

**Work Plan for Supplementary
Characterization and Investigation
of Contaminated Sediments
in Military Creek and
North Twin Lake and
Floodplain Soils Associated
With Military Creek**

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**Sediment Management and
Remediation Techniques Program**

**Bureau of Water Resources Management
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Work Plan for Supplementary Characterization and Investigation of Contaminated Sediments in Military Creek and North Twin Lake and Floodplain Soils Associated With Military Creek

1.0 WORK PLAN - INTRODUCTION

This document describes the approach and methods which will be used to collect supplementary chemical and biological data associated with the sediments from Military Creek and North Twin Lake. The creek and lake sediments are in locations that are potentially contaminated by organic chemical compounds used on-site during the operations of the C.M. Christianson Wood Treatment Facility (CWTF) and released to surface waters through storm water runoff, dipping pond overflows, discharges, and other means.

Previous work performed by the Wisconsin Department of Natural Resources (WDNR) detected the presence of pentachlorophenol (PCP), chlorinated organic pesticides, PAHs, metals, dioxins/furans, and other organic compounds in either site soils, groundwater, or creek sediments. The levels of dioxins and furans found in Creek sediments based on 2,3,7,8-TCDD toxic equivalencies are the highest found anywhere in the state.

The supplementary field sampling work described in this work plan is scheduled for October 1995 and will investigate primarily creek and lake sediments and adjacent flood plain soils for site related contamination. This work plan document contains a Sampling and Analysis Plan (SAP) and essential elements of a Quality Assurance Project Plan (QAPP). A Health and Safety Plan will be prepared as

a separate or stand alone project document. The supplementary sampling results will be evaluated and used to make further decisions on whether or not a more full scale remedial investigation is needed for the creek and lake sediments and adjacent floodplain soils.

2.0 SAMPLING AND ANALYSIS PLAN

Project Background

The Sampling and Analysis Plan (SAP) describes the methods which will be used for physical and chemical characterization of sediments and flood plain soils that may have been impacted by chemical compound releases from the CWTF site. The area of project interest includes Military Creek adjacent to the CWTF and downstream to it's point of juncture with North Twin Lake, sediments in North Twin Lake out from the mouth of Military Creek and flood plain soil adjacent to Military Creek on the CWTF property. Figure 1 shows the general project area. It should be noted that Figure 1 is based on an undated aerial photograph and some of the features are no longer present on site.

Attachment 1 contains a description of the stream classification for Military Creek and a description surrounding wetlands and soils.

Sediment sampling was conducted in Military Creek by WDNR in 1992 by Water Resources Management (Kreitlow samples) and in 1993 by the Site Evaluation Unit (SEU samples) of the Bureau of Solid and Hazardous Waste. On-land site soils were also sampled during the SEU 1993 investigation.

The evaluation of the sediment sampling results from the Kreitlow and SEU investigations are contained in a draft report entitled, Evaluation of Sediment Quality in Military Creek Associated with

C.M. Christianson Wood Treatment Facility by the Contaminant and Sediments Unit of the Bureau of Water Resources Management, April 1995.

Locations of the sediment sampling sites from both studies is shown in Figure 2. Attachment 5 contains a description of sample locations and methods from the two studies. Pertinent site evaluation information is contained in Attachment 2, Field observations of impacts; Attachment 3, Literature review on pentachlorophenol behavior in the environment; Attachment 4, Observations on contaminants; Attachment 5, Summary of on-land and sediment sampling results from the CWTF site; Attachment 6, Contaminants of potential concern at the CWTF site; and Attachment 7, shows an approach to develop sediment quality objective concentrations for pentachlorophenol to be protective of benthic organisms based on NR 105 chronic toxicity criteria to protect aquatic life.

Further supplementary sediment and initial floodplain sampling is warranted due to the following concerns based on information in the attachments:

1. CWTF site soil levels of pesticides, PAHs, and PCP are significantly elevated at the sample sites. At one soil sample site (S-14) which is within 50 feet of the creek, were PCP was analyzed, the concentration was 2300 mg/kg. The soil profile in shovel pits dug close to the west side of the creek bank shows a darker subsurface layer that carries a faint PCP odor.

The minimal sampling of creek sediments to date shows low levels of PAHs, PCP, and pesticides. However, this needs to be confirmed with further sampling at different levels in the sediment profile given the levels in site soils and potential routes of transport to the creek.

2. Based on the dioxin/ furan concentrations in creek sediments which are persistent contaminants in the manufactured PCP product, the amount of PCP released to the creek in the past was

substantial. Through degradation, weathering, and possible off-site transport, the present levels of PCP in sediment are relatively low, but still at levels that may cause chronic toxicity to benthic organisms. If only partially degraded, a number of toxic metabolites of PCP may be present in the sediments (see Attachment 6).

3. It is possible that contaminants including PCP metabolites dissolved in creek water or associated with particulate matter have been transported to North Twin Lake. Sediments in the lake out from the mouth of the creek need to be investigated for contaminant presence and impacts.

2.1 Project Objectives

WDNR has identified seven supplementary site investigation objectives. These objectives are:

1. To determine if near-bank areas (within 25 feet) on the west side of the creek on the CWTF property are contaminated and have the potential to be continuing source of contaminants to the creek.
2. To determine if sediments in the biologically active zone (approximately the top 15 cm of sediment) in the creek adjacent to and down stream of the site are toxic to aquatic organisms based on laboratory toxicity testing.
3. To determine if the benthic macroinvertebrate communities in the creek adjacent to and down stream of the site are impacted by the presence of any site related contaminants in the sediment.

4. To determine if site related contaminant distribution in the sediment deposits varies with depth, i.e., are there higher levels in the biologically active zone; do contaminants have the potential to be re-exposed by removal of overlying sediments from creek actions; or are contaminants buried under large amounts of overlying clean sediments.

5. To determine if contaminants have been transported from the creek out to the lake and are residing in the lake sediments.

6. To locate and characterize the sediment deposits in Military Creek along with characterizing features of the creek including width, water depth, flows, bank characteristics, and riparian vegetation.

7. To characterize baseline water chemistry parameters for the creek including ph, dissolved oxygen, conductivity, and temperature.

2.2 Components of the Sampling and Analysis Plan

This Sampling and Analysis Plan (SAP) is comprised of two components:

Field Sampling Plan (FSP): Describes sampling objectives, sampling design (number and location of samples), and parameters to be tested, sampling equipment and procedures, reports, and project schedule.

Quality Assurance Project Plan (QAPP): Describes field and laboratory methods for assuring data quality, including data quality objectives, analytical methods, QA procedures and reports, data validation and assessment, corrective action, and project organization and responsibilities.

3.0 FIELD SAMPLING PLAN

3.1 Site Background

Figure 1 shows the CWTF study area. The FSP focuses on investigating the creek and lake associated contamination by sampling near-bank soils and creek and lake sediments. The study area includes approximately 1200 feet of Military Creek adjacent to the CWTF and downstream to the juncture with North Twin Lake, sediments in North Twin Lake out from the mouth of the creek that may be the repository of creek delivered contaminants, and near-bank soil areas on the west side of the creek that may serve as a continuing source of contaminant input to the creek.

3.2 Field Sampling Design

This section describes the proposed design of the sampling and analysis program for the water-associated areas of the CWTF site.

3.2.1 Sample Number and Type

A. Sediment Chemistry

At present the proposed analytical plan includes a total of 17 samples to be analyzed from nine core samples taken from four areas. The number of cores from each area and the number of samples per core to be analyzed is shown in Table 1. The sediment cores are to be divided into two segments corresponding to an upper biologically active zone (generally the top 6-8 inches) and all lower remaining sedimentary material. The total core length that will be attempted to be collected at each sediment site is two feet.

Field observations of distinct strata in cores that may be associated with contamination may alter how the sediment cores are segmented for analysis. Near-bank core samples will be segmented based primarily on visual strata. Earlier reconnaissance probing indicated the presence of a darker subsurface strata with PCP or fuel oil-type smell to it in the near-bank soils. Depth of near-bank soils cores will be determined at the time of collection.

A.1 Sample Analytes

Table 2 shows the proposed testing parameters and the number of samples at each area. Table 3 lists analytes, sample volumes, and container types that will be needed for the samples collected in the sediment and soil matrices. All 17 samples will be analyzed for TOC, particle size, DRO, PCP, and chlorophenols. Testing of all the Military Creek in North Twin Lake sediments sample for PAHs and pesticides will depend on the analytical results for these compounds in the near-bank soil samples. Whether PAHs or pesticide are not detected or are at low levels in the near-bank soils will determine whether sediments will be analyzed for these compounds. Sediment samples will be collected and extracted for these compounds but not analyzed until the near-bank soil results for PAHs and pesticides are evaluated.

A brief description on the justification of each analytical parameter is provided below:

Total organic carbon (TOC) - Measures organic carbon content of soil and sediment matrix.

Organic chemical compounds may preferentially associate with organically enriched material which may in turn may determine compound bioavailability.

Particle size - Measures grain sized distribution of particles in soils and sediments. Particle size determines substrate characteristics and suitability for benthic macroinvertebrates. Coarser grained particles with less surface areas will have less tendency to adsorb contaminants.

Diesel range organics (DRO) - Measures all chromatic peaks eluting between n-decane (n-C₁₀) and n-octacosane (n-C₂₈). This measures a range of hydrocarbons that commonly make up diesel and fuel oils. Diesel or fuel oils may have been used as a carrier for the PCP in the dipping pits at the CWTF.

Pesticides and PAHs - Both are found at elevated levels in site soils. The high PAH levels suggest creosote may have been used in the wood treatment process at one time. The reason for the finding of a number of pesticides at elevated levels in site cells is unknown. If PAHs have reached the aquatic system, there is concern for effects at low level concentrations. For pesticides, bioaccumulation in the aquatic food chain is of concern.

Pentachlorophenol and Metabolite Chlorophenolic Compounds - PCP and its breakdown metabolites are toxic to aquatic organisms with many of the metabolites having mutagenic and teratogenic properties. High concentrations of PCP were found on land and near the creek. Based on dioxin-furan/ PCP relationships in the manufactured product and the amount of dioxin-furan levels in Military Creek sediments, substantial amounts of PCP have entered the creek over a period of time. Low levels of PCP in sediments presently indicates that PCP has degraded, or been transported. If degraded there is concern with chlorophenolic metabolite levels.

A.2 Sample Locations

Sample collection will occur from three areas. These three areas include Military Creek, North Twin Lake, and near-bank areas on the west side of the creek. The general area of the sampling locations are shown in Figure 3. Specific field locations will be determined at the time of sampling based on site characterization. The order of collection of sediment and soil samples will proceed in the

following manner: 1. Reference site; 2. Downstream to upstream creek sites; 3. Near-bank sites; and 4. Lake sites.

Military Creek: One site will be designated as a reference site and will be upstream out of the influence of any potential contamination releases from the CWTF. Previous background sampling sites used by WDNR will help to locate the reference site. Of the four down-stream sediment sampling sites, two will be located in sediment deposits between the CWTF property and County Highway E and two will be located down-stream below County Highway E and the mouth of the creek.

North Twin Lake: Two sediment samples will be taken. One will be at the edge of the 10-foot contour in fine sediments and out from the mouth of the creek. The other sample will be taken within the 30-foot depth contour out from the mouth of the creek.

Near-bank: Two soil cores will be taken. One will be in a southeast direction from the SEU S-14 site and within 20 feet of the creek. The other will be northeast of SEU monitoring well MW-4 and within 25 feet of the creek.

A.3 Sample Identification

Sediment and soil samples will each be labeled with a unique sample identification number as described below.

Sediment

Military Creek: Five cores will be taken in the creek, one at a reference site and four adjacent to and down-stream of the CWTF. Only one segment will be analyzed at the reference site which will be made up of the top 18 inches of material in the core. At the four down-stream coring sites, cores will be divided into two segments, 0-6 inches and 6-24 inches. The sample identification numbers that will be assigned are:

Site	Depth	
MC-1-A	0-18"	Reference Site
MC-2-A	0-6"	
MC-2-B	6-24"	Above Co. Hwy. E
MC-3-A	0-6"	
MC-3-B	6-24"	
MC-4-A	0-6"	
MC-4-B	6-24"	Below Co. Hwy. E
MC-5-A	0-6"	
MC-5-B	6-24"	

The A and B designators apply to the upper and lower segments of the core, respectively.

North Twin Lake: Two cores from the lake will be designated as follows:

Site	Depth	
NTL-1-A	0-6"	
NTL-1-B	0-24"	At 10 foot depth contour
NTL-2-A	0-6"	At 30 foot depth contour

NTL-2-B 6-24"

NTL-1 will be taken in the shallower depth contour nearest to the mouth and NTL-2 will be taken in the deep lake contour out from the mouth.

Near-bank: The near-bank sample sites will be designated FP for floodplain. The most upstream site segments will be designated FP-1-A and FP-1-B. The down-stream site segments will be designated FP-2-A and FP-2-B.

B. Sediment Toxicity Testing in Benthic Macroinvertebrate Sampling

Samples collected for toxicity testing and macroinvertebrates will represent an integration of chemical and biological information from the sites to determine if there are potential impacts to aquatic biota. The sediments for toxicity testing and macroinvertebrates will be collected as near as possible to the site where samples for sediment chemistry will be collected and will consist of the 0-6 inch sediment depth. Sediments for toxicity testing and macroinvertebrate samples will be collected from the following creek and lake sites:

MC-1-A (Reference site)

MC-2-A

MC-3-A

MC-4-A

MC-5-A

NTL-2-A

NTL-R (Macroinvertebrates only, reference site for lake benthic community)

Because the lake bottom represents a different habitat than the creek, the benthic communities will be different even under uncontaminated conditions. Therefore in addition to macroinvertebrate samples at NTL-2, macroinvertebrates will also be collected at a suitable reference site in the lake. No sediment chemistry or toxicity samples will be collected at the lake reference site. The sample container designators for toxicity testing and macroinvertebrate samples is shown in Table 4. No toxicity testing or sediment chemistry samples will be collected at the lake reference site. The sample container designators for Tox Testing and macroinvertebrate samples is shown in Table 4.

3.2.2 Sampling Equipment and Procedures

A. Field Positioning

Positioning or station-finding in the field will be achieved using a Global Positioning System (GPS). Sampling sites will also be located and marked on an aerial map of the site and related to identified reference points in the field by compass bearings and measuring distances. Based on a map with depth contours, the two lake sampling sites will be located in a southwesterly direction off of the mouth of the creek at the 10 and 30 foot depth contours. Compass bearings will be taken to three identifiable reference points on shore from each lake site in order to locate the lake sites on a map by triangulation. If the WDNR's SMART program mapping personnel are available, all sampling sites will be located by conventional survey methods.

B. Sediment Poling

Prior to sampling, locations and depths of soft sediment in the creek will be determined by the penetration of a 1 3/4 inch diameter sounding pole into the creek bottom. The sounding pole is

manually pushed into the sediments until high resistance or "refusal" is encountered. The pole is marked in 0.1 foot intervals. The water and sediment penetration depths will be recorded. The 1,200 foot length of the creek involved will be walked on shore as much as possible to locate and measure depth of soft sediments and record other creek characteristics. Creek bottom disturbance will be kept to a minimum prior to in-stream collection activities.

C. Sediment Sampling Methods

C.1 Sediment Chemistry

Sediments for chemical and physical analysis will be collected utilizing the SMART team piston core sampler using the one stainless steel or the acrylic plastic barrels of various lengths and which are 3 inches in diameter. Where the substrate conditions do not allow the use of the piston corer in the creek, a sharpshooter spade (shovel blade face 5 inches wide and 16 inches long) will be used to collect samples. Stones and rocks or hard substrate may prevent adequate penetration of the coring device to any appreciable depth. The number of core samples taken at the site will be determined by the amount of sediment materials required to do the chemical and physical analysis on each core segment. All core segments will be extruded into stainless steel mixing pans in the field and mixed with stainless steel utensils until the sample is well mixed and appears homogenous and then transferred to appropriately labeled sample containers.

C.2 Sediment Toxicity Testing

Sediments for toxicity testing from the creek and lake sites will be collected by a petite Ponar dredge or sharpshooter spade as determined by conditions and locations. The intent is to collect only the top six inches of sediment which is associated with the biologically active zone or the zone occupied by

epi- and infaunal macroinvertebrate organisms. Multiple shovel or Ponar dredge samples will be taken at each site to collect approximately four gallons of surface sediments which will be placed in a properly cleaned five gallon plastic bucket with a secure cover. The samples will be delivered to the State Laboratory Of Hygiene (SLOH) Biomonitoring Lab which will perform the toxicity tests contained in Table 5.

C.3 Sediment Benthic Macroinvertebrate Organism Samples

Macroinvertebrate samples will be taken with the SMART team corer to a depth of six inches in the sediment deposit. Five replicate core samples will be taken at each site. The replicate cores will be obtained at approximately two foot intervals at the site. Collected sediments in the retrieved cores from the zero to six inch depth will be extruded into a number 60 U.S. standard sieve bucket.

After sieving, retained materials on the sieve screen will be transferred to one liter plastic bottles and preservatives added. Five replicates are intended to provide the data required to analyze the statistical variability among the replicates and to support statistical comparisons among sampling stations.

Quantitative assessment of macroinvertebrate community structure and function will be performed by sorting and enumerating according to taxonomy all specimens from each individual replicate sample collected. Specimens will be identified to the lowest taxonomic unit possible. Taxonomic counts for each replicate from each sampling station will be used to calculate a number of indices including:

- Standing crop (numbers) of individuals by taxa per unit volume
- Species richness
- Species diversity
- Ephemeroptera-Plecoptera-Trichoptera index

- Community similarity

The core samples will be processed and evaluated for macroinvertebrates under contract with either UW-Stevens Point or UW-Superior.

D. Sample Handling, Preservation, Transportation, and Storage of Sediments and Soils

D.1 Sediment and Soils

Sediment and soil samples collected for analysis will be contained and preserved according to the specifications in Table 3. Chemical preservatives will not be added to sediment or core samples because of possible alteration of sample integrity. Collected samples will be placed in coolers on ice in the field. Samples will be segregated from melting ice within the coolers by placement in plastic bags. The coolers will be transported to refrigerated storage (4° C) facilities as soon as possible after collection until analysis. Prior arrangements are to be made with the analytical laboratory to ensure a schedule where the shortest time possible elapses between sample collection and analysis.

D.2 Macroinvertebrate Sampling Handling and Preservation

Macroinvertebrates collected by sieving cores will be handled as follows:

Benthic macroinvertebrates collected by the core sampler which includes the zero to 6 inch sediment depth will be extruded into the sieve bucket and water from the creek or lake will be allowed to come up through the bottom of the sieve for washing, agitating, and removing fine material out of the sample. No creek water will be poured or allowed to enter over the top of the edges of the sieve unless the water to be used is first pre-sieved to prevent any organisms not associated with the

sediment sample from entering the sample. If necessary to expedite sieving, the sample will be broken up by a gloved hand.

Material retained on the sieve surface will be washed into a clean sample container and 10% formalin solution added to the sample bottle to cover all organisms. After at least ten minutes of formalin preservation, the formalin will be poured off into a collection container and ethanol preservative added. The jars holding the replicate sieved core sample will be labeled using the project established labeling system. WDNR personnel will deliver properly labeled samples of macroinvertebrates for analysis to the contract laboratory.

D.3 Sample Packaging and Shipment

Sample packing and shipping to the laboratory will follow Part A.V., Shipping Requirements of the WDNR Field Procedures Manual.

Following collection, the exteriors of all sample containers will be wiped clean with a moist cloth.

The filled sample containers will not be rinsed in site water during decontamination because this water could contact sample if the container is not tightly sealed. In preparation for shipment or transport to any of the laboratories, samples will be packaged in accordance with the following procedures:

1. Each sample container will be checked to ensure that the container lid is securely tightened and the sample is appropriately preserved.
2. Each sample container will be checked to ensure that the sample label has been securely affixed to the container and completely/correctly filled out with the appropriate sample ID number, sample date, and initial of the sampler collector.

3. If necessary, sample containers will be placed in a cooler lined with a large polyethylene bag.
4. A completed chain-of-custody form identifying the contents of the sample shipment container will be placed in a large zip-lock bag. The bag will either be affixed to the outside of the shipping container (for containers transported by sampling personnel) or taped to the inside lid of the shipment container (for container shipped by carrier).
5. The cooler or box lid will be closed and sealed shut with strapping tape and the words "Enforcement Case" will be written in indelible ink across the end of the tape.
6. The sealed sample containers will either be transported by sampling personnel to the laboratory or shipped via overnight delivery by an appropriate carrier.

Sample handling, packaging, and shipment activities are the responsibility of the on-site project personnel. The project personnel will retain copies of the chain-of-custody forms. Project personnel will be responsible for contacting the lead laboratory contact and informing him/her of each shipment of samples. The project personnel will inform the laboratory of any problems encountered or noted during the field sampling that could potentially affect analysis. This information will also be noted on the chain-of-custody forms accompanying the samples.

E. Field Logbook Documentation

Field observations and other information pertinent to the collection of soil, sediment, and macro-invertebrate samples will be recorded in the field. All entries will be made in a bound, field logbook. Data to be recorded for each sample will include date, time, sample number, matrix, sample location, GPS coordinates and name of person(s) collecting the sample, depth at which sample was collected,

volume and number of containers, equipment used to collect sample, any preservatives added to the samples, and method of cleaning equipment prior to sample collection.

Field logbooks will record the names of all sampling team members present. Whenever a sample is collected a detailed description of the sample location which includes compass and distance measurements will be recorded.

Separate recording sheets will be used to record field measurement data such as conductivity, water temperature, flow velocity, water depth, wind direction and air temperature.

A separate recording sheet will be used to record characteristics of sediment samples retrieved including color (Munsell color chart readings), odor, texture, stratification and thickness of recognizable layers, depth of core tube penetration, length of retrieved core, and relative density or consistency of retrieved materials. Photos will be taken of all samples in the cores and extruded into the mixing pans.

F. Sample Custody

Chain-of-custody procedures to be followed in this project are as established in Part A, Section VI, WDNR Field Procedures Manual. Project personnel will review all field activities to determine whether proper custody procedures were followed during the field work period.

All samples will be recorded under a unique project number as discussed in Section 3.2.1.A.3, on a chain-of-custody form. For samples to be submitted to the SLOH and UW-Extension Soil and Plant Analysis Laboratory, the chain-of-custody forms shown after Page VI-3 of the WDNR Field Procedures Manual will be used. When transferring the possession of samples, the individuals

relinquishing and receiving will sign, date, and note the time on the chain-of-custody form. This record documents transfer of custody of samples from the sampler to each person that handles the sample. Each sample shipment container will be accompanied by completed chain-of-custody records identifying the containers contents.

In preparing samples for packaging and shipment, the project personnel will transfer data contained on the sample container labels to a chain-of-custody form.

Laboratory chain of custody procedures at the SLOH will be those established in Chapter 8 of the SLOH Quality Assurance Manual, Inorganic Chemistry Unit. This process will document the history of the sample containers and samples upon delivery of the sealed containers to the SLOH laboratory.

All chain-of-custody paperwork will be maintained by project personnel in a separate chain-of-custody file for the Military Creek Characterization of Contamination Study. Completed chain-of-custody forms and all raw analytical records will be retained by the laboratory for at least the three year period required for laboratory certification by WDNR. Sampling personnel will be responsible for long-term storage of data, reports from laboratories, field notebooks and field sheets, and all project reports that involve analysis of project data.

G. Preparation and Cleaning of Sampling Equipment, Containers, Utensils, and Supplies

Bottles, jars, and containers used for sediment and soil samples will be provided by the laboratory conducting the analysis.

All parts of sampling equipment (piston corer, Ponar dredge, coring spades) and sediment handling equipment (spatulas, mixing spoons, and mixing pans) will be cleaned in the laboratory prior to the sampling trip as follows:

1. Mix an adequate amount of non-phosphate detergent (1-2 tbsp) with tap water in a wash basin;
2. Wash and brush all sampling devices and sampling equipment;
3. Rinse 5-6 times in hot tap water;
4. Rinse in 10% nitric acid;
5. Rinse 3 times with deionized water;
6. Acetone rinse (except for acrylic core tubes), and
7. Air dry

All larger clean sample equipment will be wrapped in aluminum foil when dry for transport to the study site after laboratory cleaning. All smaller clean sediment handling equipment will be placed in a hard polypropylene box with cover, cleaned using the above procedures, for transport to the site. Prior to use of equipment at a sampling station, all sampling equipment to be used at that site will be rinsed with site water.

If more than one core or grab sample is needed at a sampling site, the sampling device and sampling equipment that is needed to be reused will be coarse cleaned by washing, scrubbing and rinsing with

site water. Upon completion of sample collection at a site, all sample equipment will be coarse cleaned.

Between sampling sites, the sampling device and sampling equipment will be final cleaned by washing and brush scrubbing in a non-phosphate detergent and rinsed with deionized water.

Separate scrub brushes and buckets will be dedicated to coarse cleaning and final cleaning. Brushes and buckets will be washed with soap and rinsed after use at each sampling station. All field derived final clean wash waters and rinses from decontamination will be left to fall onto the land.

3.2.3 Field Measurements

Measurements of water depths will be taken with a pole graduated into 0.1 foot increments. Lateral distances will be measured with a 200 foot fiberglass tape marked off in 0.1 foot increments.

Electronic instruments used to generate field measurements of water quality conditions of the creek and lake will be calibrated on a scheduled periodic basis in such manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications. Table 6 lists the field measurements that will be made during the project. Measurement devices will be maintained and calibrated according to the WDNR Field Procedures Manual.

3.2.4 Project Schedule

The timing of field sampling activities will be tied to the availability of a toxicity testing time slot at the SLOH Biomonitoring Lab. Collected samples have to be prepared and set up for exposure to test organisms within two weeks of field collection. Indications are now that the Biomonitoring Lab will

be set up to receive samples in early October. Evaluation of data and issuance of a report on the results will depend on when all test results become available and are reviewed. Ideally, a final report can be available by June of 1996.

4.0 QUALITY ASSURANCE PROJECT PLAN

This portion of the document comprises the Quality Assurance Project Plan (QAPP) for the Wisconsin Department of Natural Resources (WDNR's) supplementary characterization study of the contamination of the Military Creek and North Twin Lake sediments and near-bank area soils of the creek. These areas are potentially impacted from releases of organic chemical compounds associated with the operations of the C.M. Christianson Wood Treatment Facility.

The objectives of this QAPP is to match project objectives with specific measurements required to achieve those objectives. Data from the measurements will be used to support the project objectives presented in Section 2.1 of the Sampling and Analysis Plan.

4.1 Project Description

Project background is described in Section 2.0 of the Sampling and Analysis Plan.

4.2 Project Organization and Responsibilities

Project design, field sampling activities, data evaluation, and write up of a supplementary investigation report based on the data will be the joint responsibility of the Sediment Management and Remediation Techniques Team members in the project and North Central District Water Resources

personnel. The sampling effort will be coordinated with Scott Watson of the Solid Waste Program who is the project manager for the C.M. Christianson Wood Treatment Facility site.

4.3 Quality Assurance Objectives

The primary quality assurance objective is to develop and implement procedures for field sampling, chain-of-custody, field analysis, laboratory analysis and reporting which will yield data which are scientifically and legally defensible. Achieving the primary Quality Assurance objective will allow for the collection of site data of sufficient quality to meet the project objectives. This section presents target goals for data quality criteria for the project sampling program. Sampling and analytical protocols will be conducted in general accordance with appropriate state and federal guidelines and regulations including guidelines presented in Data Quality Objectives Process for Superfund 1993. Usability of the chemical data will be based on the evaluation of the precision, accuracy, representativeness, comparability and completeness. QA objectives are discussed below.

Precision is a measure of mutual agreement among individual measurements of the same property under prescribed similar conditions. Precision is measured by duplicate analysis. Sampling precision will be evaluated by analysis of duplicate field samples from a given location. Laboratory precision will be evaluated by analysis of duplicates and matrix spike/matrix spike duplicates. Specific laboratory control limits will either follow the requirements of individual methods or laboratory in-house control limits, whichever is more conservative.

Accuracy is an assessment of the closeness of a measured value to a true value. Accuracy of chemical test results will be assessed by spiking samples with known standards and measuring the percent recovery of the spike analyte, and the evaluation of procedural blanks. Known standards include matrix spikes, surrogate spikes, and standard reference materials.

Representativeness is a measure of how closely the measured results reflect the actual concentration or distribution of the chemical compounds in the matrix sample. Representativeness will be assessed by considering the recoveries of matrix and surrogate spikes.

Comparability is a qualitative parameter expressing the competence with which one data set can be compared to another. Data sets will be compared only when precision and accuracy meet the specified acceptance criteria established in this section. Sample data will be collected and reported in order to be comparable with other measurement data for similar samples and sample conditions. This goal will be achieved through using standard operating procedures to collect and then analyze representative samples through reporting analytic results in appropriate and consistent units. Each analytical procedure selected from among the acceptable options will be used throughout the work assignment, unless rationale is provided for any alteration. In essence, comparability will be maintained by consistency in sampling conditions, selection of sampling procedures, sample presentation methods, analytical methods, and data reporting units.

Completeness is a measure of the amount of valid data obtained from the analytical measurement system. Completeness will be assessed by comparing the number of valid sample results to the total number of samples planned for collection. Completeness of the data set for the level of analysis being performed is expected to be at least 90%.

4.3.1 Laboratory Quality Assurance

Quality Assurance criteria for the SLOH analysis are presented in Tables 7 through 10. During analysis of the samples, the laboratory will inform the WDNR project personnel if there is difficulty in meeting the target guidelines. Sample results and QA information will be reviewed after receipt from the laboratory.

The fundamental QA objective with respect to accuracy and precision of laboratory analysis is to achieve the QA acceptance criteria established for this project.

To the extent possible, the QA objectives in Tables 7 to 10 are consistent with method capabilities that are described in the following reference documents:

Wisconsin State Laboratory of Hygiene, July 1, 1991. Methods of Organic Analysis.

ASTM D22-63 (Particle size analysis of sediments)

4.4 Site Selection and Sampling Procedures

4.4.1 Site Sampling Locations

Section 3.2 of the Field Sampling Plan describes the proposed sampling design and sampling locations.

4.4.2 Sample Handling

Quality Assurance of data generated for this project depends on sampling procedures that are well conceived and properly implemented. The following sections provide guidance on accurate recording of field sampling forms/note books and chain-of-custody and field sampling quality control requirements.

A. Sampling Handling Procedures

Field samples will be collected according to the methods described in Section 3.2.2 of the Field Sampling Plan. To control the quality of laboratory analysis of samples, established preservation and storage measures will be followed. Recommended sample sizes, sample containers, preservation techniques, and maximum holding times for these analysis are presented in Table 3 of the Field Sampling Plan.

B. Field Notebooks/Data Sheets

Section 3.2.2.E and Section 4.5.1 below describes the documentation of field activities.

C. Field Sampling Quality Control

This section provides guidelines for the number and type of Quality Control (QC) samples proposed from the field.

Field Duplicate Samples

The purpose of obtaining and analyzing field duplicate samples is to assess the heterogeneity of sediments in close proximity at a sample site with respect to selected parameters. Duplicate sediment samples used for this purpose will be taken from two different core samples collected in close proximity to each other. Field duplicate samples will be evaluated for sediment analysis conducted for this project to assess the quality of data resulting from the field sampling program and the analytical procedures. Field duplicates will be collected and analyzed at frequency of one per every 20 or fewer investigated samples.

Field duplicates results will be used to assess the precision of the sample results. This will be used to monitor overall precision, including the reproduced ability of sampling and analytical procedures, as distinguished from the precision of analysis of laboratory replicates. Given the measurements of sediment particle size distribution are less critical to the project, no field duplicates for particle size analysis will be collected.

The project design recognizes that there will likely be considerable locational variability in concentration of contaminations in sediment. It is anticipated the "field duplicates" for the study may differ. Regardless of the magnitude of the Relative Percent Difference (RPD) it is intended that both observed values are equally valid estimates of the characteristics of the volume of material represented by the samples.

Equipment Rinsate and Field Blank Samples

The purpose of equipment rinsate and field blank samples is to assess the degree to which a parameter of interest is added or removed during field operations such as equipment decontamination between sampling sites. For this project, equipment rinsate samples will not be collected. All field sampling field personnel will familiarize themselves with and fully implement the equipment cleaning steps established for the project in Section 3.2.2.G of the Field Sampling Plan. No field blanks will be collected for either the sediment or soils.

4.5 Sample Custody

Chain-of-custody procedures are established in Section 3.2.2.F of the FSP to ensure that sample possession is traceable from the time of sample collection to delivery and handling at the analytical laboratory. Sample custody and transfer of custody will be documented.

4.5.1 Field Custody Procedures

A. Sample Handling and Preservation in the Field

Field personnel will be responsible for the care and custody of the samples until they are transferred and delivered to the analytical laboratory.

Sample bottles will be provided by the laboratory and must be subject to a Quality Assurance program to ensure uncontaminated and appropriately clean bottles are being provided. Sample identification tapes or labels will be affixed to each bottle with marking on the label being done with waterproof ink such as with a Sharpie marking pen. The label for each sample will include the sample site and segment designator as established in Section 3.2.1.A of the FSP along with the date and sampler's name or initial.

B. Field Logbook and Field Sheet Completion

Recording of data and observations for field sampling documentation is established in Section 3.2.2.E. of the FSP. All entries into logbooks or field sheets will be made with ink or with another indelible marker. All entries will be signed and dated. No erasures will be made in the logbook or accompanying logsheet entries. If an incorrect entry is made, the individual may correct the entry by crossing a single line through the error, initialing and dating the stricken item and entering the correct information.

4.5.2 Transfer of Custody and Shipping Procedures

The collected samples will be processed and delivered to the laboratory as established in Sections 4.5 of the FSP.

4.5.3 Repository of Documentation for Sampling Project

SMART team personnel participating in the project will maintain custody of the documentation of the sampling effort which includes: field logbooks, field sheets, chain-of-custody forms, correspondence, and any other relevant records. The file will be maintained at the GEF 2 Office Building, 101 South Webster Street, Madison, WI.

4.6 Analytical Procedures, Detection Limits, Accuracy and Precision for Contaminants of Potential Concern

The following section describes the analytical methods to be used for sediment and soil samples collected during the supplementary site investigation. Section 3.2.1.A. of the FSP presents the proposed analysis for the project samples.

Tables 7 to 10 present the detection limit and accuracy and precision goals for soil and sediment analysis for the contaminants of potential concern at the CWTF. The detection limit specified are those reported by SLOH in their organic analysis methods manual (Wisconsin SLOH, 1991). If an outside private laboratory is contracted to do the analytical work, the detection limits and QA objectives for precision and accuracy must be at comparable levels and the laboratory must be certified to do the analysis for the compound under NR 149.

4.7 Calibration Procedures and Frequencies

4.7.1 Laboratory Instruments and Equipment

Each laboratory instrument used by the SLOH will be calibrated prior to use as a measurement device to establish the instrumental response to known reference materials. All sample measurements will be made within the calibrated range of the instrument.

Preparation of reference materials used for calibration and the process for and frequency of calibration by the SLOH is established in the following documents:

- a. State Laboratory of Hygiene. December, 1992. Quality Assurance Manual, Inorganic Chemistry Unit, Chapter 4, Equipment and Instrumentation.
- b. State Laboratory of Hygiene. July, 1991. Methods for Organic Analysis. Section 700 Instrumentation.

WDNR does not know what calibration procedures are used for UW-Extension Soil and Plant Laboratory analysis of particle size distribution of sediments.

4.7.2 Field Measurements

Electronic instruments used to make field measurements will be calibrated on a scheduled basis according to the manufacturer's specifications. Field measurements to be made are discussed in Section 3.2.3 of the FSP.

4.8 Data Reduction, Validation, and Reporting

4.8.1 Laboratory Analysis of Chemical and Physical Parameters

State Lab of Hygiene. The SLOH will perform in-house analytical data reduction and validation to check whether project and laboratory QA criteria have been met. The SLOH data quality review procedures and information flow, data retrieval, and storage are contained in Chapter 1 of the Quality Assurance Manual, Inorganic Chemistry Unit.

SLOH will provide analytical results, in the units shown in Tables 7 to 10, for the parameters identified in the applicable methods. SLOH will provide validated data, including estimated concentrations for parameters detected at concentrations between the limit of detection and limit of quantification, and exception reports for any data points which do not meet all appropriate project and laboratory QA objectives.

Chapter 7 and Appendix A of the WDNR Field Procedures Manual discusses the transference of sample and analytical results information from the SLOH to WDNR. The SLOH lab data entry system (LDES) provides an electronic version of the analytical results. The LDES provides the project personnel access to sample results as soon as analysis is finished. Appendix A of the Field Procedures Manual discusses LDES and its interaction with WDNR data systems. Project personnel will be custodian of validated analytical data received from the SLOH. Data quality control summary reports will reside in SLOH. The project data set will be available for controlled access by the project personnel.

UW-Extension Soil and Plant Analysis Laboratory. UW-Extension Soil and Plant Analysis Laboratory will provide analytical results on particle size distribution. Paper copy data reports will identify each analyzed sample by its field sample number and laboratory number. This lab will not

evaluate any QA objectives and will provide WDNR with all raw data results in terms of percent sand, silt, and clay as determined by the referenced method.

Project personnel will be the custodian of all data reports developed by the UW-Extension Soil and Plant Analysis Laboratory for this project.

4.8.2 Macroinvertebrate Analysis

Reporting for macroinvertebrate analysis will consist of completed copies of WDNR's preprinted lab bench sheets, electronic copies of the data from the lab bench sheets, and a computer generated report, BENTSEPN, developed from one of the standard options on WDNR's Macroinvertebrate Data Management Systems. The data from this project will be mailed to project personnel as soon as those samples for the project have been analyzed. The laboratory will retain data on hard disk until it has been notified that the project team has completed data entry into its own computer storage system.

Project personnel will be the custodian of all data reports developed by the contract lab doing the macroinvertebrate analysis.

4.9 Internal Quality Control Checks and Frequency

4.9.1 Field Sample Collection

The assessment of field sampling precision and bias quality control (QC) will be made through the collection of field duplicate in accordance with the applicable procedures and frequency established in Section 4.4.2.C of the FSP.

4.9.2 Laboratory Analysis of Chemical and Physical Parameters

SLOH has written QA/QC programs which provide rules and guidelines to ensure the production of analytical data of known and documented usable quality.

SLOH programs are described in the documents mentioned above.

Laboratories control the quality of analytical methods by following standard protocols and evaluating quality control samples with each set of sample analysis.

The SLOH will analyze laboratory duplicates (or matrix spike duplicates) to assess analytical phase precision and will analyze matrix spikes to assess analytical phase accuracy. In addition, calibration procedures to control measurement quality will also be implemented.

Analysis not subject to complete internal QC checks include:

1. SLOH analysis of total organic carbon in sediment (will not be subject to matrix spikes);

4.9.3 Macroinvertebrate Analysis

It is expected that the contract laboratory doing macroinvertebrate analysis will have written QA/QC programs which include rules and guidelines to ensure the production of analytical data of known and documented usable quality.

5.0 PERFORMANCE AND SYSTEMS AUDITS

5.1 Field Audits

Internal audits of field activities (sampling and measurements) will be conducted by the designated field sampling team members. The audits will include examination of field sampling records, field instrument operating records, sample collection, handling and packaging in compliance with the established procedures, maintenance of QA procedures, chain-of-custody, and etc.

The training of the field sampling team and audits will occur at the onset of the project to assure that all established procedures are followed. Followup reviews will be conducted to ensure continuing adherence to establish procedures and to correct any deficiencies. The audit will involve review of field measurement records, instrumentation calibration records, and sample documentation.

5.2 State Laboratory of Hygiene

The SLOH does perform evaluation audits semiannually based on unknown reference samples obtained from USEPA. Reference samples are contained in conjunction with WPDES and Safe Drinking Water Act Laboratory Certification Programs. Internal reference samples are analyzed at least quarterly. These samples are either purchased from a private company or provided by USEPA. A system audit of the SLOH is conducted once a year by the Quality Assurance Officer of the USEPA Region V.

5.3 Preventive Maintenance Procedures and Schedules

Preventative maintenance on field measurement instruments will be conducted in accordance with the manufacturer specifications as established in applicable sections of the WDNR Field Procedures Manual.

The preventive maintenance protocols for laboratory equipment are contained in the SLOH Organic and Inorganic Quality Assurance Analytical Manuals. All laboratory instruments will be maintained in accordance with the manufacturer's specifications.

6.0 PROCEDURES USED TO ASSESS DATA USABILITY

6.1 Sample Collection

Determining the usability of sample results will be based, in part, on the evaluation of the completeness and representativeness of sample collection. If specified completeness falls below the stated QA objectives, project personnel will evaluate the available data set to determine whether: (1) the data set is usable but should be qualified or (2) is unusable because of limited completeness and needs to be supplemented with additional sample collection.

Failure to attain desired completeness and/or representativeness of sample collection may trigger corrective actions to attempt to rectify the problem situation.

6.2 Laboratory Analysis of Chemical and Physical Parameters

Determining the usability of analytical results will be based, in part, on the evaluation of analytical phase precision, accuracy, and sensitivity of various parameter analysis and the completeness of laboratory data reports.

If precision, as measured by RPD, and accuracy, as measured by percent recovery, meet the QA objectives identified in Tables 7 to 10, data will not be qualified and will be considered to be usable.

However, if either precision or accuracy fall outside the QA objectives, the laboratory may qualify the data and project personnel will evaluate the available data set to determine whether the qualified data should be used in spite of poor precision and/or accuracy or whether some type of corrective action is required.

Achieving method detection limits will depend on instrumental sensitivity and matrix effects.

Instrumental sensitivity will be monitored by analysis of calibration check samples and laboratory control samples as described in method documentation.

6.3 Macroinvertebrate Analysis

Macroinvertebrate community status data will be evaluated for usability based on (1) accuracy as indicated by qualitative comparisons to data from other projects and expected community character and (2) precision as indicated in an ANOVA that evaluates the variability within and among sampling stations. ANOVA results may indicate that community analysis is an insensitive parameter if variability within sampling stations is large relative to variability among sampling stations thought to represent diverse conditions.

7.0 QA REPORTS TO MANAGEMENT

The project personnel will audit the implementation of this QAPP. Each project component will deliver some type of QA report.

Reporting on the quality of field sample collection and field measurements will be the responsibility of the designated field personnel. Information from field log books, field data sheets, and calibration forms will be compiled in a summary report on field activity and prepared for the project file.

The final project report will include QA information, regardless of whether or not QA problems were observed. The final project report will include:

- a. Alterations in project design or methods from those described in this QAPP;
- b. Significant QA/QC problems, recommended solutions changes, and results of corrective actions;
- c. Discussion of whether QA objectives were met and resulting impact on decision making and technical conclusions;
- d. Limitations in use of the measurement data.

The final project report, including this QA information, will provided to the WDNR Solid Waste Project Manager.

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DIRECTIONS AND SCALE
APPROXIMATE

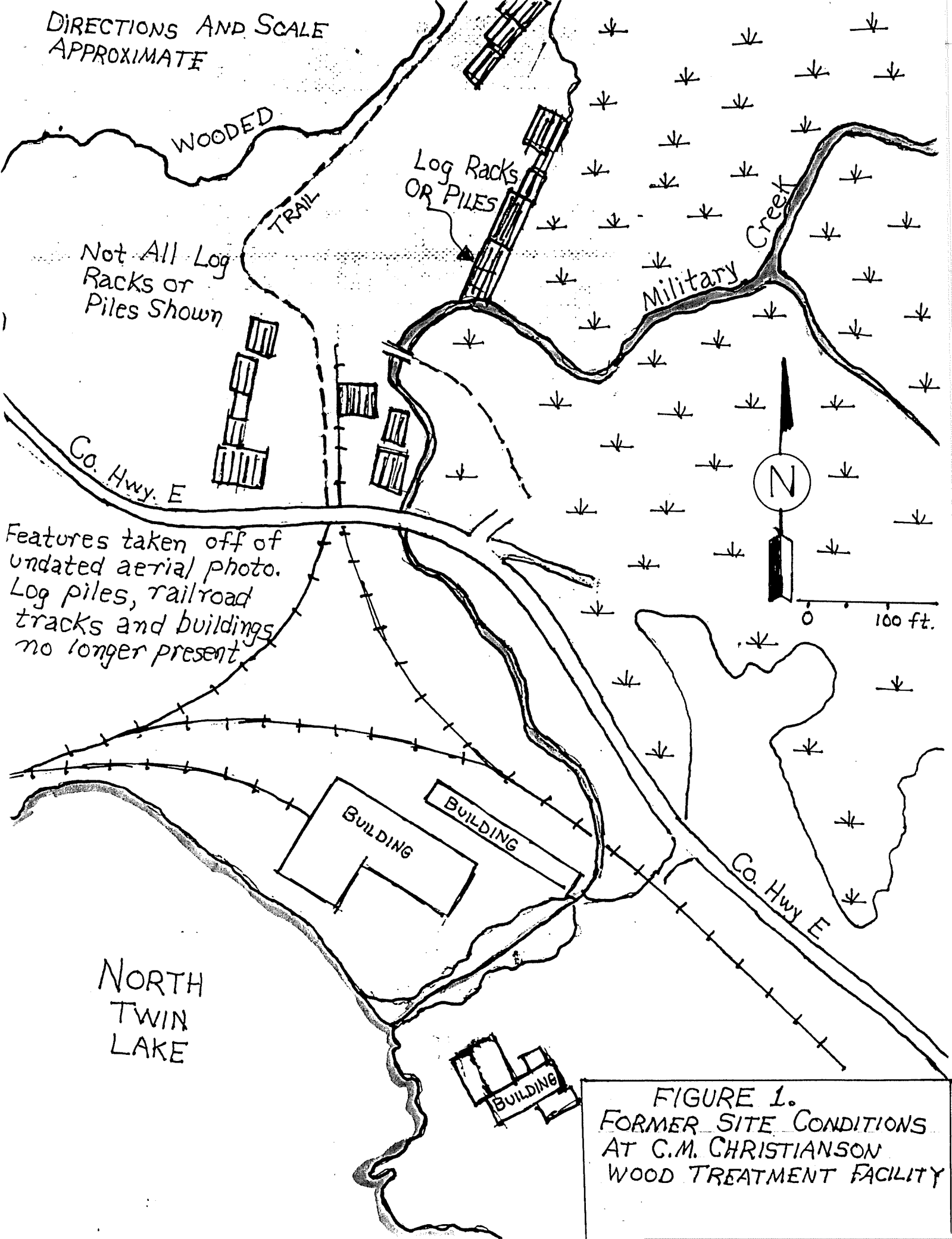


FIGURE 1.
FORMER SITE CONDITIONS
AT G.M. CHRISTIANSON
WOOD TREATMENT FACILITY

DIRECTIONS AND SCALE
APPROXIMATE

S-20
REF ● →

C.M. Christianson Wood
Treating Pole Yard
Facility

S-14

S-22/S-25
DUP

Military Creek

G-2-92

G-1-92
REF

Co. Hwy. E

S-21

G-3-92

△
Water Resources/Kreitlow - 1992
Samples - G-1-92

●
Solid Waste/ Site Evaluation Unit - 1993
Samples - S-20



North Twin Lake

10

20

30

S-23

Military Creek

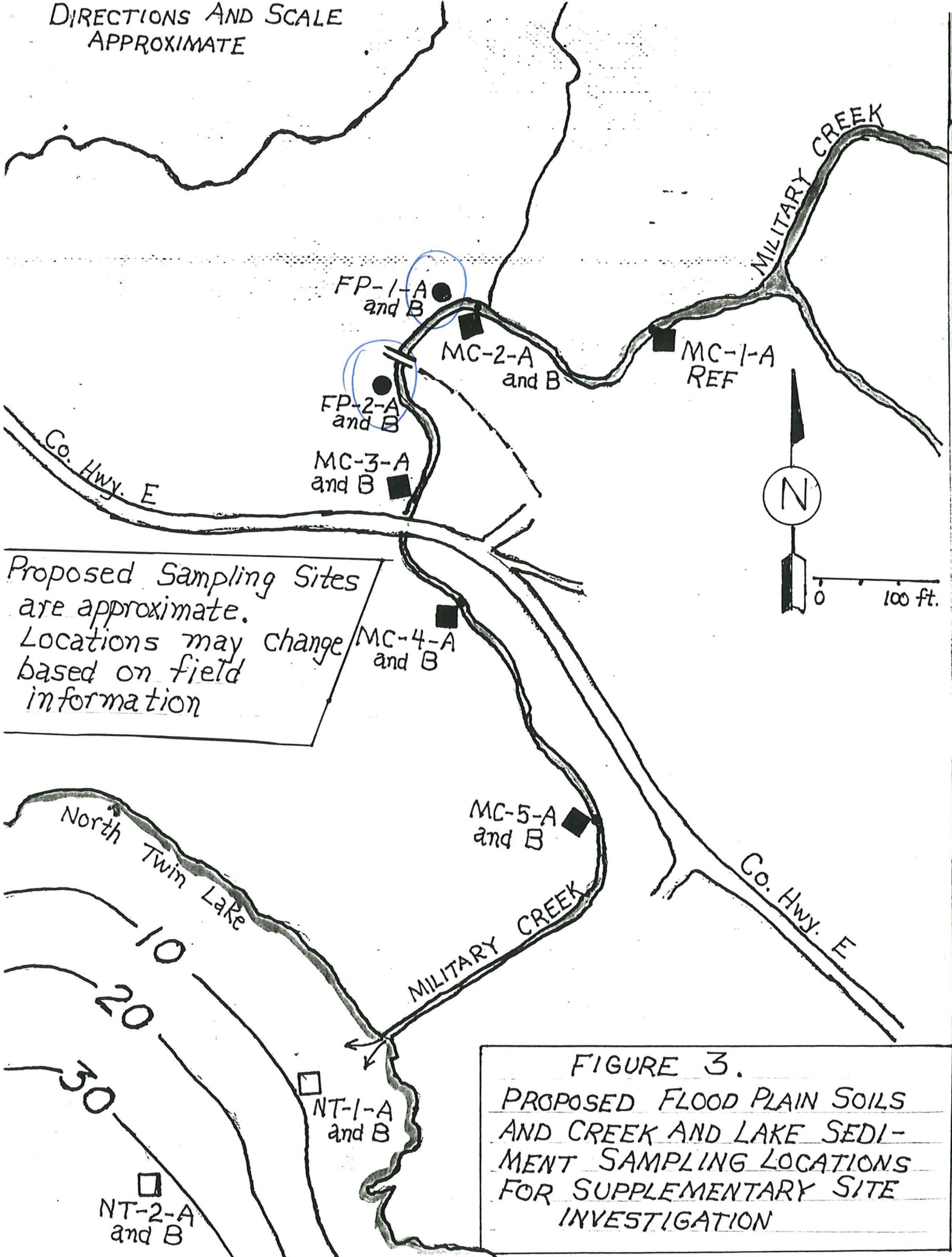
Co. Hwy. E

G-4-92

S-24

FIGURE 2.
LOCATIONS OF WDNR
SEDIMENT SAMPLING LOCATIONS
IN MILITARY CREEK IN
1992 AND 1993

DIRECTIONS AND SCALE
APPROXIMATE



Proposed Sampling Sites
are approximate.
Locations may change
based on field
information

FIGURE 3.
PROPOSED FLOOD PLAIN SOILS
AND CREEK AND LAKE SEDI-
MENT SAMPLING LOCATIONS
FOR SUPPLEMENTARY SITE
INVESTIGATION

Table 1. Christianson Wood Treatment Facility Supplementary Investigation Samples in Military Creek System.

Sample Area	Samples Within Study Area		
	Sediment/Soil Cores	Samples Per Core	Samples Analyzed
● Near-Bank Soils	2	2	4
● Military Creek	4	2	8
● Reference Site	1	1	1
● North Twin Lake	2	2	4
Totals	9	7	17

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Table 2. C.W. Christianson Wood Treatment Facility Supplementary Investigation Samples in Military Creek System.

Parameter	Sample Number and Analysis				Total Sample Number ^a
	Near-Bank Soils	Military Creek Reference Site	Military Creek	North Twin Lake	
Total Organic Carbon	4	1	8	4	17
Particle Size	4	1	8	4	17
Diesel Range Organics (DRO)	4	1	8	4	17
Pesticides	4	1	4 ^b	2 ^b	11
PAHs	4	1	4 ^b	2 ^b	11
Pentachlorophenol	4	1	8	4	17
Chlorophenols	4	1	8	4	17

^a. Total does not include field duplicates.

^b. Testing of Military Creek and North Twin Lake sediments for PAHs and pesticides will depend on the results of the near-bank soil sample results for these compounds.

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Table 3. Soil and Sediment Volume, Containers, and Sample Preservation

Sample Matrix	Analysis	Lab	Required Volume Per Sample ^a	Container Type	Preservation	No. of Samples	No. of Containers	Holding Time (from collection)
Soil and Sediment	Particle Size	UW-Ext. Soil and Plant	1x1 L	1 Qt. Ziploc Plastic Bag	Cool @ 4°C	17	17	
	Diesel Range Organics	SLOH	1x25 g	60 ml Glass Teflon Cap	Cool @ 4°C	18 ^{c.}	18 ^{c.}	Extract in 7d, analyze in 40d
	TOC	SLOH	1x1000 ml	1 quart glass jar with Teflon lined cap	Cool @ 4°C	18 ^{c.}	18 ^{c.}	28 days
	Pentachlorophenol					18 ^{c.}		
	Chlorophenols					18 ^{c.}		
Pesticides	5 (11) ^{d.}							
PAHs								
Tox. Testing	Biomonitoring Lab SLOH	4 gal.	5 gal. plastic bucket	Cool @ 4°C	6	6	14 days	

^{a.} Includes sufficient volume in each sample for any submitted sample to be used for laboratory duplicate and/or matrix spike analysis.

^{b.} Includes QC samples collected in the field (i.e. field duplicates).

^{c.} Includes a field duplicate sample analysis for DRO, TOC, PCP, and chlorophenols.

^{d.} Results of the floodplain samples for PAHs and pesticides may trigger PAH and pesticide analysis in both segments of the one lake and two creek sediment sample sites.

Table 4. Sediment Sampling Locations and Label Designations for Macroinvertebrate and Toxicity Testing.

Macroinvertebrate Samples	Toxicity Testing Samples
MC-1-A 1 through 5 ¹	MC-1-A-Tox
MC-2-A 1 through 5	MC-2-A-Tox
MC-3-A 1 through 5	MC-3-A-Tox
MC-4-A 1 through 5	MC-4-A-Tox
MC-5-A 1 through 5	MC-5-A-Tox
NTL-2-A 1 through 5	NTL-2-A-Tox
NTL-R-A 1 through 5	No Tox Testing at NTL-R-A

1 through 5 indicates the 5 replicates that are to be taken at each sample site.

MC-1-A is the creek reference site and NTL-R-A is the lake reference site.

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**STATE LABORATORY OF HYGIENE
AQUATIC LIFE TOXICITY TESTING LABORATORY
- METHODS FOR SEDIMENTS**

> ACUTE TESTS WITH SURVIVAL ENDPOINT

48 HR ACUTE TEST WITH *DAPHNIA MAGNA* *

48 HR ACUTE TEST WITH *CERIODAPHNIA DUBIA* *

10 DAY ACUTE TEST WITH *HYALLELA AZTECA* * +

**> CHRONIC TESTS WITH REPRODUCTION OR GROWTH ENDPOINTS
(AND SURVIVAL)**

**10 DAY CHRONIC TEST WITH *DAPHNIA MAGNA* *
- REPRODUCTION AND SURVIVAL**

**10 DAY CHRONIC TEST WITH *CHIRONOMUS TENTANS* * +
WEIGHT AND SURVIVAL**

Table 6. Field Measurements and Instrumentation

Measurement	Matrix	Method	Method Number	Reporting Unit	MDL
Temperature	Water	Thermistor	2101	°C	-5 to 45
Current Velocity	Water	Electro mag.	2301	ft/sec	--
Conductivity	Water	EMF	2201	umho/cm	--
pH	Water	Ag/Ag Cl Ref. Elect.	2000	s.u.	0-14
Dissolved Oxygen	Water	Polarography	2101	mg/l	0-20

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Table 7. QA Objectives for Soil and Sediment Matrices Precision, Accuracy, and MDL

Parameter	Matrix	Method	Method Number (Lab)	Reporting Unit (dry wt.)	Method Detection Limit	Precision (RPD) ^a	Accuracy ^b (% Recovery)	Completeness	Lab
Particle Size Analysis	Soils & Sediments	Gravimetric	ASTM D422-63 (1990)	% sand, silt clay (% moisture)	1% (NA)	30% (5%)	NA (NA)	90	UW-Exten. Soil & Plant Analysis Lab
Total Organic Carbon	Soils & Sediments	Slurry Method	1560	mg/kg	2000	25	75-125	90	SLOH
Penta-Chlorophenol	Soils & Sediments	GC	1540	ug/g	0.02	50	60-120	90	SLOH
2,4,5 Tri-Chlorophenol			1540	ug/g	0.10	50	70-112	90	SLOH
2,4,6 Tri-Chlorophenol			1540	ug/g	0.10	50	41-135	90	SLOH

^a Given as relative percent difference of laboratory duplicates.

^b Given as percent recovery of matrix spike.

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Table 8. QA Objectives for Soil and Sediment Matrices Precision, Accuracy, and MDL

Parameter	Matrix	Method	Method Number (Lab)	Reporting Unit (dry wt.)	Method Detection Limit	Precision (RPD) ^a	Accuracy ^b (% Recovery)	Completeness	Lab
chlorophenols	Soils and Sediments	GS/MS	1570			15	20-120	90	SLOH
4-Chloro 3-Methyphenol				ug/g	1.2				
2-Chlorophenol				ug/g	0.62				
2,4 Dichlorophenol				ug/g	0.68				
2,4 Dimethylphenol				ug/g	0.65				
4,6 Dimetro-2-Methyl Phenol				ug/g	3.3				
2,4 Dimitrophenol				ug/g	3.3				
2-Methylphenol				ug/g	0.57				
4-Methylphenol				ug/g	0.57				
2-Nitrophenol				ug/g	0.84				
4-Nitrophenol				ug/g	1.7				
Phenol				ug/g	0.62				
2,4,5-Trichlorophenol				ug/g	0.67				
2,4,6-Trichlorophenol				ug/g	0.67				

^a Given as relative percent difference of laboratory duplicates.

^b Given as percent recovery of matrix spike.

Table 9. QA Objectives for Soil and Sediment Matrices Precision, Accuracy, and MDL

Parameter	Matrix	Method	Method Number (Lab)	Reporting Unit (dry wt.)	Method Detection Limit	Precision (RPD) ^a	Accuracy ^b (% Recovery)	Completeness	Lab
<u>PAHs</u>	Soils and Sediments	GC/MS (ITD)	1580.1	ug/Kg	100 for each PAH compound	20	60-160	90	SLOH
Acenaphthene									
Acenaphthylene									
Anthracene									
Benz(a)anthracene									
Benzo(b)fluoranthene									
Benzo(k)fluoranthene									
Benzo(g,h,i)perylene									
Benzo(a)pyrene									
Chrysene									
Dibenz(a,h)anthracene									
Fluoranthene									
Fluoranthene									
Fluorene									
Indeno(1,2,3cd)pyrene									
Phenanthrene									
Pyrene									
Naphthalene									

^a Given as relative percent difference of laboratory duplicates.

^b Given as percent recovery of matrix spike.

Table 10. QA Objectives for Soil and Sediment Matrices Precision, Accuracy, and MDL

Parameter	Matrix	Method	Method Number (Lab)	Reporting Unit (dry wt.)	Method Detection Limit	Precision (RPD) ^a	Accuracy ^b . (% Recovery)	Completeness	Lab
Diesel Range Organics	Soils and Sediments	Wisconsin Modified	--	ug/g	10	20	60-130	90	SLOH
Pesticides	Soils and Sediments	GC	1571	ug/g		25	70-120	90	SLOH
Dieldrin					0.01				
o,p-DDE					0.01				
p,p-DDE					0.01				
o,p-DDD					0.01				
p,p-DDD					0.01				
p,p-DDT					0.01				
cis-chlordane					0.01				
trans-chlordane					0.01				
cis-nonachlor					0.01				
trans-nonachlor					0.01				
aldrin					0.01				
endrin					0.01				
hexachlorobenzene					0.01				
alpha-BHC					0.01				
gamma-BHC					0.01				
methoxychlor					0.05				
toxaphene					1.0				
endosulfan I					0.01				
endosulfan II					0.01				
endosulfan sulfate				0.01					
heptachlor				0.01					
heptachloroepoxide				0.01					

^a. Given as relative percent difference of laboratory duplicates.

^b. Given as percent recovery of matrix spike.

ATTACHMENT 1

STREAM CLASSIFICATION AND CHARACTERIZATION

Military Creek is in the Upper Wisconsin River, Northern Sub-basin, Tamarack/Pioneer River Watershed (UW 45).

Military Creek is approximately five miles in length. Miles 0-1.7 are classified as CLASS I and miles 1.7-5.0 are classified as CLASS II Trout Water. Also, miles 0-1.7 are classified as an Exceptional Resource Water.

The lower 1,000 feet of Military Creek above its point of juncture at North Twin Lake is potentially impacted from discharges from the C. M. Christiansen wood treatment facility. A worst case scenario has the potential input sources as being contaminated groundwater flowing into the creek, surface water runoff from the pole yard, dip pond overflows, or direct dumping or discharge of wood treatment waste or sludges or other chemicals associated with the site. There is or was a recognizable drainageway from the pole yard to the creek.

Approximately 330 feet of the creek above and north of County Highway E and approximately 660 feet below County Highway E are potential impacted from site releases. Softer sediments may exist in the approximately 330 foot stretch below the highway and before the bend in the creek where it turns in a southwesterly direction. The creek bottom in the remainder of the stretch between the bend and the juncture with North Twin Lake has harder cobble and rubble strewn materials and little areas of soft sediments. The creek bottom at the juncture with the lake is sand dominated.

The impacted 1,000 length of the creek is approximately 10 - 15 foot wide and 2 - 4 feet in depth. Military Creek has very low flows of evidence by the 2.5 and 3.7 CFS for the Q_2 and Q_{10} respectively. Military Creek originates and flows through the Nicolet National Forest before reaching North Twin Lake north of Phelps, Wisconsin. The Wisconsin Wetland Inventory Map indicates that for its 5 mile length, the creek generally flows through a narrow valley but widens at its lower end above the juncture of North Twin Lake.

North Twin Lake has a surface area of 2788 acres and a maximum and mean depth of 60 and 28 feet respectively. Musky, walleye, largemouth and smallmouth bass are present in the lake.

For its entire length, with the exception of segment below County Highway E and the lake, the creek flows through mapped wetlands. The cover type classes on the Wisconsin Wetlands Inventory Maps indicates the surrounding wetlands contain tamaracks, willows and alder shrubs, and coniferous shrubs/scrub habitat for typical spruce-tamarack lowland forest habitat. The Wetlands Inventory Map indicates there is a small amount of mapped wetlands to the west side of the segment of Military Creek above County Highway E that is on the site and potentially impacted from site discharges.

The soils in the mapped wetlands adjacent to Military Creek are classified as Seelyeville and Markey Mucks. These are typically black to dark brown mucks in the top 40 - 60 inches and are of herbaceous origin. In some areas, 1 - 4

inches of peat moss is at the surface. In places the mucks are derived from primarily from woody plants and contain wood fragments.

Soils in the upland portion of the site are Padus fine sandy loams. Permeability is moderate in the subsoil of the Padus soil and rapid or very rapid in the substratum. Poor filtering capacity can result in polluted ground water. Other soils in the watershed include champion silt loams (ChC), Padus fine sandy loams (PaC), and Rubicon sand (RoC).

ATTACHMENT 2FIELD OBSERVATIONS OF IMPACTS

Jim Kreitlow notes in a 02/01/93 memo that in his discussions with Bob Young (Water Resources Biologist) and Duke Andrews (District Fish Staff Specialist) that aquatic macroinvertebrate and trout numbers from the stretch of creek potentially impacted by the C. M. Christianson site are lower than what would be expected. In a discussion with Dave Johnson, who participated in the September 1993 SEU sediment sampling of the creek, he indicated that the stretch of creek at and below the site was largely devoid of biota. He also indicated that the cores they took were relatively homogeneous in appearance and did not contain recognizable segments or strata.

FERAL FISH COLLECTION FROM NORTH TWIN LAKE AND ANALYSIS FOR DIOXIN

Collection of white sucker and walleye from North Twin Lake were made in 1993 and analyzed for 2, 3, 7, 8 substituted dioxin and furan congeners. The fish picked up minimal levels of HpCDD and OCDD that translated into minimal TCDD-EQ. The levels in the fish may be representative of ubiquitous background sources or based on lab blank results may be from lab contamination and may not be attributable at all to the higher chlorinated dioxin and furan in the creek sediment.

Burbot and perch collected from Military Creek in 1986 had PCP concentrations in tissue as high as 0.250 ug/g.

CAGED FISH

In August of 1994, caged fish were placed at three creek locations and one in North Twin Lake out from the creek mouth. The three creek locations are the same from where Ekman dredge sediment samples were taken in 1993. A number of pesticides, trichlorophenols, pentachloroanisole and pentachlorophenols were analyzed for. No compounds were detected in fish tissue at levels above the SLOH detection limits with the exception of the fish from the 30 day exposure from the North Twin Lake site. The 0.01 ug/g value for pentachloroanisole may not be distinguishable from the reported detection level. Based on the simple partitioning model, it is predicted that based on the sediment concentration and partitioning of PCP from the organic carbon to the pore water and overlying surface water, fish would bioconcentrate PCP levels in tissue that exceeded the state SLOH detection level of 0.02 ug/g. This simple partitioning model may be over-predicting the amount of PCP that is released from the pore water to the overlying surface water. Dilution in the stream may be occurring. The PCP may be degrading in the water or metabolized in the fish. Depending on the pH, the PCP may be disassociating in the water.

ATTACHMENT 3LITERATURE REVIEW ON PCP BEHAVIOR IN THE ENVIRONMENT

In modeling, a biodegradation half life of PCP in sediment of 45 days is assumed. Environmental partitioning of PCP is pH dependent and tends to be transported from soil and sediment to water, especially at pH of around 7.0 and higher. At the pH's potential involved in Military Creek, the majority of the PCP would potentially be dissolved in water in the phenolate form.

Photolysis would be involved in the degradation of PCP in the water column. Estimated half life for dissolved PCP would be about 0.15 to 15 days. Declining aqueous concentrations could be caused by photolysis and hydraulic turnover and possibly biodegradation in sediments. The lower the pH, the more PCP in the undissociated associated pentachlorophenol form, more uptake by fish, more toxicity directly to aquatic organisms vs. higher pH's (approximately 7.0) when in the pentachlorophenate anion form.

The higher the pH, the lower the K_{ow} (octanol-water partitioning coefficient). The K_{ow} at a pH of 4 is 4 and the K_{ow} at a pH of 8 is 0.

The bioconcentration factor for PCP is 52 at pH 9 and 607 at pH of 7.

The pH is generally lower in spring and higher in autumn; therefore, most uptake in fish is potentially in spring when more pH in the un disassociated pentachlorophenol form.

The acute toxicity and bioaccumulation of PCP are a direct function of pH.

Lower pH's, lipophilic form of PCP is dominant and hydrophobic absorption of PCP to organic sediment removes PCP from the water column.

Understanding the toxicology of PCP has been confounded by the fact that commercial preparations particularly in the period up to the mid-1980's contained various amounts of toxic impurities including dioxins and furans. In studies that have compared the toxicity of pure PCP with technical or commercial grade, the toxicity has been found higher in commercial and technical grades. It has been shown to be fetotoxic (toxic to fetal life stages) and teratogenic (able to cause birth defects).

In experimental outdoor streams photolysis accounted for a 5-28% decline in initial PCP concentration compared to a 26-46% decline due to microbial degradation and loss to absorption to sediment or uptake by biota at less than 15%. PCP photochemically reduced to tri- and tetrachlorophenols and ring chlorines are replaced by hydroxyl groups. The resulting compounds are oxidized by air and subsequently dechlorinated ultimately being converted into small fragments, carbon dioxide, and hydrochloric acid.

ATTACHMENT 4OBSERVATIONS ON CONTAMINANTS

Based on existing data for the on-land and sediments for the C.M. Christianson site, the following observations are made:

1. The concentrations of PCP in site soils are approximately 1,000 times greater than the concentration in creek sediments.
2. The PAH concentrations in site soils are approximately 10 times greater than those in the creek and sediments.
3. Nineteen pesticides were detected in site soils and only three were found in the creek sediments at low-level concentrations. Pesticides in site soils are much higher in concentration for the three also found in the creek sediments. Pesticide levels in soil site S-11 are much higher than the other soil sample sites.
4. In the manufactured PCP product, the concentration ratio of PCP to dioxin/furans impurities is approximately 900 to 1. In the creek sediments, the present ratio is approximately 2.5 to 1, which may indicate differential transport of dioxins/furans to the creek compared to PCP or differential weathering and loss of PCP and persistence of dioxins and furans once the pentachlorophenol product reached the creek.
5. Metal levels and sediments do not appear to be elevated above upstream background levels. Jim Kreitlow indicated concerns with copper, chromium, and arsenic because of possible use in wood preservatives solutions. A better comparison of data could be made if particle size information was available for the samples. Zinc appears elevated at S-22 but this may be due to the indicated analytical interference. The site soils do not appear to have any significant elevations above background with exception of S-14 for zinc and S-14 and S-15 for lead.
6. At the given PCP soil concentrations, it would be interesting to know what the dioxins/furans concentrations are and TCDD-EQ. The TCDD-EQ of dioxins and furans in a manufactured PCP product can range from 1,500,000 to 2,700,000 pg TCDD-EQ/g (90% PCP content assumed).

If the PCP/dioxin impurity ratio stays the same, soil sample site S-11 at 87,000 mg/kg (8.7%) would have a TCDD-EQ of approximately 190,000 pg/g. If there has been a differential loss of PCP from weathering, and the dioxins are persistent in soil, TCDD-EQ could be much higher. The action level for human health concerns based on dermal contact is 1,000 pg/g (1 ppb).

7. The Kreitlow EKMAN dredge samples results for PCP (50, 640, and 30 ug/kg) are somewhat less than the SEU deep coring results (1,300, 1,600, 1,400, and 70 ug/kg). The differences may not be great enough to indicate PCP concentrations are elevated in deeper strata.

8. Given the higher concentrations of PCP, PAHs, and pesticides on land compared to the sediments, the following may have taken place at the facility: the facility operated from 1958 to 1978. In the intervening period between 1978 and the present the contaminated sediments could have been transported downstream into the lake or buried beneath cleaner sediments. At the time of the 1986 creek fish samples, enough PCP may have been present yet in the surface sediments to allow fish bioaccumulation either through food or water uptake. Given the amount of residual higher chlorinated dioxins and furans in the sediment which are from impurities in the commercial PCP product, (PCB/dioxin ratio in manufactured product is 900 to 1) the amount of PCP must have been substantial at one time.

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ATTACHMENT 5

Dates, Locations, and Method of Sampling Sediments from Two Studies on Military Creek.

<u>Kreitlow</u>	<u>Site Evaluation Unit</u>
<ol style="list-style-type: none"> 1. Reference - G-1-92 upgradient of pole drying area 2. G-2-92- Downstream of foot bridge below pole drying area 3. G-3-92 Downstream Co. Hwy. E 4. G-4-92- 100 ft above juncture with North Twin Lake 	<ol style="list-style-type: none"> 1. Reference S-20 upgradient 2. S-22 100 ft. east of MW-3 3. S-22 Dup 4. S-21 30 ft. upstream of Co. Hwy E culvert 5. S-23 Below Co. Hwy E bridge. 40 ft east of metal shed 6. S-24 3 ft. upstream of juncture with lake
<u>Samples Taken Kreitlow</u>	<u>Site Evaluation Unit</u>
<p>Ekman Dredge</p>	<ol style="list-style-type: none"> 1. S-20 2 ft. core 2. S-22 1 ft. core 3. S-22 Dup 1 ft. core 4. S-21 2 ft. core 5. S-23 1 ft. core 6. S-24 Trowel 2-5 in.

ATTACHMENT 5 (continued)

Sediment Samples Results from Kreitlow Collection of November 1992.

	G-1-92	G-2-92	G-3-92	G-4-92
Pentachlorophenol	< 20 ug/Kg	50 ug/Kg	640 ug/Kg	30 ug/Kg
2,4,6-TCP	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg
2,4,5-TCP	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg	< 100 ug/Kg
TOC (%)	22.4	1.14	12.6	1.37
Sand (%)	22	93	37	94
Silt (%)	51	3	51	4
Clay (%)	27	4	12	2
Pentachlorophenol ug PCP/Kg OC	--	4,380	5,080	2,190

Sediment Sample Results from Site Evaluation Unit Collection of September 1993.

	Background					
	S-20	S-22	S-22 (DUP)	S-21	S-23	S-24
Total Dioxin Isomers (ug/Kg)	0.630	646.01	562.66	286.49	15.97	19.60
Total Furan Isomers (ug/Kg)	0.070	148.11	110.34	66.07	3.26	5.00
Total Furan + Dioxin Isomers (ug/Kg)	0.700	794.12	673.00	352.56	19.23	24.60
<u>TCDD - EQUIVALENCIES</u>						
Dioxin Isomer EQ (pg TCDD-EQ/g) ppt	1.41	1611	1190	650	28.8	34
Furan Isomer EQ (pg TCDD-EQ/g)	0.92	893	623	333	8.2	14
Total TCDD EQ (pg TCDD-EQ/g)	2.33	2504	1813	983	37	48
* Because of high detection levels, other Wisconsin reference site values used.						
Pentachlorophenol (ug/Kg)	ND (800)	1300	1600	1400	70	ND (800)
Total PAHs (ug/Kg)	1630	2500	2250	3610	2340	440
Endrin (ug/Kg) ¹	ND	ND	7.2	ND	ND	ND
4.4 - DDT ¹	ND	6.9	9.6	ND	ND	ND
Endrin aldehyde ¹	ND	7.8	11.0	9.3	ND	26
pH	6.6	6.9	7.2	7.3	6.7	6.4

¹ See qualifiers associated with analytical results.

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ATTACHMENT 5 (continued)

Sediment Sample Results from Site Evaluation Unit Collection of September 1993.

	Background S-20	S-22	S-22 (DUP)	S-21	S-23	S-24
Arsenic	4.5	1.8	1.7	3.4	2.1	1.7
Cadmium	ND (7.0)	ND (1.3)	ND (1.1)	ND (1.8)	ND (1.7)	ND (4.1)
Chromium	41.5	16.0	14.3	33.7	15.8	7.1
Copper	13.3	13.7	12.8	25.8	13.2	16.9
Lead	20.2	13.3	13.6	46.3	23.8	31.1
Mercury	ND (0.94)	ND (0.20)	ND (0.16)	ND (0.28)	ND (0.24)	ND (0.58)
Nickel	16.4	8.5	9.0	20.9	8.9	ND (7.3)
Zinc	89.6	240*	179*	91.4	53.9	

* Estimated values because of interference.

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ATTACHMENT 5 (continued)
Soil Sample Results from Site Evaluation Unit Collection of September 1993.

ug/kg

	S-11	S-12	S-13	S-14	S-15	S-18	S-19
alpha-BHC	--	7.8	--	--	--	--	--
beta-BHC	4600	730	140	320	69	--	--
delta-BHC	4600	170	--	--	--	--	9.0
gamma-BHC	--	--	--	--	--	--	--
Heptachlor	--	--	11	--	--	--	--
Aldrin	13000	290	--	--	410	--	110
Heptachlor epoxide	--	180	400	160	680	1.4	84
Endosulfan	--	220	370	--	840	--	48
Diieldrin	1800	210	--	--	570	--	--
4,4 ¹ -DDE	--	200	58	480	--	--	--
Endrin	4900	--	--	500	340	--	--
4,4 ¹ -DDD	18000	190	--	390	--	--	--
Endosulfan sulphate	3000	--	--	510	--	--	86
4,4 ¹ -DDT	--	220	200	--	330	--	--
Methoxychlor	--	660	58	--	--	--	--
Endrin Ketone	4400	290	--	--	170	--	--
Endrin Aldehyde	--	190	--	490	--	--	--
alpha-Chlordane	--	150	--	240	--	--	--
gamma-Chlordane	7800	150	--	810	1100	--	--

"--" Indicates not detected.

* See data sheets in Khazae memo of 03/21/94 for qualifiers associated with reported concentrations.

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ATTACHMENT 5 (continued)

Soil Sample Results from Site Evaluation Unit Collection of September 1993.

	S-11	S-12	S-13	S-14	S-15	S-18	S-19
Pentachlorophenol (mg/Kg)	87,000	3,000	1,400	2,300	36	11	N.D.
<u>PAHs (ug/Kg)</u>							
Acenaphthene	N.D.	1,900	1,100	N.D.	N.D.	N.D.	970
Fluorene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	360
Phenanthrene	N.D.	2,100,000	N.D.	N.D.	N.D.	N.D.	690
Fluoranthene	N.D.	1,200	26,000	9,000	11,000	N.D.	22,000
Pyrene	N.D.	6,900	21,000	17,000	19,000	N.D.	16,000
Benzo(a)anthracene	N.D.	770	3,000	N.D.	N.D.	N.D.	2,600
Chrysene	N.D.	2,100	6,800	5,700	6,000	N.D.	6,000
Benzo(b)fluoranthene	N.D.	N.D.	3,000	3,300	2,100	N.D.	2,400
Benzo(k)fluoranthene	N.D.	N.D.	2,500	N.D.	N.D.	N.D.	2,000
Total PAHs (ug/Kg)	N.D.	2,112,870	63,400	35,000	38,100	N.D.	53,020
N-nitrosodi-phenylamine (ug/Kg)	N.D.	42,000	29,000	18,000	N.D.	N.D.	19,000
bis (2-ethyl-hexyl) phthalate (ug/Kg)	N.D.	1,500	800	14,000	N.D.	N.D.	490

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Contaminant of Potential Concern (COPC)

- Pentachlorophenol
- Metabolite, dissociated, and breakdown products of Pentachlorophenol. e.g. At least 32 photolytic or biodegradation products of PCP have been identified:
 - ✓ Tetra-, tri-, and dichlorophenol isomers
 - ✓ Penta-, tetra-, tri-, and dichloroanisoles
 - ✓ Tetrachlorohydroquinone
 - ✓ Tetrachlororesorcinol
 - ✓ Hydroxy quinone
 - ✓ Phenoxyphenol
 - ✓ Diphenyl ether
 - ✓ Pentachlorophenate
- Impurities in manufactured PCP commercial and technical grade product.
 - ✓ Trichlorophenols
 - ✓ 2,3,4,6 Tetrachlorophenols
 - ✓ 2,3,4,5 Tetrachlorophenols
 - ✓ Other chlorophenols
 - ✓ Penta CDF/Ds
 - ✓ Hexa CDF/Ds
 - ✓ Hepta CDF/Ds
 - ✓ Octa CDF/Ds
 - ✓ Hexachlorobenzene
 - ✓ Phenoxyphenols
 - Heptachlorophenoxyphenols
 - Octachlorophenoxyphenols
 - Nonachlorophenoxyphenols

Some of the metabolites and impurities are potentially toxic, mutagenic, or teratogenic. Thorough biological assessment is needed of any biodegraded or photodegraded PCP product to determine if any residual toxicity/teratogenicity remains due (1) intermediate metabolites, or (2) constituents that came from the impurities of the manufactured product.

Several polychlorinated phenols including 2,4,5-TCP, 2,4,6-TCP, 2,3,4,5-Tetra CP, 2,3,4,6-Tetra CP and 2,3,5,6-Tetra CP are toxic to aquatic organisms. The toxicity of technical or commercial grade PCP has been found to be greater than purified PCP.

- Diesel fuel or other petroleum products that may have been used as a carrier for the PCP in the pits used for pole treatments.
- Polycyclic Aromatic Hydrocarbons (PAHs) the relatively high levels of total PAHs in the site soils (35, 38, 53, 63, and 2,112 mg/Kg) may potentially indicate creosote may also have been used as a wood preservative on-site at one time.

Previous sampling indicates that only very low levels of PAHs have been released to the creek. It needs to be evaluated whether the on-land PAHs are from the fuel oil used as the PCP carrier, or from creosote (refined coal tars). Higher levels of PAHs may exist at lower strater in the creek sediments.

- Metals - do not appear to be a problem in sediments on site soils. Some zinc and lead elevations but either QA problems or not believed to be anything but natural variability of site soils and sediments.
- Pesticides - 19 detected in site soils, some at high levels. Only 3 detected in creek sediments at low levels. Generally persistent. If present in sediments, may be in deeper layers.


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CORRESPONDENCE/MEMORANDUM

DATE: February 7, 1990

FILE REF: 3200

TO: Larry Maltbey - NCD

FROM: Bruce Baker - WR/2 SUBJECT: Sediment Quality Criteria for Pentachlorophenol
Related to the Semling-Menke Company Contaminated
Groundwater Inflow to the Wisconsin River

At the request of NCD, the in-place pollutant staff have developed sediment quality criteria for pentachlorophenol. The developed criteria along with procedures and rationale for the criteria are attached. Sediment quality criteria are based on an approach U.S. EPA has developed and is refining that applies an equilibrium partitioning method for deriving criteria for nonpolar hydrophobic organic compounds. Because pentachlorophenol dissociates in natural waters depending on pH, adjustments were made in the partitioning model in an attempt to address for this physicochemical factor.

The sediment quality criteria are based on water quality standards in NR 102 and NR 105, Wisconsin Administrative Code. Assuming no other inputs of contaminants through groundwater inflow, successful remediation of in-place pentachlorophenol in the sediments to the levels of the attached criteria would allow promulgated state surface water standards to be met. Pentachlorophenol levels in the sediments above the calculated criteria could potentially be toxic to benthic organisms that inhabit the sediment pore water or the pentachlorophenol could potentially be released to the overlying water column at concentrations that would exceed surface water quality standards.

Also, attached is applicable literature related to pentachlorophenol characteristics and distribution in the environment.

Remediation of PCP-contaminated river bank sediments should be preceded by the cleanup and/or discontinuation of the contaminated groundwater flow toward the river. Removal of contaminated surficial sediments, bedded sediments and possibly underlying substrata materials and replacement with clean natural materials may need to be considered. A necessary buffer zone needs to be created to ensure PCP in deeper strata and soils does not continue to be transported to the sediment-water interface. The armoring or placement of an impenetrable barrier over the impacted river bottom area either alone or in conjunction with excavation and clean fill replacement is another approach to consider. The armoring of the bottom sediments should provide a more substantial barrier than only riprapping placement to prevent transport and release of PCP from and through the sediments to the overlying water column.

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Attachments

cc: Bill Jaeger - NCD
Kevin Kessler - WR/2

Comments on Approach Taken to
Derive Sediment Quality Criteria
for Pentachlorophenols

Sediment quality criteria were developed for pentachlorophenol (PCP) utilizing an equilibrium partitioning approach (EQP). The approach was developed and is currently under review by U.S. EPA. The approach is based on the established characteristics of organic compounds to partition between an organic solvent and water at a constant ratio. This physicochemical relationship is extrapolated to natural conditions by relating the sorption of organic compounds to sediment particles containing organic carbon present in organic matter.

That portion of the organic chemical compound that is partitioned to the sediment pore water is related to surface water quality criteria. It is assumed that benthic organisms have the same sensitivity to the organic compound as water column organisms used to develop the toxicological data base for water quality criteria. Water quality criteria are used to derive sediment quality criteria in the EQP approach.

The organic carbon partition coefficient value (K_{oc}) for a specific organic compound can be found experimentally or derived from the octanol water partition coefficient values (K_{ow}). The K_{ow} value is a proportionality constant characteristic of a specific compound and can be found in standard chemical references and technical papers. Any K_{oc} and K_{ow} value used needs to be assessed if references report different K_{ow} or K_{oc} values.

U.S. EPA has applied the EQP approach to only neutral, nonpolar hydrophobic compounds. The partitioning of these compounds between sediments and sediment pore waters has been demonstrated to be dependent on the organic carbon content of the sediment, with little or no dependence on or effects by any other physical or chemical factors. Sediment criteria that can be referenced or normalized to one factor such as organic carbon content can apply across a wide variety of sediment types and variable physical and chemical conditions found in the sediment environment.

The EQP approach used to describe the sorption of neutral hydrophobic organic chemicals by natural sorbents is applicable only to a limited degree to organic compounds which dissociate or ionize at natural pH values, unless appropriate considerations are made. Phenolic compounds dissociate based on pH. Chlorinated phenols are hydrophobic weak acids. Because of this characteristic, calculation of water quality criteria for PCP is based on consideration of the natural pH present in surface waters.

The K_{ow} value for PCP in most standard chemical reference text and technical papers is a value of 5.01. This value does not appear to consider the pH - dissociation relationship and assumes a total undissociated PCP concentration in the solution. Predictions of the overall distribution ratios based on simple partitioning of nondissociated species are generally in error. One study that examined the apparent octanol-water partition coefficient of PCP as a function of pH found the following relationships:

Procedures and Values Utilized in Calculating
Sediment Quality Criteria For Pentachlorophenol
in the Wisconsin River; Semling - Menke Co.,
Merrill; Contaminated Groundwater Inflow

1. Water Quality Standards for Pentachlorophenol (PCP) that Apply to the Wisconsin River Based on NR 102 and NR 105, Wis. Adm. Code

- a) Human Threshold Criteria - 840 ug/L
- b) Threshold Concentration Causing Taste and Odor in Water - 30 ug/L
- c) Chronic Toxicity Criteria (CTC)

$$CTC = e^{(V_{(pb)} + \ln CCI)}$$

pH Wisconsin River at Merrill - 7.0

$$CTC = e^{(1.005 \times 7.0 - 4.9779)}$$

$$* CTC = 7.82 \text{ ug/L}$$

* PCP CTC of 7.82 ug/L is the most stringent value, therefore it was used to derive the sediment quality criteria for pentachlorophenol applying the formula in the attached Figure 1.

2. To derive the particle organic carbon normalized partition coefficient (Koc) needed for the formula in Figure 1 to calculate sediment quality criteria, the above discussed Kow value (PCP octanol/water partition coefficient) of Log Kow = 3.32 was used in the following formula (also in Figure 1):

$$\text{Log}_{10} Koc = 0.00028 + 0.983 \text{ Log}_{10} Kow$$

$$= 0.00028 + (0.983) (3.32)$$

$$= 0.00028 + 3.26$$

$$= 3.26028$$

$$Koc = 1821 \text{ liters/Kg OC}$$

3. Insertion of the above Koc value and the Water Quality Standard into the Figure 1 formula are as follows:

Sediment Quality

Criteria	=	WQS	x	Koc
(ug PCP/Kg OC)		(ug/L)		L/Kg OC

Sediment Quality	=	7.82 ug/L	x	1821 L/Kg OC
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Criteria	=	14,240 ug PCP/Kg OC
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4. To derive site specific sediment quality criteria, the 14,240 ug PCP/Kg OC value needs to be multiplied by the concentration of Total Organic Carbon (TOC) found in sediment samples taken from the Wisconsin River in the area that is being impacted by the groundwater inflow that is

contaminated with PCP. The TOC value is the foc component in the Figure 1 formula needed to calculate site specific sediment quality criteria. Analytical results for TOC can be reported as a percent or concentration. Some interrelationships of expressing TOC values are as follows based on an example concentration:

10,000 ppm TOC = 10,000 mg TOC/Kg sediment =

1% of sediments due to particle organic carbon weight fraction =
0.01 kg OC/Kg sediments = foc

5. Applying the formula

Sediment Quality - Criteria = $7.82 \text{ ug/L} \times 1821 \text{ L/Kg} \times \text{foc (Kg OC/Kg sediments)}$

and using a range of foc values that are representative of the TOC concentrations that may be present in the Wisconsin River sediments, the following site specific sediment quality criteria were calculated:

<u>Percent Total Organic Carbon In Sediment Samples</u>	<u>Site Specific Sediment Quality Criteria (ug PCP/Kg Sediment - drv weight)</u>
0.5	71.20
1.0	142.40
2.0	284.80
3.0	427.21
4.0	569.61
5.0	712.01
6.0	854.41
7.0	996.82
8.0	1,139.22
9.0	1,281.60
10.0	1,424.00

PCP analytical results from sediment samples can be directly compared with the sediment quality criteria in the table based on TOC content of the samples. The comparison will determine whether or not the PCP levels in the sediments meet the sediment criteria.

The site specific calculated sediment quality criteria are above the Method Detection Limit of 20 ug/Kg reported by the State Laboratory of Hygiene.

Figure 1.
Formulations and Calculations
Used in Deriving Sediment
Quality Criteria

A. $SQC = WQC \times K_{oc} \times f_{oc}$

where:

SQC = Site specific Sediment Quality Criteria for a pollutant. If the calculated sediment criteria are exceeded, there is a potential for the interstitial water concentration of the pollutant to exceed the Water Quality Criteria. SQC expressed as ug/Kg.

WQC = Water Quality Criteria - can be derived from published aquatic - life water quality criteria or human health criteria documents, or criteria promulgated in regulations or codes (e.g., NR 105, Wis. Adm. Code). U.S. EPA (1988) in developing interim SQC uses chronic water quality values because it protects aquatic life from effects due to long-term exposure to contaminated sediments. WQC expressed as ug/L

K_{oc} = Organic carbon partition coefficient. K_{oc} is a measure of relative sorption potential for organics. K_{oc} indicates the tendency of an organic chemical to be adsorbed and it is largely independent of soil properties.

$$K_{oc} = \frac{\text{mg adsorbed/Kg organic carbon}}{\text{mg dissolved/liter solution}}$$

$$K_{oc} = \text{liters/Kg}$$

For nonpolar organic contaminants, the primary sorbent is the organic carbon on the sediment. The higher the K_{oc} value, the greater the affinity for the nonpolar organic compound to concentrate in organic matter in sediments and in lipid deposits of biota, and the lower the solubility in water.

Where the K_{oc} value is unknown for a compound, the octanol-water partition coefficient can be used as a surrogate to derive a K_{oc} value by use of the following formula. (U.S. EPA, 1986):

$$\text{Log}_{10} (K_{oc}) = 0.00028 + 0.983 \times \text{Log}_{10} (K_{ow})$$

f_{oc} = Fraction of organic carbon found in sediment samples expressed as a decimal. e.g. a Total Organic Carbon test result of 32,000 mg/Kg = 3.2% = 0.032 = 0.032 Kg of C/Kg sediment.

B. To find the interstitial water concentration (IWC_o) of an organic contaminant to compare with the WQC criteria value, with a known sediment concentration and organic carbon percentage, the following can be used (see tables 6-19):

$$IWC_o \text{ (ug/L)} = \frac{\text{Sediment Concentration (ug/Kg)}}{K_{oc} \times f_{oc}}$$

Where the IWC_o exceeds the WQC, the SQC value is also being exceeded.