in sections 10.2, 10.3 and 10.4 is demonstrated and documented.

10.2 Retention Time Calibration

Retention time calibration is required if the retention time criteria cannot be met.

10.2.1 The absolute retention time of CB 209 must exceed 55 minutes. Otherwise the GC temperature program must be adjusted and the test repeated until the requirement is met.

NOTE: When adjusting chromatographic conditions, the resolution requirements of sections 10.4.5.8 to10.4.5.9 must be maintained.

10.2.2 Tune the instrument to meet the mass resolution and mass accuracy requirements of section 10.3.2. Document the resolution and accuracy.

10.2.3 Analyze 2µL of each of the five individual PCB mixtures (section 7.6.3). Repeat the series twice more in succession to provide 3 runs of each mix. It is not necessary to interrupt this analytical sequence to perform a 12-hour resolution check. Set the switch-points for the MID descriptors. The switch-points must be set to insure that the first and last eluting isomer of each homolog group and the labeled internal standards are acquired properly. Determine the average retention time of each PCB congener using the elution order information in Table 11.

NOTE 1: PCB Mixture 5 (M-1668A-5) contains the first and last eluting isomer in each homolog group for the SPB-Octyl column (see Table 7).

NOTE 2: Laboratory data has indicated that the SPB-Octyl column can exhibit significant differences in performance from column to column. It has also been indicated that the column's performance can change significantly due to oxidation with subsequent changes in congener retention times and elution order. The individual PCB mixtures should be analyzed whenever the column's performance or specific congeners retention times are in doubt.

10.2.4 Calculate the relative retention times for all native and labeled congeners, using their retention time references from Table 2 (RT Ref). Calculate the relative retention time for each run in which the congener and its retention time reference are present (i.e., three RRTs will be calculated for each native congener. Fifteen RRTs will be calculated for each internal standard.) Use the calculated average retention times for all native and labeled congeners as the RT calibration source in the calculation software.

10.2.5 Calculate the relative retention time window using the absolute retention time windows (RT Window) from Table 2.

$$\text{RRT Limit Low} = \frac{RT_A - (RT_{WIN}/2)}{RT_{IS}}$$

$$\text{RRT Limit High} = \frac{RT_{A+} (RT_{WIN}/2)}{RT_{IS}}$$

Where:

RT_A = Average retention time of analyte.

RT_{IS} = Average retention time of RT reference.

RT_{WIN} = Absolute RT window in seconds from Table 2.

10.2.6 A single pair of RRT limits is used for all congeners in coeluting set. Use the RRT Limit Low that was calculated for the first eluting congener, and the RRT Limit High calculated for the last eluting congener (in the coelution set).

10.3 Initial Calibration

Initial calibration is required before any samples are analyzed for PCBs. Initial calibration is also required if any continuing calibration (section 10.4) does not meet the required criteria in section 10.4.5 after routine maintenance.

10.3.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 6a. Calibration standards should be stored at room temperature and preferably in amber vials. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.3.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). By using a PFK molecular leak, tune the instrument (see the appropriate instrument manufacturer's operating manual for tuning instructions) to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 342.97924 (PFK). For each MID descriptor group, monitor and record the mass resolution and exact m/z's of three reference peaks covering the mass range of the descriptor (see below). By using peak matching techniques, verify that the deviation between the exact m/z and the theoretical m/z for each m/z monitored is less than 5 ppm. Iteratively adjust operating parameters and tuning values until the mass resolution and mass accuracy criteria are met for each ion. Document the mass resolution and mass accuracy for each of MID group ion sets. Because of the extensive mass range covered in each MID group, it may not be possible to maintain 10,000 resolution throughout the mass range of the MID group. Therefore, resolution must be greater than 8,000 throughout the mass range and must be greater than 10,000 in the center of the mass

range for each MID group. The minimum resolution of 10,000 must be met for m/z 342.97924.

MID Group 1 PFK ions - 192.9888, 230.98563, 280.98243
MID Group 2 PFK ions - 268.98243, 292.98243, 380.97605
MID Group 3 PFK ions - 342.97924, 380.97605, 430.97285
MID Group 4 PFK ions - 404.97604, 442.97285, 530.96646

10.3.3 Inject a 2 µL aliquot of the CS 0.5 calibration solution.

10.3.3.1 Ion abundance ratios, minimum levels, and signal-to-noise ratios.

10.3.3.1.1 Measure the SICP areas for each congener or congener group, and compute the ion abundance ratios at the exact m/z's specified in Table 8. Compare the computed ratio to the theoretical ratio given in Table 9.

10.3.3.1.2 All Toxic/LOC and labeled compounds in the CS-0.5 standard must be within the QC limits in Table 9 for their respective ion abundance ratios; otherwise, the mass spectrometer must be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution must be verified (Section 10.3.2) prior to repeat of the test.

10.3.3.1.3 The peaks representing the CBs and labeled compounds in the CS-0.5 calibration standard must have signal-to-noise ratios (S/N) = 10; otherwise, the mass spectrometer must be adjusted and this test repeated until the minimum levels in Table 4 are met.

10.3.3.1.4 An exception to the ion abundance ratio and signal to noise ratio requirements is the secondary ion for dichlorinated biphenyls (m/z 223.9974). High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.

10.3.4 Analyze 2 µL of each of the other calibration standards.

10.3.4.1 Isomer specificity.

10.3.4.1.1 Use the CS-3 calibration standard to evaluate column performance. The toxic isomers must be uniquely resolved from all other congeners. Isomers may be unresolved so long as they have the same toxicity equivalency factor (TEF) and response factor and so long as these unresolved isomers are uniquely resolved from all other congeners. For example, the SPB-Octyl column achieves unique GC resolution of all Toxics except congeners with IUPAC numbers 156 and 157. This isomeric pair is uniquely resolved from all other congeners and these congeners have the same TEF and response factor.

10.3.4.1.2 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.3.4.1.3 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.3.4.1.4 Column to column variations in the SPB-Octyl phase significantly affects the resolution of isomers 156 and 157. Document the percent valley between the isomers. If the %valley is < 40% then calculate the isomers as non-coeluting peaks. If the %valley is > 40% then calculate the isomers as co-eluting peaks.

10.3.4.1.5 Classify each congener as resolved or as a member of a coelution set. To be documented as resolved, the valleys between any two isomers must be less than 40 percent of the height of the shorter of the two adjacent peaks. Each member of a coelution set is designated with a qualifier in the format of CXXX, where XXX = the

lowest numbered congener in the set. For example, if PCB 156 and PCB 157 coelute, qualify PCB 157 with “C156”.

10.3.4.2 Calculate the RRF of each compound of interest (target analytes, coelution sets, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest.
Ais = sum of the areas of the quantitation ions of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
Cs = concentration of the compound of interest.

NOTE: When calculating the RRF for a coelution set, sum the areas of all isomers in the set. Use the resulting RRF for all congeners within the set.

10.3.4.3 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (RSD) of the relative response factors for each compound of interest in the six calibration standard solutions using the following equations;

$$\overline{RRF}_{n=6} = \frac{1}{n} \times \sum_{i=1}^{n} RF_i$$

$$RSD_{n=6} = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed, otherwise repeat the

initial calibration.

10.3.5.1 The percent relative standard deviation (RSD) for the mean relative response factors for the unlabeled native analytes calculated by isotope dilution must not exceed 20 percent. The percent RSD for the mean relative response factors for the unlabeled native analytes calculated by internal standard must not exceed 35 percent. The percent RSD for the mean relative response factors for the labeled standards must not exceed 35 percent.

10.3.6 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.6.2 after completion of the ICAL prior to sample analysis. Calculate the concentration of the ICV using the RRF's from the CS-3 standard analyzed in section 10.3.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula:

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the ICV Standard.
C_{Calc} = The calculated concentration of the ICV Standard.

10.3.6.1 The criteria for acceptance of the ICV Standard are as follows:

- The %D may not exceed ±35% for more than 4 of the native and labeled compounds.
- The %D may not exceed ±50% for any native or labeled compound.

10.3.6.2 All data associated with compounds with percent differences exceeding ±35% must be reviewed before acceptance.

10.3.6.3 All data associated with compounds with percent differences exceeding ±35% shall be documented as an NCM. Corrective action must be taken and may include the following:

- Reanalyze the ICV Standard.
- Replace and reanalyze the ICV Standard.
- Evaluate the instrument performance.
- Evaluate the Initial Calibration Standards.

10.4 Continuing Calibration

10.4.1 Continuing calibration is performed at the beginning of a 12-hour period after successful mass resolution check.

10.4.2 Document the mass resolution performance as specified in section 10.3.2 at both the beginning and end of the 12-hour period.

10.4.3 Analyze 2 µL of the Continuing Calibration Verification Standard (VER). Calculate the concentration (C) of the compounds of interest (target analytes, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation:

$$C = \frac{As \times Cis}{Ais \times RRF}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest.
Ais = sum of the areas of the quantitation ions of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
RRF = mean relative response factor from section 10.3.4.2.

10.4.4 Calculate the concentrations as percentages of the test concentrations and compare them to the limits specified in Table 10 using the following equation:

$$C_{ver}\% = \frac{C_{ver}}{C_{test}} \times 100$$

Where:

C_{ver} = the concentration of the VER standard calculated in section 10.4.3
C_{tes} = the test concentration of the VER standard listed in Table 6a.

10.4.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If the acceptance criteria are met, the calibration is deemed to be in control and the RRF's generated from the initial calibration are used to quantify samples. If acceptable calibration is not achieved, identify the root cause, perform corrective action, and repeat the continuing calibration. If a second consecutive attempt at a continuing calibration fails, two consecutive calibrations must meet the criteria, or an initial calibration must be run before proceeding with client samples.

10.4.5.1 The ion abundance ratios of the peaks representing the

Toxics/LOCs and labeled standards must be within the control limits specified in Table 9.

10.4.5.2 The S/N for the GC signals present in every SICP (including those for labeled standards) must be ≥ 10.

10.4.5.3 The concentrations calculated as percentages of test concentrations (Toxic and LOC congeners, internal standards, cleanup standards, and surrogate standards) must be within the limits in Table 10.

10.4.5.4 For Toxic and LOC congeners, as listed in the first section of Table 10, the percent of the calculated concentration relative to the test concentration must be within 70-130%.

10.4.5.5 For non-Toxics/LOCs the calculated concentrations must be within 40-160% of the test concentrations.

10.4.5.5.1 If the non-Toxic/LOC calculated concentration is within 70-130% of the test concentration, then the ICAL RF for that congener is used. If the calculated concentration is not within 70-130% but is within 40-160%, then calculate the RF from the VER standard for that congener and use it to calculate any associated samples run during that 12 hour shift.

10.4.5.6 The absolute retention times (RT) of the labeled internal standards must be within ±15 seconds of the retention times obtained during initial calibration.

10.4.5.7 The relative retention times (RRT) of the Toxics/LOC congeners must be within their respective RRT limits generated in the retention time calibration in section 10.2.

10.4.5.7.1 If the RRT's or RT's are not within the limits above, the GC may not be performing properly. However, routine column maintenance may include removing short amounts of the beginning of the column when active sites or non-volatile compounds in sample extracts cause poor chromatography and loss of specificity. Shortening of the column can cause the RRT's or RT's to fall outside the above limits.

10.4.5.7.2 When the RRT of any compound or the RT of any internal standard is not within the above limits, corrective action must be taken. If the GC is not performing properly, correct the problem and repeat the test. If the GC is performing properly but the RRT's or RT's have changed due to routine column maintenance, adjust the GC or replace the GC column, then repeat the test or repeat the retention time calibration.

10.4.5.8 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.4.5.9 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.4.5.10 If PCBs 156 and 157 have been classified as uniquely resolved at the most recent initial calibration, the valley between the two must be less than or equal to 50% of the lower of the two peaks. If this cannot be demonstrated, the resolution must be reestablished, or a new initial calibration must be analyzed.

10.4.6 Daily calibration must be performed every 12 hours of instrument operation. The 12-hour shift begins with the documentation of the mass resolution followed by the injection of the Continuing Calibration Standard (VER).

11 Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgement of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Sample Extraction and Cleanup

The extraction and cleanup procedures are described in SOP KNOX-OP-0021, "Extraction of Polychlorinated Biphenyl (PCB) Isomers for Analysis by Isotope

Dilution HRGC/HRMS", current revision.

11.3 Sample Analysis

11.3.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data beginning at 8 minutes and ending after decachlorobiphenyl has eluted from the column.

11.3.2 Record analysis information in the instrument logbook. The following information is required:

- Date of analysis
- Time of analysis
- Instrument data system filename
- Analyst
- Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.3.3 Generate integrated ion chromatograms for the masses listed in Table 8 that encompass the expected retention windows of the PCB homologous series.

11.3.4 Generate a reduced peak list file from the integrations show in the ion chromatograms.

11.3.5 Load the reduced peak list file into the calculation software.

11.3.6 The RTs of the unambiguous labeled congeners (RT Markers) are used to calculate a least squares best fit regression for retention times compared to those of the retention time calibration.

11.3.7 The resulting regression is used to calculate predicted retention times for target analytes. These predicted retention times are used by the software to identify candidate peaks for targets.

11.3.8 The analyst reviews the peaks identified as targets and determines whether to accept the identification. This determination is made by evaluating the delta values (RT shift from predicted), knowledge of peak patterns and observations of localized shifting.

11.3.9 A RRT window is calculated by multiplying the RRT Limit High and the RRT Limit Low by the retention time of the designated RT reference. The software applies a qualitative flag to each peak identified as a target that has a RRT outside the RRT window.

11.4 HRGC/HRMS Troubleshooting Guide

11.4.1 Perform the instrument’s leak check: Evaluate the air spectrum. Mass

28 should be less than 5 times mass 69. If the air spectrum is not acceptable, replace transfer line ferrule and/or pump out PFK reservoir.

11.4.2 Check the voltage on the 5V power supply: If voltage is not reading 5V, adjust voltage to read 5V.

11.4.3 Check daily calibration standard: Evaluate the signal to noise (S/N), examine peak shape/chromatography, and evaluate response factors. Refer to specific SOP's requirements and acceptance criteria for all natives and internal standards. If daily calibration is not acceptable , perform the following troubleshooting options as needed and reanalyze a daily CS-3 calibration standard:

- Replace the inlet seal and clean the injection port body with methanol to improve response factor.
- Perform column/injector port maintenance and/or retune the instrument to resolve chromatography/resolution, signal to noise issues.
- Perform a gain test on the electron multiplier.
- Adjust the tuning parameters of the instrumentation to achieve optimum sensitivity and peak shape.
- Evaluate carryover from sample analyses. If carryover or contamination is suspected, run solvent rinses (nonane) under MID to evaluate the contamination.
- When troubleshooting cannot resolve an instrument problem, a manufacture's service engineer may be consulted for possible solution, or called onsite for diagnosis/repair.

12 Data Analysis and Calculations

12.1 Qualitative Identification Criteria for PCBs

For a gas chromatographic peak to be identified as a PCB, it must meet all of the following criteria:

12.1.1 The signals for the two exact m/z's in Table 8 must be present and must maximize within ±2 seconds.

12.1.2 The signal to noise ratio (S/N) for each GC peak at each exact m/z must be greater than or equal to (≥) 2.5. (This requirement does not apply to the secondary ion for dichlorinated biphenyls [m/z 223.9974]. High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.)

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 8 must be within the limits in Table 9 . Alternately, the ratios may be within ±15% of the ratio in the midpoint (CS-3) calibration or calibration verification (VER), whichever is most recent.

12.1.4 The relative retention time of the peak for a CB must be within the RRT QC limits calculated in section 10.2.5.

NOTE: For native CBs determined by internal standard quantitation, a given CB congener may fall within more than one RT window and be misidentified unless the RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. Retention time regression analysis may be employed for this purpose.

12.1.5 If identification is ambiguous, (i.e., some, but not all of the identification criteria are met for a congener) an experienced analyst must determine the presence or absence of the congener.

12.2 Quantitation for PCBs

12.2.1 Calculate the Internal Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$\text{Ris} = \frac{\text{Ais} \times \text{Qrs}}{\text{Ars} \times \text{RRFis} \times \text{Qis}} \times 100\%$$

Where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

NOTE: In some situations, such as source testing, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$\text{Qrs} = \text{Qrss} \times \text{Split}$$

Where:

Qrs = ng of recovery standard added to extract
Qrss = ng of recovery standard added to the split portion of the extract
Split = split ratio of the extract

12.2.2 Calculate the concentration of individual PCBs according to the following equation:

$$\text{Concentration} = \frac{\text{As} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{W} \times \text{S}}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest

Ais = sum of the areas of the quantitation ions of the appropriate internal standard

Qis = ng of internal standard added to sample

RRF = mean relative response factor of compound obtained during initial calibration

W = amount of sample extracted (grams or liters)

S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis)

12.2.3 If reporting results for Total Homolog Groups, calculate the total concentration of all isomers within each homolog group by summing the concentrations of the individual PCB isomers within that homolog group.

12.2.4 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$\text{EDL} = \frac{\text{N} \times 2.5 \times \text{Qis}}{\text{His} \times \text{RRF} \times \text{W} \times \text{S}}$$

Where:

N = sum of peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute

His = sum of peak heights of quantitation ions for appropriate internal standard

Qis = ng of internal standard added to sample

RRF = mean relative response factor of compound obtained during initial calibration

W = amount of sample extracted (grams or liters)

S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis. Note: do not use if results are to be reported by QuantIMS since it performs all necessary moisture corrections.)

12.2.5 If peaks are present in the region of the ion chromatogram which do not

meet the qualitative criteria listed in section 12.1, calculate an Estimated Maximum Possible Concentration (EMPC). Use the equation in section 12.2.2, except that "As" should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e., the EMPC will always be lower than the result calculated from the uncorrected areas).

12.2.6 If the concentration in the final extract of any PCB isomer exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 1/10 may be performed on the extract. If compound concentrations exceeding the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed. The lab may report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Consultation with the client should occur before compounds are reported which exceed the calibration range.

12.3 The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. The EML's for different matrices and extract volumes are listed in Table 4. Deviations from the extraction amounts or final volumes listed will result in corresponding changes in the actual sample ML.

12.4 Flag all compound results in the sample which are below the estimated minimum level with a "J" qualifier.

12.5 Flag all compound results in the sample which were detected in the method blank with a "B" qualifier.

12.6 Flag all compound results in the sample which are above the upper calibration limit with an "E" qualifier.

12.7 Flag all compound results in the sample which are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.8 Flag compound results in the sample that may contain co-eluting compounds with a "C" qualifier.

12.8.1 Flag congeners known to coelute with a higher numbered congener with a "C" qualifier.

12.8.2 Flag congeners that coelute with a lower numbered congener with a "Cx" qualifier where x is the CAS PCB number of the lowest numbered congener in the coeluting group.

12.9 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier. When ion suppression of a PFK trace occurs at greater than or equal to 20% of full scale on both the lock mass and QC mass traces, and when the suppression is sustained for greater than 4 seconds, the suppression must be evaluated to determine which, if any, PCB congeners co-elute with the suppression. Congeners that are determined to co-elute with the suppression are flagged with an "S" qualifier.

12.10 Data Review

12.10.1 Refer to Figure 3 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.10.2 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.10.3 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.10.4 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.10.5 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.10.6 All items listed on the data review checklist must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. An example data review checklist is shown in Figure 3.

13 Method Performance

13.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S006, current revision, based on 40 CFR Part 136 Appendix B. The result of the MDL

determination must support the reporting limit.

13.2 Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability**.**

14 Pollution Prevention

14.1 All attempts will be made to minimize the use of solvents and standard materials.

15 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2 Waste Streams Produced by the Procedure: The following waste streams are produced when this method is carried out.

- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container.

16 References

16.1 Knoxville Laboratory Quality Assurance Manual (QAM), current revision.

16.2 Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, EPA-821-R-00-002, December 1999.

16.3 Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS [Revision B], EPA#: 821/B-94-005a YEAR: 1994

16.4 Ballschmiter, K. and M. Zell, "Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography", *Fresenius Z. Anal. Chem*., 302:20-31 (1980).

16.5 Schulte, E. and R. Malisch, "Berechnung der Wahren PCB-Gehalte in Umweltproben I. Ermittlung der Zusammensetzung Zweier Technischer PCB-Gemische," *Fresenius Z. Anal. Chem*., 314:545-551 (1983).

16.6 Guitart, R., P. Puig and J. Gómez-Catalán, "Requirement for a Standardized Nomenclature Criterion for PCBs: Computer-Assisted Assignment of Correct Congener Denomination and Numbering," *Chemosphere*, 27(8):1451-1459 (1993).

16.7 Rigaudy, J. and Klesney, S.P., Nomenclature of Organic Chemistry, Pergamon, 1979.

16.8 Pretsch, Clerc, Seibl, Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Second Edition, Springer-Verlag, 1989.

16.9 CRC Handbook of Chemistry and Physics, 71st edition, CRC Press, 1990-1991.

17 Miscellaneous

17.1 Deviations from EPA Method 1668, Revision A.

17.1.1 Additional recovery standards are used in this procedure. The additional standards are listed in Table 1.

17.1.2 Additional labeled standards are used in this procedure as field sampling surrogates. The additional standards are listed in Table 1.

17.1.3 The method authors had observed that when their columns were degraded, PCBs 156 and 157 became resolved. The method indicates that the compounds must coelute within 2 seconds. Using constant flow conditions, this laboratory has resolved PCB 156 from PCB 157 on columns that are not degraded. This procedure does not require the coelution of the two isomers, but requires that the retention times may not change significantly in relative retention times, in accordance with section 10.4.5.6.

17.1.4 The calibration procedure in the method calls for a single point standard for the non-Toxic/LOC congeners. This procedure uses a multi-point calibration for all 209 congeners.

17.1.5 This procedure uses MID groups that differ from the method. The procedure uses 4 groups, rather than 6, to improve instrument stability, by holding the magnet current steady for longer periods. Therefore alternate PFK lock masses are monitored, to reflect the mass ranges of the procedure’s MID groups.

17.1.6 This procedure uses average retention times (and average relative retention times) produced by triplicate analyses of the 5 mixes specified, rather than single analyses of the diluted 209 standard.

17.1.7 The absolute retention times, relative retention times, and relative retention time limits used by the laboratory differ from those listed in Method 1668A. Each SPC-Octyl column used by the laboratory has exhibited slightly different retention time characteristics resulting in

different absolute retention times than those listed in the method or those observed with another SPB-Octyl column. To ensure that the correct peak assignments are made, a retention time study is performed for each new column. This study includes the triplicate analysis of the five retention time mixes listed in Method 1668A as described in Section 10.2.5 to 10.2.7. This procedure requires a minimum elution time of 55 minutes for PCB 209.

17.1.8 The calibration verification procedures in the method call for updating the retention times, relative retention times and response factors for non-Toxic compounds during daily calibration and use the retention times, relative retention times and response factors from the initial calibration for Toxic and LOC compounds. This laboratory uses the retention times and relative retention times from triplicate analyses of the 5-mix series, which contains all congeners, and uses response factors from the initial calibration for all 209 compounds. The practice of updating the relative retention times of only a subset of compounds causes significant error in the linear regression prediction formulas used by targeting software to identify the compounds. This procedure has provisions for updating all RT's and RRT's by analyzing a new retention time calibration series.

17.1.9 The EMLs listed in Table 4 differ from those listed in the reference method. The EMLs are set above the mean plus 2 standard deviations for the higher of detections or EDLs for method blanks. In no case is the EML lower than the low calibration limit. The survey period was approximately 14 months.

17.2 List of tables and figures referenced in the body of the SOP.

17.2.1 Table 1 – Polychlorinated Biphenyls Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

17.2.2 Table 2 – RT References, Quantitation References, Retention Times (RT), and Relative Retention Times (RRTs) for the 209 CB congeners on SPB-Octyl

17.2.3 Table 3 – Low Calibration Levels Based on Various Final Extract Volumes

17.2.4 Table 4 – Estimated Minimum Levels – Matrix and Concentration

17.2.5 Table 5a – Concentration of Native PCB Congener Stock and Spiking Solutions

17.2.6 Table 5b – Concentration of $^{13}C_{12}$ Labeled PCB Congener Stock and Spiking Solutions

17.2.7 Table 6a – Concentration of PCBs in Calibration Solutions

17.2.18 Table 1 - Polychlorinated Biphenyls Determined by HRGC/HRMS

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3] Number	Usage
1	2-monochlorobiphenyl	2051-60-7	$^{13}C_{12}$-2-monochlorobiphenyl	234432-85-0	Internal Std
2	3-monochlorobiphenyl	2051-61-8			
3	4-monochlorobiphenyl	2051-62-9	$^{13}C_{12}$-4-monochlorobiphenyl	208263-77-8	Internal Std
4	2,2'-dichlorobiphenyl	13029-08-8	$^{13}C_{12}$-2,2'-dichlorobiphenyl	234432-86-1	Internal Std
5	2,3-dichlorobiphenyl	16605-91-7			
6	2,3'-dichlorobiphenyl	25569-80-6			
7	2,4-dichlorobiphenyl	33284-50-3			
8	2,4'-dichlorobiphenyl	34883-43-7	$^{13}C_{12}$-2,4'-dichlorobiphenyl		Surrogate Std
9	2,5-dichlorobiphenyl	34883-39-1	$^{13}C_{12}$-2,5-dichlorobiphenyl	250694-89-4	Recovery Std
10	2,6-dichlorobiphenyl	33146-45-1			
11	3,3'-dichlorobiphenyl	2050-67-1			
12	3,4-dichlorobiphenyl	2974-92-7			
13	3,4'-dichlorobiphenyl	2974-90-5			
14	3,5-dichlorobiphenyl	34883-41-5			
15	4,4'-dichlorobiphenyl	2050-68-2	$^{13}C_{12}$-4,4'-dichlorobiphenyl	208263-67-6	Internal Std
16	2,2',3-trichlorobiphenyl	38444-78-9			
17	2,2',4-trichlorobiphenyl	37680-66-3			
18	2,2',5-trichlorobiphenyl	37680-65-2			
19	2,2',6-trichlorobiphenyl	38444-73-4	$^{13}C_{12}$-2,2',6-trichlorobiphenyl	234432-87-2	Internal Std
20	2,3,3'-trichlorobiphenyl	38444-84-7			
21	2,3,4-trichlorobiphenyl	55702-46-0			
22	2,3,4'-trichlorobiphenyl	38444-85-8			
23	2,3,5-trichlorobiphenyl	55720-44-0			
24	2,3,6-trichlorobiphenyl	55702-45-9			
25	2,3',4-trichlorobiphenyl	55712-37-3			
26	2,3',5-trichlorobiphenyl	38444-81-4			
27	2,3',6-trichlorobiphenyl	38444-76-7			
28	2,4,4'-trichlorobiphenyl	7012-37-5	$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	208263-76-7	Cleanup Std
29	2,4,5-trichlorobiphenyl	15862-07-4			
30	2,4,6-trichlorobiphenyl	35693-92-6			
31	2,4',5-trichlorobiphenyl	16606-02-3	$^{13}C_{12}$-2,4',5-trichlorobiphenyl		Recovery Std
32	2,4',6-trichlorobiphenyl	38444-77-8	$^{13}C_{12}$-2,4',6-trichlorobiphenyl		Recovery Std
33	2',3,4-trichlorobiphenyl (2,3',4'-trichlorobiphenyl)	38444-86-9			
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)	37680-68-5			
35	3,3',4-trichlorobiphenyl	37680-69-6			
36	3,3',5-trichlorobiphenyl	38444-87-0			
37	3,4,4'-trichlorobiphenyl	38444-90-5	$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	208263-79-0	Internal Std
38	3,4,5-trichlorobiphenyl	53555-66-1			
39	3,4',5-trichlorobiphenyl	38444-88-1			
40	2,2',3,3'-tetrachlorobiphenyl	38444-93-8			
41	2,2',3,4-tetrachlorobiphenyl	52663-59-9			
42	2,2',3,4'-tetrachlorobiphenyl	36559-22-5			
43	2,2',3,5-tetrachlorobiphenyl	70362-46-8			
44	2,2',3,5'-tetrachlorobiphenyl	41464-39-5			
45	2,2',3,6-tetrachlorobiphenyl	70362-45-7			
46	2,2',3,6'-tetrachlorobiphenyl	41464-47-5			
47	2,2',4,4'-tetrachlorobiphenyl	2437-79-8			
48	2,2',4,5-tetrachlorobiphenyl	70362-47-9			
49	2,2',4,5'-tetrachlorobiphenyl	41464-40-8			
50	2,2',4,6-tetrachlorobiphenyl	62796-65-0			
51	2,2',4,6'-tetrachlorobiphenyl	68194-04-7			
52	2,2',5,5'-tetrachlorobiphenyl	35693-99-3	$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	160901-66-6	Recovery Std
53	2,2',5,6'-tetrachlorobiphenyl	41464-41-9			
54	2,2',6,6'-tetrachlorobiphenyl	15968-05-5	$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	234432-88-3	Internal Std
55	2,3,3',4-tetrachlorobiphenyl	74338-24-2			
56	2,3,3',4'-tetrachlorobiphenyl	41464-43-1			
57	2,3,3',5-tetrachlorobiphenyl	70424-67-8			
58	2,3,3',5'-tetrachlorobiphenyl	41464-49-7			

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3] Number	Usage
59	2,3,3',6-tetrachlorobiphenyl	74472-33-6			
60	2,3,4,4'-tetrachlorobiphenyl	33025-41-1			
61	2,3,4,5-tetrachlorobiphenyl	33284-53-6			
62	2,3,4,6-tetrachlorobiphenyl	54230-22-7			
63	2,3,4',5-tetrachlorobiphenyl	74472-34-7			
64	2,3,4',6-tetrachlorobiphenyl	52663-58-8			
65	2,3,5,6-tetrachlorobiphenyl	33284-54-7			
66	2,3',4,4'-tetrachlorobiphenyl	32598-10-0			
67	2,3',4,5-tetrachlorobiphenyl	73575-53-8			
68	2,3',4,5'-tetrachlorobiphenyl	73575-52-7			
69	2,3',4,6-tetrachlorobiphenyl	60233-24-1			
70	2,3',4',5-tetrachlorobiphenyl	32598-11-1			
71	2,3',4',6-tetrachlorobiphenyl	41464-46-4			
72	2,3',5,5'-tetrachlorobiphenyl	41464-42-0			
73	2,3',5',6-tetrachlorobiphenyl	74338-23-1			
74	2,4,4',5-tetrachlorobiphenyl	32690-93-0			
75	2,4,4',6-tetrachlorobiphenyl	32598-12-2			
76	2',3,4,5-tetrachlorobiphenyl (2,3',4',5'-tetrachlorobiphenyl)	70362-48-0			
77	3,3',4,4'-tetrachlorobiphenyl	32598-13-3	$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	160901-67-7	Internal Std
78	3,3',4,5-tetrachlorobiphenyl	70362-49-1			
79	3,3',4,5'-tetrachlorobiphenyl	41464-48-6	$^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl		Surrogate Std
80	3,3',5,5'-tetrachlorobiphenyl	33284-52-5			
81	3,4,4',5-tetrachlorobiphenyl	70362-50-4	$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	160901-68-8	Internal Std
82	2,2',3,3',4-pentachlorobiphenyl	52663-62-4			
83	2,2',3,3',5-pentachlorobiphenyl	60145-20-2			
84	2,2',3,3',6-pentachlorobiphenyl	52663-60-2			
85	2,2',3,4,4'-pentachlorobiphenyl	65510-45-4			
86	2,2',3,4,5-pentachlorobiphenyl	55312-69-1			
87	2,2',3,4,5'-pentachlorobiphenyl	38380-02-8			
88	2,2',3,4,6-pentachlorobiphenyl	55215-17-3			
89	2,2',3,4,6'-pentachlorobiphenyl	73575-57-2			
90	2,2',3,4',5-pentachlorobiphenyl	68194-07-0			
91	2,2',3,4',6-pentachlorobiphenyl	68194-05-8			
92	2,2',3,5,5'-pentachlorobiphenyl	52663-61-3			
93	2,2',3,5,6-pentachlorobiphenyl	73575-56-1			
94	2,2',3,5,6'-pentachlorobiphenyl	73575-55-0			
95	2,2',3,5',6-pentachlorobiphenyl	38379-99-6	$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl		Surrogate Std
96	2,2',3,6,6'-pentachlorobiphenyl	73575-54-9			
97	2,2',3',4,5-pentachlorobiphenyl (2,2',3,4',5'-pentachlorobiphenyl)	41464-51-1			
98	2,2',3',4,6-pentachlorobiphenyl (2,2',3,4',6'-pentachlorobiphenyl)	60233-25-2			
99	2,2',4,4',5-pentachlorobiphenyl	38380-01-7			
100	2,2',4,4',6-pentachlorobiphenyl	39485-83-1			
101	2,2',4,5,5'-pentachlorobiphenyl	37680-73-2	$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	160901-69-9	Recovery Std
102	2,2',4,5,6'-pentachlorobiphenyl	68194-06-9			
103	2,2',4,5',6-pentachlorobiphenyl	60145-21-3			
104	2,2',4,6,6'-pentachlorobiphenyl	56558-16-8	$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	234432-89-4	Internal Std
105	2,3,3',4,4'-pentachlorobiphenyl	32598-14-4	$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	160901-70-2	Internal Std
106	2,3,3',4,5-pentachlorobiphenyl	70424-69-0			
107/109	2,3,3',4,6-pentachlorobiphenyl	74472-35-8			
108/107	2,3,3',4',5-pentachlorobiphenyl	70424-68-9			
109/108	2,3,3',4,5'-pentachlorobiphenyl	70362-41-3			
110	2,3,3',4',6-pentachlorobiphenyl	38380-03-9			
111	2,3,3',5,5'-pentachlorobiphenyl	39635-32-0	$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	160901-71-3	Cleanup Std
112	2,3,3',5,6-pentachlorobiphenyl	74472-36-9			
113	2,3,3',5',6-pentachlorobiphenyl	68194-10-5			
114	2,3,4,4',5-pentachlorobiphenyl	74472-37-0	$^{13}C_{12}$-2,3,4,4',5-pentachlorobiphenyl	160901-72-4	Internal Std
115	2,3,4,4',6-pentachlorobiphenyl	74472-38-1			
116	2,3,4,5,6-pentachlorobiphenyl	18259-05-7			
117	2,3,4',5,6-pentachlorobiphenyl	68194-11-6			

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3] Number	Usage
118	2,3',4,4',5-pentachlorobiphenyl	31508-00-6	$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	160901-73-5	Internal Std
119	2,3',4,4',6-pentachlorobiphenyl	56558-17-9			
120	2,3',4,5,5'-pentachlorobiphenyl	68194-12-7			
121	2,3',4,5',6-pentachlorobiphenyl	56558-18-0			
122	2',3,3',4,5-pentachlorobiphenyl (2,3,3',4',5'-pentachlorobiphenyl)	76842-07-4			
123	2',3,4,4',5-pentachlorobiphenyl (2,3',4,4',5'-pentachlorobiphenyl)	65510-44-3	$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	160901-74-6	Internal Std
124	2',3,4,5,5'-pentachlorobiphenyl (2,3',4',5',5-pentachlorobiphenyl)	70424-70-3			
125	2',3,4,5,6'-pentachlorobiphenyl (2,3',4',5',6-pentachlorobiphenyl)	74472-39-2			
126	3,3',4,4',5-pentachlorobiphenyl	57465-28-8	$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	160901-75-7	Internal Std
127	3,3',4,5,5'-pentachlorobiphenyl	39635-33-1	$^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl		Recovery Std
128	2,2',3,3',4,4'-hexachlorobiphenyl	38380-07-3			
129	2,2',3,3',4,5-hexachlorobiphenyl	55215-18-4			
130	2,2',3,3',4,5'-hexachlorobiphenyl	52663-66-8			
131	2,2',3,3',4,6-hexachlorobiphenyl	61798-70-7			
132	2,2',3,3',4,6'-hexachlorobiphenyl	38380-05-1			
133	2,2',3,3',5,5'-hexachlorobiphenyl	35694-04-3			
134	2,2',3,3',5,6-hexachlorobiphenyl	52704-70-8			
135	2,2',3,3',5,6'-hexachlorobiphenyl	52744-13-5			
136	2,2',3,3',6,6'-hexachlorobiphenyl	38411-22-2			
137	2,2',3,4,4',5-hexachlorobiphenyl	35694-06-5			
138	2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2	$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	160901-76-8	Recovery Std
139	2,2',3,4,4',6-hexachlorobiphenyl	56030-56-9			
140	2,2',3,4,4',6'-hexachlorobiphenyl	59291-64-4			
141	2,2',3,4,5,5'-hexachlorobiphenyl	52712-04-6			
142	2,2',3,4,5,6-hexachlorobiphenyl	41411-61-4			
143	2,2',3,4,5,6'-hexachlorobiphenyl	68194-15-0			
144	2,2',3,4,5',6-hexachlorobiphenyl	68194-14-9			
145	2,2',3,4,6,6'-hexachlorobiphenyl	74472-40-5			
146	2,2',3,4',5,5'-hexachlorobiphenyl	51908-16-8			
147	2,2',3,4',5,6-hexachlorobiphenyl	68194-13-8			
148	2,2',3,4',5,6'-hexachlorobiphenyl	74472-41-6			
149	2,2',3,4',5',6-hexachlorobiphenyl	38380-04-0			
150	2,2',3,4',6,6'-hexachlorobiphenyl	68194-08-1			
151	2,2',3,5,5',6-hexachlorobiphenyl	52663-63-5			
152	2,2',3,5,6,6'-hexachlorobiphenyl	68194-09-2			
153	2,2',4,4',5,5'-hexachlorobiphenyl	35065-27-1	$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl		Surrogate Std
154	2,2',4,4',5,6'-hexachlorobiphenyl	60145-22-4			
155	2,2',4,4',6,6'-hexachlorobiphenyl	33979-03-2	$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	234432-90-7	Internal Std
156	2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4	$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	160901-77-9	Internal Std
157	2,3,3',4,4',5'-hexachlorobiphenyl	69782-90-7	$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	160901-78-0	Internal Std
158	2,3,3',4,4',6-hexachlorobiphenyl	74472-42-7			
159	2,3,3',4,5,5'-hexachlorobiphenyl	39635-35-3			
160	2,3,3',4,5,6-hexachlorobiphenyl	41411-62-5			
161	2,3,3',4,5',6-hexachlorobiphenyl	74472-43-8			
162	2,3,3',4',5,5'-hexachlorobiphenyl	39635-34-2			
163	2,3,3',4',5,6-hexachlorobiphenyl	74472-44-9			
164	2,3,3',4',5',6-hexachlorobiphenyl	74472-45-0			
165	2,3,3',5,5',6-hexachlorobiphenyl	74472-46-1			
166	2,3,4,4',5,6-hexachlorobiphenyl	41411-63-6			
167	2,3',4,4',5,5'-hexachlorobiphenyl	52663-72-6	$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	161627-18-5	Internal Std
168	2,3',4,4',5',6-hexachlorobiphenyl	59291-65-5			
169	3,3',4,4',5,5'-hexachlorobiphenyl	32774-16-6	$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	160901-79-1	Internal Std
170	2,2',3,3',4,4',5-heptachlorobiphenyl	35065-30-6	$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	160901-80-4	Internal Std
171	2,2',3,3',4,4',6-heptachlorobiphenyl	52663-71-5			
172	2,2',3,3',4,5,5'-heptachlorobiphenyl	52663-74-8			
173	2,2',3,3',4,5,6-heptachlorobiphenyl	68194-16-1			
174	2,2',3,3',4,5,6'-heptachlorobiphenyl	38411-25-5			
175	2,2',3,3',4,5',6-heptachlorobiphenyl	40186-70-7			
176	2,2',3,3',4,6,6'-heptachlorobiphenyl	52663-65-7			

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3] Number	Usage
177	2,2',3,3',4',5,6-heptachlorobiphenyl (2,2',3,3',4,5',6'-heptachlorobiphenyl)	52663-70-4			
178	2,2',3,3',5,5',6-heptachlorobiphenyl	52663-67-9	$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	160901-81-5	Cleanup Std
179	2,2',3,3',5,6,6'-heptachlorobiphenyl	52663-64-6			
180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3	$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	160901-82-6	Recovery Std
181	2,2',3,4,4',5,6-heptachlorobiphenyl	74472-47-2			
182	2,2',3,4,4',5,6'-heptachlorobiphenyl	60145-23-5			
183	2,2',3,4,4',5',6-heptachlorobiphenyl	52663-69-1			
184	2,2',3,4,4',6,6'-heptachlorobiphenyl	74472-48-3			
185	2,2',3,4,5,5',6-heptachlorobiphenyl	52712-05-7			
186	2,2',3,4,5,6,6'-heptachlorobiphenyl	74472-49-4			
187	2,2',3,4',5,5',6-heptachlorobiphenyl	52663-68-0			
188	2,2',3,4',5,6,6'-heptachlorobiphenyl	74487-85-7	$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	234432-91-8	Internal Std
189	2,3,3',4,4',5,5'-heptachlorobiphenyl	39635-31-9	$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	160901-83-7	Internal Std
190	2,3,3',4,4',5,6-heptachlorobiphenyl	41411-64-7			
191	2,3,3',4,4',5',6-heptachlorobiphenyl	74472-50-7			
192	2,3,3',4,5,5',6-heptachlorobiphenyl	74472-51-8			
193	2,3,3',4',5,5',6-heptachlorobiphenyl	69782-91-8			
194	2,2',3,3',4,4',5,5'-octachlorobiphenyl	35694-08-7	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	208263-74-5	Recovery Std
195	2,2',3,3',4,4',5,6-octachlorobiphenyl	52663-78-2			
196	2,2',3,3',4,4',5,6'-octachlorobiphenyl	42740-50-1			
197	2,2',3,3',4,4',6,6'-octachlorobiphenyl	33091-17-7			
198	2,2',3,3',4,5,5',6-octachlorobiphenyl	68194-17-2			
199/200	2,2',3,3',4,5,6,6'-octachlorobiphenyl	52663-73-7			
200/201	2,2',3,3',4,5',6,6'-octachlorobiphenyl	40186-71-8			
201/199	2,2',3,3',4,5,5',6'-octachlorobiphenyl	52663-75-9			
202	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2136-99-4	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	105600-26-8	Internal Std
203	2,2',3,4,4',5,5',6-octachlorobiphenyl	52663-76-0			
204	2,2',3,4,4',5,6,6'-octachlorobiphenyl	74472-52-9			
205	2,3,3',4,4',5,5',6-octachlorobiphenyl	74472-53-0	$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	234446-64-1	Internal Std
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	40186-72-9	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	208263-75-6	Internal Std
207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	52663-79-3			
208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	52663-77-1	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	234432-92-9	Internal Std
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	2051-24-3	$^{13}C_{12}$-decachlorobiphenyl	160901-84-8	Internal Std

1. The BZ number is from Ballschmiter and Zell (1980). The IUPAC number, when different from the BZ, follows the recommended changes to the BZ number per Schulte and Malisch (1983) and Guitart et al. (1993).

2. The chemical structure names are from Ballschmiter and Zell (1980). IUPAC nomenclature structure names are listed in parenthesis when different from the BZ name (source CAS Registry).

3. Chemical Abstract Service Registry number (source CAS Registry and 1668A Table 1).

Table 2 - RT References, Quantitation References, Retention Times (RT), and Relative Retention Times (RRTs) for the 209 CB congeners on SPB-Octyl

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
1	1L	9L	9L	30
1	3L	9L	9L	30
1	1	1L	1L	10
1	2	3L	1L/3L	6
1	3	3L	3L	6
2	4L	9L	9L	30
2	9L	9L	9L	25
2	8L	4L	4L/15L	6
2	15L	9L	9L	20
2	4	4L	4L	10
2	10	4L	4L/15L	6
2	9	4L	4L/15L	6
2	7	4L	4L/15L	6
2	6	4L	4L/15L	6
2	5	4L	4L/15L	6
2	8	4L	4L/15L	6
2	14	15L	4L/15L	6
2	11	15L	4L/15L	6
2	13	15L	4L/15L	6
2	12	15L	4L/15L	6
2	15	15L	15L	10
3	19L	32L	32L	30
3	32L	32L	32L	6
3	31L	31L	31L	6
3	28L	31L	31L	20
3	37L	31L	31L	30
3	19	19L	19L	10
3	30	19L	19L	6
3	18	19L	19L	6
3	17	19L	19L	6
3	27	19L	19L	6
3	24	19L	19L	6
3	16	19L	19L	6
3	32	19L	19L	6
3	34	19L	37L	6
3	23	19L	37L	6
3	29	19L	37L	10
3	26	19L	37L	10
3	25	37L	37L	6
3	31	37L	37L	6
3	28	37L	37L	10
3	20	37L	37L	10
3	21	37L	37L	10
3	33	37L	37L	10
3	22	37L	37L	6
3	36	37L	37L	6
3	39	37L	37L	6
3	38	37L	37L	6
3	35	37L	37L	6
3	37	37L	37L	6
4	54L	52L	32L	20
4	52L	52L	52L	25
4	79L	81L	81L/77L	6
4	81L	52L	52L	20
4	77L	52L	52L	20
4	54	54L	54L	10
4	50	54L	81L/77L	10
4	53	54L	81L/77L	10
4	45	54L	81L/77L	10
4	51	54L	81L/77L	10
4	46	54L	81L/77L	6
4	52	54L	81L/77L	6
4	73	54L	81L/77L	6
4	43	54L	81L/77L	6
4	69	54L	81L/77L	10
4	49	54L	81L/77L	10
4	48	54L	81L/77L	6
4	65	54L	81L/77L	10
4	47	54L	81L/77L	10
4	44	54L	81L/77L	10
4	62	54L	81L/77L	10

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
4	75	54L	81L/77L	10
4	59	54L	81L/77L	10
4	42	54L	81L/77L	6
4	41	54L	81L/77L	10
4	71	54L	81L/77L	10
4	40	54L	81L/77L	10
4	64	54L	81L/77L	6
4	72	81L	81L/77L	6
4	68	81L	81L/77L	6
4	57	81L	81L/77L	6
4	58	81L	81L/77L	6
4	67	81L	81L/77L	6
4	63	81L	81L/77L	6
4	61	81L	81L/77L	12
4	70	81L	81L/77L	12
4	76	81L	81L/77L	12
4	74	81L	81L/77L	10
4	66	81L	81L/77L	6
4	55	81L	81L/77L	6
4	56	81L	81L/77L	6
4	60	81L	81L/77L	6
4	80	81L	81L/77L	6
4	79	81L	81L/77L	6
4	78	81L	81L/77L	6
4	81	81L	81L	6
4	77	77L	77L	6
5	104L	101L	101L	20
5	95L	104L	104L	10
5	101L	101L	101L	25
5	111L	101L	101L	20
5	123L	101L	127L	20
5	118L	101L	127L	20
5	114L	101L	127L	20
5	105L	101L	127L	20
5	127L	127L	127L	25
5	126L	101L	127L	20
5	104	104L	104L	10
5	96	104L	104L	10
5	103	104L	104L	6
5	94	104L	104L	6
5	95	104L	104L	10
5	100	104L	104L	10
5	93	104L	104L	10
5	102	104L	104L	10
5	98	104L	104L	10
5	88	104L	104L	12
5	91	104L	104L	10
5	84	104L	104L	6
5	89	104L	104L	6
5	121	104L	104L	6
5	92	123L	104L	6
5	113	104L	104L	10
5	90	104L	104L	10
5	101	104L	104L	10
5	83	104L	104L	12
5	99	104L	104L	10
5	112	104L	104L	6
5	119	104L	104L	16
5	108	104L	104L	16
5	86	104L	104L	16
5	97	104L	104L	16
5	125	104L	104L	16
5	87	104L	104L	10
5	117	104L	104L	12
5	116	104L	104L	12
5	85	104L	104L	10
5	110	104L	104L	10
5	115	104L	104L	10
5	82	104L	104L	6
5	111	104L	104L	6
5	120	104L	104L	6
5	107	104L	123L/114L/118L/105L/126L	10
5	124	104L	123L/114L/118L/105L/126L	10
5	109	104L	123L/114L/118L/105L/126L	6
5	123	123L	123L	6
5	106	123L	123L/114L/118L/105L/126L	6

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
5	118	118L	118L	6
5	122	118L	123L/114L/118L/105L/126L	6
5	114	114L	114L	6
5	105	105L	105L	6
5	127	105L	123L/114L/118L/105L/126L	6
5	126	126L	126L	6
6	155L	138L	101L	20
6	153L	167L	156L/157L/167L/169L	10
6	138L	138L	138L	100
6	167L	138L	138L	20
6	156L	138L	138L	6
6	157L	138L	138L	20
6	169L	138L	138L	6
6	155	155L	155L	10
6	152	155L	155L	6
6	150	155L	155L	6
6	136	155L	155L	6
6	145	155L	155L	6
6	148	155L	155L	6
6	151	155L	155L	10
6	135	155L	155L	10
6	154	155L	155L	10
6	144	155L	155L	6
6	147	155L	156L/157L/167L/169L	10
6	149	155L	156L/157L/167L/169L	10
6	134	155L	156L/157L/167L/169L	10
6	143	155L	156L/157L/167L/169L	10
6	139	155L	156L/157L/167L/169L	10
6	140	155L	156L/157L/167L/169L	10
6	131	155L	156L/157L/167L/169L	6
6	142	155L	156L/157L/167L/169L	6
6	132	155L	156L/157L/167L/169L	10
6	133	155L	156L/157L/167L/169L	6
6	165	167L	156L/157L/167L/169L	6
6	146	167L	156L/157L/167L/169L	6
6	161	167L	156L/157L/167L/169L	6
6	153	167L	156L/157L/167L/169L	10
6	168	167L	156L/157L/167L/169L	10
6	141	167L	156L/157L/167L/169L	6
6	130	167L	156L/157L/167L/169L	6
6	137	167L	156L/157L/167L/169L	6
6	164	167L	156L/157L/167L/169L	6
6	138	167L	156L/157L/167L/169L	14
6	163	167L	156L/157L/167L/169L	14
6	129	167L	156L/157L/167L/169L	14
6	160	167L	156L/157L/167L/169L	10
6	158	167L	156L/157L/167L/169L	6
6	166	167L	156L/157L/167L/169L	10
6	128	167L	156L/157L/167L/169L	10
6	159	167L	156L/157L/167L/169L	6
6	162	167L	156L/157L/167L/169L	6
6	167	167L	167L	6
6	156	156L	156L/157L	6
6	157	157L	156L/157L	10
6	169	169L	169L	6
7	188L	180L	180L	20
7	178L	180L	180L	20
7	180L	180L	180L	100
7	170L	180L	180L	20
7	189L	180L	194L	20
7	188	188L	188L	6
7	179	188L	188L/170L	6
7	184	188L	188L/170L	6
7	176	188L	188L/170L	6
7	186	188L	188L/170L	6
7	178	188L	188L/170L	6
7	175	188L	188L/170L	6
7	187	188L	188L/170L	6
7	182	188L	188L/170L	6
7	183	188L	188L/170L	6
7	185	188L	188L/170L	6
7	174	188L	188L/170L	6
7	177	188L	188L/170L	6
7	181	188L	188L/170L	6
7	171	188L	188L/170L	10
7	173	188L	188L/170L	6

Cl No[1]	IUPAC No[2,3]	RT Ref[4]	Quantitation Reference[5]	RT Win[6] (sec)
7	172	189L	188L/170L	6
7	192	189L	188L/170L	6
7	193	189L	188L/170L	6
7	180	189L	188L/170L	6
7	191	189L	188L/170L	6
7	170	189L	170L	6
7	190	189L	188L/170L	6
7	189	189L	189L	6
8	202L	194L	180L	20
8	194L	194L	194L	25
8	205L	194L	194L	30
8	202	202L	202L	10
8	201	202L	202L	6
8	204	202L	202L	6
8	197	202L	202L	6
8	200	202L	202L	6
8	198	202L	202L	10
8	199	202L	202L	6
8	196	205L	202L	6
8	203	205L	202L	6
8	195	205L	205L	6
8	194	205L	205L	6
8	205	205L	205L	6
9	208L	194L	194L	20
9	206L	194L	194L	30
9	208	208L	208L	6
9	207	208L	208L/206L	6
9	206	206L	206L	6
10	209L	194L	194L	30
10	209	209L	209L	6

1. Number of chlorines on congener.
2. Suffix "L" indicates labeled compound.
3. IUPAC Number per Table 2 of Method 1668A.
4. Retention time reference that is used to locate target congener.
5. Quantitation reference that is used to calculate the concentration of the target congener or labeled standard.
6. RT window width for congener or group of two or more congeners.

Table 3 - Low Calibration Levels (LCLs) Based on Final Extract Volumes

		20 µL Extract Volume	100µL Extract Volume
Analyte	Minimum Cal. Level CS 0.5 (ng/mL)	Water 1L (ng/L)	Solids and Tissues 10g (ng/g)
Monochlorobiphenyls	0.5	0.01[1]	0.005
Dichlorobiphenyls	0.5	0.01[1]	0.005
Trichlorobiphenyls	0.5	0.01	0.005
Tetrachlorobiphenyls	0.5	0.01	0.005
Pentachlorobiphenyls	0.5	0.01	0.005
Hexachlorobiphenyls	0.5	0.01	0.005
Heptachlorobiphenyls	0.5	0.01	0.005
Octachlorobiphenyls	0.5	0.01	0.005
Nonachlorobiphenyls	0.5	0.01	0.005
Decachlorobiphenyl	0.5	0.01	0.005

1. This value reflects the LCL. Reliable detection at this level may not be attained due to evaporative loss in adjusting the extract volume to 20 µL for these homolog groups.

2. The values for solids and tissues reflect the LCLs for Protocol 1 as described in Table 12. If the sample is prepared by another protocol described in that table, the LCLs shown in this table must be adjusted appropriately.

Table 4 - Estimated Minimum Levels - Matrix and Concentration

Parameter	Water ng/L	Solids ng/g	Tissues ng/g	Solid Wastes ng/g	100 uL Extract ng/mL
PCB 1	0.040	0.01	0.01	0.01	1.0
PCB 2	0.040	0.01	0.01	0.01	1.0
PCB 3	0.040	0.01	0.01	0.01	1.0
PCB 4	0.060	0.02	0.02	0.02	2.0
PCB 5	0.040	0.01	0.01	0.01	1.0
PCB 6	0.040	0.01	0.01	0.01	1.0
PCB 7	0.040	0.01	0.01	0.01	1.0
PCB 8	0.060	0.02	0.02	0.02	2.0
PCB 9	0.040	0.01	0.01	0.01	1.0
PCB 10	0.040	0.01	0.01	0.01	1.0
PCB 11	0.060	0.02	0.02	0.02	2.0
PCB 12	0.060	0.01	0.01	0.01	1.0
PCB 14	0.040	0.01	0.01	0.01	1.0
PCB 13	0.060	0.01	0.01	0.01	1.0
PCB 15	0.040	0.01	0.01	0.01	1.0
PCB 16	0.040	0.01	0.01	0.01	1.0
PCB 17	0.040	0.01	0.01	0.01	1.0
PCB 18	0.060	0.02	0.02	0.02	2.0
PCB 30	0.060	0.02	0.02	0.02	2.0
PCB 19	0.040	0.01	0.01	0.01	1.0
PCB 20	0.040	0.02	0.02	0.02	2.0
PCB 28	0.040	0.02	0.02	0.02	2.0
PCB 21	0.040	0.01	0.01	0.01	1.0
PCB33	0.040	0.01	0.01	0.01	1.0
PCB 22	0.040	0.01	0.01	0.01	1.0
PCB 23	0.040	0.01	0.01	0.01	1.0
PCB 24	0.040	0.01	0.01	0.01	1.0
PCB 25	0.040	0.01	0.01	0.01	1.0
PCB 26	0.040	0.01	0.01	0.01	1.0
PCB 29	0.040	0.01	0.01	0.01	1.0
PCB 27	0.040	0.01	0.01	0.01	1.0
PCB 31	0.040	0.02	0.02	0.02	2.0
PCB 32	0.040	0.01	0.01	0.01	1.0
PCB 34	0.040	0.01	0.01	0.01	1.0
PCB 35	0.040	0.01	0.01	0.01	1.0
PCB 36	0.040	0.01	0.01	0.01	1.0
PCB 37	0.040	0.01	0.01	0.01	1.0
PCB 38	0.040	0.01	0.01	0.01	1.0
PCB 39	0.040	0.01	0.01	0.01	1.0
PCB 40	0.040	0.01	0.01	0.01	1.0
PCB 41	0.040	0.01	0.01	0.01	1.0
PCB 71	0.040	0.01	0.01	0.01	1.0
PCB 42	0.040	0.01	0.01	0.01	1.0
PCB 43	0.040	0.01	0.01	0.01	1.0
PCB 73	0.040	0.01	0.01	0.01	1.0
PCB 44	0.040	0.01	0.01	0.01	1.0
PCB 47	0.040	0.01	0.01	0.01	1.0
PCB 65	0.040	0.01	0.01	0.01	1.0
PCB 45	0.040	0.01	0.01	0.01	1.0
PCB 51	0.040	0.01	0.01	0.01	1.0
PCB 46	0.040	0.01	0.01	0.01	1.0
PCB 48	0.040	0.01	0.01	0.01	1.0
PCB 49	0.040	0.01	0.01	0.01	1.0
PCB 69	0.040	0.01	0.01	0.01	1.0
PCB 50	0.040	0.01	0.01	0.01	1.0
PCB 53	0.040	0.01	0.01	0.01	1.0
PCB 52	0.040	0.01	0.01	0.01	1.0
PCB 54	0.040	0.01	0.01	0.01	1.0

Parameter	Water ng/L	Solids ng/g	Tissues ng/g	Solid Wastes ng/g	100 uL Extract ng/mL
PCB 55	0.040	0.01	0.01	0.01	1.0
PCB 56	0.040	0.01	0.01	0.01	1.0
PCB 57	0.040	0.01	0.01	0.01	1.0
PCB 58	0.040	0.01	0.01	0.01	1.0
PCB 59	0.040	0.01	0.01	0.01	1.0
PCB 62	0.040	0.01	0.01	0.01	1.0
PCB 75	0.040	0.01	0.01	0.01	1.0
PCB 60	0.040	0.01	0.01	0.01	1.0
PCB 61	0.040	0.02	0.02	0.02	2.0
PCB 70	0.040	0.02	0.02	0.02	2.0
PCB 74	0.040	0.02	0.02	0.02	2.0
PCB 76	0.040	0.02	0.02	0.02	2.0
PCB 63	0.040	0.01	0.01	0.01	1.0
PCB 64	0.040	0.01	0.01	0.01	1.0
PCB 66	0.040	0.01	0.01	0.01	1.0
PCB 67	0.040	0.01	0.01	0.01	1.0
PCB 68	0.040	0.01	0.01	0.01	1.0
PCB 72	0.040	0.01	0.01	0.01	1.0
PCB 77	0.040	0.01	0.01	0.01	1.0
PCB 78	0.040	0.01	0.01	0.01	1.0
PCB 79	0.040	0.01	0.01	0.01	1.0
PCB 80	0.040	0.01	0.01	0.01	1.0
PCB 81	0.040	0.01	0.01	0.01	1.0
PCB 82	0.040	0.01	0.01	0.01	1.0
PCB 83	0.040	0.01	0.01	0.01	1.0
PCB 84	0.040	0.01	0.01	0.01	1.0
PCB 85	0.040	0.01	0.01	0.01	1.0
PCB 116	0.040	0.01	0.01	0.01	1.0
PCB 117	0.040	0.01	0.01	0.01	1.0
PCB 86	0.040	0.01	0.01	0.01	1.0
PCB 87	0.040	0.01	0.01	0.01	1.0
PCB 97	0.040	0.01	0.01	0.01	1.0
PCB 109	0.040	0.01	0.01	0.01	1.0
PCB 119	0.040	0.01	0.01	0.01	1.0
PCB 125	0.040	0.01	0.01	0.01	1.0
PCB 88	0.040	0.01	0.01	0.01	1.0
PCB 91	0.040	0.01	0.01	0.01	1.0
PCB 89	0.040	0.01	0.01	0.01	1.0
PCB 90	0.040	0.01	0.01	0.01	1.0
PCB 101	0.040	0.01	0.01	0.01	1.0
PCB 113	0.040	0.01	0.01	0.01	1.0
PCB 92	0.040	0.01	0.01	0.01	1.0
PCB 93	0.040	0.01	0.01	0.01	1.0
PCB 100	0.040	0.01	0.01	0.01	1.0
PCB 94	0.040	0.01	0.01	0.01	1.0
PCB 95	0.040	0.01	0.01	0.01	1.0
PCB 96	0.040	0.01	0.01	0.01	1.0
PCB 98	0.040	0.01	0.01	0.01	1.0
PCB 102	0.040	0.01	0.01	0.01	1.0
PCB 99	0.040	0.01	0.01	0.01	1.0
PCB 112	0.040	0.01	0.01	0.01	1.0
PCB 103	0.040	0.01	0.01	0.01	1.0
PCB 104	0.040	0.01	0.01	0.01	1.0
PCB 105	0.040	0.01	0.01	0.01	1.0
PCB 106	0.040	0.01	0.01	0.01	1.0
PCB 107	0.040	0.01	0.01	0.01	1.0
PCB 108	0.040	0.01	0.01	0.01	1.0
PCB 124	0.040	0.01	0.01	0.01	1.0
PCB 110	0.040	0.01	0.01	0.01	1.0
PCB 115	0.040	0.01	0.01	0.01	1.0

Parameter	Water ng/L	Solids ng/g	Tissues ng/g	Solid Wastes ng/g	100 uL Extract ng/mL
PCB 111	0.040	0.01	0.01	0.01	1.0
PCB 114	0.040	0.01	0.01	0.01	1.0
PCB 118	0.040	0.01	0.01	0.01	1.0
PCB 120	0.040	0.01	0.01	0.01	1.0
PCB 121	0.040	0.01	0.01	0.01	1.0
PCB 122	0.040	0.01	0.01	0.01	1.0
PCB 123	0.040	0.01	0.01	0.01	1.0
PCB 126	0.040	0.01	0.01	0.01	1.0
PCB 127	0.040	0.01	0.01	0.01	1.0
PCB 128	0.040	0.01	0.01	0.01	1.0
PCB 166	0.040	0.01	0.01	0.01	1.0
PCB 129	0.040	0.01	0.01	0.01	1.0
PCB 138	0.040	0.01	0.01	0.01	1.0
PCB 163	0.040	0.01	0.01	0.01	1.0
PCB 130	0.040	0.01	0.01	0.01	1.0
PCB 131	0.040	0.01	0.01	0.01	1.0
PCB 132	0.040	0.01	0.01	0.01	1.0
PCB 133	0.040	0.01	0.01	0.01	1.0
PCB 134	0.040	0.01	0.01	0.01	1.0
PCB 143	0.040	0.01	0.01	0.01	1.0
PCB 135	0.040	0.01	0.01	0.01	1.0
PCB 151	0.040	0.01	0.01	0.01	1.0
PCB 136	0.040	0.01	0.01	0.01	1.0
PCB 137	0.040	0.01	0.01	0.01	1.0
PCB 164	0.040	0.01	0.01	0.01	1.0
PCB 139	0.040	0.01	0.01	0.01	1.0
PCB 140	0.040	0.01	0.01	0.01	1.0
PCB 141	0.040	0.01	0.01	0.01	1.0
PCB 142	0.040	0.01	0.01	0.01	1.0
PCB 144	0.040	0.01	0.01	0.01	1.0
PCB 145	0.040	0.01	0.01	0.01	1.0
PCB 146	0.040	0.01	0.01	0.01	1.0
PCB 147	0.040	0.01	0.01	0.01	1.0
PCB 149	0.040	0.01	0.01	0.01	1.0
PCB 148	0.040	0.01	0.01	0.01	1.0
PCB 150	0.040	0.01	0.01	0.01	1.0
PCB 152	0.040	0.01	0.01	0.01	1.0
PCB 153	0.040	0.01	0.01	0.01	1.0
PCB 168	0.040	0.01	0.01	0.01	1.0
PCB 154	0.040	0.01	0.01	0.01	1.0
PCB 155	0.040	0.01	0.01	0.01	1.0
PCB 156	0.040	0.01	0.01	0.01	1.0
PCB 157	0.040	0.01	0.01	0.01	1.0
PCB 158	0.040	0.01	0.01	0.01	1.0
PCB 159	0.040	0.01	0.01	0.01	1.0
PCB 160	0.040	0.01	0.01	0.01	1.0
PCB 161	0.040	0.01	0.01	0.01	1.0
PCB 162	0.040	0.01	0.01	0.01	1.0
PCB 165	0.040	0.01	0.01	0.01	1.0
PCB 167	0.040	0.01	0.01	0.01	1.0
PCB 169	0.040	0.01	0.01	0.01	1.0
PCB 170	0.040	0.01	0.01	0.01	1.0
PCB 171	0.040	0.01	0.01	0.01	1.0
PCB 173	0.040	0.01	0.01	0.01	1.0
PCB 172	0.040	0.01	0.01	0.01	1.0
PCB 174	0.040	0.01	0.01	0.01	1.0
PCB 175	0.040	0.01	0.01	0.01	1.0
PCB 176	0.040	0.01	0.01	0.01	1.0
PCB 177	0.040	0.01	0.01	0.01	1.0
PCB 178	0.040	0.01	0.01	0.01	1.0

Parameter	Water ng/L	Solids ng/g	Tissues ng/g	Solid Wastes ng/g	100 uL Extract ng/mL
PCB 179	0.040	0.01	0.01	0.01	1.0
PCB 180	0.040	0.01	0.01	0.01	1.0
PCB 193	0.040	0.01	0.01	0.01	1.0
PCB 181	0.040	0.01	0.01	0.01	1.0
PCB 182	0.040	0.01	0.01	0.01	1.0
PCB 183	0.040	0.01	0.01	0.01	1.0
PCB 185	0.040	0.01	0.01	0.01	1.0
PCB 184	0.040	0.01	0.01	0.01	1.0
PCB 186	0.040	0.01	0.01	0.01	1.0
PCB 187	0.040	0.01	0.01	0.01	1.0
PCB 188	0.040	0.01	0.01	0.01	1.0
PCB 189	0.040	0.01	0.01	0.01	1.0
PCB 190	0.040	0.01	0.01	0.01	1.0
PCB 191	0.040	0.01	0.01	0.01	1.0
PCB 192	0.040	0.01	0.01	0.01	1.0
PCB 194	0.040	0.01	0.01	0.01	1.0
PCB 195	0.040	0.01	0.01	0.01	1.0
PCB 196	0.040	0.01	0.01	0.01	1.0
PCB 197	0.040	0.01	0.01	0.01	1.0
PCB 200	0.040	0.01	0.01	0.01	1.0
PCB 198	0.040	0.01	0.01	0.01	1.0
PCB 199	0.040	0.01	0.01	0.01	1.0
PCB 201	0.040	0.01	0.01	0.01	1.0
PCB 202	0.040	0.01	0.01	0.01	1.0
PCB 203	0.040	0.01	0.01	0.01	1.0
PCB 204	0.040	0.01	0.01	0.01	1.0
PCB 205	0.040	0.01	0.01	0.01	1.0
PCB 206	0.040	0.01	0.01	0.01	1.0
PCB 207	0.040	0.01	0.01	0.01	1.0
PCB 208	0.040	0.01	0.01	0.01	1.0
PCB 209	0.040	0.01	0.01	0.01	1.0

The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures The values for solids, tissues and solid wastes reflect the EMLs for Protocol 1 as described in Table 12. If the sample is prepared by another protocol described in that section, the LCLs shown in this table must be adjusted appropriately. The EMLs are based on the mean plus 2 standard deviations for matrix-pooled historical blank data and calibration data obtained while performing EPA 1668A. The survey period was fourteen months, ending in February 2004. Individual EMLs may be adjusted to reflect more recent data.

Table 5a - Concentration of Native PCB Congener Stock and Spiking Solutions

Native PCB Congener	BZ/ IUPAC	Standard Source	Catalog Number	Vendor Conc (ng/mL)	LCS Spiking Solution Conc (ng/mL)
2-MoCB	1	AccuStd	S-99994-4x	4000	5.0
4-MoCB	3	AccuStd	S-99994-4x	4000	5.0
2,2'-DiCB	4	AccuStd	S-99994-4x	4000	5.0
4,4'-DiCB	15	AccuStd	S-99994-4x	4000	5.0
2,2',6-TrCB	19	AccuStd	S-99994-4x	4000	5.0
3,4,4'-TrCB	37	AccuStd	S-99994-4x	4000	5.0
2,2',6,6'-TeCB	54	AccuStd	S-99994-4x	4000	5.0
3,3',4,4'-TeCB	77	AccuStd	S-99994-4x	4000	5.0
3,4,4',5-TeCB	81	AccuStd	S-99994-4x	4000	5.0
2,2',4,6,6'-PeCB	104	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4'-PeCB	105	AccuStd	S-99994-4x	4000	5.0
2,3,4,4',5-PeCB	114	AccuStd	S-99994-4x	4000	5.0
2,3',4,4',5-PeCB	118	AccuStd	S-99994-4x	4000	5.0
2',3,4,4',5-PeCB	123	AccuStd	S-99994-4x	4000	5.0
3,3',4,4',5-PeCB	126	AccuStd	S-99994-4x	4000	5.0
2,2',4,4',6,6'-HxCB	155	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5-HxCB	156	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5'-HxCB	157	AccuStd	S-99994-4x	4000	5.0
2,3',4,4',5,5'-HxCB	167	AccuStd	S-99994-4x	4000	5.0
3,3',4,4',5,5'-HxCB	169	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4,4',5-HpCB	170	AccuStd	S-99994-4x	4000	5.0
2,2',3,4,4',5,5'-HpCB	180	AccuStd	S-99994-4x	4000	5.0
2,2',3,4',5,6,6'-HpCB	188	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5,5'-HpCB	189	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',5,5',6,6'-OcCB	202	AccuStd	S-99994-4x	4000	5.0
2,3,3',4,4',5,5',6-OcCB	205	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4,4',5,5',6-NoCB	206	AccuStd	S-99994-4x	4000	5.0
2,2',3,3',4',5,5',6,6'-NoCB	208	AccuStd	S-99994-4x	4000	5.0
DeCB	209	AccuStd	S-99994-4x	4000	5.0
All other CB congeners	NA	AccuStd	S-99994-4x	4000	5.0

Table 5b: Concentration of $^{13}C_{12}$ Labeled PCB Congener Stock and Spiking Solutions

Labeled PCB Congener	**BZ/ IUPAC**	**Standard Source**	**Catalog Number**	**Vendor Conc (ng/mL)**	Stock Conc (ng/mL)	Spiking Solution Conc (ng/mL)
Internal Standards						
$^{13}C_{12}$-2-chlorobiphenyl	1L	Cambridge	EC-4908	40,000	1000	10
$^{13}C_{12}$-4-chlorobiphenyl	3L	Cambridge	EC-4990	40,000	1000	10
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	Cambridge	EC-4911	40,000	1000	10
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	Cambridge	EC-1402	40,000	1000	10
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	Cambridge	EC-4909	40,000	1000	10
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	Cambridge	EC-4901	40,000	1000	10
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	Cambridge	EC-4912	40,000	1000	10
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	Cambridge	EC-1404	40,000	1000	10
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	Cambridge	EC-1412	40,000	1000	10
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	Cambridge	EC-4910	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	Cambridge	EC-1420	40,000	1000	10
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	Cambridge	EC-4902	40,000	1000	10
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	Cambridge	EC-1435	40,000	1000	10
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	Cambridge	EC-4904	40,000	1000	10
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	Cambridge	EC-1425	40,000	1000	10
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	Cambridge	EC-4167	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	Cambridge	EC-1422	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	Cambridge	EC-4051	40,000	1000	10
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	Cambridge	EC-4050	40,000	1000	10
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	Cambridge	EC-1416	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	Cambridge	EC-4905	40,000	1000	10
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	Cambridge	EC-4913	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	Cambridge	EC-1409	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	Cambridge	EC-1408	40,000	1000	10
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	Cambridge	EC-4199	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	Cambridge	EC-4900	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	Cambridge	EC-1419	40,000	1000	10
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	Cambridge	EC-1410	40,000	1000	10
Recovery Standards						
$^{13}C_{12}$-2,5-dichlorobiphenyl	9L	Cambridge	EC-4165	40,000	1000	100
$^{13}C_{12}$-2,4',5-trichlorobiphenyl	31L	Wellington	MBP-31	50,000	1000	100
$^{13}C_{12}$-2,4',6-trichlorobiphenyl	32L	Cambridge	EC-4163	40,000	1000	100
$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	52L	Cambridge	EC-1424	40,000	1000	100
$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	101L	Cambridge	EC-1405	40,000	1000	100
$^{13}C_{12}$-3,3',4,5,5'-pentachlorobiphenyl	127L	Cambridge	EC-1421	40,000	1000	100
$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	138L	Cambridge	EC-1436	40,000	1000	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	180L	Cambridge	EC-1407	40,000	1000	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	194L	Cambridge	EC-1418	40,000	1000	100
Cleanup Standards						
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	Cambridge	EC-1413	40,000	5000	10
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	Cambridge	EC-1415	40,000	5000	10
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	Cambridge	EC-1417	40,000	5000	10
Sampling Surrogate Standards						
$^{13}C_{12}$-2,4'-dichlorobiphenyl	8L	Cambridge	EC-5095	40,000	5000	50
$^{13}C_{12}$-3,3',4,5'-tetrachlorobiphenyl	79L	Cambridge	EC-5048	40,000	5000	50
$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl	95L	Wellington	MBP-95	50,000	5000	50
$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl	153L	Cambridge	EC-1406	40,000	5000	50

Table 6a - Concentration of PCBs in Calibration Solutions

Analyte Type	BZ/IUPAC[1]	CS 0.5 ng/mL	CS 1 ng/mL	CS 2 ng/mL	CS 3[2] ng/mL	CS 4 ng/mL	CS 5 ng/mL
Congeners							
2-MoCB	1	0.5	1.0	5.0	50	400	2000
4-MoCB	3	0.5	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.5	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.5	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.5	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.5	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.5	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.5	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.5	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.5	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.5	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.5	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.5	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.5	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.5	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.5	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.5	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.5	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.5	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.5	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.5	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.5	1.0	5.0	50	400	2000
DeCB	209	0.5	1.0	5.0	50	400	2000
All other CB congeners		0.5	1.0	5.0	50	400	2000
Labeled Congeners							
$^{13}C_{12}$-2-MoCB	1L	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6-TrCB	19L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100

Analyte Type	BZ/IUPAC[1]	CS 0.5 ng/mL	CS 1 ng/mL	CS 2 ng/mL	CS 3[2] ng/mL	CS 4 ng/mL	CS 5 ng/mL
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Cleanup Standards							
$^{13}C_{12}$-2,4,4'-TriCB	28L			5.0	50	400	--
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L			5.0	50	400	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L			5.0	50	400	--
Recovery Standards							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',5-TriCB	31L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',6-TriCB	32L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,5,5'-PeCB	127L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100
Labeled Sampling Surrogates							
$^{13}C_{12}$-2,4'-DiCB	8L			5.0	50	400	--
$^{13}C_{12}$-3,3',4,5'-TeCB	79L			5.0	50	400	--
$^{13}C_{12}$-2,2',3,5',6-PeCB	95L			5.0	50	400	--
$^{13}C_{12}$-2,2',4,4',5,5'-HxCB	153L			5.0	50	400	--

Notes:

1. Suffix “L” indicates labeled compound.

2. The CS 3 standard is also used as the calibration verification solution.

Table 6b – Preparation of Calibration Solutions

Calibration Standard ID	Parent Standards	Parent Conc. (ng/mL)	Volume Added (mL)	Final Volume (mL)	Final Conc (ng/mL)
CS 0.5	Native PCB Congener Stock Solution	40	0.0125	1.0	0.50
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
CS 1	Native PCB Congener Stock Solution	40	0.0250	1.0	1.0
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
CS 2	Native PCB Congener Stock Solution	40	0.1250	1.0	5.0
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
	Cleanup Standard Stock Solution	5000	0.0010		5.0
	Sampling Surrogate Stock Solution	5000	0.0010		5.0
CS 3	Native PCB Congener Standard Mix	4000	0.0375	3.0	50
	Internal Standard Stock Solution	1000	0.3000		100
	Recovery Standard Stock Solution	1000	0.3000		100
	Cleanup Standard Stock Solution	5000	0.0300		50
	Sampling Surrogate Stock Solution	5000	0.0300		50
CS 4	Native PCB Congener Standard Mix	4000	0.1000	1.0	400
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100
	Cleanup Standard Stock Solution	5000	0.0800		400
	Sampling Surrogate Stock Solution	5000	0.0800		400
CS 5	Native PCB Congener Standard Mix	4000	0.5000	1.0	2000
	Internal Standard Stock Solution	1000	0.1000		100
	Recovery Standard Stock Solution	1000	0.1000		100

Table 7 - GC Window Defining Mixture

SPB-Octyl

Congener Group	First Eluted		Last Eluted	
Mono	1	2-	3	4-
Di	4	2,2'-	15	4,4'-
Tri	19	2,2',6-	37	3,4,4'-
Tetra	54	2,2',6,6'-	77	3,3',4,4'-
Penta	104	2,2',4,6,6'-	126	3,3',4,4',5-
Hexa	155	2,2',4,4',6,6'-	169	3,3',4,4',5,5'-
Hepta	188	2,2',3,4',5,6,6'-	189	2,3,3',4,4',5,5'-
Octa	202	2,2',3,3',5,5',6,6'-	205	2,3,3',4,4',5,5',6-
Nona	208	2,2',3,3',4,5,5',6,6'-	206	2,2',3,3',4,4',5,5',6-
Deca	209	2,2',3,3',4,4',5,5',6,6'-	209	2,2',3,3',4,4',5,5',6,6'-

SPB-Octyl Resolution Test Compounds

23	2,3,5-trichlorobiphenyl
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)
182	2,2',3,4,4',5,6'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl

Table 8 - Ions Monitored for HRGC/HRMS Analysis of PCBs

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
1	180.9888	Lock	C_4F_7	PFK
	188.0393	M	$C_{12}H_9{}^{35}Cl$	Mono
	190.0363	M+2	$C_{12}H_9{}^{37}Cl$	Mono
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	Mono-13C12
	202.0766	M+2	$^{13}C_{12}H_9{}^{37}Cl$	Mono-13C12
	222.0003	M	$C_{12}H_8{}^{35}Cl_2$	Di
	223.9974	M+2	$C_{12}H_8{}^{35}Cl^{37}Cl$	Di
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	Di-13C
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl^{37}Cl$	Di-13C
	255.9613	M	$C_{12}H_7{}^{35}Cl_3$	Tri
	257.9584	M+2	$C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	Tri-13C
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri-13C
	280.9824	QC	C_6F_{11}	PFK
	289.9224	M	$C_{12}H_6{}^{35}Cl_4$	Tetra
	291.9194	M+2	$C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	Tetra-13C
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra-13C
2	255.9613	M	$C_{12}H_7{}^{35}Cl_3$	Tri
	257.9584	M+2	$C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	Tri-13C
	268.9824	Lock	C_5F_{11}	PFK
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri-13C
	289.9224	M	$C_{12}H_6{}^{35}Cl_4$	Tetra
	291.9194	M+2	$C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	Tetra-13C
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra-13C
	325.8804	M+2	$C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta
	327.8775	M+4	$C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta-13C
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta-13C
	359.8415	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa
	361.8385	M+4	$C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa-13C
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa-13C
	380.9760	QC	$C_{10}F_{14}$	PFK

Table 8 - Ions Monitored for HRGC/HRMS Analysis of PCBs (continued)

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
3	325.8804	M+2	$C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta
	327.8775	M+4	$C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta-13C
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta-13C
	342.9792	Lock	C_8F_{13}	PFK
	359.8415	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa
	361.8385	M+4	$C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa-13C
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa-13C
	393.8025	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta
	395.7995	M+4	$C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta-13C
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta-13C
	427.7635	M+2	$C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa
	429.7606	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa
	430.9728	QC	C_9F_{17}	PFK
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa-13C
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa-13C
4	393.8025	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta
	395.7995	M+4	$C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta
	404.9760	Lock	$C_{10}F_{15}$	PFK
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta-13C
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta-13C
	427.7635	M+2	$C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa
	429.7606	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa-13C
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa-13C
	461.7246	M+2	$C_{12}H^{35}Cl_7{}^{37}Cl_2$	Nona
	463.7216	M+4	$C_{12}H^{35}Cl_6{}^{37}Cl_3$	Nona
	473.7648	M+2	$^{13}C_{12}H^{35}Cl_7{}^{37}Cl_2$	Nona-13C
	475.7619	M+4	$^{13}C_{12}H^{35}Cl_6{}^{37}Cl_3$	Nona-13C
	495.6856	M+2	$C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Deca
	497.6826	M+4	$C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Deca
	504.9697	QC	$C_{12}F_{19}$	PFK
	507.7258	M+2	$^{13}C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Deca-13C
	509.7229	M+4	$^{13}C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Deca-13C

1. Nuclidic masses used: H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

Table 9 - Theoretical Ion Abundance Ratios and Control Limits for PCBs

Chlorine Atoms	m/z's Forming Ratios	Theoretical Ratio	Lower QC Limit	Upper QC Limit
1	m/m+2	3.13	2.66	3.60
2	m/m+2	1.56	1.33	1.79
3	m/m+2	1.04	0.88	1.20
4	m/m+2	0.77	0.65	0.89
5	m+2/m+4	1.55	1.32	1.78
6	m+2/m+4	1.24	1.05	1.43
7	m+2/m+4	1.05	0.89	1.21
8	m+2/m+4	0.89	0.76	1.02
9	m+2/m+4	0.77	0.65	0.89
10	m+2/m+4	0.69	0.59	0.79

Table 10 - Acceptance Criteria for Performance Tests

Toxic & LOC Congeners	**IUPAC**	**Test Conc (ng/mL) [1]**	**IDOC %RSD**	**IDOC %R**	**LCS %R**
2-chlorobiphenyl	1	50	40	60-140	50-150
4-chlorobiphenyl	3	50	40	60-140	50-150
2,2'-dichlorobiphenyl	4	50	40	60-140	50-150
4,4'-dichlorobiphenyl	15	50	40	60-140	50-150
2,2',6-trichlorobiphenyl	19	50	40	60-140	50-150
3,4,4'-trichlorobiphenyl	37	50	40	60-140	50-150
2,2',6,6'-tetrachlorobiphenyl	54	50	40	60-140	50-150
3,3',4,4'-tetrachlorobiphenyl	77	50	40	60-140	50-150
3,4,4',5-tetrachlorobiphenyl	81	50	40	60-140	50-150
2,2'4,6,6'-pentachlorobiphenyl	104	50	40	60-140	50-150
2,3,3',4,4'-pentachlorobiphenyl	105	50	40	60-140	50-150
2,3,4,4',5-pentachlorobiphenyl	114	50	40	60-140	50-150
2,3',4,4',5-pentachlorobiphenyl	118	50	40	60-140	50-150
2',3',4,4',5-pentachlorobiphenyl	123	50	40	60-140	50-150
3,3',4,4',5-pentachlorobiphenyl	126	50	40	60-140	50-150
2,2',4,4',6,6'-hexachlorobiphenyl	155	50	40	60-140	50-150
2,3,3',4,4',5-hexachlorobiphenyl	156	50	40	60-140	50-150
2,3',4,4',5,5'-hexachlorobiphenyl	157	50	40	60-140	50-150
2,3,3',4,4',5'-hexachlorobiphenyl	167	50	40	60-140	50-150
3,3',4,4',5,5'-hexachlorobiphenyl	169	50	40	60-140	50-150
2,2',3,4'5,6,6'-heptachlorobiphenyl	188	50	40	60-140	50-150
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	50	40	60-140	50-150
2,2',3,3',5,5',6,6'-octachlorobiphenyl	202	50	40	60-140	50-150
2,3,3',4,4',5,5',6-octachlorobiphenyl	205	50	40	60-140	50-150
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	50	40	60-140	50-150
2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208	50	40	60-140	50-150
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209	50	40	60-140	50-150
Internal Standards					
$^{13}C_{12}$-2-chlorobiphenyl	1L	100	50	35-135	30-140
$^{13}C_{12}$-4-chlorobiphenyl	3L	100	50	35-135	30-140
$^{13}C_{12}$-2,2'-dichlorobiphenyl	4L	100	50	35-135	30-140
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',6-trichlorobiphenyl	19L	100	50	35-135	30-140
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',6,6'-tetrachlorobiphenyl	54L	100	50	35-135	30-140
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	100	50	35-135	30-140
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',4,6,6'-pentachlorobiphenyl	104L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	100	50	35-135	30-140
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	100	50	35-135	30-140
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	100	50	35-135	30-140
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	100	50	35-135	30-140
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',4,4',6,6'-hexachlorobiphenyl	155L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	100	50	35-135	30-140
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	100	50	35-135	30-140
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,4',5,6,6'-heptachlorobiphenyl	188L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	100	50	35-135	30-140
$^{13}C_{12}$-2,3,3',4,4',5,5',6-octachlorobiphenyl	205L	100	50	35-135	30-140

Toxic & LOC Congeners	IUPAC	Test Conc (ng/mL) [1]	IDOC %RSD	IDOC %R	LCS %R
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	100	50	35-135	30-140
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	100	50	35-135	30-140
Cleanup Standards					
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	50	45	45-120	40-125
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	50	45	45-120	40-125
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	50	45	45-120	40-125

1 Test concentrations are based on ng/mL in the sample extract or standard solution.

Table 11 - Retention Times of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[1]

PCB Congener Mix 1 (AccustandardM-1668-1)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
1	2	4	78	6	161
2	10	4	81	6	153
2	9	5	96	6	130
2	6	5	103	6	129
2	8	5	95	6	166
2	14	5	88	6	159
2	11	5	89	6	167
3	30	5	92	6	156
3	27	5	113	7	179
3	32	5	83	7	176
3	34	5	119	7	178
3	26	5	87	7	175
3	31	5	85	7	183
3	33	5	82	7	177
3	36	5	120	7	171
3	38	5	124	7	172
3	35	5	106	7	191
4	50	5	122	7	170
4	45	5	105	7	190
4	52	5	127	8	200/201
4	49	6	152	8	204
4	75	6	136	8	199/200
4	41	6	148	8	198
4	72	6	151	8	196
4	57	6	144	8	195
4	63	6	143	8	194
4	66	6	142	9	207
4	79	6	133		

PCB Congener Mix 2 (Accustandard M-1668-2)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
2	7	4	55	6	139
2	5	4	60	6	132
2	12	5	94	6	165
3	18	5	100	6	168
3	24	5	91	6	137
3	23	5	121	6	160
3	28	5	90	6	128
3	22	5	99	6	162
3	39	5	109/108	6	157
4	53	5	117	7	184
4	51	5	111	7	186
4	73	5	108/107	7	187
4	48	5	118	7	185
4	62	5	114	7	181
4	71	6	150	7	192
4	68	6	145	8	197
4	58	6	135	8	201/199
4	61	6	149	8	203

Table 11 - Retention Times of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[1] (Continued)

PCB Congener Mix 3 (Accustandard M-1668-3)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
2	13	4	80	6	140
3	17	5	93	6	146
3	29	5	84	6	141
3	20	5	101	6	164
4	46	5	112	6	158
4	65	5	86	7	182
4	59	5	116	7	174
4	40	5	107/109	7	173
4	67	6	154	7	193
4	76	6	147		

PCB Congener Mix 4 (Accustandard M-1668-4)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
3	25	4	64	5	123
3	21	4	70	6	134
4	69	5	102	6	131
4	47	5	97	6	163
4	42	5	115	7	180

PCB Congener Mix 5 (AccustandardM-1668-5)

Cl Level	BZ No.[2]	Cl Level	BZ No.[2]	Cl Level	BZ No.[2]
1	1	4	74	6	169
1	3	4	56	7	188
2	4	4	77	7	189
2	15	5	104	8	202
3	19	5	98	8	205
3	16	5	125	9	208
3	37	5	110	9	206
4	54	5	126	10	209
4	43	6	155		
4	44	6	138		

Notes:

1 Each congener mix is analyzed in triplicate to establish the retention times of the PCB isomers in the absence of co-eluting isomers. The elution order listed here is used to assign peak identifications in the separate mixture analysis. The average retention time established in the analysis of the separate mixtures is then used to establish relative retention times. (See sections 10.2.2)

2 BZ/IUPAC Number, if different.

Table 12: Assignment of Sample Preparation Protocols

1668 Protocol	Protocol Name	Sample Amount Extracted (g)	Fraction of Extract Cleaned	IS Added (mL)	Cleanup Std Added (mL)	Recovery Std Added (µL)	Extract Delivery Volume (µL)	Prep Split Factor	Prep Dilution Factor	QuantIMS Final Volume
P1	Clean	10	1/2	1	0.5 (added aftersplit)	50	50	2	1	100
P2	Low	2	1	1	1	100	100	1	1	100
P3	Medium	1.25	1/2	2	1 (added after split)	100	250	2	2.5	200
P4	High	1	1/4	4	1 (added after split)	100	500	4	5	400

Figure 1 - Recommended GC Operating Conditions

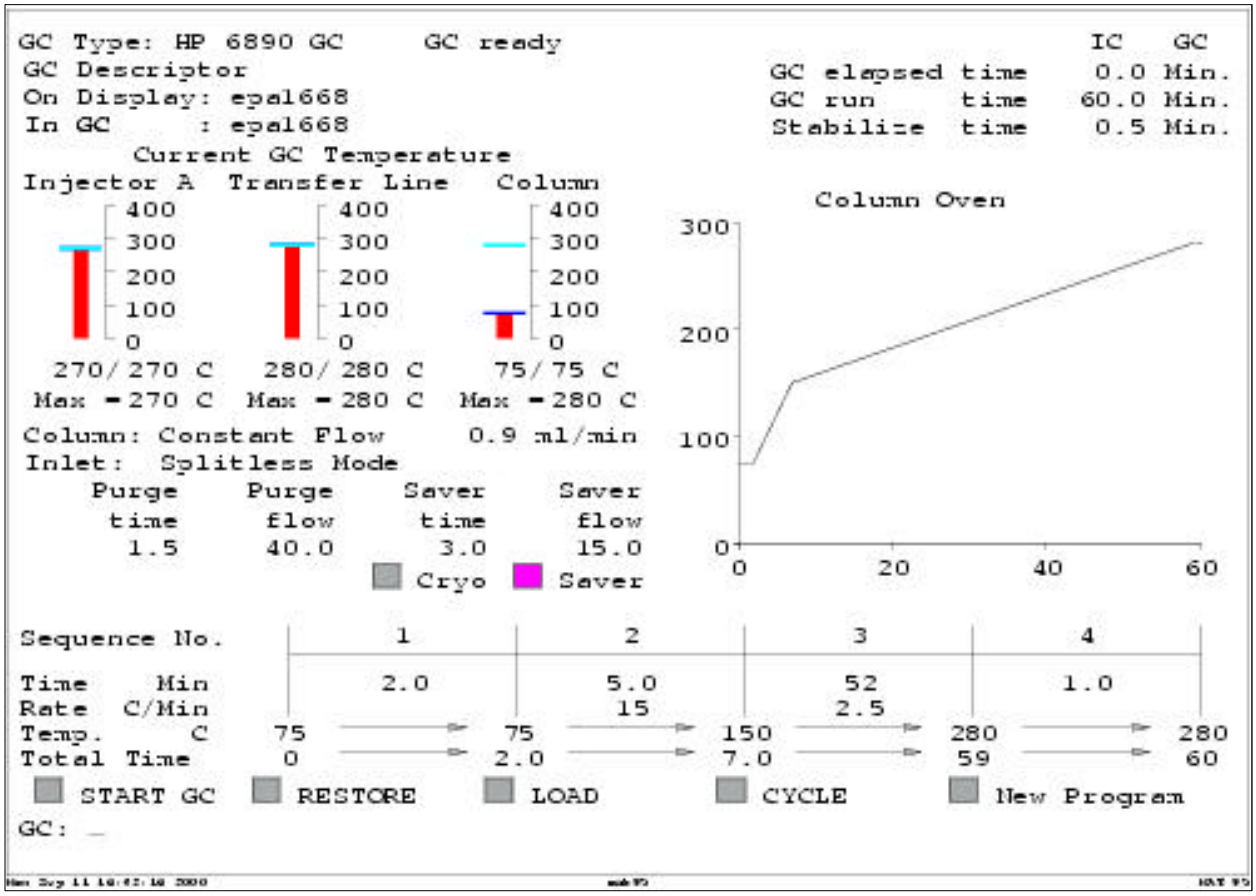
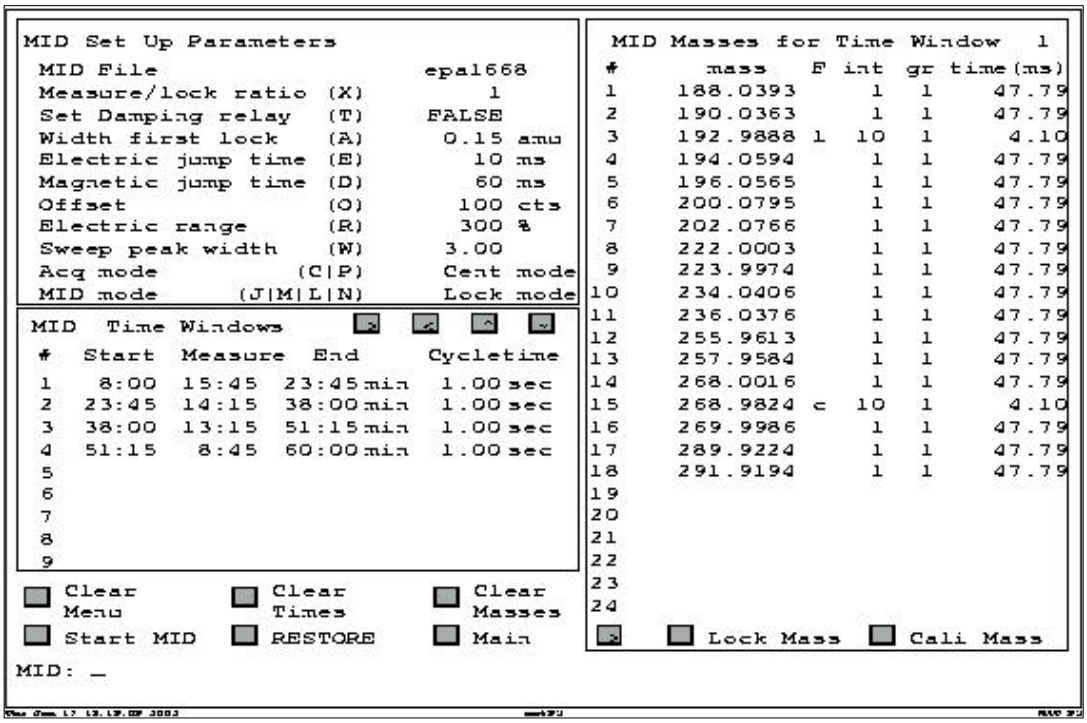


Figure 2 - Recommended MID Descriptors



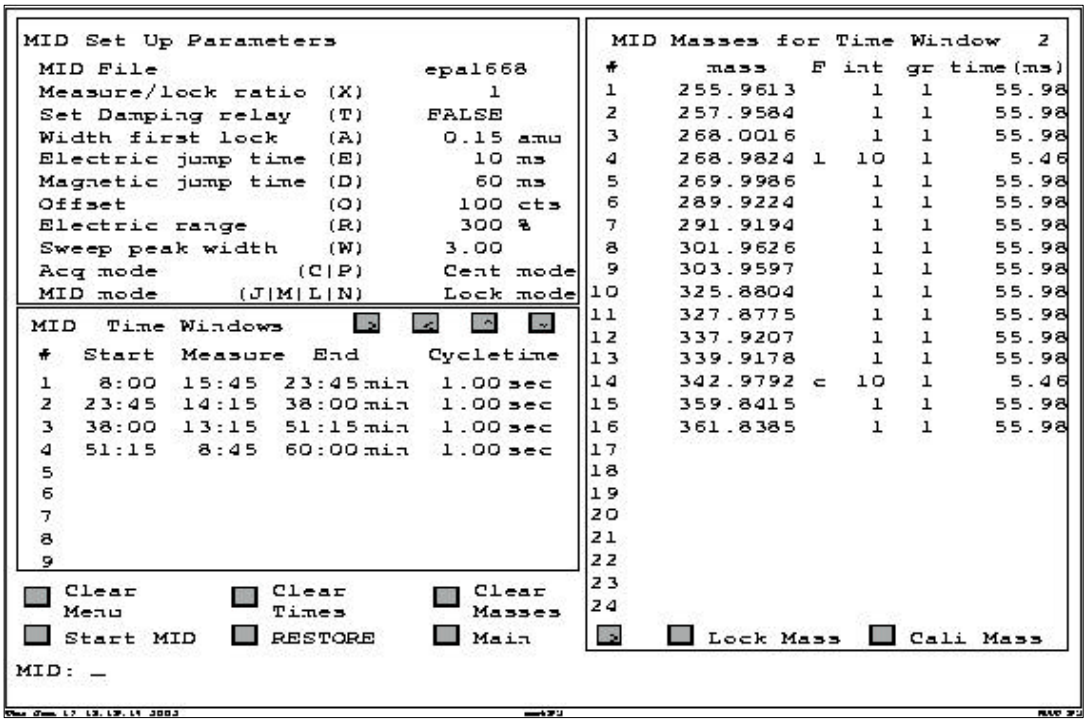
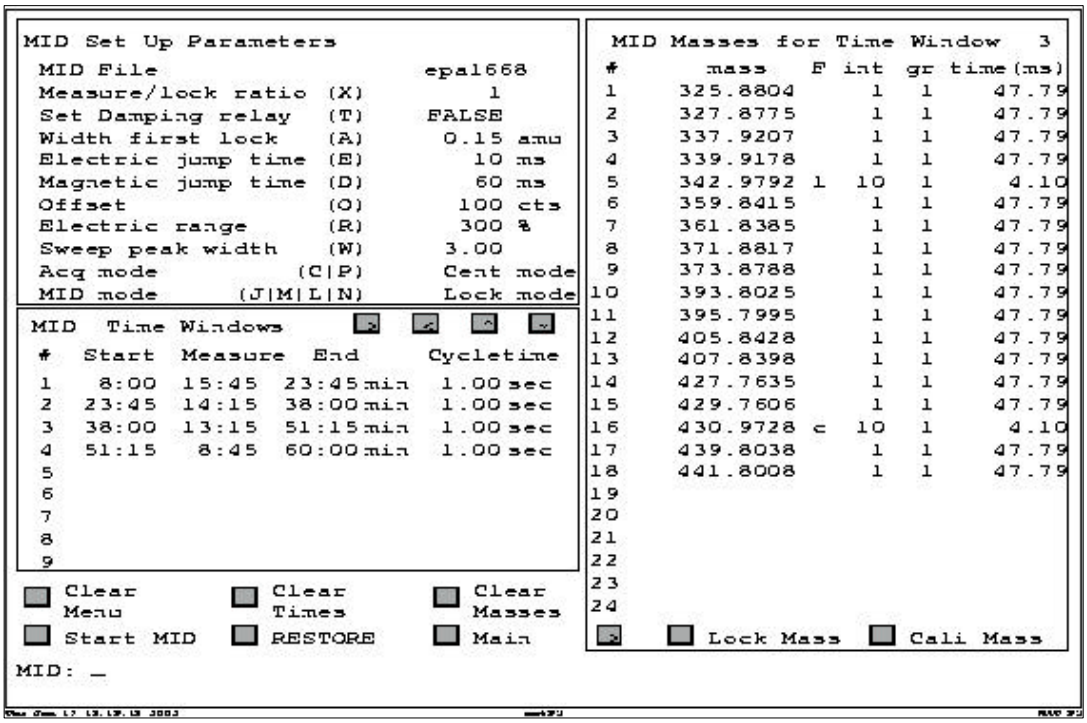


Figure 2 - Recommended MID Descriptors (Continued)



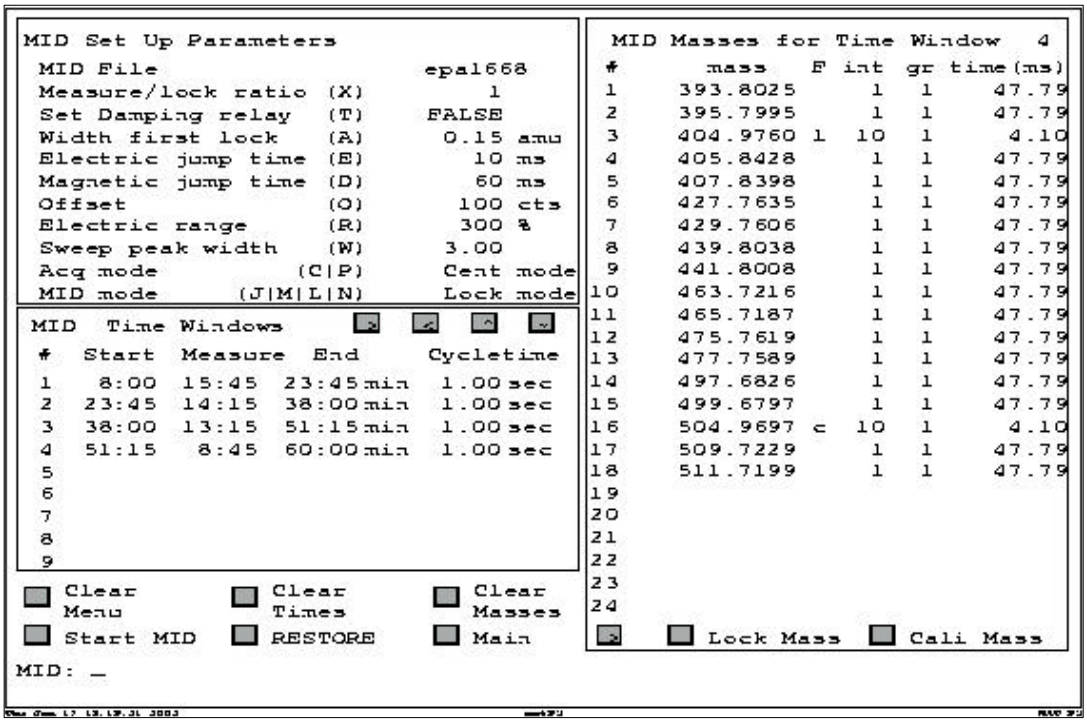


Figure 3 - Example Data Review Checklist

TestAmerica Knoxville Specialty Organics Group GC/MS Initial Calibration Data Review Checklist
Method or SOP Number: KNOX-ID-0013 Revision 9

PFK Date/Time:		Inst:		2nd Source Filename:	

CS0.5 Filename	CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution ≥8,000 throughout (≥ 10,000 for m/z 342.9792) and ≥10,000 in the center of each m/z range. PFK m/z 192.9888, *230.9856, and *280.9824? PFK m/z 268.9824, *292.9824, and *380.9760? PFK m/z 342.9792, *380.9760, and *430.9728? PFK m/z 404.9760, *442.9728, and *530.9665?					
3. Were the measured exact masses listed above within 5 ppm at reduced accelerating voltage?					
4. Have PCB Mixes 1 - 5 been analyzed in triplicate using the installed column to assign congener retention times, method retention times, and MID switch points?					
5. Were the calibration standard solutions, at the number and concentrations specified in the Method/SOP, analyzed?					
6. Was date/time of analysis verified between analysis header and logbook as correct?					
7. Was the valley height less than 40% of the height of the shorter of the two peaks for the pair PCB 23 and PCB 34, and the pair PCB 182 and PCB 187 in the CS3 standard?					
8. Was the absolute retention time of PCB 209 greater than 55 minutes in the CS3 standard?					
9. Were the response factors calculated for each labeled standard and unlabeled native analyte using the Method/SOP specified reference compound, quantitation ions, and formula?					
10. Is the %RSD acceptable for all native analytes (within ± 20% calculated by isotope dilution, within ± 35% calculated by internal standard)?					
11. Is the %RSD acceptable (within ± 35%) for all labeled standards?					
12. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards (Exception: Secondary native dichloro biphenyl channel m/z 223.9974)?					
13. Are the ion abundance ratios in the CS 0.5 within the control limits specified? (Exception: native dichlorobiphenyls)?					
14. Were all toxic congeners uniquely resolved from non-toxic congeners?					
15. Was an ICV analyzed, calculated using the CS3 RRFs, and the %D within ± 35%)?				□ < 5 outliers, none more than ±50% D.	
16. If manual integrations were performed, are they clearly identified, initialed and dated?					
17. If criteria were not met, was an NCM generated, approved by supervisor, and copy included in folder?					
18. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** run log, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

*At reduced accelerating voltage

Figure 4 - Example Data Review Checklist (Continued)

TestAmerica Knoxville Specialty Organics Group GC/MS Continuing Calibration Data Review Checklist
Method or SOP Number: KNOX-ID-0013 Revision 9

Start PFK:		End PFK:		CS3 Filename:		Inst:		ICAL Date:	

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution ≥8,000 throughout (≥ 10,000 for m/z 342.9792) and ≥10,000 in the center of each m/z range. PFK m/z 192.9888, *230.9856, and *280.9824? PFK m/z 268.9824, *292.9824, and *380.9760? PFK m/z 342.9792, *380.9760, and *430.9728? PFK m/z 404.9760, *442.9728, and *530.9665?					
3. Were the measured exact masses listed above within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Were the MID switch points set to encompass the retention time windows of each congener group?					
6. Was the valley height less than 40% of the height of the shorter of the two peaks for the pair PCB 23 and PCB 34, and the pair PCB 182 and PCB 187					
7. Was the continuing calibration performed at the beginning of the 12 hour period after successful mass resolution and GC resolution performance check?					
8. Were the %D for all toxic analytes within ± 30% (PCB 81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169, 189) Were the %D for all LOC analytes within ± 30% (PCB 1, 3, 4, 15, 19, 37, 54, 104, 155, 188, 202, 205, 206, 208, 209)					
9. Were the %D for all non-toxic/non-LOC analytes within ± 30%?					
10. If the %D for any non-toxic/non-LOC was not within ± 30, were response factors calculated from the continuing calibration for all non-toxic/non-LOC analytes with a %D greater than ± 30% but within ± 60%.					
11. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
12. Were the absolute retention times of all labeled internal standards within ± 15 seconds of the retention times obtained during initial calibration?					
13. Are %D within ± 50% for all labeled internal standards in the calibration?					
14. Are the %D within ± 30% for all labeled surrogate standards in the calibration.					
15. Are the %D within -40/+30% for all labeled cleanup standards in the calibration?					
16. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
17. Are RRTs of all unlabled toxic/LOC analytes within their respective RRT limits?					
18. If PCB 156 and 157 were classified as uniquely resolved in the most recent initial calibration, was the valley between the two less than or equal to the 50% of the height of the shorter of the two peaks?					
19. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
20. If manual integrations were performed, are they clearly identified, initialed and dated?					
21. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
22. Does the CCAL folder contain **complete** data in the following order? Data review checklist, a **complete** run log, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and both standards.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

*At reduced accelerating voltag

Figure 5 - Example Data Review Checklist (Continued)

TestAmerica Knoxville SOG GC/MS Data Review/Narrative Checklist **Lot #**_____
SOP Number: KNOX-ID-0013 Revision 9 **Page 1 of 1** **Batch #**_____

Review Items **A. Initial Calibration**	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd**
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration	**N/A**	**Yes**	**No**		**2nd**
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results	**N/A**	**Yes**	**No**		**2nd**
1. Were all special project requirements met?				See narrative	
2. Were the header information, prep factors, and dilution factors verified?					
3. Is logbook date/time of analysis correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____				□ HT expired upon receipt. □ Client requested analysis after HT expired. □ Re-extraction done after HT expired.	
5. Are internal standards within QC limits? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				□ **[sup]** Ion suppression due to matrix. □ **[low]** Low recovery. S/N >10 and EDL<ML. □ **[sam]** Not enough sample to re-extract. □ **[dil]** Dilution showed acceptable %R. □ **[mtx]** Obvious matrix interference. Further cleanup not possible.	
6. Were peaks ≥2.5 S/N, which did not meet the following criteria, properly calculated and reported as EMPCs? • All analytes within Method/SOP retention time criteria and both ions maximized within ±2 seconds. • The ion abundance ratios for all labeled and unlabeled analytes within the specified control limits.					
7. Are all results < the upper calibration level? *If no, list samples:*				□ Sample extracted at lowest possible volume	
8. If manual integrations were performed, are they clearly identified, initialed and dated?					
9. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
10. Was a narrative prepared and all deviations noted?					
D. Preparation/Matrix QC	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd**
1. LCS done per prep batch and all LCS/LCSD recoveries and RPDs within QC limits? *If no, list ID(s):*_____				□ MS/MSD %R, internal standards & surrogates %R in samples good indicating that problem was confined to the LCS.	
2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____				□ Internal standards are high and blank is free of contaminants. □ Internal standards are low, blank is free of contaminants, S/N>10 and EDL<EML.	
4. Are all analytes present in the method blank ≤ EML? *If no, list blank ID:* _____				□ Sample results are > 20x higher than blank. □ No affected analytes > RL in the samples. □ Not enough sample for re-extraction.	
5. MS/MSD done per batch and are all recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD ID:* _____				□ LCS acceptable indicating sample matrix effects. □ LCS acceptable, high analyte concentration. □ LCS acceptable, lack of sample homogeneity.	
E. Other	**N/A**	**Yes**	**No**		**2nd**
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**Analyst:**	**Date:**
Comments:		**Comments:**	

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: RECORD RETENTION AND DOCUMENT STORAGE

(SUPERSEDES: KNOX-AD-0001, Revision 9)

Prepared By: Diane Kargl

Reviewed By: Robyn M. Wagner 6/23/10
Technical Specialist

Approved By: Christopher White 07/06/10
Quality Assurance Manager

Approved By: Barry Li Charly 6-23-10
Environmental, Health and Safety Coordinator

Approved By: 7-7-10
Laboratory Director

1. Purpose

1.1. The purpose of this procedure is to ensure that records are retained appropriately and maintained for reference purposes as specified by applicable laws, regulations and contract requirements, to reduce the cost of records maintenance and to ensure that those records that have outlived their usefulness are destroyed.

1.2. This procedure establishes retention schedules for TestAmerica Knoxville records and outlines the steps required to retain records in active and inactive storage areas, to gain access to stored records, and to dispose of records in accordance with the retention schedules.

1.3. This procedure applies to all IT, client project deliverables, laboratory operations, QA/QC and project management records either received or produced at TestAmerica Knoxville.

2. Responsibilities

2.1. Employees of TestAmerica are responsible for proper use, including creation, retention, storage, and final disposition (shredding, archiving, etc.) of all company records under their control. They are responsible for maintaining their records in compliance with this procedure and the records retention schedule.

2.2. The Project Assistants are responsible for maintaining client project deliverables records in accordance with this procedure, and for initiating disposal of records.

2.3. The IT Technical Director is responsible for maintenance and destruction of all IT records as described in the TestAmerica Knoxville record retention schedule.

2.4. The Technical Director is responsible for coordinating and monitoring the records management program described in this SOP.

3. Safety

3.1. Normal office dependent safety precautions must be taken in performing this SOP. If personnel are required to perform any portion of the procedure in laboratory areas, appropriate personal protective equipment and precautions must be utilized.

3.2. Bankers boxes (larger than 12 1/2" x 15 1/2" x 10 1/2") shall not be utilized for the storage and archival of records. Larger boxes filled with paper exceed the weight limit requirement of 50 pounds.

3.3. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor.

4. Procedure

4.1. The TestAmerica Knoxville Record Retention Schedule in Appendix I provides the retention period for each record type. Record types include IT records, client project deliverables, laboratory operations records, QA/QC records and project management records.

4.2. The TestAmerica Knoxville Record Retention Schedule is designed to meet the NELAC standard retention time of five years, as well as the 10 year retention requirements of the programs listed below. This is accomplished by retaining laboratory logbooks, standard certificates and the electronic copies of all client project deliverables for 10 years rather than the NELAC required retention period of 5 years.

- Colorado – Drinking Water
- Commonwealth of MA – All environmental data 310 CMR 42.14
- Housing and Urban Development (HUD) Environmental Lead Testing
- Louisiana – All
- Michigan Department of Environmental Quality – All environmental data
- Minnesota – Drinking Water
- NY Potable Water NYCRR Part 55-2
- Pennsylvania – Drinking Water
- INVISTA Benzene Waste Operations NESHAP (Orange and Victoria)

4.3. The following programs have special record retention requirements. Projects which are received for these programs must be identified as such by the project manager:

- FIFRA – 40 CFR Part 160: Retain for life of research or marketing permit for pesticides regulated by EPA
- TSCA – 40 CFR Part 792: 10 years after publication of final test rule or negotiated test agreement

4.4. Records shall be maintained in such a manner as to reasonably protect them from loss during the retention period.

4.5. Where there are redundant copies of records (for example, paper and electronic media), the redundant archives may be destroyed at any time prior to the expiration of the data retention period.

4.6. Destruction of records will be documented by a certificate of destruction when destroyed by any person (contractor) other than the record originator (i.e., TestAmerica Knoxville). Appendices II and IV contain example certificates of destruction.

4.7. No records will be destroyed when litigation, government investigation or audit is underway (pending or imminent). Records held for litigation or audit may be released only by the organization initiating the hold.

4.8. Retention of Client Project Deliverables:

4.8.1. **Client project deliverables** include general information about the receipt of a particular shipment of samples (hereafter referred to as the **hardcopy lot folder**), raw data generated during the analysis of the samples (hereafter referred to as the **hardcopy data folder**), and **final reports** compiled in .pdf format. Client project deliverables are retained electronically and in hardcopy format as described below.

4.8.2. Hardcopy Lot Folders:

4.8.2.1. The contents of the lot folder are listed below:

- Cooler airbills
- Sub-contract lab chain-of-custody forms
- Media request forms/chain-of-custody forms
- Client analysis summary
- Sample log-in review checklist
- Lot special instructions
- Correspondence
- Data review checklists
- Metals, SOG, Wet Chemistry standard/raw data reference sheets
- Final invoice/working invoice
- Reporting review checklist
- Air bills/delivery documentation
- Sample chain-of-custody forms
- CUR checklist

4.8.2.2. The contents of the hardcopy lot folder are scanned in Adobe Acrobat (.pdf) file format in accordance with SOP KNOX-AD-0004. The electronic copies of the hardcopy lot folders are maintained for 10 years on tape.

4.8.2.3. After the contents of the hardcopy lot folders are scanned, the folders are placed on the shelves in the reporting room for 9 months. After 9 months, the contents of the associated hardcopy data folders are destroyed (section 4.8.3) and the hardcopy lot folders are filed in storage boxes in chronological order and stored on-site for 5 years from sample receipt.

4.8.2.4. After 5 years, the box of hardcopy lot folders is removed from on-site storage and placed in a bin for destruction (i.e., on-site shredding). The following information is recorded in the "Monthly Paper Copy Disposal Record" (Appendix III) in order to document the removal and destruction of the hardcopy contents of the lot folder: Lot number, date removed (i.e., put into a bin), bin number, initials of the person who removed the lot folder and the destruction date (i.e., date the bin was picked up for shredding). The vendor responsible for shredding will provide a certificate of destruction (see Appendix IV).

4.8.3. Retention of Hardcopy Data Folders and Final Reports:

4.8.3.1. Each operating group in the lab must submit final project sample data to the reporting group as defined in SOP KNOX-AD-0004 current revision, "Data Reporting". They must ensure that the original sample data review checklist is located behind the narrative, with a copy placed in the report with the data. These original data review checklists are placed in the hardcopy lot folder by the PA.

4.8.3.2. The contents of the hardcopy data folders are scanned and a final report is produced in Adobe Acrobat (.pdf) file format in accordance with SOP KNOX-AD-0004. The electronic copies of the hardcopy data folders and final reports are maintained for 10 years on tape.

4.8.3.3. After scanning, the hardcopy data folders and final reports are placed on the shelves in the reporting room, where they are stored for 9 months from the sample receipt date.

4.8.3.4. After 9 months, the hardcopy data folder/final report is removed from the shelf and placed in a bin for destruction (i.e., on-site shredding). The following information is recorded in the Monthly Paper Copy Disposal Record (Appendix III) in order to document the removal and destruction of the hardcopy contents

of the data folder: Lot number, date removed (i.e., put into a bin), bin number, initials of the person who removed the data folder and pick-up date (i.e., date the bin was picked up for shredding). The vendor responsible for shredding will provide a certificate of destruction (see Appendix IV).

4.8.4. Electronic Client Project Deliverables:

4.8.4.1. The electronic client project deliverables are maintained on the local area network in the \scandata\archive\ directory on the Knoxville file server for approximately 4 months. The electronic client project deliverables are maintained for 10 years on tape.

4.8.4.2. The electronic folder for a given receipt date and all subfolders and files are moved to an archive server by the designated PA when the 4 month time frame has elapsed. The purpose of the archive server is to allow easy retrieval of electronic project deliverables.

4.8.4.3. Refer to SOP KNOX-IT-0002, current revision for TestAmerica Knoxville's electronic data tape backup procedures.

4.8.5. Laboratory Operations Records, QA/QC Records, and Project Management Records:

4.8.5.1. Laboratory operations records, QA/QC records and project management records not included in the client project deliverable must be retained and destroyed as specified in the TestAmerica Knoxville Record Retention Schedule (Appendix I). These records may be maintained as either hardcopy original records or as electronic copies of the original records. Refer to section 4.5.

4.8.5.2. All calibration data are scanned and filed in .pdf format in the appropriate folder of the \scandata\groups\ directory on the Knoxville file server. The hardcopy data are stored in the laboratory for one year, after which time they are recycled.

4.8.5.3. Organic prep extraction records (handwritten) are scanned and filed by date range in the \scandata\groups\org prep directory on the Knoxville file server.

4.8.5.4. Dioxin prep extraction records (handwritten) are stored in the

laboratory for five years, after which time they are recycled.

4.8.5.5. Heat of combustion raw data are scanned and filed in .pdf format in the \scandata\groups\physical test directory on the Knoxville file server. The hardcopy data are stored in the laboratory for one year, after which time they are recycled.

4.8.5.6. The contents of the \scandata\groups\ directory are copied to the archive server every year.

4.8.5.7. Standard certificates are retained for 10 years from last use either as hardcopy or electronic records. After 10 years, the records are destroyed.

4.8.5.8. All laboratory logbooks are retained for 10 years, after which time they are destroyed.

4.8.5.9. Project management files are maintained electronically on TestAmerica Knoxville's public drives and/or in hardcopy form in each individual's office.

4.9. Off-Site Document Storage:

4.9.1. Prior to June 2006, some records were transferred from the laboratory to off-site storage in storage boxes. A Record Transfer form (see example in Appendix V) was completed and a bar code was assigned to each box.

4.9.2. The off-site storage contractor was Iron Mountain, located at 1407 Boruff Street, Knoxville, Tennessee 37917.

4.9.3. An off-site records inventory was used to schedule destruction of records in accordance with the TestAmerica Knoxville Records Retention Schedule (Appendix I).

Note: As of April 2010, all records in off-site storage were either destroyed by Iron Mountain or returned to the laboratory for destruction. The off-site storage contractor is no longer used.

4.9.4. The contractor provided a certificate of destruction which contained the following information: Description of records, box bar code number, destruction date, destruction method and a signature of a person supervising the destruction.

4.9.5. Upon receipt of the certificate of destruction, the PA recorded the date of destruction in the off-site records inventory and scanned the certificate of destruction and the associated Record Transfer forms in .pdf file format.

5. Definitions

5.1. Definitions can be found in the TestAmerica Knoxville Quality Assurance Manual (QAM).

6. Appendices

6.1. References

6.1.1. TestAmerica Knoxville Quality Assurance Manual (QAM).

6.2. Appendix I – TestAmerica Knoxville Record Retention Schedule

6.3. Appendix II – Example Certificate of Record Destruction

6.4. Appendix III – TestAmerica Knoxville Data Destruction Log

6.5. Appendix IV – Example Certificate of Destruction for On-Site Shredding

6.6. Appendix V – Example Record of Transfer Form

APPENDIX I - TestAmerica Knoxville Record Retention Schedule

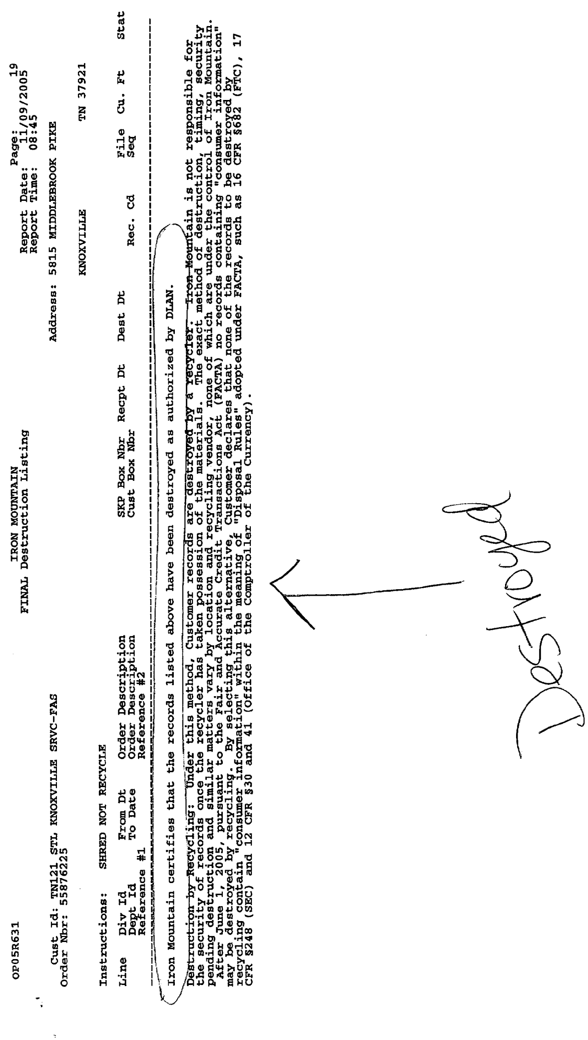
Type of Record	Hardcopy Retention	Hardcopy Location	Electronic Record Retention	Electronic Record Location
IT Records				
Daily Incremental Backups			10.25 yr	Safe
Biweekly Backups			10.25 yr	Safe
Computer Software; Distribution Media	5 yr from retirement	Computer lab	5 yr from retirement	Safe
Licenses	5 yr from retirement	QA office	5 yr from retirement	Safe
Client Project Deliverables				
Final analytical reports/QC summary reports	9 mo from sample receipt	Hardcopy data folder	10.25 yr from sample receipt	Tape
Raw sample and QC data	9 mo from sample receipt	Hardcopy data folder	10.25 yr from sample receipt	Tape
Standards data	9 mo from sample receipt	Hardcopy data folder	10.25 yr from sample receipt	Tape
Extraction records (originals)	9 mo from sample receipt	Hardcopy data folder	10.25 yr from sample receipt	Tape
Sample data review checklists (originals)	5 yr from sample receipt	Hardcopy lot folder	10.25 yr from sample receipt	Tape
Lot information	5 yr from sample receipt	Hardcopy lot folder	10.25 yr from sample receipt	Tape
Laboratory Operations				
SOG calibration/standards data	1 yr from analysis date	Reporting	5 yr	Tape
GCMS calibration/standards data	1 yr from analysis date	GCMS lab	5 yr	Tape
Metals ICP and Hg charts	1 yr from analysis date	Metals office	5 yr	Tape
GC/LC calibration/standards data	1 yr from analysis date	GC/LC lab	5 yr	Tape
Wet chemistry calibration/standards data	1 yr from analysis date	Wet Chem lab	5 yr	Tape
Physical test calibration/standards data	1 yr from analysis date	Physical Testing lab	5 yr	Tape
Heat of Combustion raw data	1 yr from analysis date	Physical Testing lab	5 yr	Tape
OP extraction records (handwritten)	1 yr	OP lab	5 yr	Tape
SOG extraction records	5 yr	SOG prep lab	NA	
Standards certificates	10 yr from last use	Lab/QA office	10 yr from last use	Safe-Tape
Instrument manuals	Retain until superseded	Lab	NA	
Internal Chain of Custody forms	5 yr	Lab	NA	

APPENDIX I - TestAmerica Knoxville Record Retention Schedule, continued

Type of Record	Hardcopy Retention	Hardcopy Location	Electronic Record Retention	Electronic Record Location
QA/QC Records				
Method & instrument validation records	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
LQM, policies, & SOPs	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
Quality assurance audits	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
Certifications & approvals	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
Employee signature list	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
MDL Studies	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
Performance testing studies	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
QA reports to management	5 yr*	QA office/OS	Determined by QA dept	Safe-Tape
Training records	7 yr from date of archival*	QA office/OS	NA	
All logbooks	10 yr from last entry	QA office/OS	NA	
Project Management Records				
Bids, Proposals & Price Quotes	2 yr from expiration	PM offices	2 yr from expiration	Safe-Tape
Project Management Files	5 yr from completion	PM offices	5 yr from completion	Safe-Tape
- Contract Copies, Work/Task Orders	5 yr from completion	PM offices	5 yr from completion	Safe-Tape
- Change Orders	5 yr from completion	PM offices	5 yr from completion	Safe-Tape
- Correspondence	5 yr from completion	PM offices	5 yr from completion	Safe-Tape
- QAPPs & Work Plans	5 yr from completion	PM offices	5 yr from completion	Safe-Tape
- Notice of Deficiencies/Requests for rework	5 yr from completion	PM offices	5 yr from completion	Safe-Tape
- Telephone Logs – project specific	5 yr from completion	PM offices	5 yr from completion	Safe-Tape

* Hardcopy records may be retained as scanned documents

Appendix II – Example Certificate of Record Destruction



OP05R631 IRON MOUNTAIN Page: 19
FINAL Destruction Listing Report Date: 11/09/2005
Report Time: 08:45

Cust Id: TN121 STL KNOXVILLE SRVC-FAS Address: 5815 MIDDLEBROOK PIKE
Order Nbr: 55876225
KNOXVILLE TN 37921

Instructions: SHRED NOT RECYCLE

Line	Div Id / Dept Id / Reference #1	From Dt / To Date	Order Description / Order Description / Reference #2	SKP Box Nbr / Cust Box Nbr	Recpt Dt	Dest Dt	Rec. Cd	File Seq	Cu. Ft	Stat

Iron Mountain certifies that the records listed above have been destroyed as authorized by DLAN.

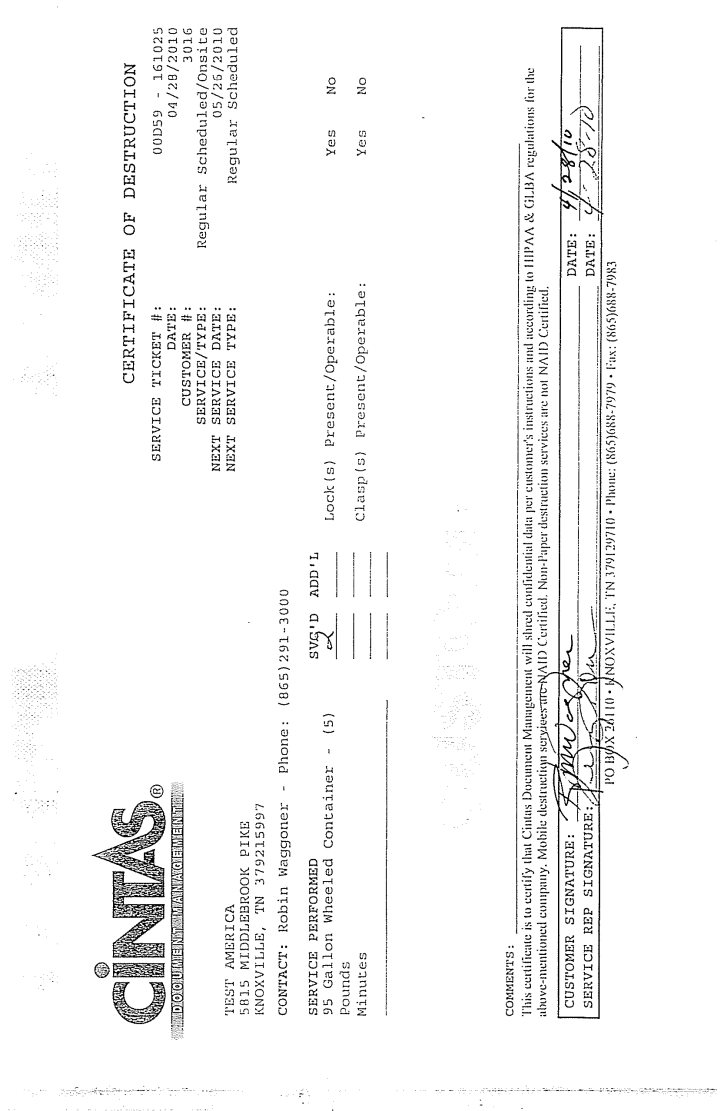
Destruction by Recycling: Under this method, Customer records are destroyed by a recycler. Iron Mountain is not responsible for the security of records once the recycler has taken possession of the materials. The exact method of destruction, timing, security pending destruction and similar matters vary by location and recycling vendor, none of which are under the control of Iron Mountain. After June 1, 2005, pursuant to the Fair and Accurate Credit Transactions Act (FACTA) no records containing "consumer information" may be destroyed by recycling. By selecting this alternative, Customer declares that none of the records to be destroyed by recycling contain "consumer information" within the meaning of "Disposal Rules" adopted under FACTA, such as 16 CFR §682 (FTC), 17 CFR §248 (SEC) and 12 CFR §30 and 41 (Office of the Comptroller of the Currency).

Appendix III – Example TestAmerica Knoxville Data Destruction Log

Monthly Paper Copy Disposal Record

Lot Number	X	Bin #	date placed in bin	Initials	bin pickup date	Notes
H9F010102	X	119835	3/29/2010	DL	3/30/2010	
H9F010104	X	119835	3/29/2010	DL	3/30/2010	
H9F010105						
H9F010120	X	119835	3/29/2010	DL	3/30/2010	
H9F010121	X	119835	3/29/2010	DL	3/30/2010	
A9F010145	X	119835	3/29/2010	DL	3/30/2010	
H9F020122	X	119835	3/29/2010	DL	3/30/2010	
H9F020149	X	119835	3/29/2010	DL	3/30/2010	
H9F020154	X	119835	3/29/2010	DL	3/30/2010	
H9F020174	X	119835	3/29/2010	DL	3/30/2010	
H9F020185	X	119835	3/29/2010	DL	3/30/2010	
H9F020200	X	119835	3/29/2010	DL	3/30/2010	
H9F020235						
C9F020240	X	119835	3/29/2010	DL	3/30/2010	
C9F020247	X	119835	3/29/2010	DL	3/30/2010	
H9F020254	X	119835	3/29/2010	DL	3/30/2010	
D9F020257	X	119835	3/29/2010	DL	3/30/2010	
H9F030102	X	119835	3/29/2010	DL	3/30/2010	
H9F030103	X	119835	3/29/2010	DL	3/30/2010	
H9F030104	X	119835	3/29/2010	DL	3/30/2010	
H9F030105	X	119835	3/29/2010	DL	3/30/2010	
H9F030107	X	119835	3/29/2010	DL	3/30/2010	
H9F030127	X	119835	3/29/2010	DL	3/30/2010	
H9F030131	X	119835	3/29/2010	DL	3/30/2010	
H9F030137	X	119835	3/29/2010	DL	3/30/2010	
F9F030138	X	119835	3/29/2010	DL	3/30/2010	
F9F030145	X	119835	3/29/2010	DL	3/30/2010	
H9F030174	X	119835	3/29/2010	DL	3/30/2010	
H9F030176	X	119835	3/29/2010	DL	3/30/2010	
H9F030180	X	119835	3/29/2010	DL	3/30/2010	
H9F030182	X	119835	3/29/2010	DL	3/30/2010	
C9F030200						
H9F030211	X	119835	3/29/2010	DL	3/30/2010	
H9F030217	X	119835	3/29/2010	DL	3/30/2010	
H9F030236	X	119835	3/29/2010	DL	3/30/2010	
H9F030246	X	119835	3/29/2010	DL	3/30/2010	
H9F030266	X	119835	3/29/2010	DL	3/30/2010	
C9F030267	X	119835	3/29/2010	DL	3/30/2010	
A9F040108	X	119835	3/29/2010	DL	3/30/2010	
H9F040110	X	119835	3/29/2010	DL	3/30/2010	
H9F040112	X	119835	3/29/2010	DL	3/30/2010	
H9F040118	X	119835	3/29/2010	DL	3/30/2010	
F9F040126	X	119835	3/29/2010	DL	3/30/2010	
H9F040127	X	119835	3/29/2010	DL	3/30/2010	

Appendix IV – Example Certificate of Destruction for On-Site Shredding



CINTAS®
DOCUMENT MANAGEMENT

CERTIFICATE OF DESTRUCTION

SERVICE TICKET #: 00D59 - 161025
DATE: 04/28/2010
CUSTOMER #: 3016
SERVICE/TYPE: Regular Scheduled/Onsite
NEXT SERVICE DATE: 05/26/2010
NEXT SERVICE TYPE: Regular Scheduled

TEST AMERICA
5815 MIDDLEBROOK PIKE
KNOXVILLE, TN 379215997

CONTACT: Robin Waggoner - Phone: (865)291-3000

SERVICE PERFORMED	SVC'D	ADD'L			
95 Gallon Wheeled Container - (5)	X		Lock(s) Present/Operable:	Yes	No
Pounds					
Minutes			Clasp(s) Present/Operable:	Yes	No

COMMENTS:

This certificate is to certify that Cintas Document Management will shred confidential data per customer's instructions and according to HIPAA & GLBA regulations for the above-mentioned company. Mobile destruction services are NAID Certified. Non-Paper destruction services are not NAID Certified.

CUSTOMER SIGNATURE: _____ DATE: 4/28/10
SERVICE REP SIGNATURE: _____ DATE: 4/28/10

PO BOX 24110 • KNOXVILLE, TN 37921-9710 • Phone: (865)688-7979 • Fax: (865)688-7983

Appendix V – Example Record of Transfer Form

TestAmerica Knoxville
RECORD TRANSFER FORM

Complete this form for each box of records being archived (Use an additional form, if necessary)
Transfer of documents shall be made to the PA or designee

Released By/Date: _____ Dept. Box ID (if applicable):_____
Dept. Name: _____ Dept. Number:_____

☐ Original ☐ Modified PAGE _____ of _____

RECORD TITLE _____

RECORD SERIES _____

TIME PERIOD COVERED _____ RETENTION PERIOD _____

DATE RECORDS TO BE REVIEWED: _____

BOX CONTENTS

PA Reviewer/Date: _____ Bar Code _____

AD004R3.DOC, 100308