Sampling Plan for Sediment Toxicity Tests and Chemical Analyses

* Manitowoc River and Kinnickinnic River MGP sites

July 11, 2014

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# Executive Summary

Sediment and water column samples will be collected from the Manitowoc and Kinnickinnic (KK) Rivers for toxicity tests and chemical analyses of contaminants of concern, primarily polycyclic aromatic hydrocarbons (PAHs) and heavy metals that are potentially associated with the manufactured gas plant (MGP) plant operations. Four investigative samples and one reference sediment samples will be collected from each site. For the KK River site, two sediment cores will be collected with two segments from each core; therefore, a total of five samples will be generated. One ambient water sample will be collected from each site. Toxicity tests will be conducted for both sediment and overlying water (or elutriate) after sediment is mixed with ambient water and settled out. The results will be used to support the evaluation of sediment quality guidelines, particularly for PAHs.

# A. Project Organization

This project will implement the routine procedures for Wisconsin Department of Natural Resources (WDNR) sediment assessment work, using internal staff for sample collection for the Manitowoc River site and getting assistance from the US EPA Great Lakes National Program Office. The Wisconsin State Laboratory of Hygiene (WSLH) will also provide support for sampling and conduct toxicity tests and both sediment and water sample analyses.

**WDNR**

WDNR is the principal investigating agency for this sediment sampling. They are responsible for developing the Scope of Work and QAPP as well as the principal client for the final data. WSLH will prepare and finalize toxicity test processes. WDNR staff associated with this project include:

***Person:***  ***Responsibilities:***

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**Laboratory**

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## Problem Definition/Background:

Contamination of sediment related to previous manufactured gas plant (MGP) operations is a statewide concern. A total of twenty eight MGP sites have been identified and under different stages of assessment and remediation.

Similar to other contaminated sediment sites, managing the MGP related sites faces challenges in assessment and remediation due to factors such as heterogeneity of sediment and complex migration pathways of contaminants associated with sediment. Based on the information obtained from sites that have been either remediated or assessed, WDNR sediment management team observed inconsistences in cleanup criteria or remedial action target levels (RATL) from one site to another. At some sites, RATL was based on site specific risk assessment, primarily sediment toxicity test results, in conjunction with chemical concentrations of contaminants of concern. The others used the WDNR consensus based sediment quality guidelines. Proposed or implemented RATL varied from 3.8 ppm at one site to more than 400 ppm of total polycyclic aromatic hydrocarbons (PAHs) at another. In addition, depending on the circumstances, the RATL was sometimes normalized by total organic carbons in sediment.

When sediment toxicity tests were conducted, they varied from one site to another showing impact under different chemical concentrations. In addition, the test organisms varied and test types differed. Some studies tested both *Hyalella azteca* and *Chironomus dilutes*, others just one of the organisms. Most of time, only Hyalella Azteca was tested At both the Manitowoc and KK River sites, toxicity tests have been conducted on sediment. Only one organism, *Hyalella azteca*, was tested and no toxicity tests were conducted on sediment elutriate, which is a concern when sediment is resuspended in the water column potentially impacting aquatic organisms.

The investigator will compile the data and analyze the results and compare to the previous test results. This project is designed to verify if the screening level proposed by WDNR can be used for establishing remedial action level.

This sampling plan and quality assurance and control plan (QA/AC) are prepared for sampling and general description of sample analyses. Laboratory analyses QA/QC is available and can be provided by the State Laboratory of Hygiene.

## Project Objectives

The primary objective of this sampling plan is to conduct sediment toxicity tests and determine contamination levels to support resolving issues related to establishing contaminated sediment remedial action target levels (RATL), particularly at MGP sites. The primary contaminants of concern are polycyclic aromatic hydrocarbons (PAHs) and heavy metals. The goal of the project is to provide information to either support or modify the current PAH sediment quality guidelines. Table 1 summarizes data quality objectives.

Table 1. Data Quality Objectives\*

|  |  |  |  |
| --- | --- | --- | --- |
| **Manitowoc River** (5 grab samples at 5 locations) | | **Kinnickinnic River** (1 grab sample at upstream location and 2 core samples with two segments from each core) | |
| **Tests** | **Objective** | **Test** | **Objectives** |
| Sediment Toxicity with ammonia | Asses impacts of sediment and elutriate (sediment and ambient mixture) samples on mortality, reproduction and growth of multiple species with different levels of contamination. | Sediment Toxicity with ammonia | Asses impacts of sediment and elutriate (sediment and ambient mixture) samples on mortality, reproductivity and growth of multiple species in both surface sediment and deeper sediment with different levels of contamination |
| Sediment and water Chemistry (described in Section B ) | Level of contamination in sediment, ambient and elutriate water for toxicity test and for analyses of potential of impact concentration for the site | Sediment and water Chemistry (details in Table 4) | Level of contamination in sediment, ambient and elutriate water for toxicity test and for analyses of potential of impact concentration for the site |
| Water Depth (Actual & Corrected) | Physical condition that may affect environmental impact of the sediment | Water Depth (Actual & Corrected) | Physical condition that may affect environmental impact of the sediment |
| Physical Descriptions of Samples | Physical condition that may affect environmental impact of the sediment | Physical Descriptions of Samples | Physical condition that may affect environmental impact of the sediment |
| Photographs of Samples | Physical condition that may affect environmental impact of the sediment | Photographs of Samples | Physical condition that may affect environmental impact of the sediment |

\*Note: Sediment/elutriate toxicity tests and ammonia determinations of elutriate/ambient water samples are covered by the WDNR basic agreement (separate funding)

## Project/Task Description and Schedule

A tentative project schedule is provided in Table 2. All personnel listed in Section A should be contacted regarding significant schedule changes.

**Table 2. Tentative Project Schedule**

|  |  |
| --- | --- |
| **Task** | **Completion Date** |
| Sampling Plan and Scope of Work | July 15, 2014 |
| QAPP Development and Approval | July 20, 2014 |
| Sediment Sampling | * July21-23, 2014 for Manitowoc River * September, 2014 for the KK River depending on the EPA’s sampling plan |
| Completion of Sediment Analysis | * September 2014 for samples from the Manitowoc River * January 2015 for samples from the KK River |
| Report Due | March 2015 |

### ***Special Equipment or Supplies***

Not applicable to this project.

### ***Personnel, Special Training Requirements or Certifications***

No special personnel or training are required beyond that required for normal job duties but Boater Safety is required to operate a state boat. Sediment sampling will require the use of the WDNR’s boat and sampling equipment.

Under normal operations, the minimum Personal Protective Equipment (PPE) required to be worn by personnel working on aboard the boat is Modified Level D Protection. Modified Level D Protection includes: boot covers, Personal Floatation Device, safety glasses, and disposable gloves. Modified Level D indicates that no respiratory protection is required. Use of dust protection masks will be optional.

This survey will require PPE suitable for normal operating conditions as described above. The main method to avoid exposure to the contaminants present is to avoid direct contact with skin. Washing hands immediately after sampling will also reduce potential exposures to the contaminants.

The State Laboratory of Hygiene is the principle laboratory for the State of Wisconsin and per manual code, staff are required to use this laboratory if the services are available. The laboratory retains certification through the Wisconsin Laboratory Certification program and through NELAP.

## Documentation and Records

Sample locations will be set up in SWIMS with the relevant locational information and the lab slips will be generated through this application. Through the automated data transmittal process, the analytical chemistry data will be linked to the sample sites to complete the record of analysis. The toxicology report will be submitted directly to Xiaochun and can be provided as PDF and/or word project. The project investigator may keep relevant project information at a local work station. Any documents relevant to evaluating data quality or decision-making for the project will be uploaded to SWIMS.

Separate SWIMS projects have been created for the toxicity testing and the sediment quality assessment to reflect the difference in funding sources.

### ***Field Records***

Field logs and other appropriate documents will be used to record appropriate sample collection information in the field.

Sediment Sample Collection Logs: A sediment sample collection log will be filled out by the field crew for each sample collected. All original field data sheets shall be turned over to the Project Coordinator at the conclusion of the field sampling and shall be kept as part of the permanent project file. A summary of sample collection information shall be maintained for each day of field sampling. Information to be recorded in the field log shall include but not be limited to: sample location ID, latitude/longitude of each sampling location, time of sample collection, water depth. Recording of soft sediment thickness is optional. Pictures of each sediment sample will be taken as records.

### ***Laboratory Records***

The laboratory will maintain records according to the procedures documented in their Quality Assurance Manual following their normal retention schedule. Laboratory chemistry data will be transmitted to DNR through the established data portal and will be available through the Lab portal Intranet and in SWIMS. Toxicity test report will follow the standard reporting convention which includes an assessment of the validity of the test, survival rates, reproduction, and growth for the test organisms (as applicable) and a statistical comparison of the results.

### ***Project File Final Disposition and Record Retention***

This project will follow standard DNR record retention procedures. Project documentation will be stored in SWIMS. Xiaochun Zhang may also retain paper or electronic documents in a working project file.

# B. Measurement/Data Acquisition

## Sampling Design

**Sediment samples**

Sampling Location and Equipment

The sampling locations are selected to provide a general coverage of the project area as well as to target the known highly contaminated area. Multiple grabs from each chosen location will insure adequate sample volume and provide better representation of the sediment quality at the sampling location.

*Manitowoc River*

Sediment samples will be collected from five locations and one of these locations is considered as a reference site. Although the “reference site” will be placed upstream of the known MGP site it does not mean sediment in this location is clean. It is designed to be compared with highly contaminated area. A Ponar or Ekman dredge sampler will be used to collect sediment samples from five locations (including reference site). Figure 1 shows the tentative sampling location from the Manitowoc and Table 3 lists the coordinates of sample locations on the Manitowoc River. Exact location will be determined on site using a GPS (Trimble Geo Explorer 3) that is accurate to at least 3 meters. Selection of exact sampling locations will be dependent upon, but not limited to site characteristics (e.g. depositional areas, physical features, flow patterns) and ability of the sampling team to collect sufficient sample material. Water depth measurements need to be accurate to within one foot.

Table 3. Coordinates for the sample location on the Manitowoc River

|  |  |  |  |
| --- | --- | --- | --- |
| ID | Lat\_Y | Long\_X | Sample type |
| MT2014Tox1 | 44.09575573510 | -87.66601925880 | Grab |
| MT2014Tox2 | 44.09765871090 | -87.66179170420 | Grab |
| MT2014Tox3 | 44.09661068080 | -87.66229192210 | Grab |
| MT2014Tox4 | 44.09689640630 | -87.66494227080 | Grab |
| MT2014Tox5 | 44.09770376340 | -87.66992784080 | Grab |

Multiple grabs at each of the 5 locations will be composited to make up the volume requirement for toxicity test and analyses of chemical and physical parameters. The sampler will be lowered to sediment along side of a sampling boat. These grab samples will be composited and thoroughly mixed. Subsamples then will be placed into appropriate storage jars and buckets for processing in the laboratory.

An ambient water sample will be collected by surface grab to containers as discussed later. The ambient water is needed to make up the elutriate samples in the lab and will be tested for acute toxicity with *Daphnia magna*.

Sampling is scheduled between July 21-23, 2014. Wisconsin DNR and SLH will collect the samples. The DNR will have a boat and sampling equipment prepared. The SLH will provide proper containers and coolers. The coolers will be used for temporary sample storage and transportation of samples for chemical analyses.

*Kinnickinnic River*

The US EPA Great Lakes National Program Office will assist sampling at the KK River site in September, 2014. Tentatively, samples from three locations, including the reference site, will be collected with a Ponar or Ekman dredge sampler. A vibrocorer will be used to collect sediment cores from two locations and the sediment core will be segmented to two sections, 0-1’ and 1’- the end of the core. Figure 2 shows the tentative sampling location and the exact location will be determined on site and Table 4 lists the coordinates of the proposed location. The two cores sites will be split into two samples to represent the surface sediment and subsurface sediment. Therefore, there will be 5 total samples for chemical and toxicological analyses.

Table 4. Coordinates for the sample location on the KK River

|  |  |  |  |
| --- | --- | --- | --- |
| ID | Lat\_Y | Lon\_X | Sample type |
| KK2014Tox1 | 43.00848636340 | -87.90803174500 | Grab |
| KK2014Tox2 | 43.01388632710 | -87.90293529850 | Core |
| KK2014Tox3 | 43.01245446720 | -87.90522475160 | Core |

An ambient water sample will be collected by surface grab to a 5-gallon container from the upstream reference site. Multiple grab samples will be collected to make up the volume needed for analyses.

*Labeling of samples*

The samples will be labeled following a notation of MT2014ToxN (where “MT” stands for the Manitowoc River; “2014” stands for the year the samples are collected; “Tox” stands for toxicity assessment and the numeral “N” stands for site ID. The water sample will be labeled as MT2014Tox1\_W.

Similar labeling approach will be applied to the KK River as KK2014ToxN\_Dstart-Dend (where “KK” stands for the Kinnickinnic River; “2014” stands for the year the samples are collected; “Tox” stands for toxicity assessment and the numeral “N” stands for site ID. Because core samples will be collected from location KK2014Tox2 and 3, following the core numbers the sediment depth will be identified as 0-1 for surface sediment and from 1 foot to the end of the core will be defined as 1-Dend depending on retrieval of sediment core length. Table 5 shows the sample labeling for the KK River. The water sample will be labeled as KK2014Tox1\_W.

Tabke 5. Sample Identification Numbers for the KK River samples

|  |  |  |  |
| --- | --- | --- | --- |
| Sample ID | Lat\_Y | Lon\_X | Sample type |
| KK2014Tox1\_0-1 | 43.00848636340 | -87.90803174500 | Grab sample |
| KK2014Tox2\_0-1 | 43.01388632710 | -87.90293529850 | Surface sediment of the cores |
| KK2014Tox2\_1-Dend | 43.01388632710 | -87.90293529850 | Subsurface sediment of the cores |
| KK2014Tox3\_0-1 | 43.01245446720 | -87.90522475160 | Surface sediment of the cores |
| KK2014Tox3\_1-Dend | 43.01245446720 | -87.90522475160 | Subsurface sediment of the cores |

### ***Field Data Collection***

Three sets of field data will be collected that are critical to the data quality objectives for this project.

*Latitude/Longitude Location*: This data is critical for use in determining where sediment samples were collected. The Global Positioning Systems (DGPS) will be used for ascertaining horizontal locations. The field team will be responsible for checking the satellite signal strength for the GPS system prior to recording this data and for ensuring that the system is recording equivalent horizontal locations. Any problems with signal strength shall be recorded in the field boring log. If problems are noted, the field team should provide a qualitative description of the sampling location utilizing any available, permanent landmarks. The GPS unit will have the accuracy checked prior to sampling activities with an accuracy of 1-3 meters.

*Water Depths:* Water depths will be taken directly over the location of the sampling site prior to sample collection. Water depths will be reported as actual depth measured with 0.5 foot accuracy and report the elevation of sediment-water interface relative to the Lake Michigan Low Water Datum. Daily and possibly hourly water levels recorded at Manitowoc, WI (Station 9087064) and Milwaukee Harbor (Station 9087057) of Lake Michigan can be obtained from the Internet at the NOAA home page for water elevations. The sediment surface depth will be converted to elevation relative to the Low Water Datum of Lake Michigan.

*Photos*: Each sediment sample will be photographed as supplemental information for future sediment quality assessment.

Analytical Parameters

*Sediment*

Samples will be analyzed for grain size distribution, PAHs, TOC, ammonia, cyanide, and selected heavy metals including arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. A final decision on parameters will be made two weeks before sampling starts.

*Water*

Ambient water samples will be analyzed for the parameters of interest as will the elutriate repared from ambient water and sediment. Parameters are similar to that for sediment samples. When sediment is prepared for elutriate toxicity test, after sediment is settled, the overlying water will be decanted for use in toxicity tests and will be analyzed for the same parameters. Phase two toxicity test will result in preparation of additional elutriate for at least one site which will result in the preparation of up to 3 more batches of elutriate which should also have chemistry done on them. A total of approximately 9 elutriate samples (6 initial samples and 3 from secondary preparation) will be analyzed if we also include the lab control elutriate sample. Suspended solids concentration will be analyzed in the elutriate samples as well?

Table 5 lists the analytical parameters for both sediment and water samples. Coordination between WDNR and SLH will finalize the parameters and analytical cost.

Table 6. Analytical Parameters for all Sample Matrix

|  |  |  |  |
| --- | --- | --- | --- |
| **Analytical Parameter** | **Water** | **Sediment** | **Elutriate** |
| PAHs | X | X | X |
| Oil and Grease | X | X |  |
| Ammonia | X | X | X |
| Arsenic | X | X | X |
| Cadmium | X | X | X |
| Chromium | X | X | X |
| Copper | X | X | X |
| Nickel | X | X | X |
| Lead | X | X | X |
| Zinc | X | X | X |
| Cyanide | X | X |  |
| Mercury |  | X |  |
| TOC | X | X | will try for 2 samples if samples volume is sufficient |
| Suspended solids | X |  | X |
| Particle size distribution |  | X | X |

Two types of sediment samples will be collected during this survey; Routine Field Samples (RFS) and Field Duplicates (FD). Each sample type is described below.

*Routine Field Samples (RFS)*: Prepared by collecting a composite grab sediment sample, homogenizing the sediment collected, and filling all required sample jars. Routine field samples will be collected at three (5) locations. Refer to Figure 1 for locations of the RFS.

*Field Duplicates (FD)*: Prepared by filling a second set of sample jars from a composite sediment grab sample after the sample has been homogenized. FDs will be collected at one (1) sampling location from each site MT2014Tox3Dup and KK2014Tox2\_0-1Dup. If budget becomes an issue, no FD will be collected from the KK river site.

*Field Replicates (FR)*: Prepared by collecting a second composite sample adjacent to the designated location, homogenizing the material separately from the RFS and filling the required sample bottles jars. FRs will not be collected for this investigation because the primary purpose of the study is to conduct toxicity tests. The samples for toxicity tests are composite from multiple sampling points at the location already.

### Type and Number of Samples

Table6 summarizes the type and number of samples to be collected during this sampling event. The estimated number of samples does include all RFS and FD samples, that is based on 1 out of 10 samples. Therefore, only one field duplicate sample will be collected. A minimum of 4 gallons of sediment per sample is needed for toxicity tests and 12 oz for chemical analyses.

**Table 7. Summary of type and number of samples to be collected from the KK River\***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample Matrix** | **Estimated Number of Samples1** | **Sample Volume** | **No. of bottle** | **Prep**  **field** | **Analyses/prep in lab** |
| Sediment | 6(including one FD) | 900ml  (quarter glass jar) | 6 | 4oC | Organics: PAHs and TOC |
| Sediment | triplicate samples from one site, then one from the other 4 sites  Total = 3+4=7 | 900ml  (quarter glass jar) | 7 | 4oC | Organics: Oil and grease |
| Sediment | 6(including one FD) | 900ml  (quarter glass jar) | 6 | 4oC | Inorganics: Ammonia, Cyanide, Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, and Zinc / nitric acid after taking aliquot for NH4 and CN |
| Sediment | 5(no FD) | 16 oz., Plastic bag | 5 | 4oC | Particle size distribution |
| Ambient water | 1 | Need 3 liters | 3 1-liter bottles | 4oC | PAHs |
| Ambient water | 1 | Need 250 ml | 1-250mil amber bottle | 4oC | TOC/sulfric |
| Ambient water | triplicates from one site | 3-quart glass jars | 3- quart jars | 4oC | O&G/sulfric |
| Ambient water | 1 | Need 250 ml | 1-250mil amber bottle | 4oC | Ammonia/sulfric |
| Ambient water | 1 | Need 250 ml | 1-250mil plastic bottle |  | Inorganics: Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, and Zinc |
| Ambient water | 1 | Special 250ml metal bottle containing Sodium Hydroxide pellets | 1-250mil metal bottle with NaOH | NaOH | Cyanide |

1- Includes field QA/QC samples and the number of samples per. Elutriate samples will be prepared in the lab and the number of samples is listed in Table 9.

\*All of the data listed in -Table 6 is considered critical to the success of this assessment project.

**Table 8. Summary of type and number of samples to be collected from the Manitowoc River\***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample Matrix** | **Estimated Number of Samples1** | **Sample Volume** | **No. of bottle** | **Prep**  **field** | **Analyses/prep in lab** |
| Sediment | 5(no FD) | 900ml  (quarter glass jar) | 5 | 4oC | Organics: PAHs and TOC |
| Sediment | 5(no FD) | 900ml  (quarter glass jar) | 5 | 4oC | Inorganics: Ammonia, Cyanide, Arsenic, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, and Zinc / nitric acid after taking aliquot for NH4 and CN |
| Sediment | 5(no FD) | 16 oz., Plastic bag | 5 | 4oC | Particle size distribution |
| Ambient water | 1 | Need 3 liters | 3 1-liter bottles | 4oC | PAHs |
| Ambient water | 1 | Need 250 ml | 1-250mil amber bottle | 4oC | TOC/sulfric |
| Ambient water | triplicate samples from one site | Need 3-quart glass jars | 3- qt jars | 4oC | O&G/sulfric |
| Ambient water | 1 | Need 250 ml | 1-250mil amber bottle | 4oC | Ammonia/sulfric |
| Ambient water | 1 | Need 250 ml | 1-250mil plastic bottle | 4oC | Inorganics: Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, and Zinc |
| Ambient water | 1 | 500 ml | 500 ml plastic quart bottle | 4oC | Total suspended solids |
| Ambient water | 1 | Special 250ml metal bottle containing Sodium Hydroxide pellets | 1-250mil metal bottle with NaOH | NaOH | Cyanide |

1- no FD samples for the KK River. Elutriate samples will be prepared in the lab and the number of samples is listed in Table 9.

\*All of the data listed in -Table 6 is considered critical to the success of this assessment project.

**Table 9. Estimated number of samples for chemical analyses for elutriate toxicity tests**

**Manitowoc River KK River**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Acute Test Elutriate sample | Chronic test Elutriate sample Day 0-6 | Chronic test Elutriate sample Day 7-13 | Chronic test Elutriate sample Day 13-21 | Total |  | Sample | Acute Test Elutriate sample | Chronic test Elutriate sample Day 0-6 | Chronic test Elutriate sample Day 7-13 | Chronic test Elutriate sample Day 13-21 | Total |
| 1 | 1 | 1 | 1 | 1 | 4 |  | 1 | 1 | 1 | 1 | 1 | 4 |
| 2 | 1 |  |  |  | 1 |  | 2 | 1 |  |  |  | 1 |
| 3 | 1 |  |  |  | 1 |  | 3 | 0 |  |  |  | 0 |
| 4 | 1 |  |  |  | 1 |  | 4 | 0 |  |  |  | 0 |
| Reference | 1 |  |  |  | 1 |  | Reference | 1 |  |  |  | 1 |
| Lab Control | 1 |  |  |  | 1 |  | Lab Control | 0 |  |  |  | 0 |
| Total | 6 | 1 | 1 | 1 | 9 |  | Total | 3 | 1 | 1 | 1 | 6 |
|  | | | | | |  |  |  |  |  |  |  |

## 

## Sample Handling and Custody Requirements

### Sample Processing

Upon retrieval of the Ponar sampler, the sampler will be carefully opened, transferred to a clean 5 gallon bucket , photographed, a description will be recorded, thoroughly homogenized, and transferred into the appropriate sample containers. Samples will be placed on ice within a cooler for shipment to the laboratory.

### EquipmentDecontamination

Immediately after the samples have been transferred from the Ponar sampler, the equipment will be scrubbed with on-site water, scrubbed with an Alconox/liquinox solution, and followed by a on-site water rinse. In case of heavy tar coating, a clean rag or paper towel may be used to wipe off the oily materials before being washed by the detergent. The sampling team will collect, properly store, and dispose of cleaning rags, paper towel, and golvers generated during the sampling effort. To be preventive, areas with known high contamination will be sampled last. The on-site water wash and rinse will? be disposed of on-site. The alconox/liquinox wash solution will be retained by the sampling team and disposed of properly at the completion of this sampling project.

### Sample Containers

*Note: The analyzing laboratory will supply all required, sample containers equipped with Teflon lined enclosures (for samples that require that), and sample coolers, including a temperature blank with each sample cooler.*

After processing, sediment samples will be placed into the appropriate sample containers as summarized in Table 10. A field sample log shall be filled out for each sampling location.

### Sample Labeling

Each sample bottle shall be individually labeled using a waterproof pen. The label shall contain, but not be limited to, the following information:

1. Unique Sample Number: MT2014Tox1 through MT2014Tox5 for the samples from the Manitowoc River. Because two core samples will be collected from the KK River, two segments will be obtained from each of the cores sampling locations. The labeling will follow the pattern of KK2014ToxX(ZZ-YY) , where X stands for sampling location (1 to 3) and ZZ-YY stands for the beginning and end of a section of the core thickness in feet. Field duplicate shall have a suffix of "Dup" following the numerical sequence of sampling locations.
2. Sample Date (MM-DD-YYYY)
3. Sample Time (HHMM, on a 24-hour clock)
4. Analysis to be performed (e.g. PAHs, As, Cyanide, Lead, etc.)
5. Client: WDNR
6. Project: Manitowoc and KK River Toxicity Tests

**Table 10. Sample Container and Preservation Requirements**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Analyses** | **Container-sediment** | **Container-Water** | **Field - Preservation  Technique** | **Holding  Times** |
| PAHs | 900ml (quarter glass jar) | 1-liter amber bottle | Cool/dark, ≤ 4 o C  7 days/40 days2 | |
| TOC | 250 ml glass amber bottle | Cool/dark, ≤ 4 o C | 7 days/40 days2 |
| Oil and Grease | 900ml (quarter glass jar) | Quarter glass mason jar | Cool/dark, ≤ 4 o C |  |
| Metals1 | 900ml (quarter glass jar) | 250 ml plastic bottle | Cool/dark, ≤ 4 o C | 28 days |
| CN | - | 250 ml metals bottle containing NaOH | Cool/dark, ≤ 4 o C | 28 days |
| Grain Size | 16 oz., Plastic bag |  | Cool/dark, ≤ 4 o C, No head space | No hold time |
| Percent Moisture | Included in organic and inorganic analyses | - | Cool/dark, ≤ 4 o C | 28 days |
| Total suspended solids | - | 500 ml plastic quart bottle | Cool/dark, ≤ 4 o C | 28 days |

1 As, Cd, Cr, Cu, Pb, Hg, Ni, Zn

2 From time of collection to extraction/From time of extraction to analysis

## Analytical Requirements

The laboratory will perform calibration and equipment maintenance in accordance with the SOPs and Quality Assurance Manual for the analytical methodologies (Table 8-9). Tthe Wisconsin State Lab of Hygiene is certified for all these parameters through WI DNR and/or NELAC and follows approved EPA or equivalent methods. All quality control data such as methods, replicate/spike results, detection limits, and control limits are available through the DNR Laboratory Liaison upon request.

## Table 11. Analytical methods for water and sediment samples ( Wisconsin State Lab of Hygiene)

|  |  |  |
| --- | --- | --- |
|  |  |  |
| **Water** | **Procedure ID** | **Procedure Name** |
|  |  |  |
| PAHs | 80642 | PAHS IN WATER -EPA 3510C |
| NH4 | 78922 | AMMONIA, DISS BY LACHAT, PRES |
| TOC | 81017 | TOC IN WATER |
| Oil and Grease | 78876 | OIL GREASE GRAV SPE-LIQUID |
| **Metals** |  |  |
| Digestion | 79524 | METALS DIGESTION FEE |
| Arsenic | 78474 | ARSENIC, TOTAL REC ICP |
| Cadmium | 78576 | CADMIUM, TOTAL REC ICP |
| Chromium | 78608 | CHROMIUM, TOTAL REC ICP |
| Copper | 78632 | COPPER, DISS TOTAL REC ICP |
| Nickel | 78712 | NICKEL, TOTAL REC ICP |
| Lead | 78722 | LEAD, TOTAL REC ICP |
| Zinc | 78850 | ZINC, TOTAL REC ICP |
| TSS | 78347 | SUSPENDED SOLIDS |
| Cyanide | 78898 | CYANIDE, TOTAL IN WATER |
| Subtotal |  |  |
| **Sediment** |  |  |
| PAHs | 80563 | PAH IN SOIL/SED DRY WT |
| NH4 | 78930 | AMMONIA BY LACHAT IN SOLIDS |
| TOC | 80539 | TOC IN SOIL/SED |
| Oil and Grease | 78878 | OIL/GREASE - SOLIDS |
| **Metals** |  |  |
| Digestion | 79524 | METALS DIGESTION FEE |
| Arsenic | 78486 | ARSENIC, SOLID ICP |
| Cadmium | 78588 | CADMIUM, SOLID ICP |
| Chromium | 78620 | CHROMIUM, SOLID ICP |
| Copper | 78634 | COPPER, SOLID ICP |
| Nickel | 78716 | NICKEL, SOLID ICP |
| Lead | 78734 | LEAD, SOLID ICP |
| Zinc | 78854 | ZINC, SOLID ICP |
| Mercury | 79465 | MERCURY IN SOLIDS |
| Particle size distribution | 79453 | %SAND, SILT, CLAY |
| Cyanide | 78904 | CYANIDE TOTAL IN SOLIDS, DRY WT |

## 

## Data Acquisition Requirements (Non-direct Measurements)

Analytical results of PAHs and heavy metals from this project may be compared with data collected previously by others. These samples were collected and analyzed under an approved QAPP and data quality. Surface sediment elevation relative to Lake Michigan Low Water Datum can be derived from the NOAA station in Manitowoc and Milwaukee.

## Quality Control Requirements

### Field

For preliminary assessments or screening level data, field duplicates will be used to assess the homogenization and sub-sampling procedure. A standard deviation of 50% will be accepted. If the results fall out of this range, additional evaluation of the data validity will be carried out and decisions will be made to whether or not the data will be useful for the purpose of this assessment.

### Laboratory

The State Laboratory of Hygiene will perform routine quality control and quality assurance specified within its Quality Assurance Manual. All procedures are documented in writing as SOPs and each SOP includes QC information, which addresses the minimum QC requirements for the procedure. All procedures are available upon request. Examples of some of the QC samples that may be used during this project include:

1. Method blanks
2. Reagent/preparation blanks
3. Instrument blanks
4. Surrogate spikes
5. Laboratory duplicates
6. Matrix Spike/Matrix Spike Duplicate
7. Laboratory control samples
8. Internal standards

## Data Management

See the Documentation and Records portion of the QAPP.

# C. Assessment/Oversight

## Assessments and Response Actions

As part of the data quality assessment, the project manager may contact the laboratory to investigate any results that appear to be anomalous.

Unusual observations of sediment physical characteristics may be investigated for potential cause or source.

## Reports to Management

The report may be shared with sediment remediation project teams on both the Wisconsin Public Service Corp Manitowoc and Solvay Coke MGP sites.

# Data Validation and Usability

For screening level assessments, the project manager uses a data review process. Reports from the laboratory indicate whether there are any quality control issues with the samples. The project manager reviews the data qualifiers to assess their effect on data usability. Results will be reviewed for any potential gross errors (e.g. units errors) or data that might not make sense (e.g. high ammonia concentration but little or no toxicity present in the sample). Holding time exceedance will be considered in data interpretation but not invalidate the data.

Additionally, the WDNR project manager will compare all field and laboratory duplicates for RPD. Based on the results of these comparisons, the WDNR project manager will determine the acceptability of the data. Reconciliation of laboratory and field duplicates shall be the responsibility of the WDNR project manager.

## Reconciliation with User Objectives

All analytical data will be compared and referenced to existing sediment quality guidelines available in the Consensus-Based Sediment Quality Guidelines developed by the Wisconsin DNR.

Sediment toxicity results will be reviewed in context of the results for the chemistry samples and in relationship to one another. If results indicate toxicity beyond what would be expected for sediments in an urban setting or the chemistry data indicate a potential sediment quality problem, the state of sediment quality will be reported to management and to the water quality biologist in the area for evaluation of potential follow up actions.

Figure 1 Sampling Locations on the Manitowoc River

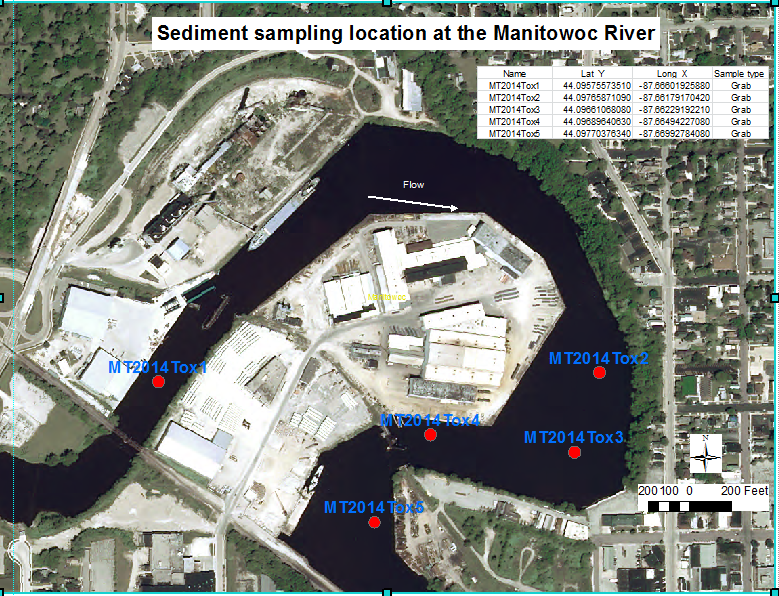


Figure 2. Sampling locations on the KK River

