Enbridge Line 6B MP 608 Pipeline Release

Marshall, Michigan

Sampling and Analysis Plan

Prepared: August 2, 2010

(Revised August 17, 2010 per U.S. E.P.A. August 17, 2010 letter)

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Table of Contents

List of Tables

List of Figures

List of Appendices

List of Acronyms/Definitions

bbd – barrels per day

Company – Enbridge Energy, Limited Partnership

DNAPL – Dense Non-Aqueous Phase Liquid – A liquid with a Specific Gravity > 1.0

DO – Dissolved Oxygen

FOSC – Federal On-Scene Coordinator

LNAPL – Light Non-Aqueous Phase Liquid – A liquid with a Specific Gravity < 1.0

MDNRE – Michigan Department of Natural Resources and Environment

NOAA – National Oceanic and Atmospheric Administration

NRDA – National Resource Damage Assessment

NREPA – Natural Resources and Environmental Protection Act

Oil Saturated Soil – Soils containing free-phase product capable of flowing or migrating as an oil

OSC – On Scene Coordinator

Remediation – Future long term corrective actions beyond those included as an initial response

Response – The initial response to remove and/or abate visible oil and/or sheen that is either currently affecting navigable waterways and/or poses the threat of release of a visible oil and/or sheen to navigable waterways.

RPDIA – Response Plan for Downstream Impacted Areas

SAP – Sampling and Analysis Plan

SAR – Source Area Response Plan

SCAT – Shoreline Cleanup Assessment Technique also known as **SCAT Assessment or SCAT Process** – A systematic approach that uses standard terminology to collect data on impacted areas, support decision-making for cleanup; reference HAZMAT Report No. 2000-1; Office of Response and Restoration, Hazardous Materials Response Division, National Ocean Service, National Oceanic & Atmospheric Administration, Shoreline Assessment Manual – Third Edition, August 2000.

SCAT Team – A team of qualified individuals using SCAT, organized and reporting to the FOSC and comprised of representatives from USEPA as the FOSC, MDNRE (as the SOSC and state NRDA trustee), NOAA or USFWS (as federal NRDA trustees) and Company to assess impacted areas and recommend cleanup methods and priorities. At least one member should have sufficient expertise in wetland and aquatic ecology to evaluate the sensitivity of impacted areas.

SCRIBE – U.S. EPA's database for warehousing environmental data

SOSC – State On-Scene Coordinator

Source Area - The primary locations impacted by the crude oil release, includes Division A (i.e. the wetland area impacted by the release due to overland flow of oil) referred to herein as the Spill Release Area and, Division B (i.e., the portion of Talmadge Creek impacted by the oil spill) referred to herein as the Creek

SAR PLAN – Source Area Response Plan - A work plan describing interim response actions designed to protect navigable waters from the crude oil release

Spill Release Area (Division A) – Area of primary spill release into wetland

Talmadge Creek (Division B) – Initial navigable water body impacted by release

U.S. EPA – Unites States Environmental Protection Agency

U.S. FWS – United States Fish and Wildlife Service

Sampling and Analysis Plan
Marshall Response to Pipeline Release

August 17, 2010

This Sampling and Analysis Plan (SAP) describes the sampling/analysis and quality assurance programs that the Company will adhere to in the short term during realization of the primary objective, which is the removal and/or abatement of visible oil and/or sheen that is either currently affecting navigable waterways and/or poses the threat of release of a visible oil and/or sheen discharge to navigable waterways. It is to be implemented in conjunction with response plans described herein. Changes to the plan should be anticipated to reflect the changing conditions during the response and the information gained as the work progresses.

1.0 Background, Spill Release Area Description, and Location

On July 26, 2010, Enbridge Energy, Limited Partnership ("Company") discovered a release of heavy crude oil (Cold Lake Blend) from Line 6B just west of milepost 608 in the vicinity its pump station located in Marshall, Calhoun County, Michigan (N½ Section 2, T3S, R6W). Line 6B is a 30-inch, 190,000 barrels per day (bpd) line transporting light synthetics, heavy and medium crude oil from Griffith, IN, to Sarnia, Ontario. The location of the release from Line 6B is located in an undeveloped area in the outskirts of town with coordinates of Latitude: 42.2395273, Longitude: -84.9662018. For the purposes of this Plan, the "Spill Release Area" is defined as the location of the pipeline breech that caused the release (Spill Release Area) and the Talmadge Creek. The Spill Release Area has limited vehicle access from Division Drive (approximate address is 16000 Division Drive).

Upon discovery of the release the pipeline was shut down and isolation valves closed, stopping the source of the oil; however, initial estimates are that approximately 19,500 barrels of crude oil may have been released.

The release entered Talmadge Creek and the Kalamazoo River. These waterways are considered to be navigable waters. Approximately 35 miles of the Kalamazoo River have been impacted. Two work plans have been prepared to control the response activities; "Enbridge Line 6B MP 608 Pipeline Release, Marshall, Michigan, *Source Area Response (SAR) Plan,* dated August 2, 2010, revised August 17, 2010 per U.S. EPA August 17, 2010 letter", and "Enbridge Line 6B MP 608 Pipeline Release, Marshall, Michigan, *Response Plan for Downstream Impacted Area (RPDIA)*, revised August 17, 2010 per U.S. EPA August 17, 2010 letter". The SAR has been ordered by the FOSC to control the response activities from the Spill Release Area along Talmadge Creek downstream to the confluence with the Kalamazoo River. The RPDIA has been ordered by the FOSC to control the response activities from the confluence of Talmadge Creek and the Kalamazoo River to the limit of the impact. These impacted areas have been divided into Divisions for cleanup operations and sampling described as follows:

- Division A – the Spill Release Area (to the constructed Flume where the release entered Talmadge Creek);
- Division B - Talmadge Creek from the Flume site to the confluence with the Kalamazoo River);

- Division C – The confluence of the Talmadge Creek and the Kalamazoo River to the Angell Street Bridge;
- Division D – Angell Street Bridge to the Kalamazoo County line; and
- Division E – Kalamazoo County Line to Morrow Lake Dam.

Copies of the SAR and RPDIA are available upon request.

The Company recognizes the health issues associated with spill contact and has published a notice explaining a suggested evacuation area and is also furnishing temporary housing for concerned residents.

Access to the Spill Release Area is now restricted by a fence and twenty-four hour security. Access to surface water is being limited by security control measures at crossings, signs, and fencing at river access points. These measures address unauthorized access to the impacted areas where practicable.

1.1 Spill Release Area Description and Location

The Spill Release Area is an approximate 5-acre parcel adjacent to the pipeline release location. (Figures 1, 2, and 3). The majority of the Spill Release Area is within a wetland adjacent to Talmadge Creek. Vegetation consists of herbaceous emergent wetland plants in low lying areas, as well as brush and trees in upland areas. Approximately five acres have been impacted by overland flow of oil in the Spill Release Area.

1.2 Area Physical Features

The surficial deposits in the area of the Spill Release Area consist of glacial outwash sand and gravel as well as post-glacial alluvium with occasional thin clay lenses. The glacial deposits in areas of the Spill Release Area are generally underlain by the Mississippian Marshall Sandstone and Coldwater Shale in Calhoun County and Coldwater Shale in Kalamazoo County, MI. The bedrock surface was mapped at 50-feet below ground surface (bgs) in much of Calhoun County and up to 200 feet in Kalamazoo County based on the State of Michigan Department of Conservation, Geological Survey Division, Drift Thickness Map, 1938.

Most of the Spill Release Area can be characterized as rural, including undeveloped and agricultural areas. The Spill Release Area and impacted sections of Talmadge Creek (Tributary) and the Kalamazoo River also include villages and cities, including developed areas.

1.3 Adaptive Management

Throughout this plan there are various forward looking statements or content, as well as, associated text that may indicate specific details may need to be worked out with relevant agencies as work progresses. It is understood that the FOSC will provide sufficient technical staff to facilitate supplementing or changing parts of the response plan (e.g., changes in sampling locations and frequencies) and strategies as such situations arise, and will work with the Company to review and approve alterations.

1.4 General Scope of SAP

The SAP will address the primary objective of the response activities in the Spill Release Area and Talmadge Creek, (collectively the Source Area), and the Downstream Impacted Area (Kalamazoo River to Morrow Lake) that are outlined in the *Source Area Response* (SAR) Plan and Response Plan for Downstream Area *(RPDIA)*. The primary objectives include: 1) removal of free phase crude oil and heavily impacted crude oil media (oil saturated soil and vegetation) from the overall Source Area; and 2) to removal and/or abatement of visible oil and/or sheen that is either currently affecting navigable water ways and/or poses a threat of a release of visible oil or sheen discharge to navigable waterways.

Within five days of an approved SAP, the Company will engage the Michigan Department of Natural Resources and Environment (MDNRE) and other agencies that may have jurisdiction over future remedial actions regarding the post-SAR and RPDIA activities consistent with Part 201 (Environmental Remediation) of the Natural Resources and Environmental Protection Act (NREPA)(1994 PA 451), as amended.

2.0 Current Conditions

The Company has mobilized to the Spill Release Area the following resources in the support of sample collection, analysis, data validation, and reporting:

- Air monitoring and data management professionals.
- Surface water, potable water, and sediment collection and data reporting professionals.
- Onsite area chemists and a mobile laboratory for on-going analytical services for rapid assessment purposes.

To date, the Company has collected the following types of discrete samples in the appropriate sample containers:

- crude oil;
- sediment;
- soil;
- groundwater (private wells and seeps);
- surface water;
- air; and,
- waste characterization.

The analytical results reflect both on-site laboratory screening samples as well as off-site laboratory analyses.

To date, the following key response actions have been completed:

- **Security:** Access to the Source Area is restricted by fencing and twenty-four hour security. Access to surface water is being limited by security control measures at crossings, signs, and fencing at creek access points. These measures address unauthorized access to the source areas.

- **Temporary Access Road:** An access road, primarily timber mats, was constructed to the site from Division Drive. Safety turn-around areas were created and grading of the site has been completed to allow for heavy equipment traffic related to response activities and pipeline repair. Timber mat access roads are also being constructed adjacent to Talmadge Creek.

- **Site Clearing and Grubbing:** Clearing and grubbing of site trees and vegetation has been performed as necessary to allow construction of access roads and removal of soils impacted by the overland flow of oil. The trees and brush will be chipped and the material mixed with excavated soil for offsite disposal.

- **Shallow Soil Excavation:** Shallow soil in the Spill Release Area (primarily peat) impacted by the overland flow of crude oil is being excavated and staged for offsite disposal. The objective associated with shallow soil excavation is to prevent further migration of oil to surface water. Spill Release Area excavation activities involve the use of a long reach backhoe staged on the access road to remove the top 6-inches to 1-foot of impacted soil/peat material. The material is direct loaded into off-road trucks and transported to the staging area where it is allowed to dewater prior to disposal. Talmadge Creek area excavation (i.e., along the banks of the Talmadge Creek) involve removal of primarily oil impacted vegetation and shallow soil/root zone material as described in the Shoreline Cleanup Assessment Technique (SCAT) Plan for Talmadge Creek. At the time this document was prepared, approximately 80 percent of the Spill Release Area excavation has been completed and 25 percent of Talmadge Creek area has been mechanically cleaned.

- **Staging Area Construction:** An approximate 2.3 acre staging area was constructed at the boundary of the exclusion zone to the north of the Spill Release Area. The staging area was constructed using Class 5 gravel to allow heavy equipment access and minimize erosion. Silt fencing and other stormwater control measures were implemented as needed. Material from the Spill Release Area and Talmadge Creek is currently being transported to the main staging area using off-road trucks.

- **Berms:** Three temporary soil berms have been constructed to remove the migration pathway for crude oil from the Spill Release Area to Talmadge Creek. The basic design of the temporary soil berms is an elongated earthen mound used to prevent the flow of water and oil. Clean on-site soils and clean granular soils were used to construct the berms. The length and height of the berms correspond with the volume of flow and drainage area required to be controlled in the Spill Release Area. All berm heights are less than five feet from the toe of the berm to the upstream bottom elevation. This berm height will ensure that the berms are not considered "dams" under Part 315 Dam Safety, of the Natural Resources and Environment Protection Act (NREPA), 1994 PA 451, as amended. As of July 30, 2010, flow of crude oil to Talmadge Creek from the Spill Release Area has not been observed.

- **Flumes:** Numerous flumes (i.e., underflow weirs) were constructed downgradient of the Spill Release Area to minimize further migration of crude oil. The basic design of a flume is a pipe, or series of pipes, that extend through a temporary flow control structure such as a berm or dam. For a crude oil release to surface water, the pipe intakes are submerged on the upstream side of the berm to allow oil-free water to flow through the pipe. This prevents the crude oil floating on top of the water from migrating further downstream. Crude oil pools on the upstream side of the berm or dam and is captured and containerized using sorbent booms, pads and vacuum trucks.

- **Oil and Water Containment and Recovery:** Oil containment and recovery operations using flumes, berms and vacuum trucks in the Source Area (i.e., from both the Spill Release Area and Talmadge Creek). Recovered oil is being reclaimed at the Company's Griffith, Indiana oil storage terminal and wastewater is being treated on-site and disposed of at the Battle Creek Publicly Owned Treatment Works (POTW).

- **Initial Receptor Survey:** An initial receptor survey was implemented and will be updated during post response activities to effectively identify potential migration pathways and potential receptors within the Source Area. The receptor survey is conducted to identify the presence and location of surface waters, water wells and surface water intakes which could be impacted by the crude oil release.

- **Federal and State Approvals:** The Company has coordinated efforts with all Federal and State level environmental stakeholders identified at the site including:

    - U.S. EPA, U.S. Fish and Wildlife Service (USFWS);
    - Michigan Department of Natural Resources and Environment (MDNRE);
    - U.S. Coast Guard;
    - Michigan Department of Agriculture (MDA);
    - Michigan Department of Community Health (MDCH);
    - Calhoun County Public Health Department (CCPHD);
    - Kalamazoo County Health and Community Services Department (KCHCSD);

- A Joint Permit Application to MDNRE and USACE for Part 303/301 and Part 31 has been submitted for general permit activities within the Spill Release Area with the SAR under a separate cover.

3.0 Project Organization

This plan describes the duties and responsibilities of the Company and its Contractors. This section provides information on project organization for the project. The project organization and the responsibilities of key personnel are defined in subsequent sections. Figure 1-1 presents the program lines of authority and the project organization.

3.1 Federal On-Scene Coordinator

Federal On-Scene Coordinator (FOSC) has regulatory oversight responsibilities for the development and approval of the documents and reports for this project. The responsibilities of FOSC include, but are not limited to, the following:

- Schedule meetings, if necessary, between agencies, and representatives of the Company;
- Review and approve proposed schedules; and,
- Review and approve documents and reports.

3.2 Company Environmental Unit Leader

Robert Steede, Enbridge Energy, Limited Partnership

The Company Environmental Unit Leader (EUL) is responsible for implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The EUL will comprise a rotation of project managers who will provide continuous management activities. The EUL will report to the U.S. EPA FOSC. All communication and reporting will be conducted through the EUL. The EUL's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The EUL will:

- Oversee project objectives and develop a detailed work schedule;
- Establish project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task;
- Acquire and apply technical and corporate resources as needed to ensure performance within schedule constraints;
- Orient all field leaders and support staff concerning the project's special considerations;
- Monitor and direct the field leaders;
- Develop and meet ongoing project and/or task staffing requirements, including mechanisms to review and evaluate each task product;

- Review the work performed on each task to ensure its quality, responsiveness, and timeliness;
- Review and analyze overall task performance with respect to planned requirements and authorizations;
- Approve all reports (deliverables) before their submission to FOSC;
- Ultimately be responsible for the preparation and quality of interim and final reports; and.
- Represent the project team at meetings and public hearing.

3.3 Sampling and Analysis Manager

The Sampling and Analysis Manager (SAM) is responsible for establishing project scope and objectives and for communicating to the project team. The SAM is also responsible for identifying internal, regulatory, and procedural requirements pertinent to the work that may differ from accepted industry standards of work. The SAM is responsible for assuring that projects are properly staffed and is ultimately responsible for the technical direction and quality of the work. He is responsible for establishing appropriate budgets and schedules, making available appropriate forms or equivalent of training, and monitoring the performance of the staff. The SAM may talk with regulatory agencies regarding methodologies and requirements. He is also responsible for monitoring the implementation of the quality assurance program.

Specific responsibilities include:

- Assure the provision of necessary resources including personnel, facilities, and equipment;
- Review and approve standard operating procedures and other project documents;
- Monitoring offsite area and onsite area laboratories for proper turnaround times;
- Support the efforts of the Field Manager, Quality Assurance Officers (QAO), and Data Manager(s) in all matters concerning the quality of work products;
- Assure effective response to corrective action requirements identified by any member of the project team of staff;
- Plan the activities of and ensure proper equipment, personnel, and subcontractor resources are allocated;
- Provide a liaison between the client, field, laboratory staff, and any other subcontractors;
- Effectively carry out the QA Program and this SAP; and,
- Assure completion of corrective actions, as needed.

3.4 Quality Assurance Officer (QAO)

The Quality Assurance Offer (QAO) is responsible for implementation of the QAPP in both field and laboratory operations. The QAO reports to the EUL and has the authority to take any actions necessary to ensure the reliability and validity of work and deliverables according to the QAPP. The QAO is responsible for developing and implementing procedures to appropriately document all project activities, to provide specific means of measuring conformance to specifications, to manage the corrective actions program, and to provide periodic reports to management. Specific responsibilities include:

- Develop, document, and carry out QA activities to ensure that appropriate Quality Control (QC) measures are being carried out and documented:
- Ensure all records related to quality assurance are documented and maintained securely and retrievably;
- Conduct periodic performance audits and/or surveillances to measure conformance to specifications;
- Prepare periodic quality reports and QA sections of final reports;
- Ensure corrective actions are carried out and documented in a way that precludes future occurrences;
- Review and approve SOPs, training records, and purchasing actions; and,
- Acquire and maintain required certifications and manage performance evaluation tests.

3.5 Field Manager

The Field Manager is responsible for implementing the SAP. The Field Manager's responsibilities include:

- Overseeing field equipment calibration, sample collection teams, field documentation, submission of samples to laboratories, and preparation of a summary report;
- Leading and coordinating the day-to-day activities of the various sample teams under their supervision;
- Implementing QC for technical data provided by the field staff including field measurement data;
- Schedule compliance, and adherence to management-developed study requirements; and,
- Identifying problems at the field team level, resolving difficulties in consultation with the SAM, implementing and documenting corrective action procedures, and provision of communication between team and upper management.

3.6 Sample/Technical Manager

The Sample/Technical Manager will be responsible for all sample collection and processing to the project organization in accordance with the QAPP. These tasks include:

- Development of the laboratory SOW;
- Procurement of laboratory services;
- Daily communication with the laboratory;
- Process samples for laboratory submittal;
- Address any chain-of-custody discrepancies or laboratory QA/QC anomalies; and,
- Logistically support Operations in the collection of samples.

3.7 Data Manager

The Data Manager is responsible for all data reporting, quality checking and reporting to the project organization in accordance with the QAPP. These tasks include:

- Receiving analytical data; checking for completeness, and making sure that appropriate QA checks have been performed;
- Performing summary validation on all samples not assigned for full validation;
- Assigning 10% of Level IV data packages for full data validation by the third party data validator;
- Entering and maintenance of sample location data;
- Entering data into databases, including US.EPA's SCRIBE system; and,
- Maintenance of appropriate security measures to ensure data integrity.

3.8 Third Party Data Validator

The Third Party Data Validator is independent from the collection of samples and will be performed by an entity not otherwise involved with the project. Level IV data packages will be provided to allow full validation of results. Full validation will be conducted on 10% of chemistry samples. Summary validation will occur on remaining samples, unless significant issues are identified on full validation.

4.0 Overview of Sampling Activities

Sampling activities will be conducted to address surface water, groundwater, sediment, and soil impacts. Background samples will be collected from all media to distinguish between pollutants related to this incident and historical conditions. The data obtained from all sampling, along with any significant field observations from the collection points (e.g., sheen, odor, etc) will be summarized and provided daily to Operations. Data and observations will be evaluated regularly during the operational period to determine if the level of effort is appropriate. A summary of information and discussions with the state and federal regulatory agencies, as appropriate, will be conducted as needed to increase or decrease the scope, including sample location, sample frequency and analyte list. All plan modifications will be approved by the FOSC and the appropriate agencies.

4.1 Data Quality Objectives

The primary objective of the environmental sampling program is to assess the natural resources and ecosystems along the potentially-affected waterways (e.g., Talmadge Creek, Kalamazoo River, and Morrow Lake) and the source/spill area for the presence, or threat of release, of visible oil and/or sheen to navigable waterways. The secondary goal is to obtain sufficient data to support a comparison of the water and sediment quality to appropriate regulatory benchmarks.

The Data Quality Objectives (DQOs) include both qualitative and quantitative descriptions for endpoint determinations. Qualitatively, for example, sediments in must be able to be disturbed at regular intervals (e.g., 50') from the Spill Release Area through the affected waterways of Talmadge Creek and in the immediate vicinity of the Spill Release Area using a rod, stick, or similar implement without producing visible oil and/or sheen, especially from high sediment depositional areas. Surface water will be continuously monitored for presence of crude oil constituents at multiple locations using remote, telemeting water quality sensors. For qualitatively evaluating visible oil and/or sheen along the Talmadge Creek banks, the primary method utilized will be the petroleum sheen test, because of the reliability and consistency of the results and the speed with which the test can be conducted. The petroleum sheen test consists of mixing a small aliquot of soil with deionized water in a glass sample container and noting if any sheen is present. Soil with a rainbow sheen is considered impacted with free-phase product. The petroleum sheen test is conducted to direct excavation activities after initial excavation of soil with visible free-phase impacts are completed. Quantitatively, the qualitative "results" of the sediment and surface water visual and water quality monitoring evaluation must be able to be confirmed by submitting an appropriate number of representative sediment and surface water (e.g., ¼-mile and 1-mile sample intervals, respectively) along the Talmadge Creek for confirmatory analysis.

In keeping with the objective of protection of public health, during the oil/sheen removal process, community air monitoring activities described in the Air Sampling and Monitoring Plan (Appendix A) will continue. As described in Section 5 therein, if community air monitoring reveals real-time benzene detections above 200 ppb, confirmation testing involving grab analytical air samples will be obtained to determine if levels in areas where community members may be exposed exceed 60 ppb. If levels in excess of 60 ppb are documented with analytical grab sampling, longer-term sampling (8 – 24 hours) will be performed. Results of these tests will be reviewed by the Public Health Unit for evaluation of actions, if any, that should be taken to address community exposure concerns. The health-based benchmark for longer-term community exposure levels is the Agency for Toxic Substances and Disease Registry's Intermediate Minimal Risk Level for benzene of 6 ppb.

4.2 Objectives, Endpoints & Metrics

The objective of this Sampling and Analysis Plan (SAP) is to evaluate and identify visible oil and or sheen that is either currently affecting navigable water ways and/or poses the threat of release of a visible oil or sheen discharge to navigable waterways. This objective will be accomplished by meeting the target endpoints for each shoreline type described below. The endpoints are based on visual field screening for the presence of materials capable of producing a release of oil or sheen to navigable water. Visual screening does not include soil that exhibits a petroleum odor and/or organic headspace. These residual impacts will be addressed as part of the long-term assessment and remediation efforts for the site.

4.2.1 Riparian Zones and Stream Banks

1. Shorelines no longer release sheens that affect navigable waterways.
2. Oil no longer rubs off on contact.
3. Oil removal to the point where recovery/re-colonization can occur without causing more harm than leaving the oil in place. Heavy oil generally weathers to a dry coat within weeks.

4.2.2 Soil, Sand and Gravel

1. Oil is no longer visible on surface.
2. No oil layers in test pits dug by inspection teams.
3. No longer release sheens that affect navigable waterways.

4.2.3 Man-made structures

1. Structure no longer generates liquid oil or sheen.
2. Oil no longer rubs off on contact.

Metric	Marshes	Soil, Sand and Gravel	Man-made Structures
Sheens no longer released to waterways	X	X	X
Oil no longer visible on surface or in test pits dug for observation purposes		X	X
Oil no longer rubs off on contact	X		X
Recovery/recolonization can occur without harm to incoming flora and fauna	X		

4.3 Surface Water Sampling

4.3.1 Overview and Rationale

This section of the SAP describes the specific surface water sampling and monitoring procedures to be utilized and implemented during response actions to remove visible oil and/or sheen that may affect navigable water ways or pose a threat of release of a visible oil or sheen discharge to navigable waterways.

4.3.2 Location and Frequency

Surface water samples will be collected where and as frequent as necessary, to assess the affect of visible oil and/or sheen to navigable water ways. The scope and frequency of the sampling may increase, as needed, based on an evaluation of the data as it is produced; or in response to "wet" weather conditions (i.e., ½-inch over a 24-hour period). It is initially anticipated that surface water sampling will be conducted twice per week, however, "wet" weather may require an increased frequency to ensure that the visible oil/sheen is contained, and does not exacerbate the extent of impact.

Surface water sampling, when scheduled, will be conducted in conjunction with sediment sampling at an initial spatial distribution of approximately one sample every two river miles starting from the Spill Release Area and heading downstream. Original sample locations will be retained and supplemented, as needed, with additional locations, which will be selected to be representative of surface water quality and for accessibility and distribution. At the request of the Kalamazoo County Health Department, additional samples will be collected at the following locations:

- Upstream on the Kalamazoo River at 23 Mile Road;
- 35th Street in Galesburg;
- River Street in Comstock;
- D Avenue in Kalamazoo;
- Downstream of Morrow Lake at M-89 in Allegan,
- M-96 Bridge in Augusta,
- H Avenue in Kalamazoo Township,
- Star Road in Plainwell,
- North Street in Otsego,
- Swan Creek and M-89,
- Kalamazoo Lake at Washington Street.

In addition to the defined areas listed above, surface water samples will be collected at sediment deposition areas along the affected waterway as they are identified and/or determined to be relevant.

Qualitative determinations of oil content of samples will be made with respect LNAPL/DNAPL characteristics. Oil and/or sheens observed floating on the surface will automatically be classified as LNAPL. With respect to soil and/or sediment samples, a representative sample, (not to exceed 1:4 volumetrically) of the subject matrix will be placed in a clear glass jar, and the jar filled with water. LNAPLs will be observed floating on the surface of the water. Non-floating oils will be classified as DNAPLs.

Surface water and subsurface water (i.e., water column) samples will be collected at each sample location to establish concentration changes with depth over time and to assure that no visible oil [light non-aqueous phase liquids (LNAPL) or dense non-aqueous phase liquids (DNAPL)] or sheen is present within the water column. For sample locations with a total river depth of six feet or less, two samples will be collected and submitted for laboratory analysis: surface and immediately above the bottom. For sample locations with a total river depth greater than six feet, three samples will be collected and submitted for laboratory analysis: surface, middle, and bottom. Additional, targeted, surface or water column sampling locations will be implemented at the request of the FOSC.

Surface water and column samples will be collected in accordance with the methods outlined in the appended SOPs (SOP-4). Sample locations are presented on Figures 3-7, by operational division (e.g., A, B, C, D, and E).

4.3.3 Surface Water Monitoring and Analysis

Water quality parameters (DO, Turbidity, temperature, pH, and conductivity) will be measured in the field at every sample location. Physical conditions such as water depth and velocity will be measured; visual observations, (including aquatic vegetation and the presence of sheen, and presence of oil/tar-like flecks) will be made at each surface water sampling location and electronically noted using a hand-held data collection device or recorded in a log dedicated to this project in accordance with SOP-4. Samples will be collected and submitted for laboratory analysis as indicated in Table 4.1.

Table 4.1 Surface water parameters, methods, and container types

Parameter	Method	Container Number, Size, and Type	Sample Preservatives
Volatile organic compounds (VOC)	EPA 8260B	3 x 40 ml VOA vials	Hydrochloric acid (HCl) to pH < 2; ice
Semi-volatile organic compounds (SVOC)	EPA 8270A	2 x 1 L Amber glass	Ice
Total Petroleum Hydrocarbons (TPH), diesel range organics TPH (DRO), oil range organics TPH (ORO)	EPA 8015B	1 x 1 L Amber glass	Ice
Gas range organics TPH (GRO)	EPA 8015B	2 x 40 mL VOA vials	HCl to pH < 2; ice
Michigan Metals: (Sb, As, Ba, Be, Cd, Cr, Hg, Cu, Co, Fe, Pb, Mn, Mo, Ni, Se, Ag, Tl, Va, and Zn)	EPA 6010 EPA 7470 (Hg)	1 x 150 mL HDPE bottle	Nitric Acid (HNO3) to pH < 2; ice
Polychlorinated biphenyls (PCBs)	EPA 8082	1 x 1 L Amber glass	Ice
Total Organic Carbon (TOC)	EPA 415.3	1 x 1 L Amber glass	Ice
Specific Gravity	NA		
Total Suspended Solids	2540D		
Hardness	EPA 130.1		

The Company has additionally established a protocol for monitoring visible oil and/or sheen on Morrow Lake and at other locations downstream of the Spill Release consisting of the deployment of direct reading instruments and daily inspections of surface water quality from multiple boats and coordinated over flights.

In order to determine that water quality (as qualitatively measured by the presence of visible oil and/or sheen) is maintained for the duration of response activities upstream, continuous monitoring of various downstream locations, including four to six locations within Morrow Lake, will be conducted. The non-Morrow Lake downstream locations will be selected with concurrence of the FOSC and are anticipated to include at a minimum six additional locations. In order to determine that water quality is maintained for the duration of response activities upstream, Company, under the procedures proposed herein, proposes to conduct continuous monitoring at and routine sampling of Morrow Lake.

Water quality parameters of Morrow Lake will be continuously collected at two established locations using a Eureka Environmental Manta 2 multi-parameter water quality real-time monitor. The data collected will be electronically logged on 15 minute intervals and will include:

- Temperature (oC)
- pH (0-14 standard units)
- Conductivity (Siemens/meter)
- Dissolved Oxygen (milligrams/liter)
- Turbidity (NTU)
- Crude Oil/Oil and Grease (parts per billion)

Continuous, remote monitoring of water quality parameters with satellite telemetry of data to a database accessible by various stakeholders including Company personnel and federal and state regulators will be performed. The water quality meters will be calibrated in accordance with manufacturer's specifications and set to alert (via text and/or email) appropriate individuals should surface water quality parameters fall outside specified ranges (i.e., "actionable" values). Proposed actionable values are presented in Table 4.2. Please refer to the appendix to the SOPs for product information on Eureka Environmental Manta 2 multi-parameter water quality real-time monitor.

Table 4.2 Proposed Actionable Values

Parameter	Proposed Actionable Value	Units
Temperature	--	--
pH	6.5 < x > 9.0	Standard Units
Conductivity	--	Siemens/m
Dissolved Oxygen	5.0	mg/L
Turbidity	300 or 30% greater than background, whichever is greater	NTUs
Crude Oil	Instrument detection Level (i.e., any detection)	ppb

In the event that an alert is received, the results will be confirmed using a hand-held, properly calibrated multi-parameter water quality meter. A re-evaluation of the controls and containment measures deployed upstream of the alarming water quality meter would occur in the event of a confirmed reading.

To demonstrate acceptability of data obtained by the remote surface water monitoring units, discrete confirmation samples will be collected and submitted for laboratory analyses. It is anticipated that initial samples will be collected daily from locations immediately adjacent to the water quality monitoring units and the results expedited; however, as the initial analytical results are reviewed, is anticipated that sampling frequency, sample turn around, and/or sample locations may be revised with concurrence of the FOSC. Samples will be submitted for analysis of parameters identified in Table 4.1 above. Sampling will be documented in field notebooks and/or with hand-held data collectors in accordance with Sample Handling Procedures outlined in the attached SOPs. A map of current established sampling locations is available in the attached Figures. The FOSC will be consulted if deviations are made to the above-described protocols noted above.

In addition to the water quality meters in Morrow Lake, water column sampling will be collected at two grid nodes approximately one-third of the distance from the east and west ends of the lake on the long axis. Buoys will be placed at those locations and logged by GPS. This will aid in replicability of the sampling locations if the buoys are damaged or moved. These sample points will be accessed and column sampling (surface, mid depth, and bottom) will be conducted on a twice weekly basis, as per the analysis outlined below. The Company will adjust the number, analyses and frequency of sampling based on the results of the analyzed samples, in conjunction with the FOSC.

Field sampling will be carried out according to SOP-4 which is appended to this Plan. Surface water sample parameters are presented on Table 4.1.

4.4 Sediment Sampling

4.4.1 Overview and Rationale

Sediment sampling will provide a base-line evaluation of the current conditions as well as confirm the presence or absence crude oil impacts. Sediment samples will be collected using hand-operated equipment in accordance with SOP-4.

4.4.2 Location and Frequency

Sediment samples will be collected at a minimum once weekly from Talmadge Creek, the Kalamazoo River, Morrow Lake, Wenke Park, immediately upstream of Ceresco Dam, M-96 Bridge in Augusta, and various background locations (e.g., several locations upstream of the Spill Release Area on Talmadge Creek and the Kalamazoo River). The specific locations will be selected in the field based on topography, erosion features, water depth, water velocity, and other indicators of sediment deposition. Conceptually, the spatial distribution of sediment sample locations is anticipated to be approximately every 2 miles from the Spill Release Area to Morrow Lake; however, in actuality, an assessment of the features of the affected waterways and location of sediment deposition will determine the actual sediment sample locations. In areas of low potential for sediment deposition (i.e., straight, narrow, and/or swiftly moving waterways) sediment samples will be collected from the surface sediments to 2 inches in depth. At locations with a high potential for sediment deposition (i.e., meandering, broad, and/or slowly moving waterways) sediment samples will be collected from the surface sediments to 6 inches in depth to assess the potential for dense non-aqueous phase liquids (DNAPL) impacts.

In the affected waterway immediately upstream of the Ceresco Dam, the initial sediment deposition at the confluence of Morrow Lake, and any other locations of obvious sediment deposition between the Spill Release Area and Morrow Lake, representative sediment samples, consisting of transect and/or grid samples, will be collected. The transect and/or grid sample distribution/interval will be determined following the qualitative assessment of the Kalamazoo River and Morrow Lake sediments, as described in the RPDIA, Sections 4.1.1 and 4.1.2, respectively, dated August 2, 2010, revised August 15, 2010 and submitted for the FOSC approval.

Results will be evaluated upon receipt of analytical results and further actions (e.g., increasing or decreasing sample locations) will be made with concurrence of the FOSC.

Coordinates at sediment sample locations will be recorded to allow subsequent sampling from the same location to establish concentration changes over time. Sediment samples will be collected from the fine sediment column in accordance with SOP-4.

4.4.3 Sediment Analysis

Collected samples will be transported to a fixed-base laboratory and analyzed as indicated in Table 4.3. Excess material generated during sampling will managed in accordance with Section 2.3 of the Waste Treatment, Transportation, Disposal Plan (WTTP).

Table 4.3 Sediment parameters, methods, and container types

Parameter	Method	Container Number, Size, and Type	Sample Preservatives
Volatile organic compounds (VOC)*	EPA 8260B	3 x 4 oz wide-mouth glass	Methanol; ice Method 5035A
Semi-volatile organic compounds (SVOC)	EPA 8270A		Ice
Total Petroleum Hydrocarbons (TPH), diesel range organics TPH (DRO), oil range organics TPH (ORO)	EPA 8015B		
Gas range organics TPH (GRO)	EPA 8015B		
Michigan Metals: (Sb, As, Ba, Be, Cd, Cr, Hg, Cu, Co, Fe, Pb, Mn, Mo, Ni, Se, Ag, Tl, Va, and Zn)	EPA 6010 EPA 7471A (Hg)		
Polychlorinated biphenyls (PCBs)	EPA 8082		

*Note: In the event that water saturated sediments are to be analyzed for VOCs, the samples should not be preserved with methanol.

4.5 Groundwater Sampling/Monitoring Approach

As a result of the release, there is concern that crude oil constituents may impair groundwater in the vicinity of the Spill Release Area and affected water bodies. MDNRE and various county departments of health (e.g., Calhoun County, Kalamazoo County, etc.) are providing the FOSC with a list and description of wells within the affected area. However, realizing that departmental lists may not accurately reflect all private wells (Wells) within the affected area, the Company, or its contractors, will be conducting a visual survey to identify private wells located within a 200-foot buffer zone (in accordance with the direction of the Calhoun County Public Health Department) on either side of the affected water bodies (e.g., Talmadge Creek, Kalamazoo River, and Morrow Lake). The survey is anticipated to be conducted house-to-house, from the shore where access allows, and from boats, canoes, and/or other watercraft.

Other sources of information, including township tax records for property owner names and addresses, electronic database searches, and mailings to all affected property owners asking for information about their wells will be utilized to assist in locating wells. Information gathered from the private well surveys will supplement information obtained from property queries and database searches and is anticipated to include location, coordinates, depth to zone of extraction (if known), and age. Wells identified during the visual survey and obtained from agency-provided lists will be sampled as part of this SAP, pending approval from the well-owners within the 200-foot buffer zone.

In addition to sampling the wells identified in the visual survey, other wells may also be sampled to address citizen calls to the Company Call Center in accordance with the "Environmental Procedure Call Center Operations" protocol, submitted to the FOSC for approval separately from this document.

4.5.1 Location and Frequency

The locations of the wells will be plotted on maps based on coordinates recorded during the survey. All owners/operators of the identified wells will be contacted for permission to sample their respective wells. The respective County Health officials will be notified at least 48 hours in advance of the well sampling event to allow the county time to observe and/or split the sampling event. The results of the analyses will be provided to the landowner, resident, and the FOSC, if requested. Wells will initially be sampled once every other week.

4.5.2 Groundwater Sample Analyses

Samples collected from the groundwater sampling events will be submitted to a Safe Drinking Water Act (SDWA)-certified laboratory for laboratory analysis of VOCs, SVOCs, metals and Total Petroleum Hydrocarbons (TPH) (TPH/DRO, GRO, ORO), as shown on Table 4.4. The proposed laboratory for this effort is Merit Laboratories, Inc. (Merit) located at 2680 East Lansing Drive, East Lansing, MI 48823. Representatives for Merit have indicated that the laboratory is a Michigan SDWA-certified laboratory for VOC and metals analysis. At the request of the Company, Merit will obtain Michigan SDWA certification for SVOCs, and until that time, will subcontract the SVOCs analysis to a Michigan accredited laboratory. Merit has requested and is awaiting the necessary state-performed audit of its facilities.

Table 4.4 Groundwater parameters, methods, and container types

Parameter	Method	Container Number, Size, and Type	Sample Preservatives
Volatile organic compounds (VOC)	EPA 524.2	3 x 40 ml VOA vials	Hydrochloric acid (HCl) to pH < 2; ice
Semi-volatile organic compounds (SVOC)	EPA 525	2 x 1 L Amber glass	Ice
Total Petroleum Hydrocarbons (TPH), diesel range organics TPH (DRO), oil range organics TPH (ORO)	EPA 8015B	1 x 1 L Amber glass	Ice
Gas range organics TPH (GRO)	EPA 8015B	2 x 40 mL VOA vials	HCl to pH < 2; ice
Metals: (Sb, As, Ba, Be, Cd, Cr, Hg, Cu, Co, Fe, Pb, Mn, Mo, Ni, Se, Ag, Tl, Va, and Zn)	200.7(ICP), 200.8 (ICP-MS) 245.2	1 x 150 mL HDPE bottle	Nitric Acid (HNO3) to pH < 2; ice
Polychlorinated biphenyls (PCBs)	EPA 508	1 x 1 L Amber glass	Ice
Total Organic Carbon (TOC)	EPA 415.3	1 x 1 L Amber glass	Ice
Total Suspended Solids	2540D		Ice
Hardness	EPA 130.1		

4.6 Soil Sampling

4.6.1 Overview and Rationale

Soil investigation and response activities, including excavation and source removal, for the purposes of this plan, will continue in areas where there remains qualitative (i.e., visual evidence of oil) or quantitative (i.e., confirmation sampling of representative sample from 0-6 inch depth interval submitted for laboratory analysis in accordance with SOP-8 evidence of oil that poses a threat of release of a visible oil or sheen discharge to navigable waterways, especially after significant precipitation events. The Source Area Remediation (SAR) Plan submitted separately to FOSC for approval addresses some of the additional soil screening and sampling activities which will be conducted; however, it is anticipated that longer term monitoring and soil sampling will be required.

4.6.2 Location and Frequency

Soil removal from the Spill Release Area will continue until oil is no longer qualitatively (i.e., visually) identified; sample locations cannot be established definitively at this time. The area(s) of investigation will be determined by the extent of initial response (e.g., excavation and source removal) and/or the Shoreline Cleanup Assessment Technique (SCAT) Team activities. Soil verification sampling locations will be established based on discussions with the MDNRE.

4.6.3 Soil Sample Analyses

It is anticipated that analytes, sample preservation and analytical methods will be as found in Table 4.5.

Table 4.5 Soil parameters, methods, and container types

Parameter	Method	Container Number, Size, and Type	Sample Preservatives
Volatile organic compounds (VOC)*	EPA 8260B	3 x 4 oz wide-mouth glass	Methanol; ice Method 5035A
Semi-volatile organic compounds (SVOC)	EPA 8270A		Ice
Total Petroleum Hydrocarbons (TPH), diesel range organics TPH (DRO), oil range organics TPH (ORO)	EPA 8015B		
Gas range organics TPH (GRO)	EPA 8015B		
Metals: (Sb, As, Ba, Be, Cd, Cr, Hg, Cu, Co, Fe, Pb, Mn, Mo, Ni, Se, Ag, Tl, Va, and Zn)	EPA 6010 EPA 7471A (Hg)		
Polychlorinated biphenyls (PCBs)	EPA 8082		

4.7 Waste Characterization Sampling

4.7.1 Overview and Rationale

Response activities related to this release generate multiple waste streams requiring appropriate characterization for proper disposal determination. Examples of anticipated waste generated from the response activities may include, but are not limited to:

- crude oil;

- impacted soil, water, sediments, Morrow Lake, Talmadge Creek, and the Kalamazoo River;
- vegetation;
- saturated absorbent materials;
- used disposable personal protection equipment (PPE);
- biological material associated with wildlife rescue operations; and,
- animal carcasses.

4.7.2 Location and Frequency

Waste is being generated and managed at various locations. Water and crude oil are being stored in portable storage tanks (e.g., frac tanks) at a centralized location north of the pumping station on Division St. in Marshall, MI. Soiled absorbents and PPE are held in roll-off boxes at the major centers of activity, such as the Spill Release Area, Kalamazoo River skimmer locations, and boom maintenance sites. Vegetation, soil, and sediment samples will be generated in areas that will be subject to restoration. Samples will be collected in accordance with the Waste Treatment, Transportation, and Disposal Plan, approved with comments by FOSC August 3, 2010, on an as-needed basis as activities and accumulated quantities dictate.

4.7.3 Soil Sample Analyses

Soil sampling of soils in the storage area will be performed as a preventive measure, so that contaminants in the soil are known in the event that leakage of contaminants from the stockpile occurs. Soils shall be analyzed for the same parameters as the other waste streams identified.

4.7.4 Waste Characterization Analysis

Collected samples will be transported to a NELAC certified fixed-base laboratory and analyzed by medium as indicated in Table 4.6.

Table 4.6 Waste characterization parameters, methods, and container types

Parameter	Method	Container Number, Size, and Type		Sample Preservatives
Volatile organic compounds (VOC)	EPA 8260	Liquid	3 x 40 ml VOA vials	Hydrochloric acid (HCl) to pH < 2; ice
		Solid	1 x 4 oz wide-mouth glass	Ice
Semi-volatile organic compounds (SVOC)	EPA 8270	Liquid	2 x 1 L Amber glass	Ice
		Solid	1 x 4 oz wide-mouth glass	

Parameter	Method	Container Number, Size, and Type		Sample Preservatives
Toxicity Characteristic Leaching Procedure (TCLP) Metals	SW 6020	Liquid	1 x 150 mL HDPE bottle	Ice
		Solid	1 x 8 oz wide-mouth glass	
Flashpoint (Closed cup)	D93	Liquid	From 1 L Amber glass	Ice
		Solid	From 8 oz wide-mouth glass	
pH	9040	Liquid	From 1 L Amber glass	Ice
	9045	Solid	From 8 oz wide-mouth glass	
Polychlorinated biphenyls (PCBs)	EPA 8082	Liquid	1 x 1 L Amber glass	Ice
		Solid	1 x 4 oz wide-mouth glass	
Paint Filter	EPA 9056	Liquid	3 x 1 L Amber glass	Ice
		Solid	2 x 8 oz wide-mouth glass	

TPH/DRO, GRO, ORO analysis will be added if required by disposal firms for waste coordination or characterization purposes.

4.8 Product Sampling

Product samples will be collected, as necessary and prudent, to support forensics investigations. On July 27, 2010, an unweathered sample of the released crude oil was collected from the Spill Release Area. The sample of the material was placed in an airtight container and refrigerated. Following sample collection, an aliquot of this material was analyzed by an on-site, mobile laboratory for use as a standard. Additional samples may be collected from the pipeline during repair operations to serve as additional standards. The Company will collect representative samples of sheen, oil/tar-like flecks from downstream areas and submit them for comparative fingerprint analysis if they meet one of the following criteria: the oil/tar-like flecks appears in a new location or is observed for the first time in a location; the oil/tar/like flecks that are observed currently are different in color, size, or form from something previously observed; or, the oil/tar-like flecks are group in a large quantity or cover a large surface area. See Table 4.7 below. The chromatograms of the additionally collected representative sample and the sample used as the standard will be submitted to an independent laboratory for comparative interpretation. Interpretation of the results will occur following receipt of analyses. Following a review of the interpretive results, additional samples may be warranted, especially near heavily populated or industrial areas following precipitation events.

Table 4.7 Product Parameters/Forensic Fingerprinting (may change as needed)

Parameter	Method	Container Number, Size, and Type	Sample Preservatives
Volatile organic compounds (VOC)	EPA 8206B	3 x 40 ml VOA vials	Hydrochloric acid (HCl) to pH < 2; ice
Semi-volatile organic compounds (SVOC)	EPA 8270A	2 x 1 L Amber glass	Ice
Diesel range organics (DRO)/Oil range organics (ORO)	EPA 8015B	1 x 1 L Amber glass	Ice
Gas range organics (GRO)	EPA 8015B	2 x 40 mL VOA vials	HCl to pH < 2; ice

5.0 Sample Management

Samples will be managed in accordance with the requirements set forth in the referenced analytical method and/or laboratory SOPs.

Field samples will be contained and preserved in accordance with appropriate U.S. EPA specifications. Sampling containers and preservatives will be provided by the laboratory. Samples will be placed in individual pre-cleaned containers for shipment to the laboratory. Samples will be collected and stored in accordance with U.S. EPA specifications, laboratory SOPs, and analytical methods currently under development for this project, as specified in the Quality Assurance Project Plan (QAPP, August 2010).

Sample container orders, when shipped by the laboratory, will include a packing list that details the number and type of bottles shipped, the bottle lot numbers, chemical preservatives, and the packer's signature. The COC Records will be completed by field sampling personnel and returned to the laboratory with the samples.

Samples will be stored according to the applicable storage criteria from the time of collection until the time of analysis by the laboratory. Field personnel will keep samples cold by placing ice in the coolers in which samples will be stored until delivery to the analytical laboratory personnel. After receipt of the samples, it is the laboratory's responsibility to store the samples according to the applicable preservation conditions until preparation and analysis has been initiated.

Samples have a finite holding time (the time between sample collection, sample digestion, and sample analysis) to limit the potential for degradation of the analytes. The holding times for required analyses are measured from the verified time of sample collection. When possible, samples will be shipped by overnight carrier or hand delivered by same-day courier to minimize the time between collection and laboratory receipt.

Samples will be preserved per the appropriate EPA method, immediately placed in a cooler following sample collection, and maintained at 4 degrees C. Shipping or transporting of samples to the laboratory will be done within a timeframe such that recommended holding times are met.

5.1 Sample Labeling

Sample jars and vials will be clearly labeled with, at a minimum, the following information:

- Unique sample identification;
- Sample Type (discrete or composite area);
- Sampler name or initials;
- Date sample collected;
- Time sample collected; and
- Analysis to be performed.

The unique sample designation will include a matrix prefix, a numerical designation, and a unique series of information including the month, day, time, sampler initials, and QA sample designation. The following matrix prefixes will be used: "SO", "SE", "WS", "WP", and "WG" which designate soil, sediment, surface water, potable water, and groundwater, respectively. Agricultural wells will be considered groundwater. A photograph will be taken at each sampling location. The photograph will include the sample designation, date, and time showing the immediate surrounding area and any distinctive feature that can be found in the future.

5.2 Chain of Custody Procedures

A primary consideration for environmental data is the ability to demonstrate that samples have been obtained from specific locations and have reached the laboratory without alteration. Evidence of collection, shipment, laboratory receipt, and laboratory custody while samples are in the laboratory's possession will be documented by maintaining a COC that records each sample and the individuals responsible for sample collection, shipment, and receipt at the project laboratory. Samples that are collected will be accompanied by a COC Record. The following information will be recorded to complete the COC Record:

- Project name and number.
- Name of sampler.
- Sample identifier/name, location, date and time collected, and sample type.
- Analyses requested.
- Special instructions and/or sample hazards, if applicable.
- Signature of sampler in the designated blocks, including date, time, and company.

- Sample condition (including temperature) upon receipt as reported by the analytical laboratory.

Copies of COC Records will be maintained under customary business practices and on-Spill Release Area by the Sample Manager. Duplicates of all COC Records will be retained by the as part of the Project File.

6.0 Analytical Approach

Water and sediment samples, as well as confirmatory soil samples will be submitted to a full-service, qualified, subcontracted commercial laboratory for the analyses as specified in the QAPP. During the initial response period, sample turnaround times (TATs) be expedited to assist in making quantitative driven decisions. After a review of the data, it may be agreed upon by the FOSC that expedited TATs may be scaled back to a standard TAT.

Level II data packages will be required for validation for 90% of the samples analyzed. Level IV data packages will be required for full data validation of the remaining 10% of the samples analyzed. Lab contacts and shipping information are as follows:

Merit Laboratories, Inc.
2680 East Lansing Drive
East Lansing, MI 48823
Cell: 517-202-1340
Maya Murshak

TestAmerica, Inc.
2417 Bond Street
University Park, IL 60484
708-534-5200

Pace Analytical Services, Inc.
7726 Moller Road
Indianapolis, IN 46268
Phone:317-875-5894
Karl Anderson

ALS | Environmental
3352 128th Avenue
Holland. MI 49424
Direct Phone 616-738-7346
Office Phone 616-399-6070 Ext. 525
Mobile 616-218-5574
FAX 616-399-6185
www.alsglobal.com

New Age/Landmark, Inc.
160 Veterans Blvd.
South Haven, Michigan 49090
Phone: (888) 685-1628
Fax: (269) 637-5664

7.0 Quality Assurance

Sampling will be carried out in conjunction with a defined quality assurance (QA) program. The goal of the field QA program is to document that samples are collected without introducing a bias (i.e., the effects of accidental cross- or systematic contamination are eliminated) and refers to the sampling, analysis, and data validation procedures for generating valid and defensible data. To provide QA for the proposed sampling, the following sampling, analysis, and data validation procedures will be performed in addition to the Quality Assurance Project Plan (QAPP) prepared for this project and submitted to the FOSC under a separate cover letter for review.

7.1 Initial Field Evaluation

7.1.1 Surface Water Samples

Surface water sample containers collected for VOC analysis will be evaluated for "acceptability" in the field prior to submittal to the laboratory. VOA vials containing air bubbles will be judged unacceptable. Containers containing air bubbles will be re-opened and an additional aliquot of representative sample carefully decanted into the container to remove any air bubbles in the sample without losing any of the preservative.

7.1.2 Sediment

The sediment sample will be retrieved aboard the boat and evaluated for "acceptability". For example, a sediment sample will be considered "acceptable" if it meets all of the following characteristics for "representativeness":

- Sediment surface is not against the top of the sampler (i.e., not over-filled);
- Sediment surface is relatively flat indicating minimal sediment disturbance;
- Overlying water is present indicating minimal leakage;
- Overlying water has minimal turbidity indicating minimal sample disturbance; and,
- Desired penetration is achieved.

7.1.3 Groundwater

Groundwater sample containers collected for VOC analysis will be evaluated for "acceptability" in the field prior to submittal to the laboratory. VOA vials containing air bubbles will be judged unacceptable. Containers containing air bubbles will be re-opened and an additional aliquot of representative sample carefully decanted into the container to remove any air bubbles in the sample without losing any of the preservative. Groundwater will be purged the appropriate volume (i.e., three volumes) prior to sample collection to achieve representativeness.

7.1.4 Soil

Soil samples collected for VOC analysis will be evaluated for "acceptability" in the field prior to submittal to the laboratory. Ten milliliters of methanol will be combined with 10 grams of soil in the appropriate soil sample container.

7.2 Field Duplicate Sample

Field duplicate samples are used to check for sampling and analytical error, reproducibility, and homogeneity. For approximately every twenty (5%) samples collected in the field, one field duplicate will be collected and submitted for laboratory analyses to verify the reproducibility of the sampling methods. Field duplicates will be prepared by separately submitting an aliquot from the same sample location to the laboratory for analysis consistent with the proscribed analyses. For sediment samples, the duplicate will be obtained by collecting a sample from an area adjacent to the routine sample or by collecting a separate aliquot of sediment from within the same core (i.e., co-located sample), whichever is more appropriate for the type of sample/sampling technique (i.e., surface or subsurface sediment sample). At least one field duplicate will be collected each day that samples are collected.

7.3 Equipment Rinsate Sample

Collection and analysis of equipment rinsate blanks are performed to assess the efficiency of field equipment decontamination procedures in preventing cross-contamination between samples. Each day of sampling, one equipment rinsate sample will be collected and submitted for laboratory analysis. The rinsate sample will be collected by decanting deionized water over the post-decontaminated non-disposable sampling equipment (e.g., ponar sampling device, stainless steel bowls and spoons used for sample collection) into laboratory-supplied sample containers. The deionized water comprising the rinsate blank will make contact with each piece of decontaminated sampling equipment used in the collection of the sample.

7.4 Trip Blanks

Trip blanks will be prepared by the lab and included in coolers containing water samples to be analyzed for VOCs. The trip blanks will be used to assess the potential for contamination of the containers during handling and transit.

7.5 Field Split Samples

Field split samples refer to samples collected by the regulatory agency or its designee from the same sampling location and independently submitted to a different laboratory for analysis. Field split samples may be requested at the discretion of representatives of the regulatory agency or the FOSC.

7.6 Laboratory QA

Laboratory quality control procedures will be conducted in a manner consistent with relevant State and federal regulatory guidance. Level II data packages will be required for validation for 90% of the samples analyzed. Level IV data packages will be required for full data validation of the remaining 10% of the samples analyzed. Internal laboratory quality control checks will include method blanks, matrix spikes (and matrix spike duplicates), surrogate samples, calibration standards, and laboratory control standards (LCSs). A Level IV data package will additionally be requested for 10% of samples submitted for laboratory analyses as a result of this sampling event.

7.7 Matrix Spike/Matrix Spike Duplicate Sample

Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples refer to field samples spiked with the analytes of interest prior to being analyzed at the laboratory to gauge the quality of analysis. Approximately one in twenty samples will be analyzed as MS/MSD samples.

7.8 Data Validation

Validation of the data generated by the laboratory performing the analyses will include at a minimum, sample holding times, accuracy, precision, contamination of field generated or laboratory method blanks, and surrogate compound recovery. Accuracy will be determined by evaluating LCS and MS recovery. Precision will be determined by evaluating laboratory and field duplicate samples.

Ten percent of the analytical samples with Level IV data packages from each matrix will be submitted to a third party laboratory for data validation. Level II summary validation will occur on the remaining 90% of samples, unless significant concerns are raised during the validation process. Level II validation typically consists of an audit for compliance with analytical holding times, GCMS calibration, (initial calibration, continuing calibration verification standards), and internal standard and ICP interference check against accepted criteria in accordance with the EPA Functional Guidelines. Data are reviewed for compliance with accuracy limits for surrogate recovery, laboratory control samples, matrix spikes, matrix spike duplicate recoveries. Laboratory method blank and field blank results will be reviewed for evidence of contamination and potential impacts on project data quality results. The data validator will attach appropriate qualifiers to the data to reflect data quality for future use in decision making.

8.0 Sampling Equipment Decontamination Procedures

Decontamination procedures refer to the steps undertaken to minimize the potential for offsite area contamination and cross-contamination between individual sampling locations. Prior to collecting any sample described in this SAP the following decontamination procedures will be undertaken: non-disposable sampling equipment such as the ponar sampling device, stainless steel bowls and spoons which come into contact with sampling media will be decontaminated using a bristled brush and a solution comprised of a laboratory grade, non-phosphate detergent (e.g., Alconox or Liquinox) and deionized water. The sampling equipment to be decontaminated will be placed in the first bucket containing the detergent solution and thoroughly washed using a bristled brush. The items will then be transferred to the second 5-gallon bucket containing deionized water for rinsing. Following the initial rinsing, the item will be held over the third 5-gallon bucket while deionized water is carefully decanted over each item. Decontaminated items will be wrapped in clean aluminum foil for transit to the next sampling location.

All decontamination will be conducted according to SOP-5, appended to this Plan.

9.0 Waste Disposal and Investigative Derived Waste

Excess sediment generated during sediment sampling shall be handled, characterized, and disposed of as an Investigation Derived Waste (IDW) in accordance with the *Waste Treatment, Transportation, and Disposal Plan*.

10.0 Data Management

Data obtained as part of this response will be managed in accordance with the *Data Management Plan*, submitted for approval to the FOSC on August 1, 2010.

10.1 Sampling and Analytical Data

Sampling data is recorded on paper forms or captured using Motorola MC-55 Enterprise Digital Assistants (MC-55 EDAs). Analytical laboratory data sheets are provided from the laboratory as a Portable Document File (PDF) and an Electronic Data Deliverable (EDD).

10.2 SIERA Data

Sample Instrument Event Receptor Awareness (SIERA) is a program developed to provide situational awareness to a project. Field personnel utilize SIERA to geographically tag photographs, establish sampling locations, and document important events that may influence, interfere, or otherwise bias a particular sample. SIERA data points are collected on a MC-55 and synchronized to the off-site data warehouse.

10.3 Data Flow

Sampling data, including but not limited to, hand-written field notes, photographs, real-time monitoring parameters, SIERA data, will be entered into an off-site data warehouse, managed by the Company's contractor, daily following the sampling event to the extent possible information will be collected using a Motorola MC-55 Enterprise Digital Assistants (MC-55 EDAs), or equivalent, to facilitate synchronized to the database. Data which has undergone Level II validation will be published to the centralized Scribe.NET database being maintained by EPA's Environmental Response Team (ERT).

10.4 Data Backup

Daily backups are performed on-site to a removable storage drive using off-the-shelf commercial backup hardware and software. Every evening an off-site dump is performed to the Company's Contractor's corporate file server over the network. Every night, this fileserver is backed up to tape and stored off-site.

11.0 Records Management

Records management refers to the procedures for generating, controlling, and archiving project-specific records and records of field activities. Project records, particularly those that are anticipated to be used as evidentiary data, directly support current or ongoing technical studies and activities, and provide historical evidence needed for later reviews and analyses, will be legible, identifiable, retrievable and protected against damage, deterioration, or loss on a centralized electronic database. Handwritten records will be written in indelible ink. Records will likely include, but are not limited to, the following: bound field notebooks on pre-numbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of custody forms, maps and drawings, transportation and disposal documents, reports issued as a result of the work, procedures used, correspondences, and any deviations from the procedural records. Documentation errors will be corrected by drawing a single line through the error so it remains legible and will be initialed by the responsible individual, along with the date of change, and the correction will be written adjacent to the error.

Figures

ENBRIDGE

0 50 100 150 200 Miles

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 1: Site Location

DATE ISSUED:	Aug 11, 2010
DATE REVISED:	
SCALE:	1:1,500,000
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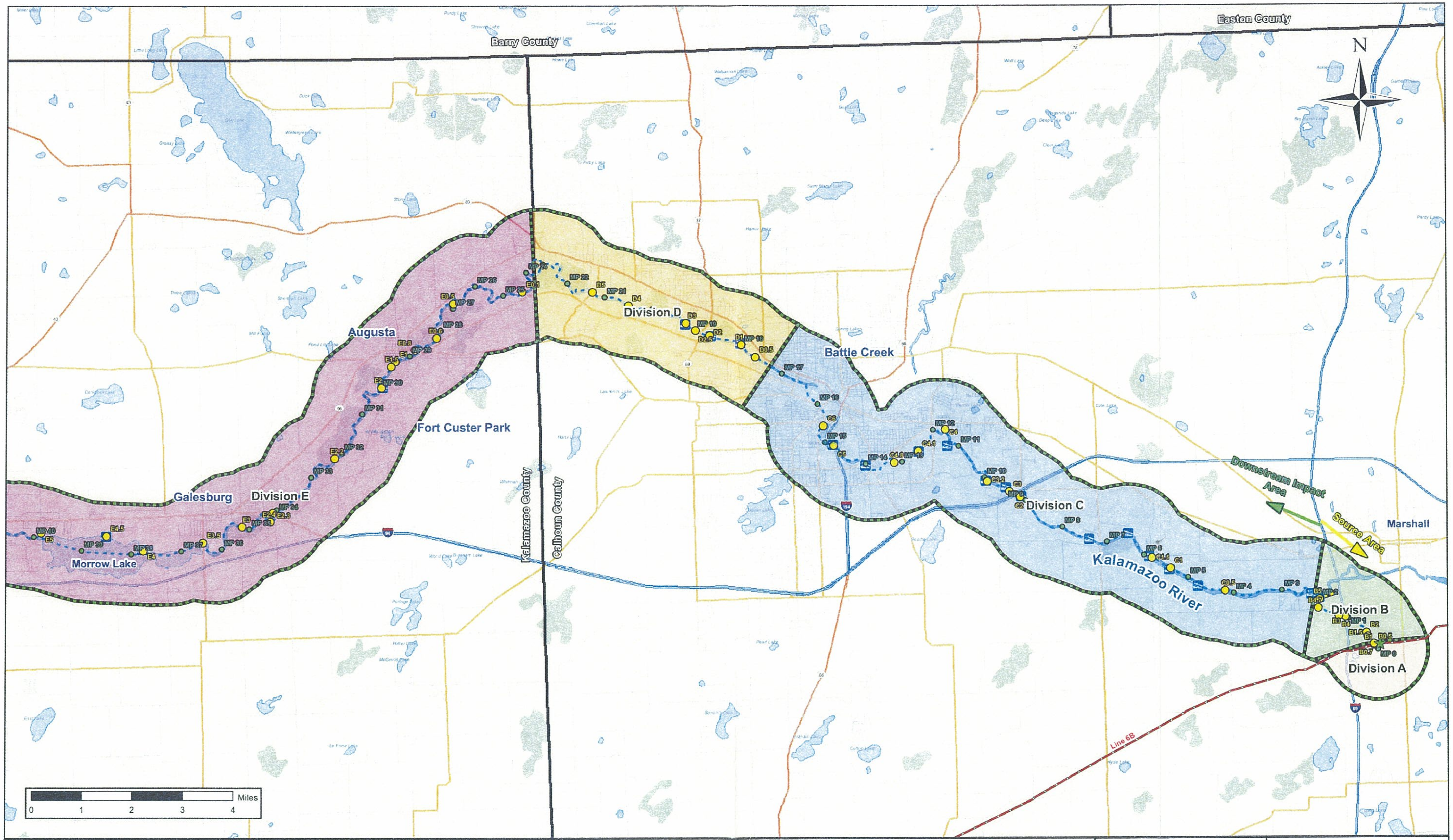

ENBRIDGE

Legend

Enbridge Pipeline 6B
River Centerline
Major Road
Division Boundary
● Containment Site (Boom)
Water Access
★ Release Location
● Downstream Milepost

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 2: Division Designation Map

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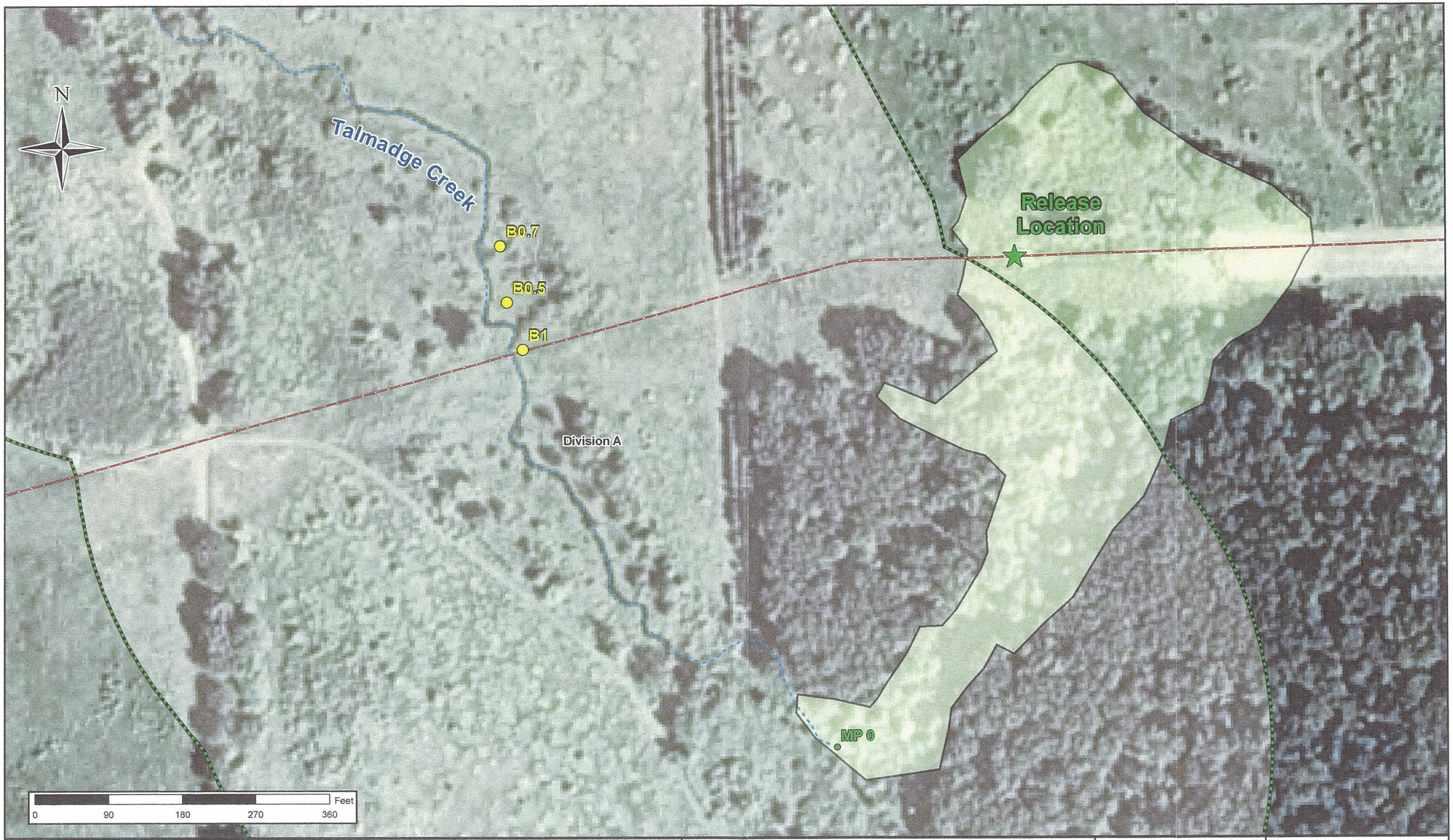

ENBRIDGE

Legend

- Division Boundary
- Enbridge Pipeline 6B
- River Centerline
- Major Road
- ○ Extent Of Pooled Oil on Land
- ★ Release Location
- ● Downstream Milepost
- ● Containment Site (Boom)
- ● Surface Water Sample
- ● Potable Well Sample
- ● Sediment Sample
- ○ Soil Sample
- Water Access

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan

Figure 3: Division A - Multiple Media Sampling Locations

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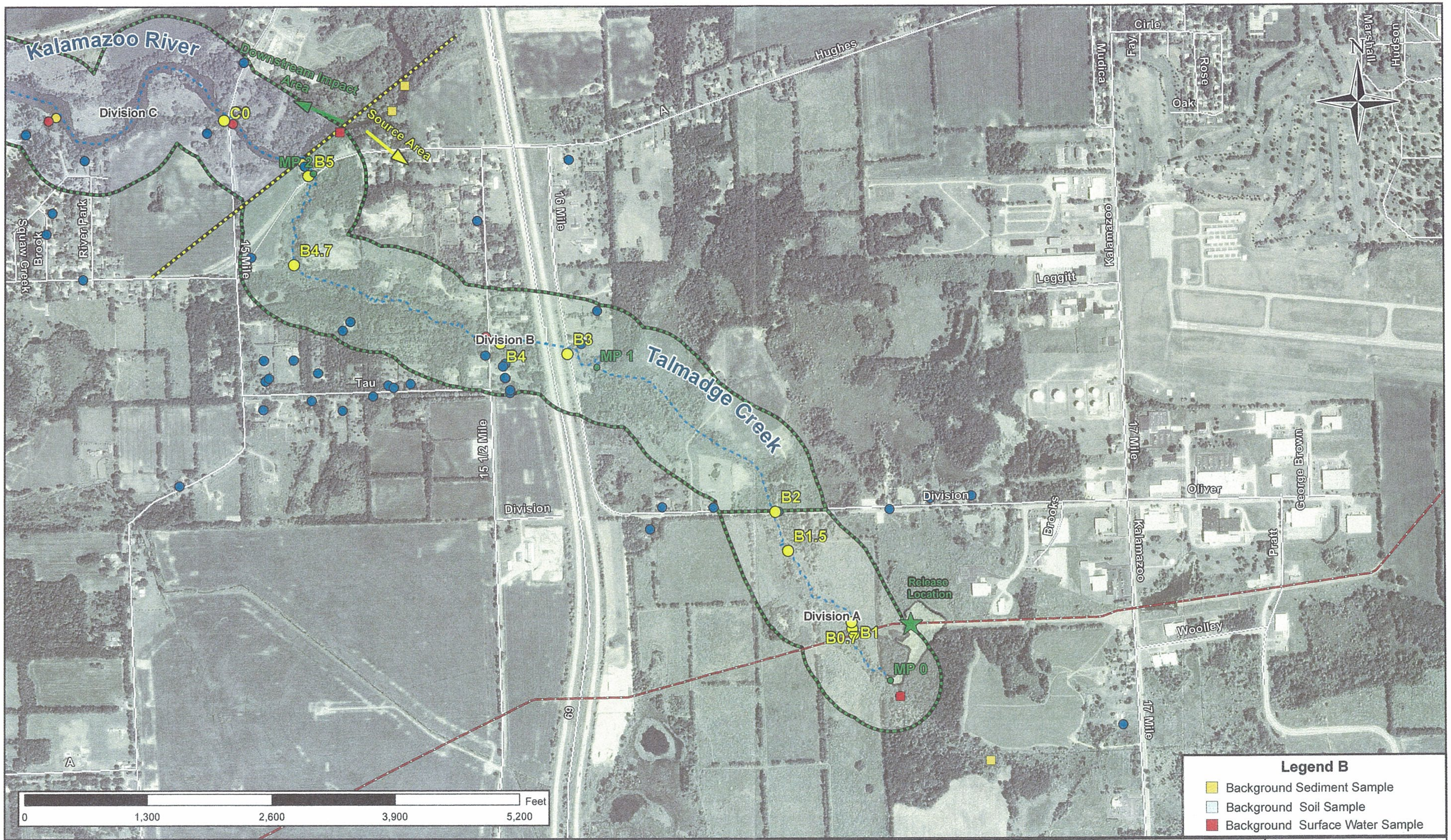

Legend B

🟨 Background Sediment Sample

☐ Background Soil Sample

🟥 Background Surface Water Sample

Legend A

Enbridge Pipeline 6B	★ Release Location	● Potable Well Sample
River Centerline	● Downstream Milepost	● Sediment Sample
Major Road	● Containment Site (Boom)	○ Soil Sample
○ Extent Of Pooled Oil On Land	● Surface Water Sample	Water Access

ENBRIDGE

Enbridge Energy, Limited Partnership

Enbridge Line 6B MP 608 - Marshall, MI

Sampling and Analysis Plan

Figure 4: Division B - Multiple Media Sampling Locations

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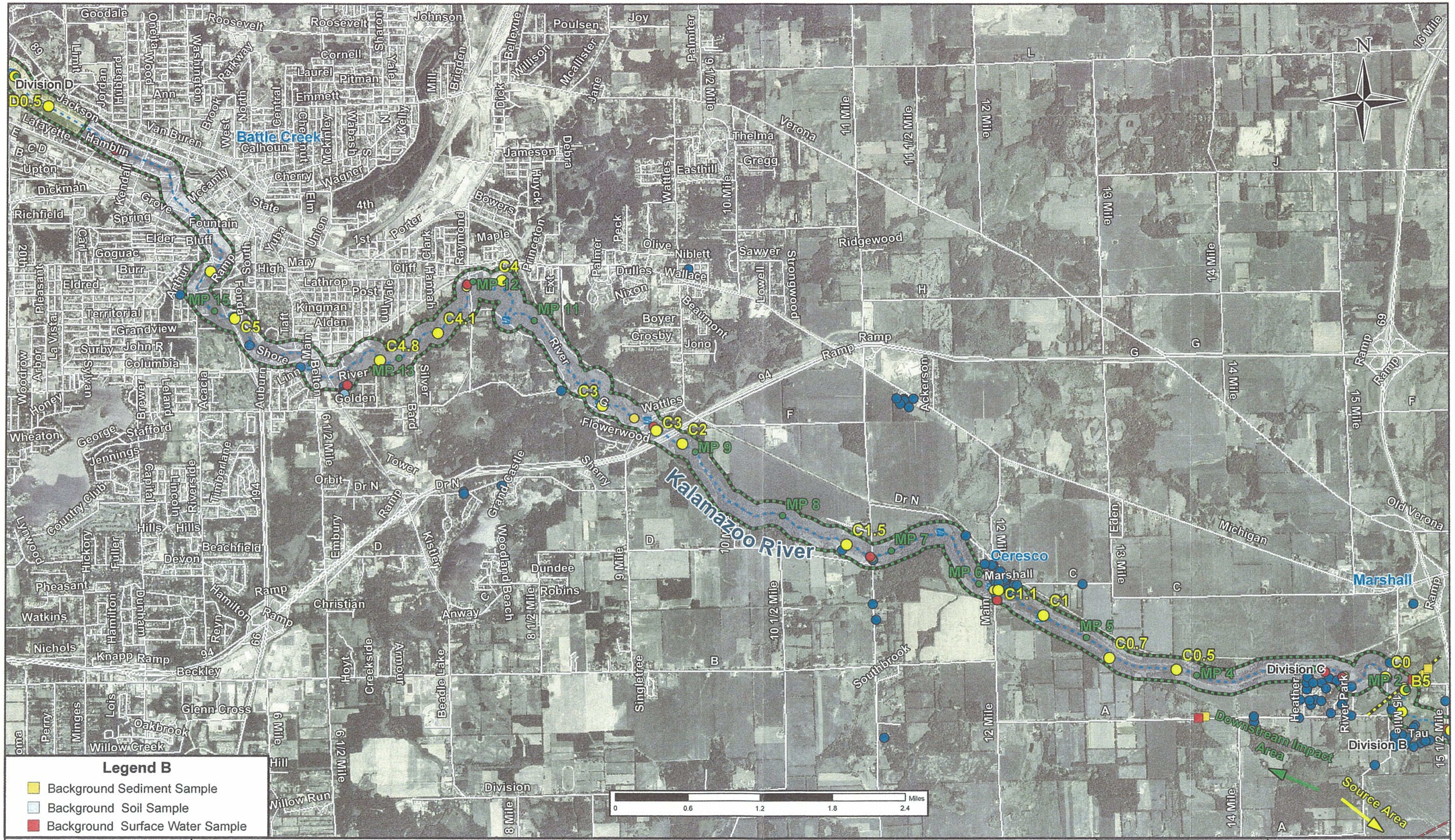

Legend B

- 🟨 Background Sediment Sample
- ☐ Background Soil Sample
- 🟥 Background Surface Water Sample

Legend A

- Division Boundary
- Enbridge Pipeline 6B
- River Centerline
- Major Road
- ○ Extent Of Pooled Oil on Land
- ★ Release Location
- ● Downstream Milepost
- ● Containment Site (Boom)
- ● Surface Water Sample
- ● Potable Well Sample
- ● Sediment Sample
- ○ Soil Sample
- Water Access

ENBRIDGE

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 5: Division C – Multiple Media Sampling Locations

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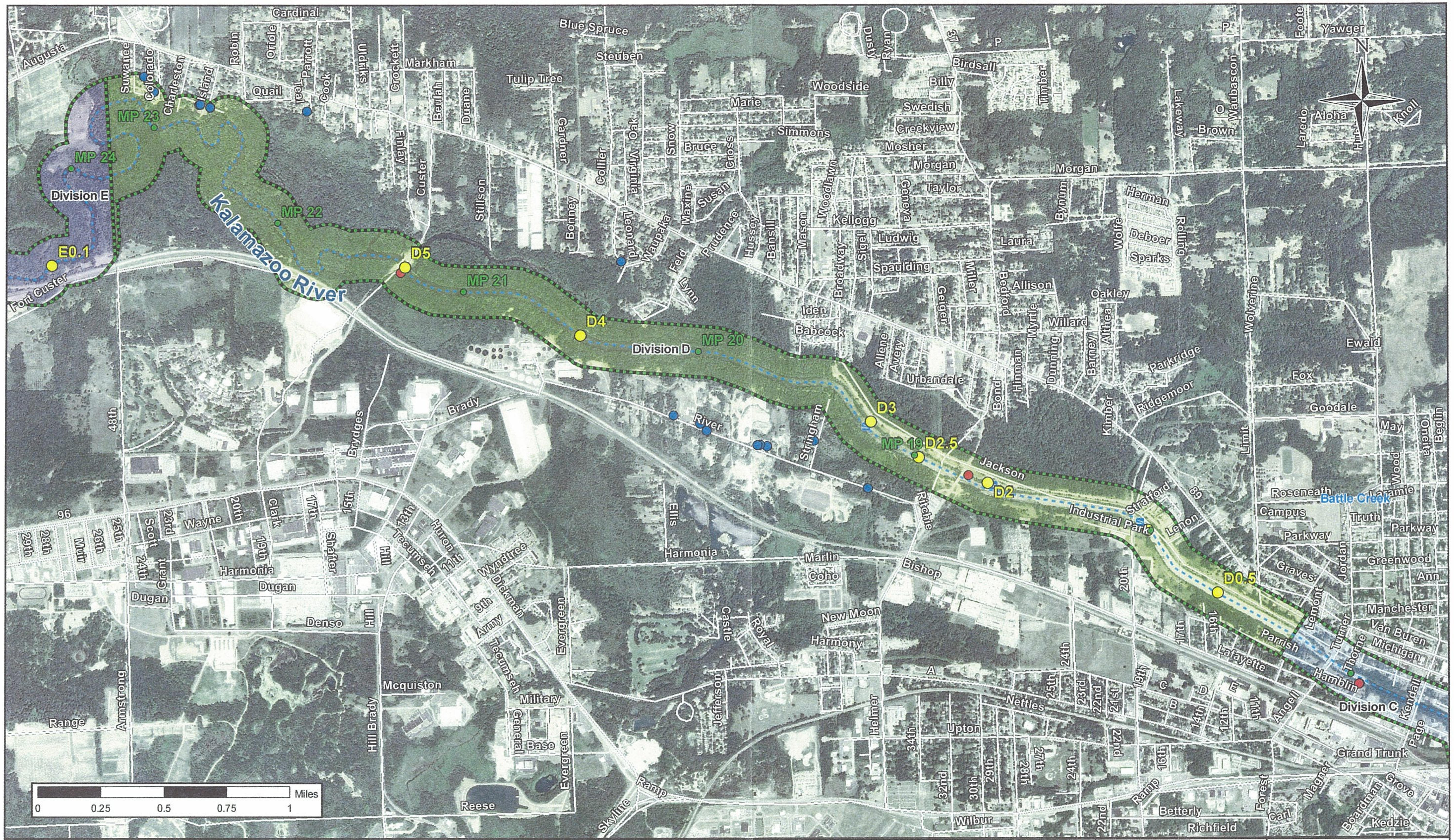

ENBRIDGE™

Legend

Division Boundary

Enbridge Pipeline 6B

River Centerline

Major Road

Extent Of Oil Pooled On Land

★ Release Location

● Downstream Milepost

● Containment Site (Boom)

● Surface Water Sample

● Potable Well Sample

● Sediment Sample

○ Soil Sample

Water Access

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 6: Division D - Multiple Media Sampling Locations

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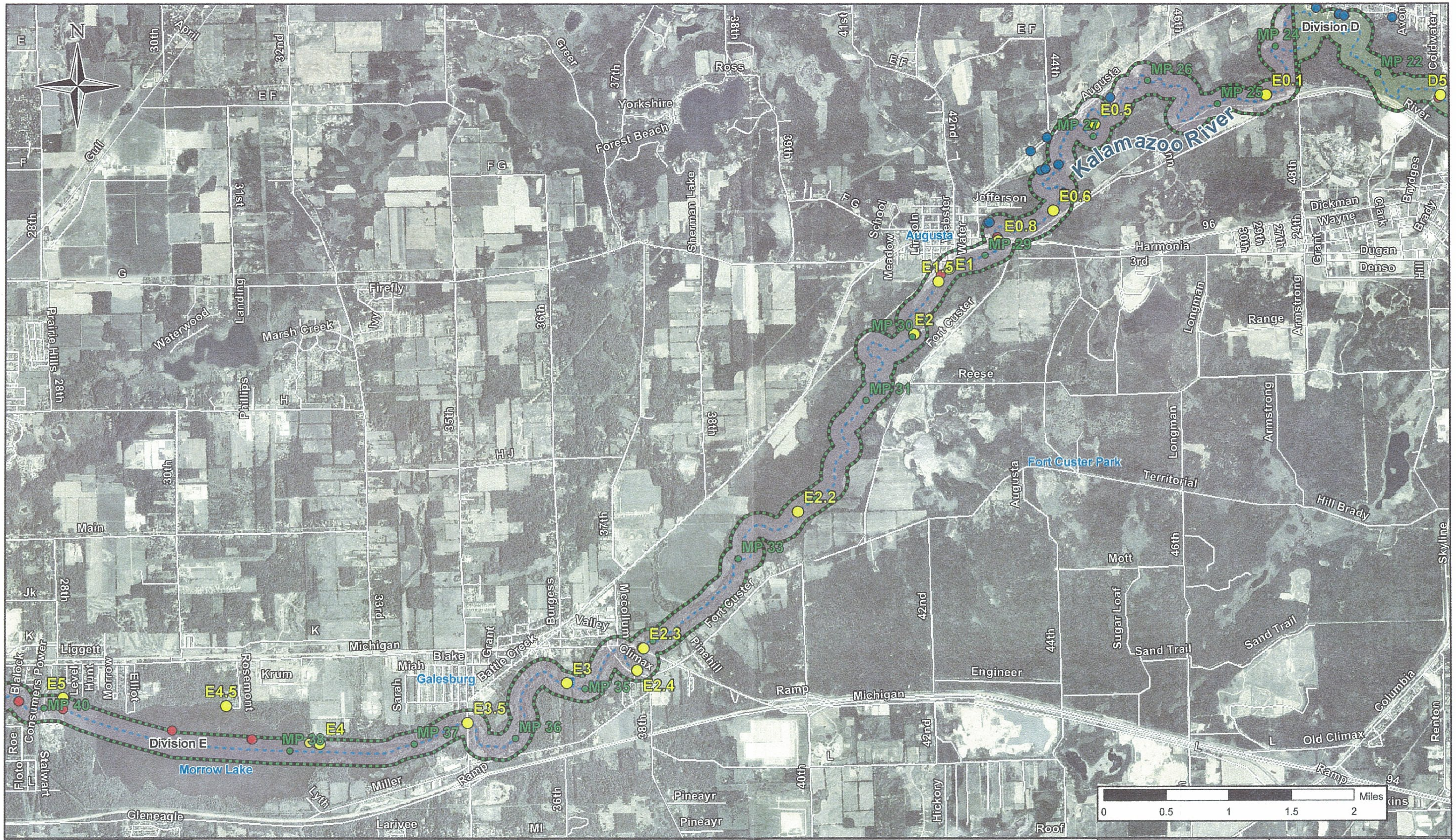

Legend

- ▭ Division Boundary
- ▬ Enbridge Pipeline 6B
- ┅ River Centerline
- ─ Major Road
- ○ Extent Of Pooled Oil on Land
- ★ Release Location
- ● Downstream Milepost
- ● Containment Site (Boom)
- ● Surface Water Sample
- ● Potable Well Sample
- ● Sediment Sample
- ○ Soil Sample
- ▨ Water Access

ENBRIDGE

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 7: Division E - Multiple Media Sampling Locations

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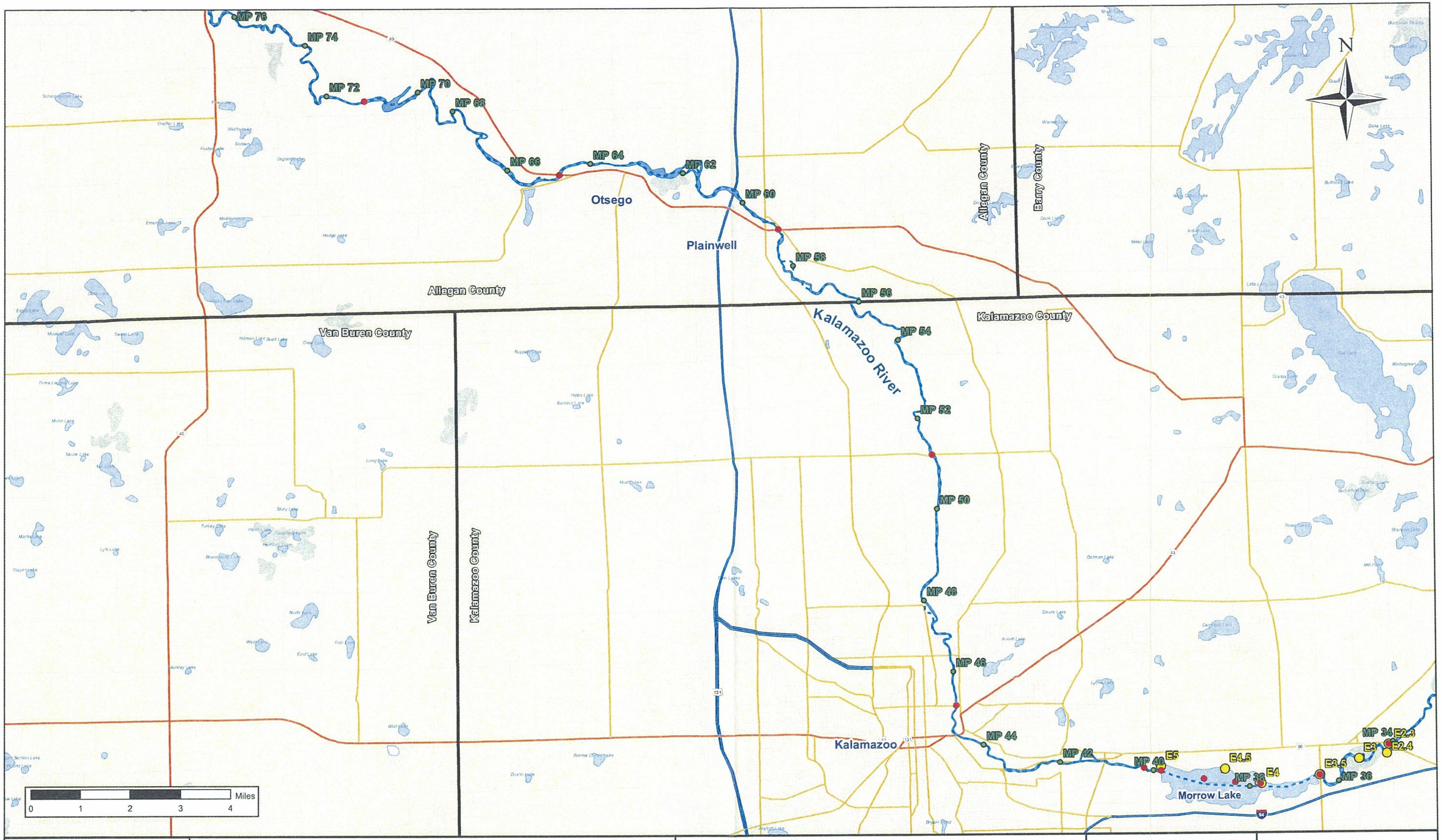

ENBRIDGE

Legend

- - - - River Centerline
— Major Road
● Downstream Milepost
○ Containment Site (Boom)
● Surface Water Sample
● Sediment Sample
🌊 Water Access

Enbridge Energy, Limited Partnership

Enbridge Line 6B MP 608 - Marshall, MI

Sampling and Analysis Plan

Figure 8: Downstream Surface Water Sampling Locations
Morrow Lake to MP 76

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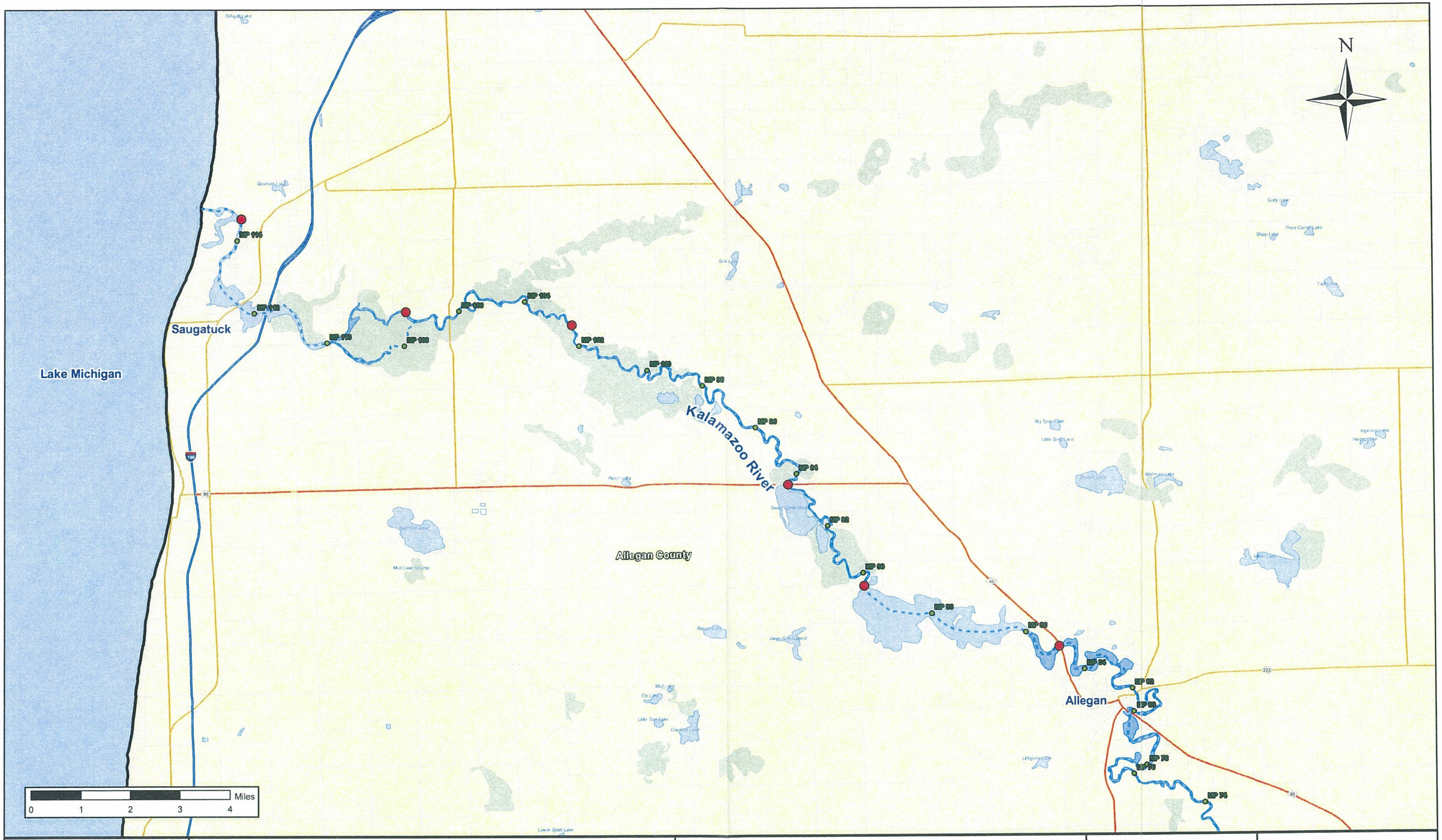

ENBRIDGE™

Legend

- - - - River Centerline
● Downstream Milepost
—— Major Road
● Surface Water Sample
▨ Water Access

Enbridge Energy, Limited Partnership

Enbridge Line 6B MP 608 - Marshall, MI

Sampling and Analysis Plan

Figure 9: Downstream Surface Water Sampling Locations
MP 74 to Lake Michigan

DATE ISSUED: Aug 13, 2010
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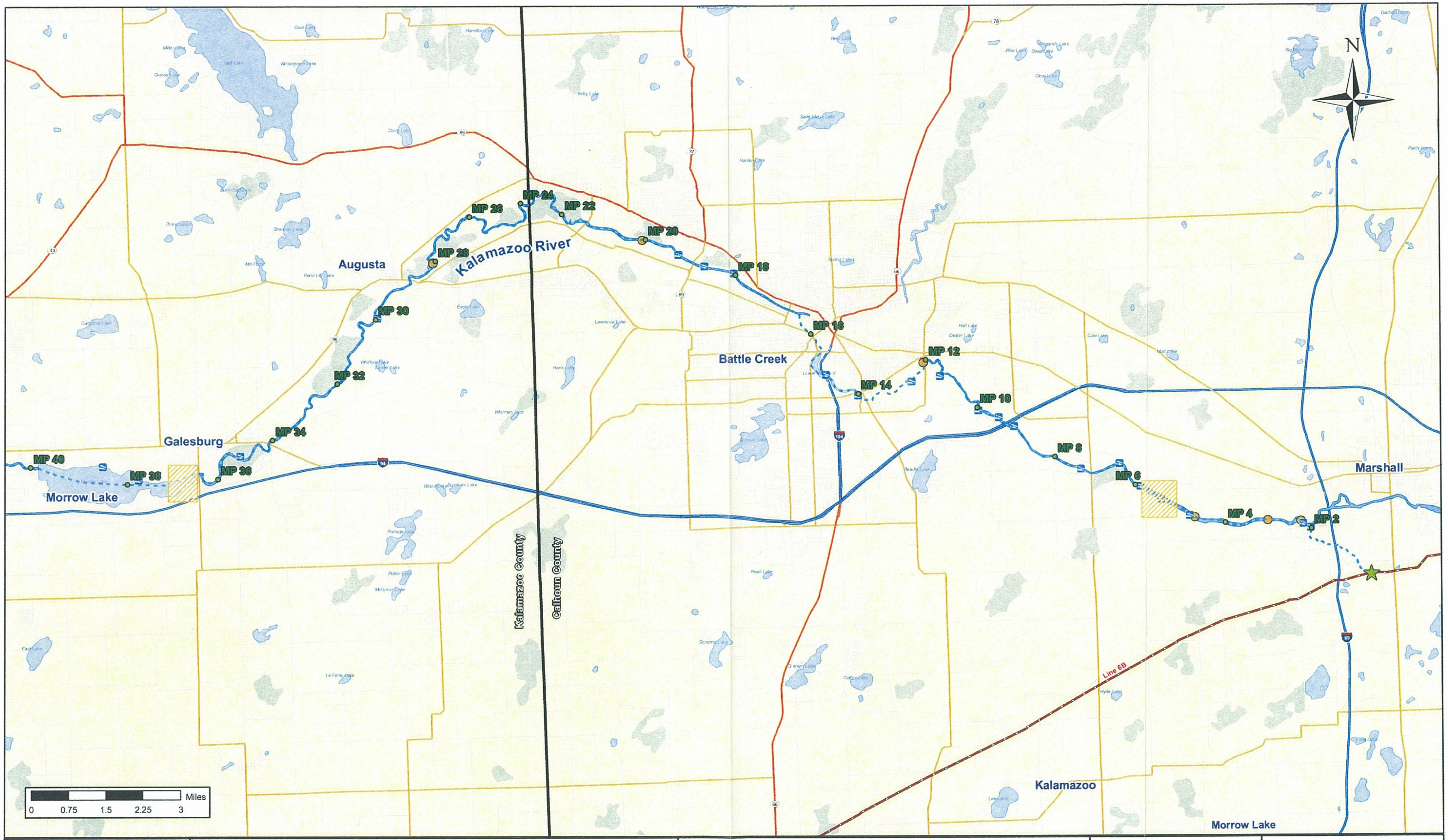

ENBRIDGE™

Legend

Enbridge Pipeline 6B	
River Centerline	★ Release Location
Major Road	● Downstream Milepost
● Proposed Sediment Sample Location	Water Access
▨ Proposed Sediment Sample Location Following Assessment	

Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan

Figure 10: Proposed Sediment Sample Locations

DATE ISSUED: Aug 15, 2010
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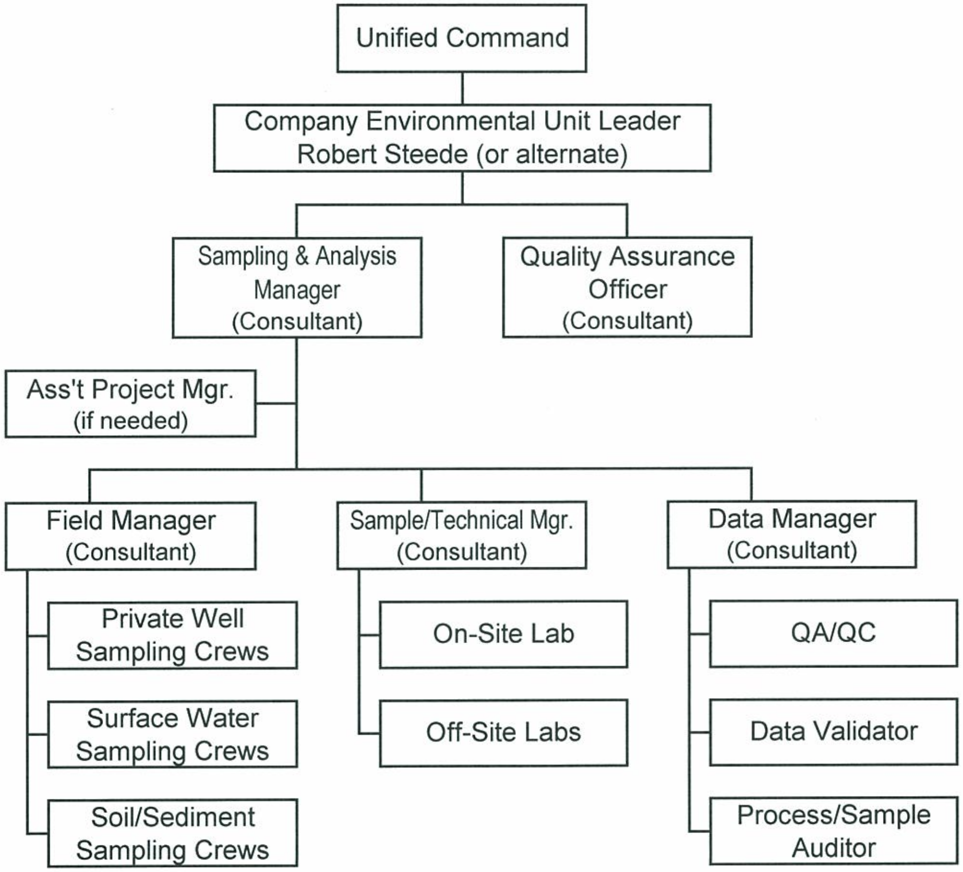
Figure 11

Enbridge Line 6B, MP 608
Quality Assurance Project Plan
Organization Chart



Appendix A

Air Sampling and Monitoring Plan
Dated July 31, 2010 (Air Sampling QAPP)

CTEH
Center for Toxicology and Environmental Health, L.L.C.
5120 N. Shore Drive, North Little Rock, AR 72118 Phone: 501.801.8500 www.cteh.com

AIR SAMPLING AND MONITORING PLAN

ENBRIDGE ENERGY OIL SPILL

MARSHALL, MICHIGAN

JULY 31, 2010

Revised August 15, 2010

PREPARED BY:

CENTER FOR TOXICOLOGY AND ENVIRONMENTAL HEALTH, L.L.C.
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Table of Contents

Table of Tables

1. Purpose

Center for Toxicology and Environmental Health, L.L.C. (CTEH®) was requested to respond in support of site operations for the Enbridge Energy crude oil release on Monday, July 27, 2010. CTEH® is providing air monitoring, air sampling, and toxicology support to address public health concerns resulting from the crude oil spill. CTEH® has been conducting community air monitoring and sampling in communities to protect human health.

This work plan addresses air monitoring and sampling in communities potentially affected by fumes from the crude oil spill. The purpose of this sampling includes the following:

- Air monitoring and sampling in the community potentially impacted by the presence of crude oil vapors and/or fumes from the spill.
- Air monitoring and sampling throughout the community during mitigation activities to evaluate the potential for exposure.
- Perform air monitoring and sampling in response to reports of odors in the community.
- Provide personnel monitoring for CTEH and EPA contractors performing air sampling and monitoring to protect against overexposure to chemicals in crude oil vapors and/or fumes.

CTEH® will conduct community air monitoring in support of Unified Command actions. Data from air monitoring and sampling will be evaluated to make decisions regarding the need for additional monitoring and sampling. Data will be reported to Unified Command, Enbridge representatives and USEPA, as soon as available.

Two types of air monitoring will be conducted, analytical and real-time. These are discussed at greater length in the following sections of this report.

2. Air Monitoring

Air monitoring will be conducted using a number of real-time instruments including the MultiRAE Plus, AreaRAE, Gastec colorimetric detector tubes, and/or UltraRAE/ UltraRAE 3000 throughout impacted communities. The major sampling routes are show in Figure 1. Monitoring locations may be modified based on operational requirements. The air monitoring equipment used is listed in Table 1.

Figure 1
Major Sampling Routes for Air Monitoring

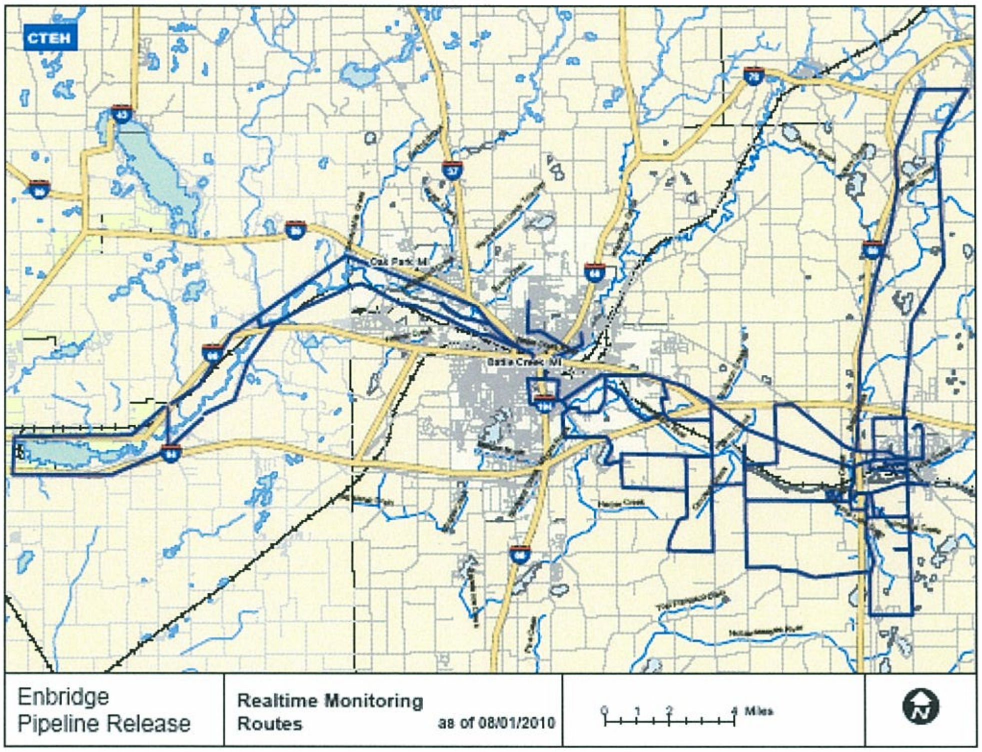


Table 1
Real-Time Air Monitoring Equipment

Instrument	Chemical	Detection Limit
AreaRAE	VOCs	0.1 ppm
AreaRAE	H_2S	1.0 ppm
MultiRAE PID	VOCs	0.1 ppm
MultiRAE H_2S electrochemical sensor	H_2S	1 ppm
MultiRAE SO_2 electrochemical sensor	SO_2	0.1 ppm
UltraRAE/UltraRAE 3000 PID with benzene sep filters	Benzene	0.05 - 0. 1 ppm
Gastec detector tube with pump	Benzene	0.05 ppm*

* Gastec detection limits are based upon detector tubes used

CTEH personnel will perform continuous air monitoring in the community using an AreaRAE or MultiRAE Plus. Real-time data using these instruments will be collected for volatile organic compounds (VOCs), hydrogen sulfide (H_2S), oxygen (O_2) and lower explosive limit (LEL). Benzene levels will be monitored using an UltraRAE, UltraRAE 3000 and/or benzene specific colorimetric tubes.

2.1 Sampling Frequency and Coverage

Roaming vehicles in the community will operate 24 hours per day. Air monitoring will be conducted throughout the communities near affected waterways. In addition, real-time air monitoring will be conducted as needed to respond to potential concerns raised on or off-site, and for air quality during operations performed by Fish and Wildlife or first responders.

Two readings will be taken at locations along the length of the spill, returning multiple times to monitor areas with detectable VOCs or benzene levels. Multiple readings in the same location will be used as one method to determine if VOC and/or benzene detects from instantaneous readings from real-time instrumentation are due to transient elevations or spikes in air concentration or if the elevated air concentrations are sustained. If sustained, further air monitoring and/or sampling would be initiated. Benzene readings will also be taken in all areas with detectable VOCs or where an odor is present.

AreaRAEs with data-logging capabilities may also be used at some fixed locations and in roaming to supplement analytical data.

3. Air Sampling

Analytical air sampling will be conducted in community areas close to the waterways impacted by the spill. Analytical samples will be taken in fixed locations (Figure 2) in the community, at locations selected to represent background (Figure 3), at community receptors near oil collection points (Figure 4) and as needed due to changing site conditions, odor complaints, wind direction, and evaluation of benzene or oil-related other air concentrations for possible evacuation and re-entry. Background stations may be eliminated after sufficient data are collected to establish background VOC concentrations. The GPS coordinates of initial analytical stations is included in Appendix A. Methods may include either NIOSH Method 1500/1501 and/or EPA TO-15.

Initial fixed community sampling and background locations were chosen with input from Unified Command representatives and Enbridge industrial hygienist, Daniel Lu, PhD, CIH. Air samples will be collected 2 -3 times per day at each location during a 24-hour period (sorbent tubes or regulated evacuated canisters) or for a 24-hour sampling interval (regulated evacuated canisters) each day. The criteria that will be used to select sampling locations will include proximity to residences, areas of oil collection, and areas downwind of the oil release point. Air samples collected using sorbent tubes will be analyzed for aromatic hydrocarbons using NIOSH method 1500/1501 (Table 2). Canister samples will be analyzed for VOCs using EPA Method TO-15 (Table 3). Methods are summarized in Table 4.

Table 2

Aromatic Hydrocarbons Detected using NIOSH 1500/1501

Group A	Group B
Benzene	Cumene
Toluene	Styrene
Ethylbenzene	p-tert butyl toluene
Xylene	methyl styrene

Table 3

Predominant Crude Oil VOCs Detected by TO-15

Benzene	Heptane, n-
Butane, 2-methyl-*	Hexane, n-
Cyclohexane	Naphthalene
Cyclohexane, 1,3-dimethyl-*	Nonane*
Cyclohexane, 1,3-dimethyl-, cis-*	Octane*
Cyclohexane, butyl-*	Octane, 4-methyl-*
Cyclohexane, ethyl-*	Pentane, 2-methyl-*
Cyclohexane, methyl-*	Toluene
Cyclohexane, propyl-*	Trimethylbenzene, 1,2,4-
Decane*	Trimethylbenzene, 1,3,5-
Dodecane*	Undecane*
Ethylbenzene	Xylene, m&p-
Ethyltoluene, 4-	Xylene, o-

***- Tentatively identified compound (TIC)**

Table 4

Summary of Integrated Air Sampling Method

Analyte	Analytical Method	Sample Media	*Flow Rate (ml/min)*
VOCs	EPA TO-15	Canisters	NA

Aromatic hydrocarbons	NIOSH 1500/1501	Coconut shell charcoal	200

Figure 2
Location of Fixed Analytical Stations

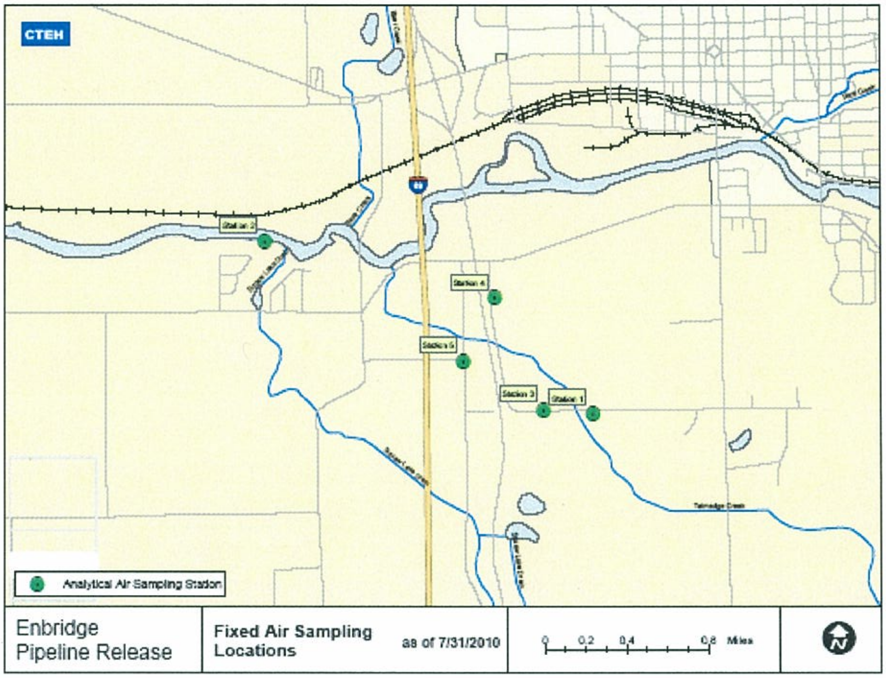


Figure 3
Background Locations

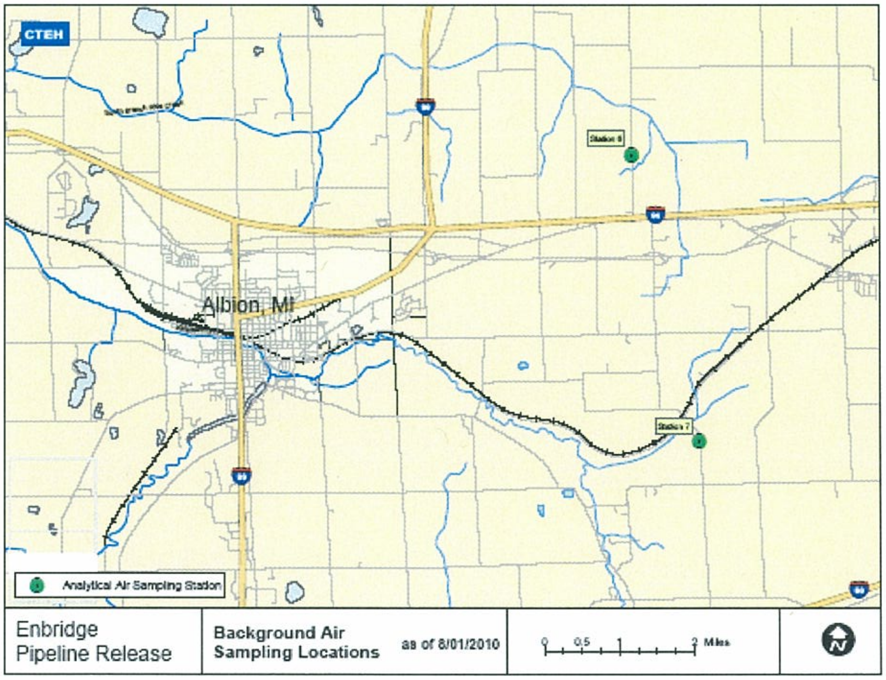
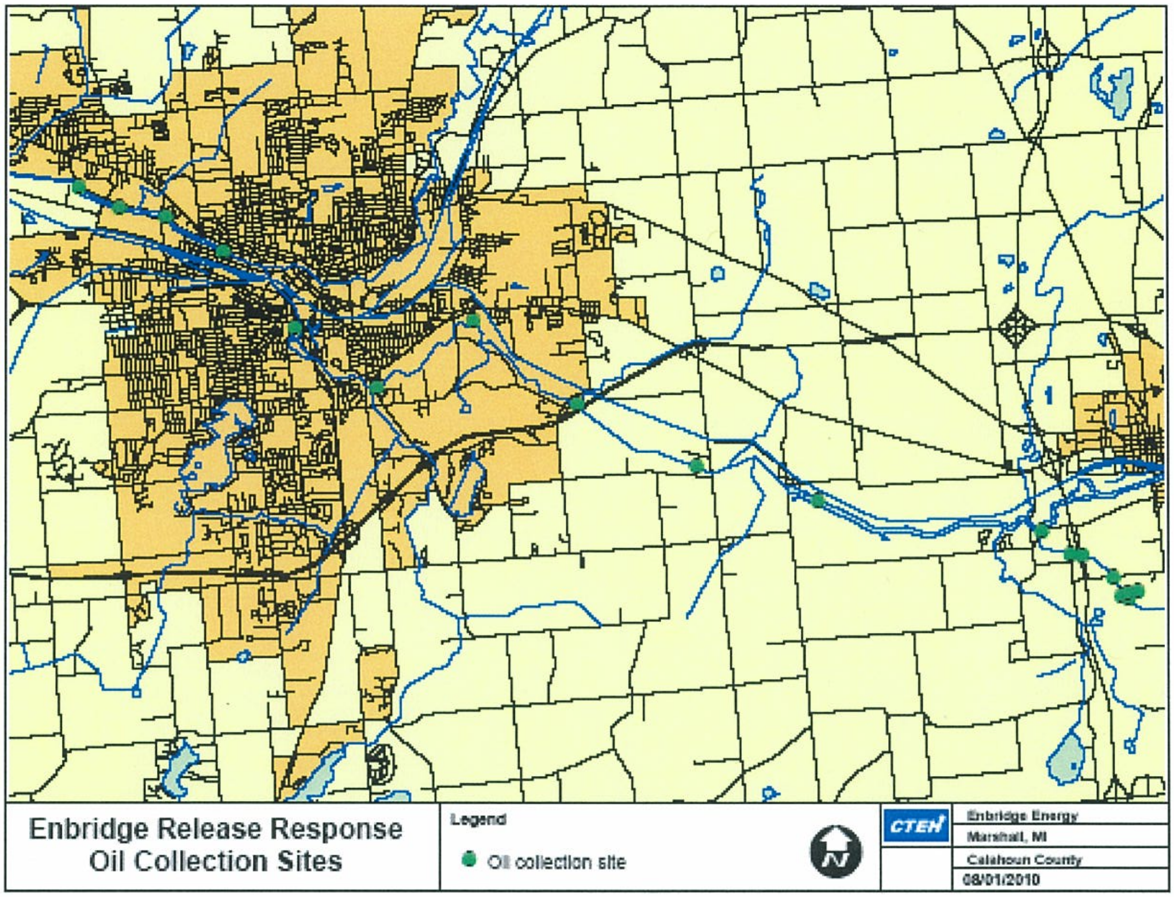


Figure 4
Location of Oil Collection Sites



Evacuated canisters may also be used to collect air samples to address community concerns about odors. Canister samples will consist of either grab or regulated 12 or 24-hour collections. The collection time will be based on monitoring needs. For instance, a grab sample will be collected for confirmatory purposes in response to data from real-time instruments. Longer sampling times may be appropriate for evaluation of air concentrations over time. A 12-hour sampling period would be used for analysis of air concentrations during mitigation activities over a work shift, while 24-hour sampling would be appropriate for evaluating the potential for exposure at certain receptor sites like homes and daycare centers.

All collected air samples will be sent to Galson Laboratories, an American Industrial Hygiene Association (AIHA) accredited laboratory, in East Syracuse, New York. Samples will be expedited for shipping and analysis. A 1 – 2 days turnaround is anticipated for data is anticipated.

4. Odor Investigation

A CTEH team will be designated as the Odor Response Team. The Odor Response Team will be deployed as soon as possible after receiving odor complaints/concerns referred by the hotline, Enbridge, and Unified Command staff. The response team will additionally include representatives USEPA and the Calhoun County Public Health Department, as available. Air monitoring equipment (e.g. MultiRAE Plus, AreaRAE, Gastec colorimetric detector tubes, and/or UltraRAE) will be used to evaluate the levels of VOCs and specific oil-related chemicals in the air. The evaluation of the results should follow the decision process described below.

5. Decision Tree and Action Levels

A decision process has been developed for the evaluation of air monitoring results for VOCs, NIOSH 1500/1501, and real-time detections for benzene. For VOC detections, a trigger level of 1 ppm will be used to designate the need for chemical-specific sampling. The decision process for the evaluation of benzene levels from Ultra RAE, GASTEC, NIOSH 1500/1501, and HAP analysis (Tedlar bag collection) is summarized in Figure 5. If benzene levels are detected above 200 ppb, then confirmation with the HAP instrument should be employed. If benzene levels exceed 60 ppb, then an 8-24 hr time-weighted sample should be collected. The target for longer-term exposures to benzene has been set at 6 ppbv. Air sampling will be performed as need to meet requirements established by the Public Health Unit.

6. Sample Station Locations

Real-time and integrated sampling locations will be selected based on the presence of communities near impacted waterways (Figure 1) and in addressing specific community concerns. Mobile AreaRAE data will be mapped using GPS coordinates. Additional, manually logged real-time data will be collected and reported on CTEH® electronic field and/or paper forms.

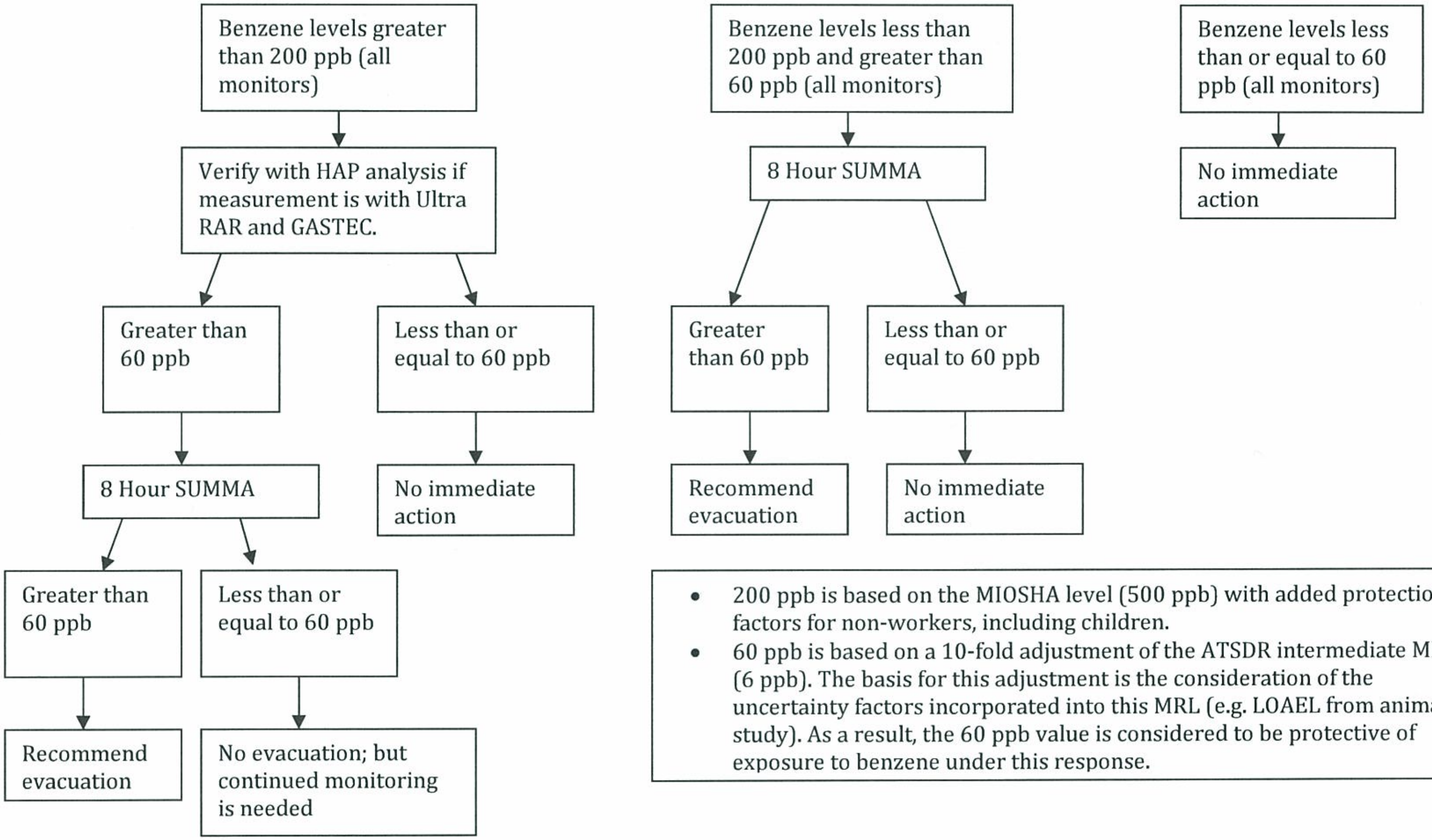
7. Data Quality and Management

Integrated air samples will be sent to Galson Laboratories located in Syracuse, N.Y. Air sampling preliminary results will be provided to Enbridge Energy's designated representative and the USEPA within 1-2 days of receipt by the laboratory. The expedited turnaround time for Galson is one business day. All data will undergo a

Level II data validation by eDATApro prior to release to the EPA SCRIBE data base. The CTEH QAPP is included as Appendix B of this report.

All air sampling and air monitoring data will be provided in a format compatible with SCRIBE. The data management plan can be found in data management plan (Appendix C).

Figure 5
Real-time monitoring for benzene (Ultra RAE, GASTEC, NIOSH 1500/1501, and HAP Analysis) (ppb)



- 200 ppb is based on the MIOSHA level (500 ppb) with added protection factors for non-workers, including children.
- 60 ppb is based on a 10-fold adjustment of the ATSDR intermediate MRL (6 ppb). The basis for this adjustment is the consideration of the uncertainty factors incorporated into this MRL (e.g. LOAEL from animal study). As a result, the 60 ppb value is considered to be protective of exposure to benzene under this response.

8. Project Organization

CTEH will be responsible for the following:

- Toxicological support
- Air data quality assurance/quality control
- Data evaluation and reporting

10. Calibration and Maintenance of Field Instruments

The calibration and maintenance of field equipment and instrumentation will be in accordance with each manufacturer's specifications or applicable test/method specifications, and will be recorded in CTEH calibration logs. Standard operating procedures for each type of instrument are in Appendix D.

11. Chain of Custody (COC)

Each sample will be identified on a chain of custody record. The integrated sample numbering system will include site name, date, analyte, and identification code unique to each sample.

12. Sample Labels

Sample labels will be securely affixed to the sample container. They will clearly identify the particular sample and should include the following information:

- Sampling location
- Date and time the sample was collected.
- Analysis requested.
- Unique identifier

14. Packaging and Shipping

Packaging and shipping of samples will vary depending upon sample media, contaminant concentration, preservation technique, and sample container. The person packaging the samples is responsible to ensure that the sample packaging is in suitable condition for shipping.

Appendix A

GPS Coordinates

Table 1

GPS Coordinates at Fixed Analytical Locations

station_name	latitude	longitude	type
Station 1	42.24643	-84.9762	analytical
Station 2	42.25891	-85.0074	analytical
Station 3	42.24675	-84.9809	analytical
Station 4	42.2547	-84.9855	analytical
Station 5	42.25024	-84.9885	analytical
Station 6	42.28166	-84.6543	background
Station 7	42.22631	-84.6379	background

Table 2
GPS Coordinates at Oil Collection Sites

Site Name	Division	Boom	X	Y
Approx Release Site	Division A		-84.97153654	42.24328227
608	Division A		-84.97595329	42.24275523
A1 Release Site	Division A		-84.97404082	42.24220305
B1 MP 0.0	Division B		-84.97420968	42.24318202
B2 MP 0.3	Division B	Y	-84.97747813	42.24652001
B3 MP 0.9	Division B	Y	-84.98531523	42.2513746
B4 MP 1.00	Division B	Y	-84.98831667	42.25165
B5 MP 1.7	Division B	Y	-84.99537766	42.25689902
C1 MP 5.1 (Add Boom)	Division C		-85.05361235	42.26667246
C2 MP 7.0 (Add Boom)	Division C		-85.08484296	42.27576335
C3 MP 8.9	Division C	Y	-85.11479057	42.29010592
C4 MP 11.1 (Add Boom)	Division C		-85.14015217	42.30864478
C5 MP 13.1 (Add Boom)	Division C		-85.16711736	42.29720573
C6 MP 14.8 (Add Boom)	Division C		-85.18716213	42.3102401
C7 MP 16.4 (Add Boom)	Division C		-85.20406232	42.32651713
E 3.0 MP 33.8	Division C		-85.41261846	42.28422964
E1 MP 25.5	Division E		-85.32282535	42.35359682
E2 MP 28.9	Division E	Y	-85.35818541	42.32421571
Sheen Limit (5:30pm EST 7/27)	Division E		-85.3856568	42.30063438
E2.5 MP 33.3	Division E		-85.40592243	42.28830782
River Oaks County Park Access	Division E		-85.44507052	42.28831395
E4 MP 36.4	Division E		-85.45037364	42.27698084
Sheen Location (9:30 am EST 7-28)	Division E		-85.44282317	42.27655843
E5 MP 38.5	Division E		-85.49021375	42.28348629
D1 MP 17.4	Division D	Y	-85.21820616	42.33452887
D2 MP 17.9	Division D	Y	-85.23023889	42.33697579
D3 MP 18.7	Division D		-85.24040801	42.34165021
D4 MP 19.8 (Add Boom)	Division D		-85.26219413	42.34642123
D5 MP 20.6	Division D		-85.27544835	42.35048898
E1 MP 25.5 Priority 3	Division E		-85.3228204	42.35358879
E2 MP 28.9 Custer Boat Launch (400' boom, 1 Vac Truck, 1 Skimmer)	Division E		-85.35818046	42.3242077
Sheen Limit (5:30 pm EST 7/27)	Division E		-85.38565184	42.30062637
E 2.5 MP 33.3	Division E		-85.40591746	42.28829981
River Oaks County Park Access	Division E		-85.44506554	42.28830594
E4 MP 36.4 Priority 1 Morrow Lake Boat Launch (10500' available boom, 2 Vac Tankers)	Division E		-85.45036866	42.27697283
Sheen Location (9:30 am EST 7-28)	Division E		-85.44281819	42.27655042
E5 MP 38.5 Priority 1A	Division E		-85.49020876	42.28347829

Appendix B

CTEH QAPP

CTEH

Center for Toxicology and Environmental Health, L.L.C.

5120 N. Shore Drive, North Little Rock, AR 72118 Phone: 501.801.8500 www.cteh.com

Quality Assurance Project Plan
Enbridge Pipeline Crude Release

July 29, 2010

Prepared For:
Incident Command

Prepared By:
Center for Toxicology and Environmental Health, L.L.C.
5120 North Shore Drive
North Little Rock, AR 72118

Table of Contents

1. Purpose

This Quality Assurance Project Plan ("QAPP") has been prepared to provide assurance that community air monitoring and sampling activities conducted as part of the response to the Enbridge Pipeline crude oil release meet performance goals. In addition, the methods and procedures described herein were developed in general accordance with conventionally-accepted Quality Assurance and Quality Control (QA/QC) objectives.

2. SCOPE AND OBJECTIVES

This QAPP represents the foundation of QA/QC that will be utilized to assess and verify that sampling, testing, and analysis activities are executed in a manner consistent with applicable guidance and conventional QA/QC objectives. The procedures described in the QAPP are intended to assess the data generated in terms of representativeness, precision, accuracy, completeness and comparability.

Details about the sampling methodologies can be found in the individual work plans prepared for each activity type. Much of the field sampling QA/QC methodology and rationale is described in the individual work plans and, for conciseness, is not reproduced herein. Rather, this QAPP presents the following:

- Project Organization and Responsibility
- Data Quality Objectives
- Sampling Procedures and Field Measurements
- Sample Handling, Documentation and Custody
- Quality Assurance Procedures for Laboratory Activities
- Quality Assurance Procedures for Field Activities
- Data Reduction, Assessment and Validation
- Audits
- Corrective Action

This QAPP is applicable to the work plans approved as of the date of this document. To the extent that other work plans are written and approved that this QAPP is applicable to, those activities will be incorporated by reference to the scope of the QAPP herein.

3. Project Organization and Responsibility

This section describes the project organization and specifies personnel responsibilities. The project organization presented in this section has been developed to guide and assess the quality of sampling and testing procedures for obtaining reliable data, and to facilitate effective communication and decision-making during the project.

3.1. Project Organization

The principal entities relevant to this QAPP that are involved in activities related to the -Enbridge Pipeline Crude Release, and their respective roles, include the following:

- *Enbridge Energy* – Responsible Party
- *Unified Command Health and Environmental Representatives* – review and approval for procedures and deliverables
- *Center for Toxicology and Environmental Health* (CTEH) – complete all site investigation work, including data validation.
- *Sampling Manager* - CTEH project manager responsible for sampling activities

3.2. Responsibility for Quality Assurance and Quality Control

The responsibilities of key members of the proj ct team are summarized in the following subsections.

3.3. Qualified Individual (QI)

Enbridge Energy and their representatives will have full authority to direct, supervise, and coordinate the project team, and to commit resources as deemed necessary. One or more Enbridge Energy designates will be the focal point of communications for contractual matters with the Project Managers and all subcontractors. The QI will oversee all project planning and will review and approve project specifications, plans, and procedures. The QI will have ultimate project responsibility for assuring that the project is completed according to plan.

3.4. Project Manager

CTEH Sampling Managers will be responsible for the preparation of project plans, specifications, and reports within their defined scope of work. The PMs will attend meetings and conferences between Unified Command and any other project participants. They will ensure that the necessary equipment, facilities, and staffing are available to implement their portion of the project.

Sampling Managers are responsible for maintaining the schedule of the work and will regularly advise the QI of the progress of the project. Each PM will provide direction to the field staff and subcontractors involved in field sampling activities within his scope so that the project is completed in accordance with the Work Plans and QAPP. The PM will consult with any subcontractors to discuss compliance with the relevant Work Plans and QAPP, and to evaluate corrective measures if problems occur.

The PM will also be responsible for the development and execution of QA/QC activities in all phases of the project, including plan design, execution, data reduction, and reporting for the scope of work. Each PM will serve as an in-house consultant to the QI in the development of a project-specific internal QC system, as well as providing an independent review of the project approach, methods and design.

3.5. Laboratory Subcontractors

Integrated air samples will be sent to Galson Laboratories and, if resource limitations require, Pace Analytical Services, Inc. and Air Toxics Ltd located in Syracuse. NY, Minneapolis, MN, , and Folsom, CA, respectively. Galson Laboratories is AIHA Accredited, and Pace and Air Toxics are NELAP certified.

3.6. DATA QUALITY OBJECTIVES

This section on Data Quality Objectives (DQOs) presents the intended data usage and QA objectives for the sampling and analysis that will be performed during the project. The overarching DQO is to generate validated data that is suitable for its intended use.

3.7. Intended Data Use and Objectives

The data collected during field activities will be used to characterize the chemical properties of media collected during the response. The data collected during field activities will be used to characterize potential exposures of members of the public to constituents potentially related to the release of oil from the Enbridge Energy pipeline, by reporting on chemical constituents found in the environment at the time and location of sample collection. The data may also be used to inform decisions related to appropriate protective actions necessary to ensure health and safety of members of the community.

3.8. Data Quality/Measurement Objectives

The purpose of DQOs is to establish a target level that can be measured against whether data that is collected (through the sampling and analysis program) are of appropriate quality to produce documented, consistent, and technically defensible results. These results ultimately will define the characteristics and chemical constituent concentrations present at the Site.

The quality of measurements made and the data generated will be evaluated in terms of the following characteristics:

1. Representativeness
2. Precision and Accuracy
3. Completeness
4. Comparability

Specific objectives for each characteristic are established to develop sampling protocols and identify applicable documentation, sample handling procedures, and measurement system procedures. These objectives are established based on Site conditions, objectives of the project, and knowledge of available measurement systems. In addition, the following criteria for chemical sample handling and analysis will help attain the DQOs:

- Standard chain-of-custody procedures
- Analytical testing will be performed according to approved laboratory methods with data packages prepared that are consistent with Level 2 protocol (a Level 3 and 4 CLP protocol may be required in some instances).

3.9. Representativeness

Measurements will be made so that analytical results are as representative as practical of the actual field conditions. Sampling protocols will be utilized to help assure that samples collected are reasonably representative of the media present in the field. Appropriate sample handling protocols, including such tasks as storage, transportation, and preservation, will be used to protect the representativeness of the samples gathered during the project. Proper documentation in the field and the laboratory will verify whether protocols have been followed, and whether sample identification *and integrity* have been preserved.

Representativeness will be assessed also by comparing the results of co-located samples to determine the spread in the analytical results. The results of QC blanks will be examined for evidence of contamination unrelated to the Site on sampling activities. Such contamination may be cause for invalidation or qualification of affected samples. Sample analytical data classified as "questionable" or "qualitative" by any of the above criteria may be invalidated.

It is also anticipated that CTEH sampling activities in some instances may be conducted in cooperation with EPA or other agency personnel. If available, results of co-located samples may be evaluated to address representativeness of samples.

3.10. Completeness

The characteristic of completeness is a measure of the amount of valid data (or samples) obtained as compared with the amount that was specified to be obtained under normal conditions. The objective for completeness is to provide enough valid data to ensure the goals of the field investigation are met. Completeness will be evaluated for each sampling event specified relative to each activity on an individual basis.

3.11. Comparability

The characteristic of comparability expresses the confidence that one set of analytical data may be compared with another. Data sets that can be used for comparison include results of studies conducted previously in the area. Comparability is maintained by use of standard analytical methods, and units consistent with those used in previous studies. Also, the personnel involved in data acquisition and reduction must operate measurement systems within the calibrated range of the particular instrument as well as utilize analytical methodologies that produce comparable results. The comparability of field investigation tasks will be maintained by following the applicable EPA Technical Guidance documents, and/or the applicable Work Plan.

3.12. Analytical Methods and DQOs

Analytical testing will be performed according to the methods outlined in the approved Work Plans.

4. SAMPLING PROCEDURES AND FIELD MEASUREMENTS

The objectives of air sampling procedures and field measurements are to obtain samples and measurements that are representative of the environment being investigated. Through the use of proper sampling tools, sampling techniques, and equipment decontamination procedures, the potential for cross contamination due to trace levels of chemicals will be reduced. These procedures are described further in the individual Work Plans.

5. SAMPLE HANDLING, DOCUMENTATION, AND CUSTODY

The purpose of specific procedures for sample handling, documentation and custody is to maintain the integrity of samples during collection, transportation, analysis and reporting. These procedures are necessary to validate the history of sample data, from collection through reporting, by providing adequate documentation. The sampling handling, documentation and custody procedures are provided in the individual Work Plans. QA/QC checks will be performed during the field activities to assess whether the procedures elaborated in the Work Plans are followed. An appointed representative will perform the QA/QC check prior to packaging the samples and transportation to the designated laboratory.

6. QUALITY ASSURANCE PROCEDURES FOR LABORATORY ACTIVITIES

Qualified laboratories will perform chemical sample analyses of samples collected under the direction of CTEH. Each laboratory maintains an internal *Quality Assurance Plan*. These plans include the respective laboratory's internal QA/QC procedures that cover all aspects of QA/QC during implementation of laboratory procedures. The technical quality systems that are described in the *Quality Assurance Plans* include the following:

- Personnel Qualifications and Training
- Demonstration of Capability
- Standard Operating Procedures
- Documentation and Record-Keeping
- Analytical Test Methods and Procedures
- Method Detection Limits
- Method Quantitation Limits and Reporting Limits
- Traceability, Preparation of Standards, and Reference Materials
- Measurement Process
- QC Samples
- Control Charting
- Performance Evaluation
- Corrective Action
- Preventative Maintenance
- Sample Handling and Management

In addition, the plan includes the following information that will be utilized for this project:

- Test Procedures and Standard Operating Procedures Performed
- Data Quality Acceptance Criteria
- Calibration and QC Requirements
- Containers, Preservation, and Holding Times
- Instrumentation, Software, and Applications
- Preventative Maintenance Schedule
- Training Certification Statements

The Galson Laboratories QAPP has been reviewed and are available from the lab upon request.

7. QUALITY ASSURANCE PROCEDURES FOR FIELD ACTIVITIES

This section describes the general QA/QC procedures related to field activities during the collection, handling, labeling, packaging, preservation, and custody of samples for chemical analysis. Specific procedures for field activities are described in the individual Work Plans. Field QA/QC samples will be used to verify that the sample collection and handling process has not affected the quality of samples that will be subjected to chemical analyses. This section discusses the preparation and collection frequency of field QA/QC samples constituting of blanks and duplicates. This section also provides a general guidance on maintaining QA/QC on the subsequent activities to ensure the goals of the field activities are met.

7.1. Internal Quality Control

Field QA/QC samples will follow the procedures set forth below and in accordance with the individual Work Plans. The required analyses and the amount of sample needed to complete the analyses will be evaluated prior to the initiation of the sampling event. The required quantity of sample matrix to perform all the analyses will be collected.

Co-located Samples – True duplicates of many media types are not typically possible because chemical constituents are rarely distributed uniformly in the media, even within small volumes. For this reason, duplicate samples collected during this project will be referred to as co-located samples. They are samples that are collected at the same time and place.

Co-located samples will be collected for each media type at a rate of approximately 10% of samples collected or at least 1 duplicate sample per day per media type, whichever is greater. USEPA region 5 has been invited to shadow field operations and will collect co-located samples at a rate that they determine necessary.

7.2. Equipment

Appropriate tools and equipment will be utilized for collecting samples during the field investigations. Using the correct equipment for sampling is important in meeting the objectives of QA/QC. Laboratory supplied equipment such as sample containers are generally uncontaminated. However, a simple visual QA/QC check of any containers in cases that were opened may identify certain potential issues. Sample labels will be clearly printed in waterproof, indelible ink and placed directly on the sample container(s).

7.3. Sampling Equipment Decontamination

No sample equipment decontamination procedures are anticipated for this project.

7.4. Calibration, Operation and Maintenance

Instruments and equipment utilized for field measurements will be calibrated in accordance with the frequency requirements and instrument manufacturer's instructions. More frequent calibration may be performed if deemed appropriate. Appropriate methods and calibration material (gases, etc.) will be used and the procedures documented in the field records. The field measurement instruments will be operated and maintained in accordance with the manufacturer's instructions and industry standard specifications/procedures in order to maintain the consistency and reliance of the measurement capacity of each instrument.

7.5. Field Documentation

Field logs, documentation forms, and calculation work sheets utilized during the field investigations will be maintained accurately and in accordance with the requirements of the individual Work Plans. Field logs and form may be collected in electronic format, if deemed appropriate. Copies of paper field logs will be included in the project reports as appropriate.

7.6. Procedures to Assess Precision, Accuracy, Completeness and Comparability

No quantitative levels for precision and accuracy have been specified for field measurements. However, proper maintenance and operation of instruments will be followed to ensure instrument accuracy so that reliable results will be obtained. Multiple readings and analysis of duplicate samples will be performed to measure the precision of field measurements.

7.7. Corrective Action

If QA audits of data result in identification of unacceptable data, the field sampling project manager will be responsible for developing and initiating corrective action. Corrective action for sampling procedures may include evaluating and amending sampling procedures or re-sampling.

8. DATA REDUCTION, ASSESSMENT AND VALIDATION

8.1. Laboratory Data

Reduction of laboratory measurements and laboratory reporting of analytical parameters will be in accordance with the procedures specified for each analytical method (i.e., perform laboratory calculations in accordance with the method-specified procedure). Upon receipt of the laboratory data, the data will be processed according to the Data Management Plan (DMP) included as Appendix B.

8.2. Field Measurement Data

Project data personnel will perform assessment of field measurement data. Data assessment will be performed (as appropriate) by checking calibration procedures utilized in the field, evaluating duplicate and control sample analyses, and by comparing the data to previous measurements obtained at the specific location. Large variations, depending on matrix type, will be examined in association with changes in local conditions and general trends. In some instances, instrument drift or malfunction may be detected. If this is apparent, the data may be disregarded, but a record of the evaluation will be maintained in the project records. If variations in data cannot be explained, the data will be qualified and will be used for appropriate purposes.

8.3. Data Management

Upon successful completion of the data assessment process, the data generated for the investigations will be stored in a central location and/or database. Data summaries and results will be submitted in accordance with the DMP. Further data management details are provided in the DMP.

8.4. Data Validations

All data packages will receive a data package completion check from the corresponding laboratory generating the data package to ensure that the deliverable requirements specified for this project have been satisfied. A Level II data validation will be performed on all sample delivery groups prior to release of the data. Third party data reviews will be conducted on all data as the data are received to assess whether the QC criteria established for the associated analytical methods established for this project have been met. In addition, third party data Level IV validation will be conducted on a minimum of 10 percent of the data packages generated. Further details about data validation are included in the DMP.

9. AUDITS

Quality assurance audits will be performed to assess whether the QA/QC measures are being utilized to provide data of acceptable quality. Further, audits will be completed to verify that subsequent calculation, interpretation, and other project outputs are checked and validated.

9.1. Field Systems Audit

Field auditors will visit field sampling teams periodically to observe the designated control procedures that are set forth in this document and in the individual Work Plans. These audits will address whether field tools, analytical instruments, and reporting processes are selected and used to meet the requirements specified by the project objectives stated in this plan and other project Work Plans. Equipment and facilities provided for personnel health and safety will also be evaluated. Calibration and documentation procedures for instruments used in the field will receive special attention. Field documentation and sample custody records will be reviewed. During the audit, the sampling manager will review data handling procedures with the appropriate personnel. Accuracy, consistency, documentation, and appropriate selection of methodologies will be discussed.

9.2. Laboratory Audit

Laboratory audit procedures are described in the DMP.

10. CORRECTIVE ACTION

Corrective or preventive action is required when potential or existing conditions are identified that may have an adverse impact on data quality. Corrective action can be immediate or long term. In general, any member of the project staff who identifies a condition adversely affecting quality can initiate corrective action by notifying in writing their supervisor or the sampling manager. The written communication will identify the condition and explain how it may affect data quality.

Corrective action in the field is the responsibility of the on-site staff. This includes reviewing the procedures to be followed prior to sampling events and checking the procedures taking place after the sampling event is completed. Corrective action with regard to laboratory analyses are the responsibility of the selected laboratory.

10.1. Immediate Corrective Action

This type of corrective action is usually applied to spontaneous, nonrecurring problems, such as instrument malfunction. The individual who detects or suspects nonconformance to previously established criteria or protocol in equipment, instruments, data, methods, etc., will immediately notify his/her supervisor. The supervisor and the appropriate task leader will then investigate the extent of the problem, if any, and take necessary corrective steps.

If a large quantity of data is affected, the sampling manager must prepare a memorandum to the QI. These individuals will collectively decide on a course of action to correct the deficiencies while the project continues to proceed. If the problem is limited in scope, the task leaders will decide on a corrective action measure, document the solution, and notify the sampling manager.

10.2. Long-Term Corrective Action

Long-term corrective action procedures are devised and implemented to reduce the potential for the recurrence of a potentially serious problem. The sampling manager and the QI will be notified of the problem and will conduct an investigation to determine the severity and extent of the problem. Corrective actions may be initiated as a result of other activities such as audits.

The sampling manager will be responsible for documenting all notification, recommendations, final decisions, and notifying project staff and implementing the agreed upon course of action. The development and implementation of preventive and corrective actions will be timed, to the extent possible, to minimize any adverse impact on project schedules and subsequent data generation/processing activities. However, scheduling delays will not override the decision to correct the data collection deficiencies before proceeding with additional data collection. The sampling manager also will be responsible for developing and implementing routine program controls to minimize the need for corrective action.

Appendix C

CTEH DMP

Data Management Plan

Table of Contents

Table of Tables

Enbridge Pipeline Release
Environmental Sampling Data Management Plan

1. Executive Summary

This plan describes the initial data management needs and workflow for the air sampling activities being conducted by CTEH for the Enbridge Pipeline Release in Marshall, MI.

2. General Information

2.1 Background

Center for Toxicology and Environmental Health, L.L.C. (CTEH®) was requested to respond in support of site operations for the Enbridge Energy crude oil release on Monday, July 27, 2010. CTEH® is providing air monitoring, air sampling, and toxicology support to address public health concerns resulting from the crude oil spill. CTEH® has been conducting community air monitoring and sampling in communities to protect human health.

2.2 Special Considerations

CTEH is collecting approximately 1,000 data points per day, spanning a geographic area along the Kalamazoo River from Marshall, MI to Greater Galesburg, MI. There are over 10 teams working around the clock collecting samples in this area. Managing data in this scenario requires consistent communications to the project managers, field teams, and data management team.

Currently EPA Region 5 is independently managing their data. CTEH will also operate in this fashion, maintaining a local master Scribe database which is published to the merged Scribe.NET.

2.3 Data Management Plan (DMP) Revision History

Document Version	Date of Revision	Author	Description of Changes
Initial Release (1.0)	8/1/2010	Anton Avguchenko	NA

3. Data Workflow and Warehousing

3.1 Real-Time Monitoring Data

CTEH field personnel retrieve readings from hand-held air monitoring devices and enter them into their Motorola MC-55 Enterprise Digital Assistant (MC-55 EDA). After each monitoring data point is entered they are synchronized to CTEH's off-site data warehouse.

3.2 Sampling and Analytical Data

Field analytical data is collected on paper forms and entered directly into Scribe. Meta information about each sample is collected and synchronized using MC-55's (sample ID, latitude, longitude, station name, sample date/time).

3.3 SIERA Data

Sample Instrument Event Receptor Awareness (SIERA) is a program developed by CTEH to provide situational awareness to a project. Field personnel utilize SIERA to geographically tag photographs, establish sampling locations, and document important events. SIERA data points are collected on a MC-55 and synchronized to CTEH's off-site data warehouse.

3.4 EPA Data

EPA Region V is individually maintaining on-site Scribe databases. Their data is published to the centralized Scribe.NET database being maintained by EPA's Environmental Response Team (ERT).

3.5 Roles and Responsibilities

Field Sampling Personnel:

- Operate and maintain the sampling and monitoring equipment
- Collect samples
- Input data into MC-55 EDA.

Sample Handling Personnel:

- Package and ship samples to laboratory
- Generate Chain of Custody (COC)
- Input field sample data into on-site Scribe database

Site Data Manager(s):

- Maintain on-site Scribe database by importing lab EDD's
- Monitoring and field sampling data from CTEH Data Warehouse and SIERA data.

QAQC Team:

- Assist with data processing
- Perform quality control by checking for completeness and accuracy
- Interviewing field personnel to resolve data issues.

3.6 Backup

Daily backups are performed on-site to a removable storage drive using off-the-shelf commercial backup hardware and software. Every evening an off-site dump is performed to CTEH's corporate file server over the network. Nightly, CTEH's fileserver is backed up to tape and stored off-site.

4. Data Collection

4.1 Field Data Collection Methodology and Data Deliverables

Table 1 Field Data Collection Methodology and Data Deliverables

Monitoring/ Sampling/ Analytical Type	Instrument or Method	Data Collection Tool	Data Collection Instructions	File Type	Comments
Real-Time Air Monitoring	MultiRAE	Input direct read-out into MC-55 EDA	Download from CTEH Data Warehouse, import into Scribe	.csv	
Real-Time Air Monitoring	Gastec Color metric Tubes	Input direct read-out into MC-55 EDA	Download from CTEH Data Warehouse, import into Scribe	.csv	
Real-Time Air Monitoring	UltraRAE	Input direct read-out into MC-55 EDA	Download from CTEH Data Warehouse, import into Scribe	.csv	
Air Sampling	Summa	Input field sampling data into MC-55 EDA, fill out paper field forms	Download from CTEH Data Warehouse, import into Scribe	.csv	
Air Sampling	Passive Dosimeter	Fill out paper forms	Download from CTEH Data Warehouse, import into Scribe	.csv	
Air Sampling	Sorbent Tube	Input field sampling data into MC-55 EDA, fill out paper forms	Download from CTEH Data Warehouse, import into Scribe	.csv	
Photos	Digital Image	MC-55 EDA	Synchronized to CTEH Data Warehouse	.jpg	Available through CTEH Data Warehouse

4.2 Data Collection SOP's and Checklists

See Table 1 for data collection SOP's. Additional data streams will be added to the table as they are identified.

5. Data Management

5.1 Data Processing

Table 2 Data Processing

Monitoring, Sampling, or Analytical Type	Instrument or Method	Data Collection Tool	Data Processing Instructions	File Type	Comments
Real-Time Air Monitoring	MultiRAE	Input direct read-out into MC-55 EDA	Download daily CSV in Scribe format, import using custom Scribe import for Monitoring Data.	.csv	
Real-Time Air Monitoring	Gastec Color metric Tubes	Input direct read-out into MC-55 EDA	Download daily CSV in Scribe format, import using custom Scribe import for Monitoring Data.	.csv	
Real-Time Air Monitoring	UltraRAE	Input direct read-out into MC-55 EDA	Download daily CSV in Scribe format, import using custom Scribe import for Monitoring Data.	.csv	
Air Sampling	Summa	Input field sampling data into MC-55 EDA, fill out paper forms	Enter sample ID, date/time and location information directly into Scribe GUI.	.csv	Handwritten field forms are faxed/emailed by field personnel to site data manager.
Air Sampling	Sorbent Tube	input field sampling data into MC-55 EDA, fill out paper forms	Enter sample ID, date/time and location information directly into Scribe GUI.	.csv	Handwritten field forms are faxed/emailed by field personnel to site data manager.

Monitoring, Sampling, or Analytical Type	Instrument or Method	Data Collection Tool	Data Processing Instructions	File Type	Comments
Photos	Digital Image	MC-55 EDA		.jpg	Photos are geographically tagged as well as associated with specific samples and instrument locations

5.2 Scribe Import Mappings

Real-time air monitoring data is exported from the CTEH Data Warehouse using a custom designed format with native Scribe field names. Analytical results from each laboratory are imported after verification and/or validation using a custom import mapping. See appendix A for mapping.

5.3 Data Element Dictionary

The tables below identify what should be considered the minimum data requirements for the identified data source. These elements may increase or have their description changed as a result of a change in operational requirements. A complete list of all data elements in Scribe can be found at http://www.epaosc.org/scribe.

Table 3 Monitoring Data Elements

Scribe Fields	Description	Type	Length	Primary Key?	Req?
Mon_Time	Monitoring Time (hh:mm:ss)	Text	30	PK	Yes
Mon_Parameter	Pollutant	Text	30	PK	Yes
Mon_Date	Monitoring Date (Required)	DateTime	0	PK	Yes
Location	Monitoring Location Code (Required)	Text	30	PK	Yes
InstrumentID	Instrument ID (Required)	Text	50	PK	Yes
Mon_Operator	Organization That Collected the Sampling	Text	50	No	No
Mon_Measurement	Monitoring Measurement	Numeric	0	No	No
Mon_Meas_Units	Monitoring Measurement Units	Text	40	No	No
EventID	Identifies the date of the reporting period and the start/stop time a value is associated with	Text	50	No	No
Latitude	Latitude	Numeric	0	No	No
Longitude	Longitude	Numeric	0	No	No
Coord_Sys_Desc	Coordinate System				
Mon_Qualifier	Monitoring Criteria such as detection limit; action limit or other criteria	Text	10	No	No
Mon_Remark	Monitoring Data Remark	Text	255	No	No
Mon_Source	Describes the averaging period of the result (ie 1-hr avg)	Text	50	No	No

Table 4 Air Sampling Data Elements

Scribe Fields	Description	Type	Length	Primary Key?	Req?
Samp_No	Sample Number. Scribe requires a unique sample number (Required)	Text	25	PK	Yes
Location	Sampling Location Code (Required)	Text	30	No	Yes
EventID	EventID. Use to group data by sampling events. Defaults to 'Sampling' (i.e. EOC; Site Assessment)	Text	50	No	No
Latitude	Latitude	Numeric	0	No	No
Longitude	Longitude	Numeric	0	No	No
Matrix	Sample Matrix (i.e. Air; Vapor)	Text	40	No	No
SampleCollection	Sample Collection Method (i.e. Grab; Composite; Discrete Interval)	Text	30	No	No
SampleDate	Date Sample Taken	DateTime	0	No	No
SampleMedia	Sampling Media (i.e. Summa Canister)	Text	30	No	No
Sampler	Sampler Name	Text	30	No	No
SampleTime	Time Sample Taken (hh:mm)	Text	5	No	No
SampleType	Sample Type (i.e. Field Sample; Field Duplicate; Lab QC; Spike; Trip Blank)	Text	30	No	No
Total_Time	Total Sampling time	Numeric	0	No	No
Volume	Air Sampling Volume. Wipe Sampling Area.	Numeric	0	No	No
Volume_Units	Volume Units	Text	20	No	No

5.3 Entity Relationship Diagram

See Appendix B

5.4 Database Inventory

Table 5 Database Inventory

Name	Database Type	Description	Manager
Enbridge_Oil_Spill.MDB	Scribe	Community/Area Air Monitoring, Air Sampling Data	Anton Avguchenko
Enbridge_Oil_Spill_personnel.MDB	Scribe	Personnel Sampling	Anton Avguchenko
Enbridge_arearae.mdb	MS Access	Community AreaRAE sampling from initial response phase	Anton Avguchenko
Enbridge_Oil_Spill_reporting.MDB	MS Access	Staging/Reporting for Community/Area Air Monitoring, Air Sampling Data	Anton Avguchenko

6. Data Communication

Table 6 Data Communication

Data Source	Owner	Contains	Communication Method	Data Release Frequency	Comments
Real-Time Air Monitoring	MultiRAE	Input direct read-out into MC-55 EDA	Download daily CSV in Scribe format, import using custom Scribe import for Monitoring Data.	.csv	
Real-Time Air Monitoring	Gastec Color metric Tubes	input field sampling data into MC-55 EDA	Download daily CSV in Scribe format, import using custom Scribe import for Monitoring Data.	.csv	
Real-Time Air Monitoring	UltraRAE	Input direct read-out into MC-55 EDA	Download daily CSV in Scribe format, import using custom Scribe import for Monitoring Data.	.csv	
Air Sampling	Summa	Input field sampling data into MC-55 EDA, fill out field forms	Enter sample ID, date/time and location information directly into Scribe GUI.	.csv	Handwritten field forms are hand delivered by field personnel to site data manager.
Air Sampling	Sorbent Tube	Input field sampling data into MC-55 EDA, fill out field forms	Enter sample ID, date/time and location information directly into Scribe GUI.	.csv	Handwritten field forms are hand delivered by field personnel to site data manager.

Data Source	Owner	Contains	Communication Method	Data Release Frequency	Comments
Photos	Digital Image	MC-55 EDA		.jpg	Photos are geographically tagged as well as associated with specific samples and instrument locations

7. Data Verification and Validation

7.1 Verification SOP's and Checklists

See Appendix C

7.2 Data Verification

Prior to import into Scribe, all analytical data will go through level II data verification by third party. The following Quality Assurance/Quality Control (QA/QC) parameters are reviewed during level II:

Chain-of custody: completeness and sample custody

Holding time: time of collection to time of sample preparation and analysis

Preservation: temperature and chemical

Blank Contamination: laboratory and field blanks

Matrix: precision and recovery of matrix spikes, laboratory control samples, duplicates and system monitoring compounds (Organics)

7.2.1 Level II Laboratory Data Report

Level II data reports will also be delivered with the EDD's from the laboratories. The project laboratory will provide reports as a deliverable suitable for data verification. Each data validation package will include, but is not limited to, the following information for review:

- Case Narrative,
- Chain-of-Custody,
- Method blank summary,
- Matrix spike/matrix spike duplicate summary,
- Laboratory control sample recovery summary,

- System monitoring compounds recovery (Organics)

A hard copy and an electronic disk deliverable of the analytical results, consistent with the format specified by the data validator, will be issued by the laboratory. The samples to be included in each SDG will be efficiently grouped such that holding times are not jeopardized for any of the analyses.

8. Data Analysis and Reporting

8.1 Data deliverables

Unified Command (UC), EPA ERT, Enbridge representatives

8.2 Reporting Requirements

Monitoring, sampling, and analytical data will be stored in a normal fashion. All report and map products will identify exceedances of action levels setup in the CTEH's Air Sampling Plan.

8.3 Reporting SOP's and Procedures

Developing these will be the responsibility of the initial site data manager and remote support personnel.

8.4 SQL Reporting Queries:

Developing these will be the responsibility of the initial site data manager

8.5 GIS / Spatial Data Visualization Requirements

Map products are produced using an Arc-Scribe OLE Database Connection to the On-Site Scribe database.

8.6 Site Specific Requirements

Required Tools:

- Scribe (3.8.0)
- Computer/Laptop running Windows XP, Vista, Windows 7 OS
- Network connection to internet (for Scribe.NET subscriptions)
- ArcGIS
- Microsoft Access
- Microsoft Excel
- Web Browser (Chrome, Mozilla Firefox, Safari etc.)

Reference Files:

- CTEH Analytical Results to Scribe Import Data Map
- CTEH Real-Time Air Monitoring to Scribe Import Data Map

Appendix A

Lab Result EDD to Scribe

Data Mappings

Global Lab EDD to Scribe Data Mapping

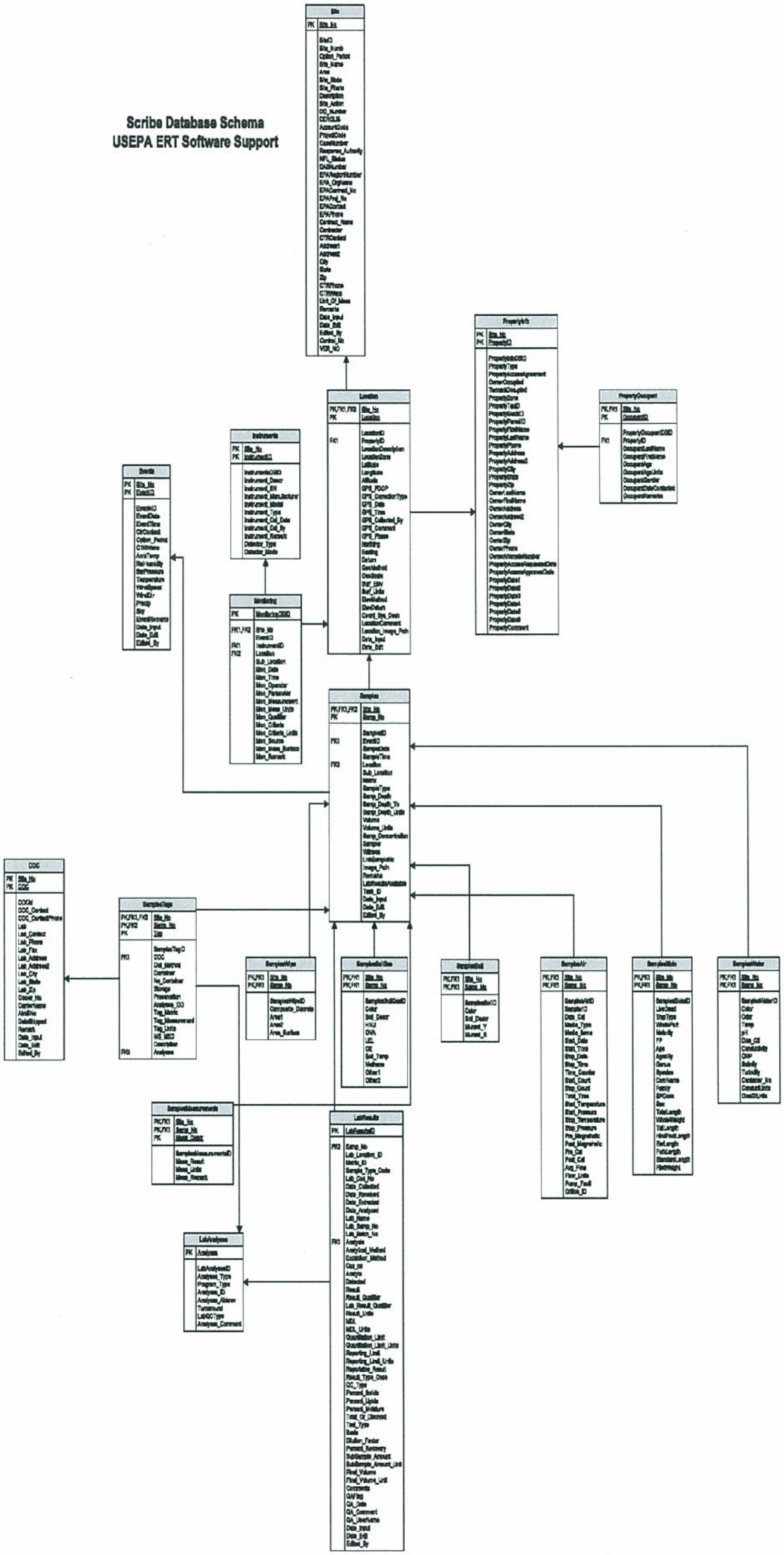
Scribe Fields (Destination)	Import Fields (Source)
Analysis	Analytical_Fraction
Analyte	Parameter_Name
Result_Units	Result_Units
Samp_No	Sample_Point_ID
Analytical_Method	Analytical_Method
Basis	
CAS_NO	CAS_Number_Equivalent
CLP_Sample_No	Project_ID
Comments	Field_Sample_Classification
Date_Analyzed	Analysis_Date_Time
Date_Collected	Sampling_Date_Time
Date_Extracted	Extraction_Date_Time
Date_Received	Preparation_Date_Time
Detected	
Dilution_Factor	Dilution_Factor
Extraction_Method	
Final_Volume	Retention_Time
Final_Volume_Unit	
Lab_Batch_No	Instrument_ID
Lab_Coc_No	SDG_ID
Lab_Location_ID	Site_Sample_ID
Lab_Name	Laboratory_ID
Lab_Result_Qualifier	Laboratory_Qualifier
Lab_Samp_No	Lab_Sample_ID
Matrix_ID	Matrix
MDL	
MDL_Units	
Percent_Lipids	
Percent_Moisture	Percent_Moisture
Percent_Recovery	
Percent_Solids	
QA_Comment	Top_Depth
QA_Date	Middle_Depth
QA_UserName	Bottom_Depth
QAFlag	
QC_Type	
Quantitation_Limit	
Quantitation_Limit_Units	
Reportable_Result	
Reporting_Limit	Reporting_Limit
Reporting_Limit_Units	
Result	Laboratory_Result
Result_Qualifier	

Scribe Fields (Destination)	Import Fields (Source)
Result_Type_Code	Analyte_Type
Sample_Type_Code	Lab_Sample_Type
SubSample_Amount	
SubSample_Amount_Unit	
Test_Type	
Total_Or_Disolved	Filtration_Method

Appendix B

Entity Relationship Diagram

Scribe Database Schema
USEPA ERT Software Support



Appendix C

Data Management SOP's and Checklists

Data Quality Control for Real-Time Air Monitoring QA/QC SOP

- Log into Samples.cteh.com
- Click “Projects” on the left panel
- Click “40005” on the project list
- Click “Realtime Readings” on the left panel
- Click on QAQC Next (#### remaining)

This brings you to your first reading. Review all fields for accuracy. When complete, click Mark QAQC Complete and Next.

Primary fields that require information are:

- Project number
- Reading date (Date should make sense. If a reading has been taken in 2006, this needs to be corrected.)
- Latitude, Longitude
- Region
- Location Category (description of type of monitoring/work being done)
- Indoor/Outdoor (should always be Outdoor)
- Matrix (should always be Air)
- Instrument – Barcode (make sure it is the instrument serial number, not CTEH ID)
- Analyte (VOC, SO2, H2S, PM2.5, Benzene)
- Concentration (only when positive detection) with Units
- Detection flag (always “<”) & Limit - both of these fields should be populated when there is no positive detection
- Initials
- Comments (will not always be filled, but this is where personnel should note visible oil or crude oil odor)

MultiRAE Detection Limits

Analyte	Detection Limit	Unit
VOC	<0.1	ppm
H2S	<1.0	ppm
SO2	<0.1	ppm

UltraRAE Detection Limits

Analyte	Detection Limit	Unit
Benzene	<0.1	ppm

Gastec Tube Detection Limits

Analyte	Tube #	Detection Limit	Volume	Unit
Benzene	121L	<0.05	500mL	ppm
Benzene	121SP	<0.1	300mL	ppm

If a chemical does not have a positive detection, the concentration should never be reported as "0.0." Instead, the detection limit for that chemical should be used based on the sampling equipment used. Particulate matter should always have a concentration.

Enbridge QA

This is a selection on the main page under each project number in Samples. It will take you to a site that has been designed to display the readings for that day that fit certain parameters, such as being VOC detections, incorrect detection limits and missing barcodes. These readings should be the top priority for the QA/QC for that day, although all readings should be QA/QC'd on a daily basis if at all possible.

Changing/Adding information in records:

Information will sometimes need to be changed and/or added during the QA/QC process. When this occurs please note what information was changed or added in the QA/QA comments box. You should also add what prompted the change (ie talked with personnel to correct information).

Quality Flag:

Sometimes a reading will be determined to be not of good quality due to equipment problems, personnel error or some other issue. This drop down box will add a qualifier that will make that reading not included in the reportable data.

There are classifications, for not usable, drift, non-sustained, or sustained. These will cover various scenarios.

Calling field personnel/supervisors:

We will often need to contact the field personnel and/or supervisors to obtain more information or to clarify certain information. The phone numbers for personnel can be found in the Dabble database or on the various organizational charts. Please note in the QA/QC comments that the information was obtained from an interview with field personnel and/or supervisors.

Load Failures:

Occasionally the readings will get hung up in the samples system due to an entry that is not recognized by the system. These will be placed into the Load Failures section on the main page. These readings will need to be opened, then scroll to the bottom to see the reason for the load failure. This will need to be corrected and then the reading will be processed along with the other samples from that day. This should be checked several times a day.

Appendix D

Equipment SOPs

CENTER FOR TOXICOLOGY AND ENVIRONMENTAL HEALTH, L.L.C.

Toxicology Emergency Response Program (June 3, 2008)
STANDARD OPERATING PROCEDURE NO. (Version 1.1)

SUBJECT: SKC Universal Pump Model 224-PCXR8 (5 to 5,000 mL/min)

***Description of the SOP*:** This procedure is intended to provide instruction on the proper use of SKC Universal Sample Pump Model #224-PCXRA for analytical air sampling.

Calibration Instructions:

1. There are two settings for the pump, high flow (≥500 mL per minute) and low flow (<500 mL per minute). To adjust it to high flow or low flow un-screw the smaller copper colored screw located on top of the pump (Figure 1 #18) and you will see a slotted screw (set screw).

2. For high flow sampling:

   a) Turn the set screw (Figure 1 # 18) in a clockwise position all the way down and replace the copper colored screw to the top of the pump.

   b) Attach an approximately 3 foot piece of plain Tygon tubing to the pump intake (Figure 1 #13) on the right hand side of the pump.

   c) Place air sampling media on the end of the tubing not attached to the pump (insure proper directionality of sampling media), with the arrow on the media pointing towards the tubing.

   d) Use a Bios Drycal or DC- Lite to attach to the open end of the air sampling media.

   e) Turn on the SKC pump using the black toggle switch (Figure 1 #8) on the front of the pump.

   f) Adjust the flow rate using the small set screw on the front of the SKC pump labeled "flow adjust" (Figure 1 #11) to the desired flow rate. To increase the flow rate, turn the set screw clockwise. To decrease the flow rate, turn the set screw counterclockwise. Continue to adjust flow rate until calculated flow rate has been achieved. Write your pre-cal on the analytical data sheet (see example).

3. For low flow sampling:

   a) Without any Tygon tubing attached to the pump, turn the set screw (Figure 1 #18) in a clockwise position all the way down.

   b) Using the set screw (Figure 1 #11) and the flow indicator on the front of the SKC pump (Figure 1 #17); adjust the ball so that it is approximately at 1.5.

   c) Turn the set screw on top of the pump (Figure 1 #18) counterclockwise 5 full turns and replace the copper colored screw.

   d) Attach a piece of Tygon tubing to the pump intake (Figure 1 # 13) located on the right hand side of the pump.

   e) An "adjustable low flow holder," (Cat. No. 224-26-01, 224-26-02, 224-26-03, 224-26-04 for single, dual, tri, and quad, respectively) should be attached to the free end of the Tygon tubing.

Cat. No. 224-26-01

Cat. No. 224-26-02

Cat. No. 224-26-03

   f) Place air sampling media on the end of the tubing not attached to the pump (Insure proper directionality of sampling media).

   g) Use a Bios Drycal or DC-Lite to attach to the open end of the air sampling media.

   h) Turn on the SKC pump using the black toggle switch on the front of the pump (Figure 1 #8).

   i) Adjust the air sampling flow rate using the set screw located on the adjustable low flow holder to the desired flow rate. To increase the flow rate, turn the set screw clockwise. To decrease the flow rate, turn the set screw counterclockwise. Continue to adjust flow rate until calculated flow rate has been achieved. Write your pre-cal on the analytical data sheet (see example).

Equipment Use Instructions (step by step)

This instrument has six keys on the front that perform a variety of functions. The following is a review of each key function:

1. The top left hand key is labeled "START/HOLD." When the pump is turned on, push the "START/HOLD" key to pause the pump, the screen will say hold (no air will be pulled through the sampling media). To restart the pump, push the key again.
2. With the pump on hold, press the SET-UP key to enter the "Delayed Start" mode. Enter the number of minutes delay before the sampling period begins by pressing the DIGIT SELECT and DIGIT SET keys. The DIGIT SELECT key advances the flashing digit and the DIGIT SET key increases the value of the flashing digit.
3. Press the MODE key to enter the "Sample Period" mode. Press the DIGIT SELECT and DIGIT SET keys to enter the sampling time period in minutes.

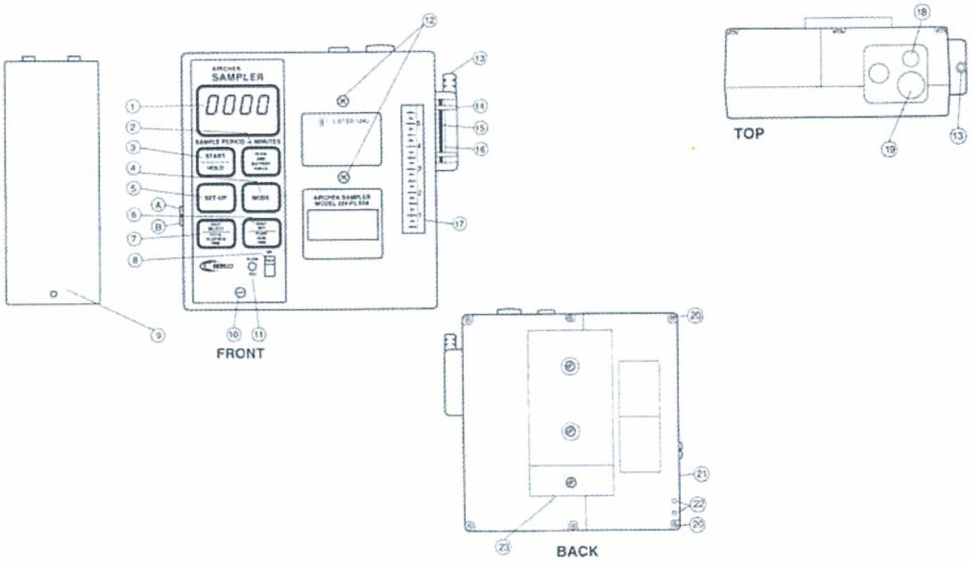
<u>NOTE:</u> The sample period is the *total* time of the sampling event.

4. Press the MODE key to enter the "Pump Period" mode. This is the actual running time of the pump. Use the DIGIT SELECT and DIGIT SET keys to enter the pump run time in minutes. If intermittent sampling is not desired, set the sampling period equal to the pump period.

<u>NOTE:</u> The pump period is the time in which the pump is actually pulling air through the media. Pump period is always equal to or less than the sample period.

5. Press the start button to begin sampling.

Figure 1



Cassette Notes: When using cassettes, the calibration will require a hose with an adaptor tip to insert into the cassette. The cassettes generally require holders, make sure the side of the cassette the air comes in through says inlet.

Placement Notes:

-Pump should be set up so the media is at breathing level.

-Tubing should not be pinched or crimped by position.

-Media should be horizontal to maximize exposure.

-Media should be facing downwards to discourage moisture build up.

-Always cover the pumps if rain is likely. However, media should still be exposed to the outside air. Be sure to tape the sample tag and use a tube cover if applicable.

-If not at an AreaRAE station, make sure to GPS the location for later mapping.

Media Note:

-Some analytes require the use of a tube and a cassette.

-Example: PAH sampling. The air is first pulled through a cassette, which is connected to a tube.

-Some analytes are sensitive to UV rays, these must be handled a certain way after sampling.

-Example: PAH. The tube must be wrapped in foil. The cassette must be pried open using the crescent-ended tool in the media bag. The cassette filter must be picked up with forceps (also in media bag) and placed into an amber bottle. It helps to make double labels for the media. One set on the media, and one set for the bottle and the wrapped tube.

Labeling Note: Especially if rain is expected, using clear tape over the labels will keep the number from smearing. Always make the sample number is as easy to read as possible, do not confuse the letter o from the number zero, etc...

Additional Media Needed for This Equipment:

Air sampling media appropriate for the analyte of concern.

Notification Procedures for Equipment Failure:

1. Tiffani Ray
2. Contact SKC Gulf Coast at 1-800-225-1309 and request a Return Authorization form. Fill it out and ship the damaged equipment with the included form to:

   SKC, Inc
   Attn: Repair Department
   863 Valley View Road
   Eighty Four, PA 15330
   1-800-752-8472

Specialized Training Required or Recommended:

Chemical specific sampling techniques

References and Further Assistance:

1. SKC Universal Sample Pump Operating Instructions for Cat. No. 224-PCXR8
2. SKC 2004 Comprehensive Catalog & Air Sampling Guide
3. http://www.skcgulfcoast.com/
4. Jack Shriver
   9827 Whithorn Drive
   Houston, TX 77095
   1-800-225-1309

Review Date for this SOP

Emily Schmitz and Ben Gehring; June 3, 2008

CTEH®

CENTER FOR TOXICOLOGY AND ENVIRONMENTAL HEALTH, L.L.C.

Toxicology Emergency Response Program (6/17/08)
STANDARD OPERATING PROCEDURE NO. (Version 1.1)

SUBJECT: MultiRAE Plus

Description of the SOP. This SOP describes the set-up and use of the MultiRAE Plus.

Calibration Instructions: Calibration should be done at least once a shift.

To get to Calibration Screen

1) Turn on MultiRAE by pressing and holding the MODE button. Wait for the instrument to warm up.
2) To get to the calibration screen press the MODE and "No" buttons at the same time. Hold until screen says "Calibrate Monitor", press Y/+.
3) When the message "Fresh Air Calibration?" appears, make sure before pressing Y/+ you have either a fresh air environment or are using zero grade air. When calibrating sensors for the first time, do not Fresh Air calibrate.

For Multiple Sensor Calibration

1) To calibrate multiple sensors at the same time in the MulitRAE, select Y/+ at the multiple sensor calibration screen.
2) To accept these chemicals for multiple sensor calibration, press Y/+
3) To change the chemicals for the multiple sensor calibration, press N/- at the "OK?" screen
4) The "Pick" screen will appear. To choose other sensors, press MODE scroll from one sensor to the next and press Y/+ to select a sensor and N/- to deselect a sensor.
5) An asterisk (*) will appear by the sensors that are selected to be calibrated with the multiple sensor calibration.
6) The instrument will recognize the Calibration gas and begin counting down from 59 seconds.
7) After 59 seconds, the instrument will show "Calibration Complete"

NOTE: Quad gas allows for the calibration of CO, H_2S, O_2, and LEL.

For Single Sensor Calibration

1) To calibrate single sensors, select y/+ at the single sensor calibration screen.
2) Use the MODE button to navigate between sensors. Press Y/+ to select the sensor.

3) After pressing Y/+ on the VOC sensor, the MultiRAE will ask you to Apply Gas = Isobutylene.
4) When you apply the calibration gas to MultiRae, it will begin a countdown from 59 sec.
5) At the end of the 59 sec., the instrument will show "Calibration Complete, Turn off cal gas"

NOTE: The MultiRae is set to calibrate to a specific concentration of calibration gas. For each sensor, the calibration gas and concentration will be different.

Using a Different Calibration Gas: If you need to calibrate your instrument with a calibration gas that is not sold to you by Rae Systems, you will need to check the span gas value which should equal concentration of the calibration gas.

1) To modify span gas value, press Y/+ when the "Modify Span Gas Value" screen appears.
2) Use the MODE button to scroll from digit to digit and the Y/+ and N/- buttons to adjust values.
3) Before calibration, the span gas values need to represent the calibration gas concentrations.

Bump Calibration: This is done to check a sensor's function; this does not take the place of a standard calibration.

1) Can be done in either diagnostic mode in the raw screen or in standard mode in the readings screen.
2) Attach the calibration gas that coincides with that sensor to the MultiRAE
3) Expose the instrument to the gas (example: isobutylene to check VOCs)
4) Watch the readings and make sure they reach the correct value. (RAW values have an acceptable range. The ranges for the most commonly used sensors will be provided at the end of the SOP)

NOTE: Always record a calibration in the calibration log, there will be an example form at the end of the SOP.

NOTE: Always calibrate the instrument in the environment it will be used in. If there is too large a change in humidity and temperature, the instrument will not react properly

NOTE: There are special case calibrations for some sensors.
Example: HCl and HF sensors. These sensors have a 4 minute calibration time.

NOTE: Some sensors need to be "burned in" for a period before fully operable.
Example: Cl2, HCL, HF, NO, NH3 sensors: There "burn in" periods are recommended to be between 12-24 hours.

Equipment Use Instructions (step by step)

Battery Replacement and Monitor Start Up

1) Remove the water trap, if applicable, from the inlet. (replace water trap if there is visible dirt or it has been in humid environment)
2) Remove the instrument from its casing.
3) Loosen the screws on the backside of the instrument and remove the front cover.
4) Replace the batteries, and screw the cover back on.
5) Press and hold the mode button until the monitor comes on.
6) Place the instrument back into its protective cover and put the water trap back on unless you are using chemical sensors which call for the water trap to be left off (see MultiRAE handbook for list of sensors).
7) Allow the MultiRAE to go through its startup procedures.

User Mode- Main Screen Menus

1) While the Instrument is showing readings, press MODE to scroll through the main screens.
2) Press MODE once to view the PEAK value.
3) Press MODE again to view the MINIMUM value.
4) Press MODE again for the STEL values. STEL values are only shown for TOX1, VOC, and TOX2.
5) Press MODE again for TWA values. TWA values are also only shown for TOX1, VOC, and TOX2.
6) Press MODE again to view the Battery Power screen.
7) Press Mode once again to view the Date, Time, Temperature, and Time the instrument was turned on.
8) Pressing MODE again will take you to the "Start Datalog?" Screen. Press Y/+ to Start Datalog then the screen will display Stop Datalog. When you stop the datalog, this will complete one event.
9) Press mode once to view the LEL gas= screen. This tells you what calibration gas your LEL is set.
10) Press MODE once more to view the calibration gas to which the PID is set.
11) Press MODE again for the "Print Reading?" Screen.
12) Press MODE again for the "Communicate with PC?" screen. To download information off of the Multi Rae to your computer, press Y/+.

Program Mode - to go into Program Mode, PRESS and HOLD MODE and N/- for 5 seconds. (It is sometimes easier to hold the N/- button first then hold MODE)

Change Alarm Limits

1) All sensors come from Rae Systems with a default alarm limit.
2) These limits can be found in the "Change Alarm Limits" screen on the Multi Rae.
3) Press mode and no at the same time. Use the mode button to scroll through the menu.
4) When the "Change Alarm Limits" screen appears, select Y/+.
5) You will have the option of changing the High alarm, Low alarm, STEL alarm, and the Average alarm limits.
6) Press N/- to scroll to the Alarm limit that you would like to change.
7) Select Y/+ on the alarm limit that you intend to change.
8) Use the MODE button to scroll from digit to digit and the Y/+ and N/- buttons to select digits.
9) To save your changes, hold down the MODE button.

Change Real Time Clock

1) Hit MODE when the command Monitor Setup? appears on the screen.
2) Select "Change Real Time Clock?" to adjust the date and time showing on the MultiRae, then use Y/+ and N/- to adjust the time.

NOTE: ALWAYS do this, and double check it, before you start a datalog.

View or Change Datalog

1) Press MODE and N+/ at the same time. Scroll through the menu by pressing the MODE button.
2) To view or change the Datalog function, press Y/+ at the "View or Change Datalog?" screen.
3) The first option will be to "Clear all Data?"
4) Select Y/+ to clear all of the data in the datalog memory.
5) The next option is to "Reset the Peak and Minimum?"
6) When you select Y/+ to "Reset the Peak and Minimum?" the Multi Rae will prompt "Are you sure?"
7) Select Y/+ to reset your values that you see when scrolling the main menu.
8) The next option is to Enable/Disable datalog? If a * is displayed next to a sensor name, data will be recorded. Use mode to move from sensor to sensor. An asterisk (*) means

the sensor is enabled; no asterisk means the sensor is disabled. Press Y/+ to select, and N/- to deselect. To save changes, press MODE until Save? appears. Then press Y/+ to accept. Otherwise, hold MODE to escape and cancel changes.

NOTE: Do not datalog an instrument that is in diagnostic mode, it will record RAW values. Always restart first then begin datalog.

Change Backlight

1) You can change the backlight mode by pressing Y/+ at the "Change Backlight Mode?" screen.
2) To turn on the backlight, hold the N/- button down.

Change Pump Speed

1) To change Pump Speed continue until Change Pump Speed? appears on screen. Press Y+/ or N+/ to change speed different than what it is previously set. Once you determine which speed you prefer then hold the Y+/ to save.
2) Low pump speed- (default) used when operating conditions that are slow to change, prolongs pump motor life, LEL sensor life and battery run time.
3) High pump speed- use for long lengths of tubing or when rapid changes in input conditions are expected, such as HazMat response or when used for measuring heavy, low vapor pressure compounds like jet fuel.

NOTE: Make sure to note it somewhere on an equipment tag when you have changed the pump speed from a default setting, include your initials and date

NOTE: When using tubing as an extension, we must use Teflon tubing. Tygon tubing readily absorbs volatiles, especially benzene.

Sensor Configuration

1) Hit MODE and N/+ at the same time.
2) Change LEL/VOC Gas Selection?
3) Enable/Disable Sensors?
4) Sensors have assigned sockets. These are identified on the PCB. High bias toxic in socket 1/A.
5) Change PID Lamp Type? This only applies to PID monitors. The PID sensor can utilize either a 10.6 eV or an 11.7 eV UV. Since each lamp type has a different correction factor table, it is important to select the correct lamp type.

NOTE: 11.7 lamps have a much shorter lifespan, be aware of the expiration date and leave Tiffani a note when you mobilize with them.

Using the MultiRAE

1) After recognizing your chemical of concern, look in the technical and application notes and locate the correction factor for that chemical that corresponds with the lamp in your MultiRAE
2) When two or more chemicals of concern need to be monitored, a general rule of thumb is to use the highest correction factor and the chemical with the lowest PEL for action level purposes.

NOTE: Correction factors are very important, for both the VOC and LEL sensors. Look through both TN-106 (PID) and TN-156 (LEL).

NOTE: The new NH3 sensors are un-biased. However the NO sensors are still high-bias.

How to clean a lamp

1) Acquire a lamp cleaning kit. Make sure it includes cotton swabs, methanol, tweezers. Gloves can be found in the ER GO BAG if there are none in the kit.
2) Remove the front cover from the instrument.
3) Remove the metal casing from the PID using the tweezers and wearing gloves. Set it aside.
4) Using the tweezers carefully remove the top of the PID housing, it is usually fairly secure, do not use too much force. Set it aside.
5) Carefully remove the lamp from the base, and securely hold it while you swab with cotton soaked in the methanol. Be careful not to allow cotton fibers to stick to the lamp.
6) Give the lamp a few seconds to dry, then place back into base.
7) Carefully swab the metal screen in the top of the PID housing, and give it a few seconds to dry before replacing.
8) Replace metal casing. If it appears dirty, swab with methanol also.
9) Replace cover on the instrument.

NOTE: If replacing an expired or faulty lamp, please place the old lamp in box the new lamp came out of. Mark the box with the serial number and date removed, and return to Tiffani. It may not have expired yet and be available for replacement.

NOTE: Other than lamp cleaning/replacement or sensor changes, do not manipulate the other components within the instrument. Red tag the unit and return to Tiffani.

Additional media needed for this equipment: (i.e. calibration gas or chemcassettes)

MultiRAE technical and application notes; MultiRAE users manual

Calibration gases appropriate to the sensors being used.

Lamp cleaning kit.

Notification Procedures for Equipment Failure (i.e. Rae Systems tech support number and CTEH contact)

RAE Systems 408.723.4800   CTEH- Tiffani Ray 801.501.8580

RED TAG inoperable equipment properly, example following SOP

References and Further Assistance

Review Date for this SOP

Emily Schmitz and Ben Gehring June 17, 2008

Attachments

Excerpt from TN-123
Calibration Log example
Red Equipment Tag example

CENTER FOR TOXICOLOGY AND ENVIRONMENTAL HEALTH, L.L.C.

Toxicology Emergency Response Program April 14, 2009
STANDARD OPERATING PROCEDURE NO. (1)

SUBJECT: ***MiniCan*** or Mini-canister

Description of the SOP. The purpose of this SOP is to instruct the user about proper methods and operation for collecting a Mini-Can air sample. Upon completion of this manual the user should be able to collect both a grab sample and a time released air sample using a Mini-Can air sampling instrument.

Calibration Instructions

1. All cleaning and calibration should be conducted at the laboratory by authorized personnel.

Grab Sample Equipment Use Instructions (step by step)

1. Ensure that the sampler is not wearing any of perfume, cologne, or aerosol. These products may affect the sample.

2. Remove protective cap from the Mini-Can sampler tip..

3. Using a grab sample regulator, slide the connection collar back.

4. Position the canister on its side in the direction of the area intended to sample.

5. Insert the sampler tip into the regulator and release the collar. ***NOTE: There should not be a gap between the regulator and the canister.***

6. Allow the canister ample time to fill (20-30 seconds)

7. Once the canister has been successfully filled with sample air pull back on the connection collar to release the regulator.

8. Place protective cap on sampler tip.

9. Complete a Chain of Custody form and ship sample in accordance to laboratories shipment instruction.

Additional media needed for this equipment:

Quick Grab Sample Regulator

Time Released Equipment Use Instructions (step by step)

1. Ensure the sampler is not wearing any sort of perfume, cologne, or aerosol. These products may affect the sample.

2. Remove protective cap from the Mini-Can sampler tip.

3. Using a time release regulator, slide the connection collar back.

4. Place canister in area intended for sampling and insert sampler tip into regulator. ***NOTE: For stationary sampling the canister should be placed on its side. For personnel sampling the canister should be fastened using a holster belt with a sampling tube attached to the regulator and clipped to the collar of the individual that is being sampled.***

5. Release the connection collar. ***Note: There should not be any gap between the regulator and the canister.***

6. Allow the sample canister ample time to fill. ***NOTE: Progress can be monitored by checking the vacuum gauge located on the regulator. The pressure should decrease over time****.*

7. Once sample time is complete and canister has been successfully filled with sample air pull back the connection collar to release the regulator.

8. Place protective cap back on the Mini-Can sampler tip.

9. Complete a Chain of Custody form and ship sample in accordance to laboratories shipment instruction.

Additional media needed for this equipment:

Time Released Grab Sample Regulator

Belt holster (depending on sample)

Sample tubing (depending on sample)

Notification Procedures for Equipment Failure

Galson Laboratories
6601 Kirkville Road
East Syracuse, NY 13057

Phone: 315-432-LABS (5227)
Toll Free: 888-432-LABS (5227)
www.galsonlabs.com
mail@galsonlabs.com

Center for Toxicology and Environmental Health (CTEH)
5120 North Shore Drive
North Little Rock, AR 72118
Phone: 501-801-8500
Emergency: 1-866-TOX-CTEH (869-2834)
Fax: 501-801-8501
www.cteh.com

References and Further Assistance.

Centek Laboratories, LLC
143 Midler Park Drive
Syracuse, New York 13206
Phone: 315-431-9730
Fax: 315-431-9731

Review Date for this SOP

Chris Talley

04-14-09

CENTER FOR TOXICOLOGY AND ENVIRONMENTAL HEALTH, L.L.C.

Toxicology Emergency Response Program (June 3, 2008)
STANDARD OPERATING PROCEDURE NO. (Version 1.1)

SUBJECT: Gastec GV-100 and Colorimetric Detector Tubes

Description of the SOP: This procedure is intended to provide instruction on the proper use of the Gastec piston pump (GV-100) with real-time colorimetric detector tubes for a wide range of analytes.

Calibration Instructions:

Factory Calibrated.

Equipment Use Instructions (step by step):

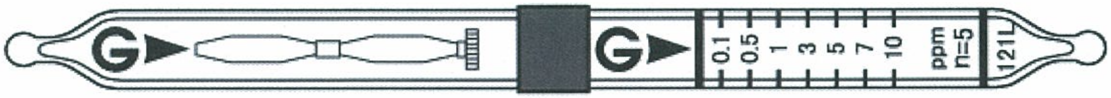
1. Determine your analyte of concern.
2. Pick out a box of detector tubes and insure the following items (The following instructions assume you have picked out a previously un-opened box):
   a) The box of detector tubes is not expired (Expiration date is printed on the top of the box).
   b) The measuring range is appropriate for the sampling you are performing.
3. Determine if the analyte you are sampling for is a single tube method or a dual tube method. To determine this, look on the front of the detector tube box and look at the number of tests. If it says 10 tests, it is a single tube method, if it says 5 tests; it is a dual tube method (example: Benzene 121L).
4. Assuming it is a single tube method:
   a) Break off both ends of the glass detector tube in the tip breaker located on the Gastec pump.
   b) Insert the glass tube in the end of the Gastec pump with the arrow on the glass detector tube pointing towards the pump.
5. Assuming it is a dual tube method:
   a) There will be ten glass tubes in the box, 5 pre-treatment tubes and 5 detector tubes.
   b) Locate a pre-treatment tube (usually in the back row of the box and is identified as a tube with no measuring scale printed on it), a detector tube (usually in the

front row of the box and is identified as a glass tube with a measuring range printed on it), and a pink piece of tubing located between the two rows of tubes.

c) Break off both ends of both tubes using the tip breaker on the side of the Gastec pump.

d) The pretreatment tube should be placed in-line with the measuring tube using the pink piece of tubing. The pretreatment tube should be in front of the detector tube for sampling. The detector tube has the measuring range delineated on it, and should be the one inserted into the pump while the other, pretreatment tube, filters the air before it reaches it.

Note: The arrows on both glass tubes should be pointing towards the Gastec pump.



e) Insert the measuring tube in the Gastec pump.

6. To determine the appropriate number of pump strokes, look at the instructions located in the detector tube box. There are two types of pump strokes, a full stroke (100 mL) and a half stroke (50 mL). To pull a full stroke or a half stroke line up the arrow on the Gastec pump handle with the appropriate volume (either 100 mL or 50 mL). Every analyte has a different measuring range, but generally the more pump strokes that are pulled, the lower the detection limits.

   NOTE: Insure that you are pulling enough pump strokes to get below the particular standard or guideline with which you are comparing your results. Also, the "number of pump strokes" in the directions refers to full (100 mL) pump strokes.

7. The pump stroke is complete when the "Flow Finish Indicator" is visible on the end of the pump handle. The "Flow Finish Indicator" is a white disc that becomes visible after pulling the pump stroke anywhere from 30 seconds to 5 minutes depending on the analyte.

8. To read the airborne concentration of the analyte of concern, look at the measuring scale on the detector tube. Consult the instructions for the appropriate reagent color change that you should expect if the analyte is present in the air at detectable levels. There is a statement on every detector tube such as "n=X", this indicates the number of full pump strokes that you must pull to read the concentration directly from the

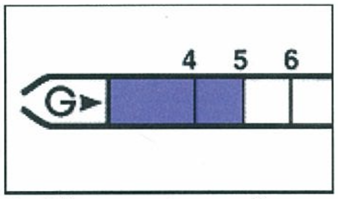
detector tube. If you pull more or less than this number, you must apply a correction factor that you will find in the instructions.

9. Note that all colorimetric detector tubes have chemical interferences as well as corrections for humidity, pressure, and temperature. Consult the instructions for details.

10. Do not re-use a detector tube or pretreatment tube if you have a color change in the reagent (a detection).

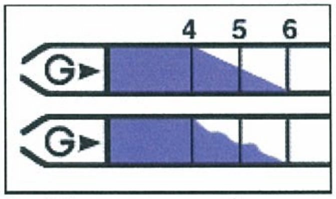
Tips for detector tube reading

When the end of the color change layer is flat, simply read the value at the end.



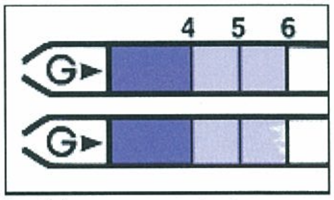
In this case, the reading would be 5%.

When the end of the color change layer is slanted, read the value in the middle of the slant.



In this exaggerated case, the reading would be 5%.

When the demarcation of the color change layer is pale, the mean value between the dark and the pale layer ends is taken.



In this exaggerated case, the reading would be 5%.

Tip for easier reading

When you mark the color change with a pen as soon as the sampling is complete, it is more convenient to read.

Note: It is possible to have a positive detection that is not measurable. This occurs when there is a positive color change, but it is not within the marked, measurable part of the tube. To record this properly you would state that the reading was above the detection limit, but below the measuring range. Example, >1 ppm ,<5 ppm.

11. Dispose of the pretreatment and detector tube according to local governmental standards.

Additional media needed for this equipment:

Detector tubes are available for a wide variety of analytes. We have at least one box of most of the detector tubes that are manufactured by Gastec.

Notification Procedures for Equipment Failure:

Notify: Tiffani Ray

Specialized Training Required or Recommended:

None

References and Further Assistance:

1. Refer to the Gastec Handbook 2nd Edition or later

2. Nextteq, LLC
   8406 Benjamin Road, Suite J
   Tampa, FL 33634
   Phone: 877-312-2333
   Fax: 877-312-2444
   http://www.nextteq.com/

3. http://www.gastec.co.jp/english/index.php

Review Date for this SOP:

Emily Schmitz and Ben Gehring 6/3/2008

Appendix B

Crude MSDS

EnCana Corporation Material Safety Data Sheet

SECTION 1 – MATERIAL IDENTIFICATION AND USE

Material Name: HEAVY CRUDE OIL/DILUENT MIX (CHRISTINA LAKE/FOSTER CREEK)
Use: Process stream, fuels and lubricants production
WHMIS Classification: Class B, Div. 2, Class D, Div. 2, Sub-Div. A and B
NFPA: Fire: 2 **Reactivity**: 0 **Health**: 3
TDG Shipping Name: Petroleum Crude Oil
TDG Class: 3 **UN**: 1267
TDG Packing Group: II (boiling point 35 deg. C or above, and flash point less than 23 deg. C)
Manufacturer/Supplier: ENCANA CORPORATION
#1800, 855 - 2nd Street S.W., P.O. BOX 2850,
CALGARY, ALBERTA, T2P 2S5
Emergency Telephone: 403-645-3333
Chemical Family: Crude oil/condensate mix

SECTION 2 – HAZARDOUS INGREDIENTS OF MATERIAL

Hazardous Approximate C.A.S. LD50/LC50 Exposure
Ingredients Concentrations (%) Nos. Specify Species Limits
& Route
Crude oil 50 - 70 8002-05-9 LD50,rat, skin,>2 g/kg 5 mg/m3 (OEL,TLV)
Hydrocarbon Diluent 30 - 50 N.Av. N.Av. 900 mg/m3 (OEL)*
Benzene 0.03 - 0.3 71-43-2 LD50,rat,oral,930 mg/kg 1 ppm (OEL),
LC50,rat,4 hr,13200 ppm 0.5 ppm (TLV)
Hydrogen Sulphide <0.5 7783-06-04 LC50, rat, 4 hrs, 444 ppm 10 ppm (OEL,TLV)
OEL = 8 hr. Alberta Occupational Exposure Limit; TLV = Threshold Limit Value (8 hrs) *OEL for gasoline

SECTION 3 – PHYSICAL DATA FOR MATERIAL

Physical State: Liquid **Vapour Pressure (kPa)**: 2.5 – 36.5 @ 20C
Specific Gravity: 0.65 – 0.75 **Odour Threshold (ppm)**: N.Av.
Vapour Density (air=1): 2.5 -5.0 **Evaporation Rate**: N.Av.
Percent Volatiles, by volume: 20 - 30 (estimated) **Boiling Pt. (deg.C)**: 40 - 180
pH: N.Av. **Freezing Pt. (deg.C)**: <0
Coefficient of Water/Oil Distribution: <0.1
Odour & Appearance: Brown/black liquid, hydrocarbon odour
(N.Av. = not available N.App. = not applicable)

SECTION 4 – FIRE AND EXPLOSION

Flammability: Yes **Conditions**: Material will ignite at normal temperatures.
Means of Extinction: Foam, CO2, dry chemical. Explosive accumulations can build up in areas of poor ventilation.
Special Procedures: Use water spray to cool fire-exposed containers, and to disperse vapors if spill has not ignited. Cut off fuel and allow flame to burn out.
Flash Point (deg.C) & Method: <-35 (PMCC)
Upper Explosive Limit (% by vol.): 8 (estimated) **Sensitivity to Impact**: No
Lower Explosive Limit (% by vol.): 0.8 (estimated) **Sensitivity to Static Discharge**: Yes, at normal temperatures
Auto-Ignition Temp. (deg.C): 250 (estimated) **TDG Flammability Classification**: 3
Hazardous Combustion Products: Carbon monoxide, carbon dioxide, sulphur oxides

SECTION 5 – REACTIVITY DATA

Chemical Stability: Stable **Conditions**: Heat
Incompatibility: Yes **Substances**: Oxidizing agents (e.g. chlorine)

Reactivity: Yes **Conditions**: Heat, strong sunlight

Hazardous Decomposition Products: Carbon monoxide, carbon dioxide, sulphur oxides

EnCana Corporation Material Safety Data Sheet

Heavy Crude Oil/Diluent Mix – Christina Lake/Foster Creek Page 2 of 2

SECTION 6 – TOXICOLOGICAL PROPERTIES OF PRODUCT

Routes of Entry:

Skin Absorption : Yes **Skin Contact**: Yes **Eye Contact**: Yes

Inhalation: **Acute**: Yes **Chronic**: Yes **Ingestion**: Yes

Effects of Acute Exposure: Vapour may cause irritation of eyes, nose and throat, dizziness and drowsiness. Contact with skin may cause irritation and possibly dermatitis. Contact of liquid with eyes may cause severe irritation/burns.

Effects of Chronic Exposure: Due to presence of benzene, long term exposure may increase the risk of anaemia and leukemia. Repeated skin contact may increase the risk of skin cancer.

Sensitization to Product: No.

Exposure Limits of Product: 1 ppm (Alberta 8 hr OEL for benzene)

Irritancy: Yes

Synergistic Materials: None reported

Carcinogenicity: Yes **Reproductive Effects**: Possibly **Teratogenicity**: Possibly **Mutagenicity**: Possibly

SECTION 7 – PREVENTIVE MEASURES

Personal Protective Equipment: Use positive pressure self-contained breathing apparatus, supplied air breathing apparatus or cartridge air purifying respirator approved for organic vapours where concentrations may exceed exposure limits (note: cartridge respirator not suitable for hydrogen sulphide, oxygen deficiency or IDLH situations) – see also Storage below).

Gloves: Viton (nitrile adequate for short exposure to liquid)

Eye: Chemical splash goggles. **Footwear**: As per safety policy **Clothing**: As per fire protection policy

Engineering Controls: Use only in well ventilated areas. Mechanical ventilation required in confined areas. Equipment must be explosion proof.

Leaks & Spills: Stop leak if safe to do so. Use personal protective equipment. Use water spray to cool containers. Remove all ignition sources. Provide explosion-proof clearing ventilation, if possible. Prevent from entering confined spaces. Dyke and pump into containers for recycling or disposal. Notify appropriate regulatory authorities.

Waste Disposal: Contact appropriate regulatory authorities for disposal requirements.

Handling Procedures & Equipment: Avoid contact with liquid. Avoid inhalation. Bond and ground all transfers. Avoid sparking conditions.

Storage Requirements: Store in a cool, dry, well ventilated area away from heat, strong sunlight, and ignition sources.

Caution: hydrogen sulphide may accumulate in headspaces of tanks and other equipment, even when concentrations in the liquid product are low. Overexposure to hydrogen sulphide may cause dizziness, headache, nausea and possibly knockdown and death. Factors increasing this risk include heating, agitation and contact of the liquid with acids or acid salts. Assess the exposure risk by gas monitoring. Wear air supplying breathing apparatus if necessary.

Special Shipping Provisions: N.App.

SECTION 8 – FIRST AID MEASURES

Skin: Flush skin with water, removing contaminated clothing. Get medical attention if irritation persists or large area of contact. Decontaminate clothing before re-use.

Eye: Immediately flush with large amounts of luke warm water for 15 minutes, lifting upper and lower lids at intervals. Seek medical attention if irritation persists.
Inhalation: Ensure own safety. Remove victim to fresh air. Give oxygen, artificial respiration, or CPR if needed. Seek medical attention immediately.
Ingestion: Give 2-3 glasses of milk or water to drink. DO NOT INDUCE VOMITING. Keep warm and at rest. Get immediate medical attention.

SECTION 9 – PREPARATION DATE OF MSDS

Prepared By: EnCana Environment, Health and Safety (EHS)
Phone Number: (403) 645-2000 Preparation Date: October 15, 2008 Expiry Date: October 15, 2011

Appendix C

Sampling SOPs

STANDARD OPERATING PROCEDURES 2010

STANDARD OPERATING PROCEDURES 2010 - 1

Multi-Media Sampling

Contents

1.0 Sampling Objectives

To collect representative samples of oil; oil derivatives; source oil; oily media and debris; feathers; vegetation, contaminated PPE, contaminated booms and absorbent, etc. for analysis. Call dispatches will originate with the Enbridge call center or Enbridge management individual.

2.0 Equipment

- Clipboard, pencils
- Digital camera
- Field logbook (bound with numbered pages)
- Chain-of-custody (COC) forms
- 30 m waterproof measuring tape
- Disposable spatulas
- Disposable plastic tongs
- 1-qt heavy-duty freezer bags
- 1-gallon heavy-duty freezer bags
- 4-oz pre-cleaned glass jars
- 8-oz pre-cleaned glass jars
- VOA vials prepared for sheen sampling
- Ice chest & 10 lbs. of bagged ice
- Appropriate PPE, incl. disposable powder free nitrile gloves
- Decontamination supplies
- Garbage bags (for investigation derived waste)
- GPS
- “Attachment 1” scale for sample photographs
- Hand-held data collectors
- Pens with water-proof ink
- Custody seals

3.0 Deployment Protocol

The field manager will be notified of any reported media needing evaluation and sampling in the area. The field manager will notify the team in the closest vicinity of the report. The field team will deploy to the location of the media.

4.0 Sampling Methods

4.1 General

Field teams should consist of two technicians. One technician should be the note-taker. The note-taker will record location and date and time of collection, and other appropriate data in their field logbook. The note-taker should also note landmarks that will assist in relocating the sampling site, if necessary. Refer to _SOP-3 Field Documentation_ for procedures to ensure that all notes are complete and detailed.

Important notes:

- Data or other information that is entered incorrectly into the log book should have a single line drawn through it, and be initialed, and dated.
- A vertical line should be drawn and initialed by the writer at the end of each day and at the end of each incomplete page.
- Once project is complete the word "END" should be written below the last entry, dated, and initialed.
- No pages shall be removed from the log book.
- Field notebooks will be relinquished to Field Operations Command once the notebook has been filled or upon completion of the sampling event.

4.2 Sample Photographs

Photograph all sampled oil, reference, and potentially contaminated assemblages. Take obliquely oriented photographs of habitat and structure from approximately 30 feet and nearly normally oriented photos of sampled materials. Any photographs of samples should use the scale included as "Attachment 1" for reference. For photographs taken with a digital camera, keep a detailed photo log so that each photo can be labeled and located as to the oil zone it represents. Label each photo with a unique code, such as team home base and sample number. Photos taken with hand-held data collectors will automatically be linked to the sampling file when data is uploaded. Other photos should be e-mailed to the team leader at the end of the day.

4.3 Complete Sample Collection Form

(A copy of this form is included as "Attachment 3")

4.4 Sample Collection

- Put on gloves; at least one on each hand.
- Determine if a composite or grab sample is most appropriate for the sample.
- Collect sample.
  - For solid materials:
    - Collect sample using disposable sample spatulas/tongue depressors.
    - If the sample cannot be easily collected with a sample spatula/tongue depressor, collect sample utilizing disposable plastic tongs. Samples can also be collected by gloved hand if the materials to be sampled are best handled in that fashion.
    - If the sample is a composite, place sample in plastic clean sample jar or pyrex bowl, and using disposable sample spatula/tongue depressor, homogenize.
    - Dispense sample into appropriate containers.
    - To split the sample for fingerprint analysis, use tongue depressor and remove 2 to 10 grams (approximately the weight of two nickels) and place into two sample containers.

    - Samples of boom, absorbent, or PPE may need to be cut in order to place in sample jars. For safety purposes, care should be taken in cutting the materials. Cutting tools will need to be decontaminated according to accepted methods prior to use on other samples (see SOP-5 Decontamination).
  - For liquids (product):
    - Use a clean sample jar to collect free product.
    - Dispense product into fresh sample container, taking care to avoid contaminating the external surface of the sample jar.
    - Properly Dispose of the jar used to collect and dispense product samples per the waste management plan.
  - For sheen
    - Prepare sheen net apparatus.
    - Slowly drag Teflon sheen net through the sheen. Several passes may be necessary to collect .adequate sample, especially if the sheen is light.
    - Deposit oiled net into 4-ounce jar.

- Three jars will need to be collected. For sheen sampling, three net samples should be collected.
- Custody seal your sample jars.
- All sampling equipment will be disposable and should only be used once then properly disposed per the waste management plan.

4.5 Sample Preservation and Storage

Bag ice in one-gallon freezer bags. Seal sample jars before placing in protective wrap. Seal ice chest with custody seal on the ice chest opening. Cover custody seal with clear packaging tape with two entire wraps around the cooler and transport samples and forms to the analytical lab. Label each ice chest so any courier can easily identify which ice chest should go to which lab.

4.6 Important Sampling Notes

- If portable, Investigative Derived Waste will be disposed of at the Enbridge staging area in the appropriate receptacles. If too large to move, it will be stored at the point of generation awaiting proper disposal.
- All information contained in the field notebook, sample label, Sample Collection Form and Chain of Custody should match, identically. Any deviations could invalidate the sample.

5.0 References

USEPA Region 4, *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual* (EISOPQAM), November 2001

USEPA Region 4, Ecological *Assessment Standard Operating Procedures and Quality Assurance Manuel* (EISOPQAM), January 2002

Attachment 1

Photographic Scale

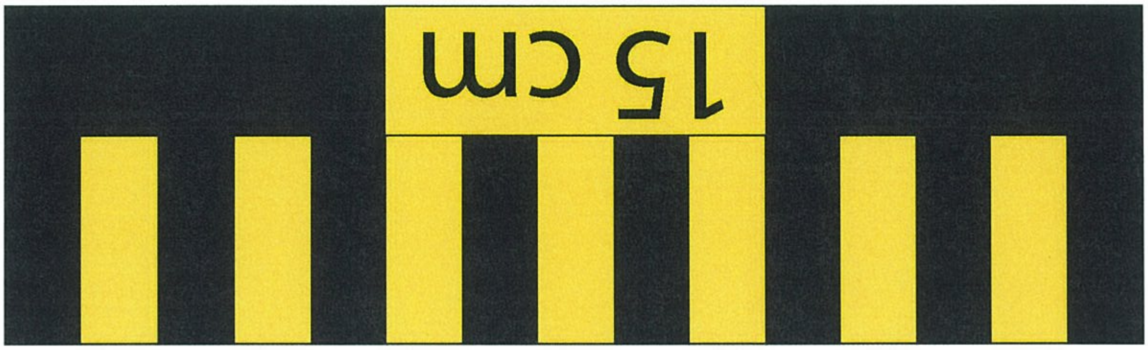
Carlos M. Gutierrez
Secretary, U.S. Department of Commerce

Vice Admiral Conrad C. Lautenbacher, Jr., USN (Ret.)
Under Secretary for Oceans and Atmosphere and NOAA Administrator

John H. Dunnigan
Assistant Administrator,
Ocean Services and Coastal Zone Management
NOAA Ocean Service

August 2007

U.S. Department of Commerce • National Oceanic and Atmospheric Administration • NOAA Ocean Service



Attachment 2

USCG RESPONSE FORM
(Located in front of binder)

Attachment 3

SAMPLE COLLECTION FORM
(attached)

Project Name: ______________________ **Project Number:** ______________

Sample Collection Data Sheet

SAMPLE #	DATE	TIME	SAMPLE LOCATION (State, Latitude, Longitude)	COMMENTS	Name

Notes: ____

STANDARD OPERATING PROCEDURES 2010 - 2

Sample Identification and Nomenclature

Sample Identification/Nomenclature

Matrix Code	
AB	Absorbent or Boom
PD	Product
SE	Sediment
SO	Soil
WC	Waste Characterization
WG	Groundwater
WP	Potable Water
WS	Surface Water

Enbridge Divisions	
A	Release Site to 1st Talmadge Flume
B	Flume Site to Confluence of Talmadge Creek and Kalamazoo River
C	Confluence of Talmadge Creek and Kalamazoo River to Angell Road
D	Angell Road to County Line
E	County Line to Morrow Dam
F	Downstream of Morrow Dam
0	Upstream of Release

Nomenclature:

For ALL samples:

-First two letters will be Matrix Code (see above)

-Third letter will be Division Code (see above)

-Four numbers denoting the date (i.e. 0727 for July 27, 2010)

-Four digit time (i.e. 1300 for 1:00 PM)

-Sampler's initials (i.e. PDS)

-Lastly-the sample type: 1 – Sample; 2 – Duplicate; 3 – MS/MSD; 4 – Rinsate; 5 – Trip blank; 6 – Duplicate

EXAMPLE: Surface water sample collected from Division B on August 12, 2010 at 1:00 PM by PDS - **WSB08121300PDS1**

STANDARD OPERATING PROCEDURES 2010 - 3

Field Documentation

1.0 PURPOSE

This standard operating procedure (SOP) describes requirements associated with the documentation of field investigation (sampling) activities conducted during response activities. Procedures described in this SOP include documentation of field logbooks, sample labels, and chain-of-custody forms.

2.0 GENERAL CONSIDERATIONS

Field documentation is important for both technical and legal reasons. Proper documentation of field activities is a critical aspect of the field investigation (sampling) process. Documentation must be thorough and maintained at all times to track the possession and handling of samples from time of collection through delivery to the laboratory. This documentation is mandatory to locate the sampling site in the future; record sampling methodology and equipment used, and identify personnel responsibilities. In addition, this document also describes the actions and protocols for field data entry into the field logbooks, labeling of samples, and chains-of-custody.

3.0 PROCEDURES

The following sections describe the procedures for proper documentation of sampling events. In the event where these procedures cannot be followed as outlined in the SOP, field technicians must contact their team leader, or supervisor, to get approval for any deviations to the SOP prior to conducting field activities.

4.0 FIELD LOGBOOKS

Field documentation is a critical element of field activities; therefore, field technicians shall strictly adhere to the logbook protocol. During sampling events, a field log book to document sampling activities will be maintained by the field team leader. Information in this log book must be written legibly, and in a clear and concise manner. The following information must be included in the logbook for each sampling event: (first three bullets must appear on the top of every page)

- Your name
- Project Name
- Date of sample collection
- Name of Field team leader, partner in field, and/or auditor or other sampling personnel (USEPA, MDNRE, etc.)
- Name and location of sampling site
- Date of sample collection
- Time of sample/data collection
- Sample identification for each sample. This does not apply to field chemistry

- GPS coordinates (latitude and longitude in decimal degrees) collected from either a MC-55 (handheld) or other approved GPS device
- Daily Sampling Plan (brief description of task and purpose for the day)
- Time of arrival on site
- Time of safety briefing
- Name of on-site coordinator
- Weather conditions
- Pertinent field observations
- Summary of equipment used
- Description of physical characteristics of sample acquired: color, texture, odor, appearance, etc.
- Specific sample characteristics, such as depth, temperature, turbidity, specific conductivity, pH, dissolved oxygen, etc. (if applicable)
- Record of contact with individuals at the site (site safety personnel, federal or state agency personnel, etc. (and company affiliation if known)
- Management and disposal procedures of investigation-derived wastes (IDW) if generated

Logbooks will be provided. Key procedures of field documentation are described below:

- Logbooks must be bound
- Logbooks include consecutively numbered pages.
- Entries into the logbook should be chronological, so that each time notation introduces a new entry.
- Use only indelible ink for logbook entries.
- Record all entries directly and legibly in the log book for each event.
- Strike out any errors with a single line, initial and date the correction.
- Do not leave spaces between entries into the logbook.
- Strike a diagonal line through any spaces at the bottom of each page of documentation in the logbook. On the diagonal line sign and date each page of the logbook.

Logbooks carried into the field shall have the completed pages copied and placed into the appropriate project binders in the office locations. The copies shall be made weekly at a minimum. However, copying daily is preferred to reduce the possibility of loss or accidental destruction of data within the field logbooks. Upon completion of all pages in a field logbook, the logbook becomes part of the project file and will be retained by the water sampling office for future reference.

5.0 SAMPLE LABELS

Sample label must include the following information:

- Preservative
- Parameter
- Sample ID (unique nomenclature for each sample)
- Date
- Time sample was acquired
- Sampler's (technician's) initials
- Type of sample (composite or grab)

Sample labels should be completed with as much of this information as possible prior to departing to the field and will be placed on laboratory glassware only immediately prior to each sampling event. Information such as time must be filled out immediately prior to taking the sample at each location. When completing the sample labels, field technicians should employ the same documentation techniques as previously described in the field logbook section of this document.

6.0 CHAIN-OF-CUSTODY

The Chain-of-Custody (COC) form is a legal record of possession of samples from the time the sample was collected to completion of laboratory analysis. Therefore, strict adherence to the COC protocol must be performed at all times. The COC will be provided to the sampling technician prior to being deployed to the field for each days sampling events, and must accompany the samples at all times. The COC should be completed by the field team leader, or technician, at the time of sample collection and thus should indicate the personnel responsible for collecting, handling and securing the samples. The field team leader will maintain the COC during the sampling event. The following information must be included on each COC (some information may already be completed):

- Client name
- Client Number

- Name of laboratory and address
- Reporting information for results
- Project Name/Number
- Sampler's name and company name
- Matrix
- Date sample was collected
- Time (2400) sample was collected
- Sample type (composite or grab)
- Sample Identification
- Number of containers for the sample
- Preservative
- Parameters (analysis being performed)
- Number of containers for each parameter

When completing the COC's, the field technician will employ the applicable field documentation techniques as previously described in the field logbook section of this document. Blank spaces will be addressed in the same manner as field logbooks, and should be lined through unless it is obvious from the nature of the COC section that information will be added to those sections at a later time, e g. spaces marked "for lab use only". Strike a diagonal line through any spaces at the bottom of the sample field box on the COC. On the diagonal line, sign and date the COC.

Upon completion of the quality assurance /quality control (QA/QC) inspection the original COC and the samples will be relinquished by the technician to the Field Sampling Manager or other qualified supervisor. A working copy of the COC will be retained in the working files within the mobile office for reference. The receiving laboratory will provide a completed copy of the COC as part of the data deliverables and will become part of the Project Files.

7.0 REFERENCES

- U.S. EPA. *A Compendium of Superfund Field Operations Methods.* Office of Solid Waste and Emergency Response. Directive 9355.0-14, 1987, http://www.hanford.gov/dqo/project/level5/Sfcompnd.pdf.

- U.S. EPA. *Compliance-Focused Environmental Management System-Enforcement Agreement Guidance.* National Enforcement Investigations Center. EPA-330/9-97-002R,2005. http://www.epa.gov/ocearth/resources/policies/neic/cfems_05.pdf.

- U.S. EPA. *Contract Laboratory Program Guidance for Field Samplers.* Office of Superfund Remediation and Technology Innovation. OSWER 9240.0-44, EPA 540-R-17-06, July 2007: http://www.epa.gov/superfund/programs/clp/download/sampler/clp_sampler_guidance.pdf.

- U.S. EPA. *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA.* Office of Solid Waste and Emergency Response. Directive 9355,3-01, 1988. http://www.epa.gov/superfund/policy/remedy/pdfs/540g-89004-s.pdf.

- U.S. EPA. *Guidance for Performing Preliminary Assessments Under CERCLA.* Office of Solid Waste and Emergency Response. Directive 9345.0-01A, 1991. http://www.epa.gov/superfund/sites/npl/hrsres#PA%20Guidance.

- U.S. EPA. *Guidance for Performing Site Inspections Under CERCLA.* Office of Solid Waste and Emergency Response. Directive 9345.1-05.1991. http://www.epa.gov/superfund/sites/npl/hrsres#PA%20Guidance.

- U.S. EPA. Region 4, *Logbook Operating Procedure.* Document #SESDPROC-010-R3. November 2007.

End of Document

STANDARD OPERATING PROCEDURES 2010 - 4

Surface Water and Sediment Sampling

Table of Contents

Surface Water and Sediment Sampling SOP

1.0 Purpose

The purpose of this standard operating procedure (SOP) document is to describe methods for sampling water and sediment.

Water sampling will consist of recording water chemistry data as well as collecting water samples for further water quality laboratory analysis, while sediment sampling will consist of solely collecting samples for further laboratory analysis. Water samples will be collected from the middle of the main channel. Sediment samples will be collected from the middle of the main channel, with the exception of the locations where transects are specified in the SAP. The list of analytes will continue to be updated based on results and may be reduced based on repeated evidence of non-detection. Any changes to the analyte schedule will be made in consultation with Unified Command.

The data obtained from these samples, along with any significant field observations taken at collection points (e.g., sheen, odor, etc), will be recorded in the sampling record..

2.0 General Considerations

2.1 Safety

A copy of the health and safety plan should be easily accessible on the vessel, in the vehicle, or on the sampler's person.

2.2 Safety briefing

Before sampling each day, a site safety briefing must be conducted. The briefing will be recorded on the Safety Briefing Form and should address potential safety hazards and describe courses of action in the event of an emergency or in climate weather. All team members and samplers from other agencies should be included in the daily safety briefing (as needed). Additional site-specific safety considerations should be addressed by the team as they arise.

2.3 Personal Protective Equipment (PPE)

Samplers must wear proper PPE at all times that is specific to the work they are doing and the hazards they may encounter. This may include but is not limited to long pants, close-toed, steel-toed shoes/boots, hard hats, Tyvek suit (if needed), and proper sun protection such as hat and safety glasses, and fire retardant clothing as directed by the Company. A PFD (Personal Flotation Device) must be worn when within 10 feet of a water body or when on a boat, dock, or bridge. If a question arises concerning what is appropriate site specific PPE that determination will be made by the Site Safety Officer, Field Team Leader, supervisor, or water sampling manager. During water sampling, powder-free nitrile gloves must be worn at all times with the exception being to collect or record water chemistry data with field instruments. However, while calibrating the instrument, gloves must be worn. In all cases, nitrile gloves will be changed before and after the decontamination process and between each sampling event; also when clean gloves are contaminated by touching contaminated equipment or surfaces.

2.4 Sampling Safety and Access

For all water quality and sediment sampling from a vessel, the boat will be anchored and all the motors and gas powered generators powered off before sampling begins. The sampling location should be approached from downstream, and the sample shall be obtained from the upstream side of the boat. If a safety issue arises such that it becomes a danger to either anchor or power off the motor(s) water quality/sediment samples will not be collected. If only water chemistry data are to be recorded, the boat need not be anchored nor motor powered off to collect data. This is not recommended and should only be conducted if a safety issue arises, and after consultation with the Field Team Leader. In any case, sampling should be conducted away from the boat motor or bilge pump if located on the vessel. In all cases, the sample should be taken from the upstream side of the boat.

Appropriate on-land safety protocols will be followed as outlined in the site specific Health and Safety Plan.

2.5 Sample Sites

The sample sites are predetermined sites based on the operations analysis for the project. These sites are subject to change as sampling goals and directives change, and are available in the Project Work Plan.

2.6 Labeling

Labels for samples will be written in a clear and concise manner which is legible. Sample labels are written in permanent marker and include sampler, analysis, date, time, sample ID and preservative. Additionally, those samples must be taped completely around each piece of laboratory glassware with a clear packing tape. It is also acceptable to write the sample Identification Number on each lid of laboratory glassware; however, if those sample labels are taped it is not required to write on the lid. A detailed description of relevant Standard Operating Procedures (SOPs) for field note documentation and labeling can be found in as a corresponding attachment to this SOP.

2.7 Note Taking

Daily field notes will be written in field books in a clear and concise manner which is legible. Each page of field notes must have three main pieces of information: your name (and affiliation), the project name and number, and the date.

Below that, you will note each sample taken in the following format (for example purposes only):

> 10:14 30.59623, -88.151809. Tar ball collected. No odor, brown in color, about the size of a nickel with a thickness of one half inch. Noticed a high abundance of green algae washed up on shore covering about 75% of the beach at the shoreline. Skies are clear, ~85 °F, with calm winds.

Notes, as shown above, will include time, GPS coordinates, Sample ID (if a sample is collected), and any factual observation

At each location, observations of aquatic vegetation, water depth and/or water velocity shall be made.

- Aquatic Vegetation: visually describe quantity and types of aquatic vegetation observed.
- Water Depth: using a marked staff, weighted line, or similar device, record the water depth at the sampling location.
- Water Velocity: using a Watermark Model 6200 "USGS type" current flow meter, record the water velocity at the sampling location.

2.8 Daily document submission

Daily field notes, safety briefing, and chain of custody forms must be copied and inserted into the specific binder after completion of each sampling day. These documents are to be kept in chronological order by geographical river division rather than by individual sampler.

2.9 Preventing Contamination

Samples will be collected with a variety of sampling equipment. All equipment will be used according to manufacturer recommendations and instructions. Decontaminated equipment and new expendable sampling gear will be used for each successive sample to prevent sample contamination.

1) Nitrile powder-free gloves must be changed between calibration and sampling events, between sampling sites, and whenever clean gloves come into contact with a surface that has not been decontaminated.
2) The sampler nozzle (if used) cannot come into contact with any potentially contaminated surface, including boat surfaces, clothes, ungloved hands, etc. Be especially sure when filling laboratory glassware the lip of the vial/bottle does not touch the sampler nozzle.
3) Do not let the lip of the clean bottles/vials come into contact with any potentially contaminated surface, including but not limited to: pant legs, boats, ungloved hands, weights (for bottles), rinseate solution, sun screen, diesel fumes, etc.
4) Use a clean decontaminated surface to set unfilled and filled sample bottles before they are placed on ice and only open the sample vial immediately before collecting sample.
5) Fill preserved vials without overflow as the preservatives will exit the bottle and not effectively preserve the sample; also, this overflow may damage clothing or working surfaces as well as labels.

3.0 Field Water Quality Measurements

3.1 Water Chemistry

Water depth will be measured at each sampling location. Sample depths will be based on the water depth at the chosen location. Three samples will be collected from the water column.

One sample will be collected from the surface, one sample at the approximate mid point of the column and one sample from within 6"-1' of the sediment layer or bottom.

Water chemistry parameters include those collected from a field instrument (YSI or equivalent) and turbidimeter (or equivalent) (Water Temperature (°C), pH, Specific Conductivity ($^{mS}/_{cm}$), and Dissolved Oxygen ($^{mg}/_{L}$)) and have a minimal recommended holding time. Dissolved oxygen, pH, specific conductivity, and water temperature data are collected using a YSI Multi-probe Professional Plus, YSI 556MPS, or equivalent. Both YSI (or equivalent) units and turbidimeters will be calibrated once at the beginning of each sampling day, unless abnormal readings, damage, or malfunction of the YSI occurs throughout sampling. If any of these events occur, the sampler should calibrate the instrument again before taking the next sample. The dissolved oxygen parameter must be calibrated in the field while those other parameters can be calibrated in another prior location. Each day's calibration must be documented on the Calibration Log (Appendix B).

3.2 Turbidity (NTU)

If requested by the state or USEPA, a turbidity reading will be taken at each sampling site as well. Turbidity is calculated using a HACH 2100Q turbidimeter (or equivalent), which should be calibrated at the beginning of each sampling day.

4.0 Water Quality Sampling

A. *Surface Water Samples*

1) In the event that free phase oil is observed on the surface, no samples will be attempted.
2) The surface samples will be taken by dipping the bottles into the surface of the water, being careful to not lose any of the preservative.
3) In the event a sheen is noted on the surface, a sheen sample will be taken as described in Section 4.4 of *SOP-1 Multi-media Sampling*

B. Potential sampling methods for deeper samples are Kemmerer bottle or peristaltic pump.

1) Peristaltic Pump

i. The peristaltic pump will use disposable poly tubing that will be changed between sampling locations. The tubing will be attached (avoid the use of any tape within 1' of the end of the tube) to a marked staff or marked weighted line and lowered to the desired depth. The pump will be turned on and purged for a period of one minute.

ii. In the event a sheen is noted on the surface, the tubing shall be connected to the peristaltic pump as described in B(1)i above, and air pumped down the tubing to create positive pressure and prevent the entry of sheen into the tubing . The tubing will then be attached (avoid the use of any tape within 1' of the end of the tube) to a marked staff or marked weighted line and lowered to the desired depth. The pump will then be turned on and purged for a period of one minute.

   iii. After the bottles are filled for that depth, the tubing will be lowered to the next depth and the process repeated.

2) Kemmerer Bottle

   i. Obtain the sampler and check the knot at the bottom of the sampler for tightness and size. The knot should be sufficiently large so that it will not pull through the central tube of the sampler.

   ii. To prepare the sampler for making a cast, cock the sampler by pulling the trip head into the trip plate. Holding the top and bottom stoppers and giving a short, hard pull to the bottom stopper does this.

   iii. Tie the free end of the line to the railing of the vessel. This is done to prevent accidental dropping of the sampler should the person operating the sampler let go of the line.

   iv. Lower the sampler to the desired depth. When the sampler is at the desired depth, attach a messenger to the line. This is best done with the messenger held over the deck until it is securely attached to the line.

   v. Release the messenger. It will slide down the line to the sampler where it will trigger the stoppers and they will close the ends of the tube. The stoppers seal by their own weight.

   vi. Retrieve the sampler. Untie the line from the railing and carry the sampler to the sample prep area where the water sample can be transferred to clean sample glassware for storage and transport to the laboratory.

   vii. In the event additional sample is required, repeat steps I – vi as necessary

4.1 Sample Kits

Bring appropriate bottles as outlined in the sampling plan.

4.2 Bottle Procedures

1) Nitrile powder-free gloves must be worn when decontaminating and sampling.
   a. Used gloves will be changed for clean before and after both decontamination and sampling events.
2) Decontaminate the sampler following the Decontamination procedure described in the Decontamination SOP.
3) Record the time, depth range, GPS coordinates, any factual observations/ descriptions, and sample identification number in the field notebook.
4) Allow some sample water to purge from the nozzle or sampling equipment into the decontamination bucket below before beginning sample collection.
5) Fill all 11 pre-labeled sample bottles.

   a. The 3 40-mL Volatile Organic Analysis (VOA) vials are filled first. To fill VOA vial, allow sample water to form a meniscus while preventing overflow of the vial. Keep vial perpendicular to ground and screw lid on, making certain there are no air bubbles in the vial. To check for air bubbles, invert the vial and hit against palm of hand. If an air bubble is observed the vial must be refilled until no air bubbles are detected. However, make sure not to pour sample over vial to avoid contamination and loss of preservative.

6) Place all sampling bottles back into bubble wrap, into their respective zip lock bags (which are also labeled with the sample ID and hold an entire sampling kit), and then in cooler of ice (4±2°C).
7) A Chain of Custody (COC) form is filled out before a Quality Analysis/Quality Control check of samples is complete. Samples are then sent out to the appropriate laboratory. See *Standard Operating Procedures for Field Documentation* (Appendix D).
8) Those samples will be relinquished after all bubble-wrap and zip lock bags have been sealed and coolers have been taped shut over their respective custody seals.

4.3 Split Samples

In the event that split samples are collected by state or federal representatives for submission to independent, third party laboratories, sample containers will be provided by those agencies or their designates if requested in advance.

Split samples are taken from the same grab sample. Often two grabs are needed to obtain enough source water for all 20 bottles of the split sample. The VOA vials are filled first. All amber bottles are filled halfway first and then filled completely with the second grab sample. Split samples are documented in the field notebook along with the time they were taken.

4.4 Duplicate Samples

For water quality sampling, a duplicate sample will be collected on a 5% interval basis; at a minimum, one per day.. A duplicate is a second sample at a certain site that will be submitted to the same laboratory under a different sample ID. This duplicate is to verify consistency in sample collection and decontamination techniques. The duplicate sample is taken in the same manner as a split sample; each of two grabs taken will fill half of all sample glassware to homogenize the sample. Field notes must document from which sample a duplicate was taken, along with all other pertinent information that should be included in sample documentation.

4.5 Rinseate Samples

Equipment rinseate blanks will be collected after completion of each day's sampling events and used to monitor the effectiveness of each team's decontamination process. The rinseate sample is taken after the final decontamination. Rinseate blanks will be prepared by passing deionized water through and over the surface of decontaminated water sampling equipment (although deionized water is always preferred, distilled water is acceptable but must be documented in field log book and in the comments section of MC-55 or MC-35 handheld or equivalent). The rinse water will be collected in appropriate sample bottles, preserved, and handled in the same manner as other samples collected that day. One rinseate blank will be collected for each day of sampling for initial sampling events. If impacted surface water is identified in sampling events the frequency of rinseate blanks will be evaluated for modification.

4.6 Trip Blanks

A set of trip blanks is to be present in each cooler that will hold a VOA vial during the sample day. A trip blank set consists of three pre-filled VOA bottles, which will need to be labeled at the start of each sampling day. The trip blanks are to be kept on ice (4±2°C) in the cooler and sent through the quality assurance/quality control process at the conclusion of the sampling day (for proper labeling procedures see Appendix D). These trip blanks are also sent to the appropriate lab with samples collected.

5.0 Sediment Sampling

Sediment sampling will be performed in two types of locations;

1. Programmatic sediment sampling will consist of a single sample collected from the middle of the main channel using a dredge sampler.
2. Transect sediment samples will be taken at selected locations and deeper samples will be taken using a coring device or bucket auger.

5.1 Sample Site Locations

Sediment sampling sites are determined by the project team in conjunction with other stakeholders and are subject to change. Those locations will be available in the figures in the concurrent SAP. All sampling should be performed in depositional areas; the exact location to be decided based on field conditions evaluated by the sampling team. Once the location is determined, it shall be surveyed and marked on the bank so that subsequent sampling events can easily and with confidence be performed at the same location.

5.2 General Considerations

For all water quality and sediment sampling from a vessel, the boat will be anchored and all the motors and gas powered generators powered off before sampling begins. The sampling location should be approached from downstream, and the sample shall be obtained from the upstream side of the boat. If a safety issue arises such that it becomes a danger to either anchor or power off the motor(s) water quality/sediment samples will not be collected. If only water chemistry data are to be recorded, the boat need not be anchored nor motor powered off to collect data. This is not recommended and should only be conducted if a safety issue arises, and after consultation with the Field Team Leader. In any case, sampling should be conducted away from the boat motor or bilge pump if located on the vessel. In all cases, the sample should be taken from the upstream side of the boat.

Also, if dense product is observed on the surface, no sampling will occur at that sampling site for that day. However, if only a light sheen or pockets of floating product is present, the ultimate decision of whether or not to sample belongs to either the Field Team Leader or his/her supervisor.

5.3 *Sediment Sampling Procedure*

Sediment samples from sampling locations 2 inches or less from the surface may be collected with a stainless steel trowel or stainless steel Ponar or Ekman dredge to obtain a sample from the upper 2" of sediment. Samples collected from the transects will be obtained using a bucket auger or a Wildco core sampler to obtain samples from the upper 6" of sediment. The sample will be mixed in a Pyrex baking dish or on a new piece of aluminum foil. The sediment samples are placed in either four 4-oz sediment jars or one 8-oz and two 4-oz sediment jars that are pre-labeled.

Protocol for collecting sediment samples in deep water:

1) Place tarp or protective covering on flat surface of vessel (boat)
    - Decontaminate all sampling equipment (Ponar/Ekman dredge, Wildco® Hand Corer, Pyrex dish, and stainless steel sampling spoon, etc.) prior to sample collection.
2) Sample Collection
    a. When only the top two inches of bottom sediment sample is required for laboratory analysis, the Ponar/Ekman dredge will be used.
        - Determine Ponar/Ekman dredge is locked in open position by the safety pin, and lower into water.
        - Make sure to keep Ponar/Ekman rope taught while lowering as to not let safety pin disengage.
        - Also, industrial work gloves should be worn while lowering and lifting Ponar/Ekman (clean nitrile powder-free gloves must be worn before any sample may be handled).
        - After equipment has reached sediment, either send messenger down rope to trigger the device closed (Ekman), or slowly pull rope toward surface to close equipment with sediment inside (Ponar).
        - Raise Ponar/Ekman carefully onto boat avoiding sample contamination and vessel damage.

    b. When deeper bottom sediment samples are required (such as in the transect locations), the Wildco® Hand Corer will be used.
        - Insert CAB liner into tool
        - Attach line to clevis pin in head of tool. Attach additional weights if necessary
        - Drop tool to bottom and push to a depth sufficient to recover a 6-inch sample.
        - After corer penetrates bottom, twist and pull free to retrieve sample.

3) Sediment sample will be collected into Pyrex mixing bowl
    a. Ekman – the upper two inches of sample may be accessed by opening flap on top of instrument. Those two inches will be used to fill VOA 4-oz laboratory glassware first.
    b. Ponar – All collected sample will be emptied into Pyrex mixing bowl
        - The top two inches will be used to fill 4-oz VOA laboratory glassware first.
        - The resulting sediment may be homogenized (stainless steel spoon) and collected into remaining laboratory glassware.
    c. Wildco® Hand Corer
        - Empty the top 6" of the sediment from the sampling device into the bowl or onto the clean foil.
4) If necessary, lower the sampling tool back into the water and repeat steps 2) and 3) until enough sediment is obtained to fill all laboratory glassware (This will be done before homogenization).
    - If sampling events are within 15 minutes of each other, this may still be classified a grab sample.
5) Collect sample for laboratory analysis as specified in SAP
6) All sample glassware will then be placed in bubble wrap and preserved on ice at 4±2 °C
7) A COC form will be completed for all sediment samples before returning to the office for QA/QC protocols. Wastes generated during these sampling operations will be segregated, containerized and disposed of properly.

Protocol for Wadeable Samples

If sediment samples are to be collected in shallow water that is accessible on foot or is wadeable, the following procedures will be followed:

1. Approach sample location from downstream direction.
2. The Wildco® Hand Corer, bucket auger or shovel may be used to obtain samples
    a. Wildco® Hand Corer
        - Insert CAB liner into tool
        - Attach line to clevis pin in head of tool. Attach additional weights if necessary
        - Drop tool to bottom and push to a depth sufficient to recover a 6-inch sample.
        - After corer penetrates bottom, twist and pull free to retrieve sample

b. Bucket Auger

   - Utilize 4-inch to 6-inch conductor pipe, wrapped (capped) with plastic cling wrap, or similar film.
   - Place capped conductor pipe on the sediment bed and utilize a decontaminated tool (hand auger, probe, coring tool, etc.) to breach the film and access the sediment.
   - Using bucket auger, obtain 6-inch sediment sample.

c. Shovel

   - A shovel may be used where the depth and/or velocity of the water will not cause the sample quality to deteriorate due to washing.
   - The analytical sample will be collected from the center of the sample mass

3. All sample remnants will be containerized and disposed of per the Waste Management Plan. Sediment sample will be collected into Pyrex mixing bowl.
4. If necessary, repeat steps 2) and 3) until enough sediment is obtained to fill all laboratory glassware (This will be done before homogenization).
5. Collect sample for laboratory analysis as specified in SAP
6. All sample glassware will then be placed in bubble wrap and preserved on ice at 4±2 °C
7. A COC form will be completed for all sediment samples before returning to the office for QA/QC protocols. Wastes generated during these sampling operations will be segregated, containerized and disposed of properly.

5.4 Split Samples

In the event that split samples are collected by state or federal representatives for submittal to independent third party laboratories, sample containers will be provided by those agencies or the Company's designates if requested in advance. If split sampling is requested, VOA glassware for each team will be filled first, followed by remaining glassware. All remaining sediment sample glassware will be filled once enough sediment has been collected and homogenized; these two sets of glassware will be filled in alternating order. Sediment sampling is conducted according to above steps.

5.5 Duplicate Samples

One duplicate field sample will be collected for every 20 field samples. A duplicate is a second sample at a certain site that will be submitted to the same laboratory under a different sample ID (Appendix E). This duplicate is to verify consistency in sample collection and decontamination techniques. The duplicate sample is taken in the same manner as a split sample; sediment samples for all analyses, following VOA jars, will be homogenized then distributed to each laboratory sample jar. Field notes must document from which sample a duplicate was taken, along with all other pertinent information that should be included in sample documentation.

5.6 Rinseate Blanks

Equipment rinseate blanks will be collected after completion of each day's sampling events and used to monitor the effectiveness of each team's decontamination process. The rinseate sample is taken after the final decontamination of the sampling equipment. Rinseate blanks will be prepared by passing deionized water through and over the surface of decontaminated sediment sampling equipment. The rinse water will be collected in (11) sample bottles, preserved, and handled in the same manner as other samples collected that day. One rinseate blank will be collected after decontamination following each day's final sampling event. If impacted surface water is identified in sampling events the frequency of rinseate blanks will be evaluated for modification.

5.7 Trip Blanks

Throughout the entire sampling day a set of trip blanks is to be present in each cooler that will hold a sample for volatile organic compounds analysis. A trip blank set consists of three pre-filled VOA bottles which will need labeled at the start of each sampling day. The trip blanks are to be kept on ice (4±2 °C) in the cooler and sent through the QA/QC process at the conclusion of the sampling day. These trip blanks are also sent to the appropriate laboratory with samples collected.

5.8 Temperature Blanks

Temperature blanks will monitor the temperature at which each day's samples are kept during transportation. These temperature blanks will be received from the laboratory at the start of each day, not be opened only labeled, and kept in the same cooler as those samples collected throughout the day. These, as well as all samples collected, must be kept on ice (4±2 °C).

STANDARD OPERATING PROCEDURES 2010 - 5

Decontamination

Purpose:

The purpose of this Standard Operating Procedure (SOP) is to provide a description of the methods used for preventing, minimizing, or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during hazardous waste operations as per 29 Code of Federal Regulations (CFR) 1910.120.

These are standard operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitation, or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

METHOD SUMMARY

Removing or neutralizing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances. Gross contamination can be removed by physical decontamination procedures.

These decontamination methods will be used for sampling tools, equipment, containers, etc.

Step One, a soap (Alconox or equivalent) and water wash, removes all visible particulate matter and residual oils and grease. This may be preceded by a steam or high pressure water wash to facilitate residuals removal.

Step Two, involves a triple rinse with tap water and/or a distilled/deionized water rinse to remove the detergent. Rinsate blanks can be collected at this time if desired.

The decontamination procedure described above may be summarized as follows:

1. Physical removal by scrubbing or pressure washing or steam cleaning
2. Non-phosphate detergent wash
3. Tap water rinse
4. Distilled/deionized water rinse
5. Air dry

EQUIPMENT/APPARATUS

Decontamination equipment, materials, and supplies are generally selected based on availability. Other considerations include the ease of decontaminating or disposing of the equipment. For example, softwash and rinse solutions. Children's wading pools can also be used. Large plastic garbage cans 5-gallon buckets or other similar containers lined with plastic bags can help segregate contaminated equipment. Contaminated liquid can be stored temporarily in metal or plastic cans or drums. Most equipment and supplies will be provided by Enbridge.

The following standard materials and equipment are recommended for decontamination activities:

Decontamination Solutions

- Non-phosphate detergent
- Tap water
- Distilled or deionized water

Useful Decontamination Tools/Supplies

- Long and short handled brushes
- Bottle brushes
- Drop cloth/plastic sheeting
- Paper towels
- Plastic or galvanized tubs or buckets
- Pressurized sprayers (H O) 2
- Aluminum foil

Post Decontamination Procedures

Please refer to the Waste Handling and Disposal Plan for details concerning the handling of solid and liquid waste.

- Empty all soap and water waste liquids from basins and buckets into drums or other appropriate containers. Refer to the DOT requirements for appropriate containers based on the contaminant of concern. Dispose of residual liquids properly.
- Place all solid waste materials generated from the decontamination area (i.e., gloves and plastic sheeting, etc.) in an approved DOT drum. Refer to the DOT requirements for appropriate containers based on the contaminant of concern. Dispose of discarded materials properly.
- Write appropriate labels for waste and make arrangements for disposal. Consult DOT regulations for the appropriate label for each drum generated from the decontamination process

Adapted from: USEPA Publication, **SAMPLING EQUIPMENT DECONTAMINATION** SOP#: 2006 DATE: 08/11/94 REV. #: 0.0

STANDARD OPERATING PROCEDURES 2010 - 6

Equipment Calibration

Purpose: The purpose of this SOP is to ensure accurate and consistent field chemistry, water level, and organic vapor measurements using measurement equipment such as pH meter, conductivity meter, dissolved oxygen meter and probe, water-level indicator, photoionization detector, etc.

Field personnel are responsible for the calibration, calibration verification and maintenance of the equipment in accordance with this procedure and manufacturer maintenance/ calibration instructions. Calibration is essential for field equipment whose measuring accuracy is critical to monitoring for safe work conditions and in gaining accurate reading of environment indicators.

Calibration Records

Each piece of monitoring equipment must have its own calibration/maintenance logbook. The following information should be documented in the calibration/maintenance logbook:

A. Date of entry and initials of the individual recording the entry.
B. Results of the calibration or calibration verification.
C. Information on the standards and method used for calibration or verification, including standard preparation details.
D. Maintenance performed.
E. Operator comments.
F. The calibration or verification status (i.e., “calibrated” or “not calibrated”).

Equipment Calibration/Maintenance

Calibration of all field instruments will be conducted according to the equipment manufacturer’s recommendations. Field equipment maintenance shall be conducted according to the manufacturers recommended schedule.

STANDARD OPERATING PROCEDURES 2010 - 7

Private Well Sampling

Private Water Well Monitoring Plan

PURPOSE

This Private Water Well Monitoring Procedure has been developed to direct a potable water well monitoring program for private wells located within the area of concern.

A. Objective

The objective of this SOP is to describe the proper sampling techniques to be used as part of the private well monitoring plan.

SAMPLING

A. Sample Identification

Unique sample numbers will be assigned to identify and describe each potable well sample according to procedures described in *SOP-2 – Sample Identification and Nomenclature*.

Blank and duplicate samples will be identified by false or dummy numbers selected by the staff conducting the sampling, followed by the date the sample was collected (for blanks, the date the sampling event occurred).

B. Sample Labeling

Each sample container will be clearly labeled, following procedures described in Section 5.0 of *SOP-3 – Field Documentation*, using an indelible ink pen on adhesive labels.

C. Sample Collection and Handling

All water samples will be collected using the following procedures:

1. Select a sampling location that is upstream or ahead of any water softening or filtering devices.
2. Select a sample tap that best represents the water in the system between the pump and any softening or filtration devices. Avoid poor sample sites such as swivel faucets, hot and cold mixing faucets (with a single lever), leaky or spraying faucets, drinking fountains, janitorial sinks, frost-free hose bibs, and faucets below or near ground level.
3. Remove any attachments from the faucet, including aerators, screens, washers, and hoses.
4. Turn on the cold water only and let it run in a steady stream for at least fifteen minutes. Before collecting the sample, don latex, nitrile or similar disposable gloves and turn the water down to a thin ¼" stream, then let the water continue to run for one minute.
5. Physical parameters will be allowed to stabilize prior to a sample being collected.
6. To avoid contamination while taking the sample, hold the bottle near the bottom with one hand, hold the top of the cap with the other, and then unscrew the cap. DO NOT set the

cap face down, touch any part of the cap that touches the bottle, or let anything touch the rim or inside of the cap. Hold the bottle under the stream of water, being careful not to let the bottle touch the sample tap. Fill the bottle to the neck or indicated fill line, but do not allow it to overflow. Remove the bottle from the water flow and replace the cap.

7. Complete the sample label and chain of custody form.
8. Place the sample in the chilled cooler (approximately 4°C or ~39°F).

D. Sample Storage and Preservation

Sample bottles will be supplied by the mobile laboratory for all sampling events and will include the appropriate preservatives. Sample containers will be kept closed until each is to be filled. Sample containers will be filled as outlined above and capped immediately. Immediately following the sample collection, samples will be labeled, as described above, and placed into a chilled cooler awaiting transportation to the laboratory. Samples will be delivered to the laboratory at the end of that sampling day.

E. Documentation

The sample location and number will be recorded in the field log book. Sample conditions and observations will be recorded in the log as well. After data is received, all potable sample addresses will be located on a site map for the whole area. Documentation will include the chain-of-custody and any field notes that are generated.

F. Chain-of-Custody Form

A chain-of-custody form will be completed by the staff for every day's sampling event. Samples will be transferred to subsequent custodians (the mobile laboratory), the chain-of-custody form will be signed by each person relinquishing and accepting custody of the samples. The chain-of-custody forms will be included in the Superior project file and will also be maintained by the laboratory. The chain-of-custody form will contain the sample location and number as outlined above.

SAFETY

Site Safety

All staff must have attended the contractor orientation safety seminars and have received the appropriate certifications prior to entering any field operation. Staff shall adhere to safety policies and will also adhere to the Project and/or Corporate Safety Manual and site specific HASP for all field activities. All staff members will have received 40-Hr OSHA HAZWOPER training and annual refresher. Numerous staff will be qualified as Site Supervisors under OSHA. Each will also have attended first aid and CPR training classes.

STANDARD OPERATING PROCEDURES 2010 - 8

Soil Sampling

Table of Contents

1.0 – Soil Classification and Logging

Purpose

The purpose of this technical practice is to provide a general guideline for the classification and logging of soil.

Equipment/Materials

Unified Soil Classification System (USCS) Field Chart

Procedures

Soil descriptions shall be precise and comprehensive with enough detail to allow interpretation by the project geologist. Field loggers shall minimize interpretation beyond soil type. The field logger shall strive to capture sufficient detail.

The following format and order for soil descriptions shall be recorded on the log:

- Soil name (USCS Group name and symbol) or fill
- Color
- Mottles, if present
- Estimate of particle size percentages
- Plasticity
- Moisture
- Consistency
- Sedimentary structure, if present
- Bedding, if present
- Organic material, if present
- Lithologic contact
- Special features such as chemical staining, nodules, and caliche
- Potential hydrocarbon or other impacts

2.0 – Soil Sampling for VOCs

Purpose

The purpose of this technical practice is to provide a general guideline for collecting and handling soil and sediment volatile organic compound (VOC) samples.

Equipment/Materials

- 4 oz jar for dry weight sample
- Methanol preserved 40 ml vial
- Nitrile gloves

Procedures

1. VOC sample should be collected first, before any other aliquot.
2. Collect undisturbed soil sampling in 10 ml syringe.
3. Inject soil filled syringe into pre-weighted, methanol preserved 40ml vial.
4. Replace cap and invert as many times as necessary to ensure that soil is saturated with methanol.
5. Collect 4oz jar of undisturbed soil for dry weight analysis.

NOTE:

A. In the event that low level soil VOC testing is determined to be necessary, the methods and procedures outlined Michigan Department of Natural Resources and Environment, Remediation and Redevelopment Division (MDEQ/RRD) Operational Memorandum No. 2, Attachment 6, page 3: Method 5035A, Low Concentration Method shall be followed.

B. All soil testing results shall be reported on a dry weight basis.

References

MDNRE/RRD Operational Memorandum 2, Attachment 4
MDNRE/RRD Operational Memorandum 2, Attachment 6

3.0 – Near Surface Soil Sampling

Purpose

The purpose of this technical practice is to provide a general guideline for collecting and handling soil samples obtained from the surface to 6 inches below the surface.

Equipment/Materials

- Appropriate level of personal protective equipment (PPE)
- Shovel or hand trowel
- Photo-ionization detector (PID)
- Appropriate sample containers provided by the analytical laboratory
- Alconox
- Scrub brush
- Distilled water
- 5 gallon pail

Procedures

1. Clear ground surface of vegetation, debris, and loose material to expose undisturbed soil.
2. Use tools to gently obtain the appropriate sample volume.
3. Decontaminate the tools between each sample location.
4. Each sample will be screened with a PID for the presence of volatile constituents. A boring log will be constructed based on observations from the soil samples. USCS information, including soil type, grain-size, color, moisture content, and PID reading, will be recorded on a field boring log.
5. Collect soil sample (see Section 2.0 of this document and/or Section 4.5 of the SAP for recommended parameters and preservation, storage and analytical methods and procedures)
6. Following completion of sampling, the location will be backfilled with any remaining cuttings.

4.0 – Soil Sampling – Manual Soil Boring

Purpose

The purpose of this technical practice is to provide a general guideline for the manual collection and handling of subsurface soil samples.

Equipment/Materials

- Appropriate level of PPE
- Hand auger
- PID
- Appropriate sample containers provided by the analytical laboratory
- Alconox
- Scrub brush
- Distilled water
- 5 gallon pail

Procedures

1. The hand auger shall be decontaminated prior to the first, and between each soil boring.
2. Using the hand auger, manually advance the soil boring to obtain the requisite samples. Soil samples will be obtained from the lower half of the auger bucket at six inch intervals.
3. Each sample will be field screened with a PID for the presence of volatile constituents.
4. A field boring log will be constructed based on observations from the soil samples. The following information will be recorded:
    - USCS information, including soil type, grain-size, color, moisture content
    - PID reading

- Collect soil sample (see Section 2.0 of this document and/or Section 4.5 of the SAP for recommended parameters and preservation, storage and analytical methods and procedures)

5. Following completion of the boring, the borehole will be backfilled with any remaining cuttings. At a minimum, the upper 2 feet of the borehole will be backfilled with bentonite pellets. Surface features, such as pavement, asphalt, soil, etc., will be utilized to restore the site to its original status.

5.0 – Drilling and Sampling Using Direct Push Techniques

Purpose

The purpose of this technical practice is to provide a general guideline for the collection of soil samples using direct push techniques.

Equipment/Materials

- Appropriate level of PPE
- Geoprobe®, or equivalent hydraulically-actuated direct-push drill rig
- Plastic sampling sleeves
- Razor knife
- PID
- Appropriate sample containers provided by the analytical laboratory
- Alconox
- Scrub brush
- Distilled water
- 5 gallon pail

Procedures

1. The stainless steel coring sleeve and drill rod shall be decontaminated prior to the first, and between each boring.
2. When drilling with a direct-push drill rig, the drilling contractor will follow methods and procedures outlined in American Society for Testing and Materials (ASTM) D6282-98(2005). The drilling contractor will use hydraulic drive core/direct-push sampling techniques. Continuous soil samples will be collected from the soil borings at appropriate (generally 5-foot, 4-foot and/or 2-foot) intervals, according to ASTM. A clean, plastic sampling sleeve will be used for each sample interval.
3. Every 2-foot section of the sample core will be field screened with a PID for the presence of volatile constituents.
4. A field boring log will be constructed based on observations from the soil samples. The following information will be recorded:
    - USCS information, including soil type, grain-size, color, moisture content
    - PID reading

- Collect soil sample (see Section 2.0 of this document and/or Section 4.5 of the SAP for recommended parameters and preservation, storage and analytical methods and procedures)

5. Following completion of boring, the borehole will be backfilled with any remaining cuttings. At a minimum, the upper 2 feet of the borehole will be backfilled with bentonite pellets. Surface features, such as pavement, asphalt, soil, etc., will be utilized to restore the site to its original status.

6.0 – Drilling and Sampling Using Hollow Stem Auger (HSA) Techniques

Purpose

The purpose of this technical practice is to provide a general guideline for the collection of soil samples using hollow-stem auger (HSA) techniques.

Equipment/Materials

- Appropriate level of PPE
- Drill Rig
- Hollow-stem augers
- Appropriate sample containers provided by the analytical laboratory
- PID
- Alconox
- Scrub brush
- Distilled water
- 5 gallon pail

Procedures

1. The hollow-stem augers shall be decontaminated prior to the first, and between each boring.
2. When drilling with hollow stem augers, the drilling contractor will follow methods and procedures outlined in ASTM D6151-97(2003). While drilling with hollow-stem augers, soil samples will be collected at 5.0-foot-intervals using a 2-foot-long, 2-inch-diameter clean stainless steel split-spoon sampler. The stainless steel split-spoon sampler will be decontaminated between each sample.
3. Each sample will be screened with a PID for the presence of volatile constituents.
4. A field boring log will be constructed based on observations from the soil samples. The following information will be recorded:
    - USCS information, including soil type, grain-size, color, moisture content
    - PID reading

- Collect soil sample (see Section 2.0 of this document and/or Section 4.5 of the SAP for recommended parameters and preservation, storage and analytical methods and procedures)

5. Following completion of boring, the borehole will be backfilled with a cement/bentonite slurry (90/10 mixture). Soil cuttings will be handled in accordance with appropriate investigative-derived waste practices. Surface features, such as pavement, asphalt, soil, etc., will be utilized to restore the site to its original status.

7.0 – Soil Sampling – Test Pit Sampling

Purpose

The purpose of this technical practice is to provide a general guideline for investigating subsurface soils using test pit techniques to collect soil samples for visual and chemical characterization.

Equipment/Materials

- Appropriate level of PPE
- Backhoe or other powered excavating equipment
- Appropriate sample containers provided by the analytical laboratory
- PID
- Alconox
- Scrub brush
- Distilled water
- 5 gallon pail

Procedures

1. Brush the backhoe bucket clean of loose dirt before beginning excavation of the test pit.
2. Begin excavation away from the target feature, and work towards the feature.
3. Dig pits in 2-foot increments with a backhoe. Excavate pits perpendicular to the long axis of the target features, if possible and appropriate for the work plan.
4. A field logger is to record all activities, soil characteristics, and other observations in the field. The field logger will record the appearance of the excavated soil and the appearance of the sidewalls.
5. Use clean gloves and collect a full set of soil samples at each depth increment specified in the field sampling plan. The backhoe will scoop the samples from the appropriate sample layer. Collect the sample directly from the backhoe bucket. At no time is the field logger to enter the excavation if it is greater than 3 feet deep.
6. See Section 2.0 of this document and/or Section 4.5 of the SAP for recommended parameters and preservation, storage and analytical methods and procedures.
7. Continue excavating until the test pit extends to one of the following:
    - The local water table
    - Depth specified in the field sampling plan
8. At termination of excavation, backfill test-pit with spoils of excavation. Compact the material from time to time during backfilling with pressure from the backhoe bucket.

SOP 8 – SOIL SAMPLING

Appendix 1

MDEQ/RRD Op Memo 2, Attachment 4
'Sample Preservation, Sample Handling, and Holding Time Specifications'

Remediation and
Redevelopment Division
Michigan Department of Environmental Quality

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: SAMPLING AND ANALYSIS - ATTACHMENT 4 SAMPLE PRESERVATION, SAMPLE HANDLING, AND HOLDING TIME SPECIFICATIONS

Key definitions for terms used in this document:

NREPA:	The Natural Resources and Environmental Protection Act, 1994 PA 451, as amended
Part 201:	Part 201, Environmental Remediation, of NREPA
Part 211:	Part 211, Underground Storage Tank Regulations, of NREPA
Part 213:	Part 213, Leaking Underground Storage Tanks, of NREPA
MDEQ:	Michigan Department of Environmental Quality
RRD:	Remediation and Redevelopment Division
U.S. EPA:	United States Environmental Protection Agency
Criteria or criterion:	Includes the cleanup criteria for Part 201 and the Risk-based Screening Levels as defined in Part 213 and R 299.5706a(4)
Facility:	Includes "facility" as defined by Part 201 and "site" as defined by Part 213

PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides sampling handling, preservation, and holding time specifications. This attachment applies to site assessments, site investigation and response activities under Part 201, Part 211, and Part 213.

SAMPLE CONTAINERS AND PRESERVATIVES

Containers and preservatives should be obtained from the laboratory performing the analysis whenever possible. When this is not possible, arrangements must be made with the selected laboratory to ensure the sample containers and preservatives to be used are appropriate. Preservatives must be provided with appropriate identification marks, safety information, instructions for use if necessary, and with expiration dates. The preservatives and expiration dates must be recorded into field logbooks as samples are collected so that each preserved sample is cross referenced with the added preservative(s).

The specific size, types of containers, and associated container codes used by the MDEQ laboratory are identified in Table 1. Preservatives normally used are listed in Table 2. Appropriate containers for each contaminant are specified with their respective bottle codes in Table 3.

Chemical preservatives should be used in their recommended dosages. If a little preservative is good, more is not necessarily better. Preservatives must be replaced at intervals specified by the manufacturer or laboratory and whenever contamination is suspected. Chemical preservatives should not be added to soil samples, except when specified in a sampling protocol, e.g., methanol preservation of soils analyzed for volatile organic compounds. Chemical preservatives should never be added to unknown or untreated liquid wastes and to samples of unknown matrix or source. Violent reactions can occur as acids are added to basic waste or conversely when bases are added to acidic waste. Adding acids to samples containing high cyanide or sulfide levels could result in generation of dangerous quantities of cyanide or sulfide gas.

Sample preservation should be performed immediately upon sample collection or arrangements made with the laboratory to preserve samples within the specified time. For composite samples, when possible, each aliquot used to make the composite should be preserved at the time of collection. When use of an automated sampler prevents preservation of each aliquot, the aliquots should be maintained at about four degrees centigrade (4° C) until composite samples can be preserved.

If a sample reacts vigorously when preservatives are added, discard the sample and obtain a new sample without preservation. Label the sample appropriately to advise the laboratory that it is not preserved; record the behavior of the sample in the field logbook and on chain of custody or sample receipt forms so that it is appropriately communicated to the laboratory.

CONTAMINATION FROM SAMPLE CONTAINERS OR PRESERVATIVES

Documentation must be maintained by the laboratory to uniquely identify the source of the material used to make each preservative. The results of methanol blanks, trip, and field blank samples should be routinely reviewed for evidence of contamination from preservatives or sample containers. In the event preservative and sample containers cannot be ruled out as contamination sources, relevant information must immediately be provided to the laboratory, and suspect supplies not used until their suitability can be established. If the laboratory determines that preservative or sample containers are possible sources of contamination, the laboratory should then inform their clients as appropriate.

HOLDING TIMES

Samples should be processed and/or analyzed as soon as possible after collection. Table 3 specifies the maximum amount of time the sample and any sub-sample generated from the sample can be held. Samples not meeting these specifications must receive a holding time code or other data qualifier. Where more than one holding time is specified, all applicable holding times should be used to validate results. Samples may be held for longer periods only if the laboratory has data on file to show that the specific types of samples under study are stable for longer periods.

Sample collection and delivery to the laboratory must ensure holding times will not be exceeded. Laboratory sample schedules are contingent upon priorities of other samples and unforeseen events such as instrument malfunction. Schedules can change after samples have been delivered to the laboratory. To minimize the impact of schedule changes, it is important to provide instructions to the laboratory, before or during sample receipt at the laboratory, concerning actions to take when a schedule change affects the ability to meet holding times.

Results from samples analyzed past the holding times are not necessarily unusable. When holding times are exceeded, the usability of the data will depend on such factors as the relationship between sample levels and cleanup criteria, the type of decisions to be based on the data, the presence of other data from other samples, and other factors relative to whether the data establishes a reliable representative concentration of the hazardous substance. When holding times are exceeded, results should be interpreted as a minimum concentration.

VOLATILE CONTAMINANTS

Specifications for collecting soil samples using methanol preservation are provided in RRD Operational Memorandum No. 2, Attachment 6. The preservation of samples to be analyzed for volatile contaminants is dependent upon the requirements provided in SW-846, Method 5035A.

This method should be consulted for guidance. Table 3 below has the requirements taken from Method 5035A. Future revisions of Method 5035A may alter these requirements.

DE-CHLORINATION

Water samples existing naturally in the environment should not need de-chlorination. De-chlorination procedures may be required for some samples taken from water sources where chlorination is used. De-chlorination is accomplished using the instructions provided in Table 3, footnote number 4, under De-chlorinate. Specific procedures for methods and contaminants may apply and should be used when possible. Applicable contaminants for which de-chlorination procedures may be required are provided below.

Acetonitrile
Acrolein
Acrylonitrile
Acrylamide
Benzidines
Chlorinated Acids/Herbicides
Chlorinated Pesticides
1,2-Dibromo-3-Chloropropane
1,2-Dibromoethane (EDB)
Nitrosamines
Organophosphorus Pesticides
Phenolics
Polychlorinated biphenyls
1,2,3-Trichloropropane
Semivolatiles
Volatiles

ANALYSIS OF GASOLINE OXYGENATES

High temperature purging during analysis of acid preserved samples can cause ethers to degrade which may result in underreporting of some ethers. When a sample is collected and preserved with acid for the analysis of volatiles that include gasoline oxygenate compounds, methyl(tert)butylether, t-Butyl alcohol, Di-isopropyl ether, Ethyl(tert)butylether, Ethyl alcohol, Methyl alcohol, and Tertiaryamylmethylether, the acid-preserved samples should be neutralized prior to analysis. Trisodium phosphate dodecahydrate (TSP) has been determined by the U.S. EPA to be effective and safe for this purpose. Separate samples may be collected specifically for the analysis of oxygenates, and preserved using TSP to adjust the pH to > 11 rather than preserving them with acid.

SAFETY

Be aware of dangers associated with chemical preservatives and their handling. Obtain Material Safety Data Sheets (MSDSs) from the laboratory providing the preservative prior to the sampling event to determine appropriate safety precautions and first aid. MSDSs should accompany personnel in the field. Preservatives must be stored in sealed containers away from other preservatives, and away from environmental and quality control samples. Use safety glasses and appropriate gloves to handle chemicals and properly place them into a closed chamber at the site until proper disposal can be arranged.

APPLICABILITY

Many published methods include specifications for sample containers, preservation, and holding times that may be specific for certain contaminants analyzed using the specific method. Those specifications may be more detailed than the specifications provided in Table 3 or in similar generic tables. When samples are collected for analysis by a method not specifically listed in Table 3, the method-specific requirements for sample containers, preservation, and holding times must be followed.

There are additional sources of holding time and preservation guidance, including the Clean Water Act, the Resource Conservation Recovery Act, the Safe Drinking Water Act, and the U.S. EPA CLP. The guidelines and specifications in this document are applicable to water and soil matrices and for contaminants regulated under Parts 201, 211, and 213. These guidelines and specifications may not be applicable to other matrices or to cleanups conducted under other regulatory programs. When samples are required to meet the criteria of another regulatory agency, the requirements for sample preservation, sample containers, and holding time of that agency should be applied.

Questions concerning this memorandum should be directed to Mr. A. Ralph Curtis, RRD, at 517-373-8389; or email to curtisar@michigan.gov.

The following documents are rescinded with the issuance of this attachment:

- Environmental Response Division Operational Memorandum 16, Sample Preservation, Sample Handling, and Holding Time Guidelines for the Act 307 Program, dated January 4, 1995.
- Storage Tank Division Operational Memorandum 14, Analytical Parameters and Methods, Sample Handling, and Preservation for Petroleum Releases, Table 4, Container, Preservation, and Holding Time Requirements for Common Petroleum Product Sampling and Analysis, dated June 12, 1998.

APPENDED TABLES:
Table 1. Sample Containers and Container Codes
Table 2. Preservatives
Table 3. Specifications for Sample Containers, Preservation, and Holding Times

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This memorandum and its attachments are intended to provide direction and guidance to foster consistent application of Part 201, Part 211, and Part 213 and the associated administrative rules. This document is not intended to convey any rights to any parties or create any duties or responsibilities under the law. This document and matters addressed herein are subject to revision.

Table 1. Sample Containers and Container Codes

Container Code	Size ml	Bottle Type	Container Code	Size ml	Bottle Type
DO	250	Glass, glass stopper	BNA	1000	Glass, amber
GN	500	Plastic	MS	250	Glass, wide mouth
GA	500	Plastic	GS	250	Glass, wide mouth
GG	250	Glass, screw cap	OS/BNA	250	Glass, wide mouth
GB	500 250	Plastic Plastic	VOA	40	Glass, septum vial (soils require MeOH kit)
S	250	Plastic	SCD	NA	Soil coring device [1,2]
MA	500	Plastic	MO	250	Glass, wide mouth
MAD	500	Plastic	OL	250	Glass, wide mouth
MD	500	Plastic	HW	250	Glass, wide mouth
MN	500	Plastic	MX	250	Glass, wide mouth
OG	250	Glass, wide mouth	OX	250	Glass septum jar
VOA	40	Glass Septum vial	L	500	Fluoropolymer [1,3]
ON	1000	Glass, amber	M	250	Glass or HDP[1]
Sealed Vial	Varies	Laboratory Specific	HDP	125	High Density Polyethylene[1]

1. SCD, L, M and HDP are not MDEQ Lab bottle codes.
2. The syringe type coring device, SCD, refers to the samplers listed in Method 5035A, or other validated samplers.
3. Contact the lab regarding availability and cleaning instructions.

Table 2. Preservatives

The following table represents the preservatives normally used for sampling and the approximate amounts to meet a targeted preservation.

Preservative	Concentration	Preservation	Approximate Amount
Sulfuric Acid (H2SO4)	Conc.	pH < 2	5 drops per 250 ml.
Nitric Acid (HNO3)	1:1	pH < 2	5 ml per 250 ml.
Hydrochloric Acid (HCl)	1:1	pH < 2	5 drops per 40 ml.
Sodium Hydroxide (NaOH)	10 N	pH > 9	2 drops per 250 ml.
		pH > 12	10 drops per 250 ml.
Chloroacetic Acid	0.1 N	pH 4-5	Varies with sample
Trisodium phosphate dodecahydrate (TSP)	Powder	pH> 10	Varies with sample
MeOH	Lab Grade	1:1	10 ml per 10 gr soil.
Ascorbic Acid	Powder	Oxidizing Agents	About 0.6 gr per L.
Sodium Arsenite	0.1 N	Oxidizing Agents	5 ml per L.
Zinc Acetate (ZnAc)	2 N	Interferences	10 drops per 250 ml.
Disodium EDTA	2.5 %	Interferences	1 ml per 100 ml.
Ethylenediamine	Powder	Interferences	50 mg per L.

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants [2]	Methods [3]	Container Codes [1]		Preservation [4]	Holding Time [5]
		Soil	Water		
Specific Contaminants					**Collection to Analysis**
Acidity	305.1		MN	4° C	14 Days
Alkalinity	310.1		MN	4° C	14 Days
Anions by Ion Chromatography	9056 300.1		MN	Contaminant Specific [6]	
Acetate			MN	4° C	2 Days
Formate			MN	4° C	2 Days
Bromide			MN	None Required	28 Days
Chloride			MN	None Required	28 Days
Fluoride			MN	None Required	28 Days
Nitrate or Nitrite-N			MN	4° C	48 Hours
Nitrate and Nitrite-N			MN	pH < 2 H2SO4, 4° C	28 Days
Ortho-Phosphate-P			MN	4° C	48 Hours
Sulfate			MN	4° C	28 Days
Bromate			MN	None Required	28 Days
Chlorate			MN	None Required	28 Days
Chlorite			BNA	50 mg Ethylenediamine per L. 4° C	14 Days
Asbestos	100.1		GN	4° C	48 Hours
Biochemical Oxygen Demand	405.1		GN	4° C	48 Hours [7]
Bromide	320.1	GS	MN	None Required	28 Days
Chemical Oxygen Demand	410		GA	pH < 2 H2SO4, 4° C	28 Days
Chloride	325	GS	MN	None Required	28 Days
Chlorine, Total Residual	330		GN	None Required	Immediately
Color	110		GN	4° C	48 Hours
Conductance, Specific	9050A	----	MN	4° C	28 Days
Fluoride	340.1	----	MN	None Required	28 Days
Hardness	130.2	----	MA	pH < 2 1:1 HNO3 / H2SO4, 4° C	6 Months
Hydrogen Ion, pH	9040, 9045	GS	MN	None Required	24 Hours

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers		Preservation	Holding Time
		Soil	Water		
Specific Contaminants					**Collection to Analysis**
Iodide	345.1	----	MN	4° C	28 Days
Odor	SM 2150B	----	GN	4° C	24 Hours
Total Organic Carbon (TOC)	415.1	----	GA	pH < 2 H_2SO_4 / $HCl/NaHSO_4$, 4° C	28 Days
Fraction of Organic Carbon	Walkley-Black	GS	GN	4° C	28 Days
Fraction of Organic Matter	D2974	GS	GN	4° C	28 Days
Oxygen, Dissolved, Probe	360.1	----	DO	None Required	Immediately
Oxygen, Dissolved, Winkler	360.2	----	DO	Fix on site with DO Kit [10], avoid aeration, store at 10-20° C in dark.	8 Hours
Perchlorate	340.1 9058	GS	MN	None Required	28 Days
Petroleum Hydrocarbon Material[8]	1664 9071B	2xOG	2xOG	pH < 2 HCL, 4° C. For dry soils cool to 4° C. For pourable sediments and soils add 2 ml 1:1 HCl per 100g, 4° C	ASAP [9]
Phenolics	420.2	----	GG/GP	pH < 2 H_2SO_4, 4° C	28 Days
Phosphorus, Ortho, Dissolved	365	----	GN(D)	Filter on site immediately, 4° C	48 Hours
Phosphorus, Elemental		----	GA	4° C	48 Hours
Phosphorus, Total	365.4	----	GA	pH < 2 H_2SO_4, 4° C	28 Days
Residue, Total	160.3	----	GN	4° C	7 Days
Residue, Filterable (TDS)	160.1	----	GN	4° C	7 Days
Residue, Non-Filterable (TSS)	160.2	----	GN	4° C	7 Days
Residue, Settleable	160.5	----	GN	4° C	48 Hours
Residue, Volatile	160.4	----	GN	4° C	7 Days
Silica	370.1	----	GN	4° C	28 Days
Sulfate	375.1	----	MN	4° C	28 Days

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers		Preservation	Holding Time
		Soil	Water		
Specific Contaminants					**Collection to Analysis**
Sulfide	9030 376.1	GS		See Footnote 11	7 Days
			S	Cover surface of collected soil with 2 M ZnAc until moistened. No headspace.	
Sulfite	377.1	----	HDP	Avoid contact with air, cool < 50° C and add 1 ml EDTA [12] per 100 ml., < 50° C	Immediately
Temperature	170.1	----	----	Not Applicable	On site
Total Recoverable Petroleum Hydrocarbons (TRPH)	8440 [13]	GS	----	4° C	ASAP [9]
Turbidity	180.1	----	GN	4° C	48 Hours
Biological Tests					
Coliform, Fecal and Total	9131 9132	----	M	4° C	8 Hours [14]
Fecal Streptococci	SM 9230	----	M	4° C	6 Hours
Cyanides					
Cyanide, Total	9010B	GS	----	See Footnote [15]	14 Days
				Unpreserved	24 Hours
Cyanide, Available	OIA1677	GS	GB	See Footnote [15]	14 Days
				Unpreserved	24 Hours
Cyanide, Amenable (Free)	D4298-02	----	GB	pH ≥ 12 NaOH, store in dark, 4° C	24 Hours to diffusion
Nitrogen Forms					
Ammonia – N	350.1	GS	GA	pH < 2 H2SO4, 4° C	28 Days
Kjeldahl – N	351.1	GS	GA	pH < 2 H2SO4, 4° C	28 Days
(Nitrate + Nitrite) – N	353.2	GS	GA	pH < 2 H2SO4, 4° C	28 Days
(Nitrate + Nitrite) – N	353.2	GS	GA	4° C	24 Hours
Nitrate – N or Nitrite – N	353.2	GS	GN	4° C	48 Hours

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers		Preservation	Holding Time	
		Soil	Water			
Mercury					**Collection to Analysis**	
Mercury, Total	7470 7471	MS	MA	pH < 2 1:1 HNO3 , 4° C	28 Days	
Mercury, Low Level	1669/1631	MS	L	10 ml 1:1 Hg-free HNO3 per L, 4° C	28 Days	
Hexavalent Chromium						
Chromium VI (waters)	7199	----	HDP	Use buffer solution [16] to adjust pH 9-9.5 (check with pH paper or pH meter) 4° C	24 Hours	
	7196	----	MN	4° C	24 Hours	
					Collection To Preparation	**Preparation To Analysis**
Chromium VI (soils)	3060A [17]	MS	----	4° C, Store field-moist.		
				Dry Soils:	2 Days	7 Days
				High moisture soils and sediments:	30 Days	7 Days
Low Molecular Weight Acids	5560 C	GS	GN	None Required	NA	NA
Glycols	8015C	GS	GN	None Required	NA	NA
Phosphorus, White [18]	7580	OX	VOA	Limit contact with air. No headspace, 4° C, store in dark. Tightly seal extracts and refrigerate.	5 Days	
				Extracts:		
				Ether Extract	----→	8 Hours
				Iso-Octane Extract	-----→	30 Days

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers		Preservation	Holding Time	
		Soil	Water			
Metals					**Collection To Analysis**	
Metals, Totals	6010/6020	MS[19]	MA	pH < 2 1:1 HNO3, 4° C	6 Months	
Metals, Dissolved	6010/6020	----	MD MA(D)	Filter and preserve < 24 Hours of sampling. pH < 2 1:1 HNO3 , 4° C	6 Months	
Specific Organic Compounds						
Acetonitrile	8033	----	2 x VOA	pH < 2 H2SO4, 4° C	14 Days	
Acrolein	603 8316	----	2 x VOA	pH 4-5 HCl, 4° C	14 Days	
Acrolein	603	----	2 x VOA	4° C	3 Days	
Acrylonitrile	603	----	2 x VOA	4° C	14 Days	
Acrolein and Acrylonitrile	603	----	2 x VOA	pH 4-5 HCl, 4° C	14 Days	
Acrolein and Acrylonitrile	603	----	2 x VOA	4° C	3 Days	
Acrylamide	8032	----	2 x VOA	pH < 2 HCL/H2SO4, 4° C	14 Days	
Specific Organic Compounds					**Collection to Preparation**	**Preparation to Analysis**
Benzidines	605 8270C	OS BNA	BNA	Adjust pH 2-7 using H2SO4 and 10 N NaOH. If 1,2-dephenylhydrazine is expected to be present, adjust pH to 3.8-4.2 H2SO4 and 10 N NaOH 4° C, store extracts in inert atmosphere in dark	W: 7 days	7 days
Carbamates	8318	OS BNA	BNA	Cool, pH 4-5 using 0.1 N Chloroacetic Acid, 4° C, store sample and extracts in dark	W: 7 days S: 7 days	40 days 40 days
Carbonyls	8315A	OS BNA	BNA	4° C	W: 3 days S: 3 days	3 days 3 days

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

		Containers				
Contaminants	**Methods**	**Soil**	**Water**	**Preservation**	**Holding Time**	
Specific Organic Compounds					**Collection To Preparation**	**Preparation To Analysis**
Chlorinated Acids/Herbicides	8151A	OS/B NA	BNA	4° C, store samples and extracts in dark	W: 7 Days S: 14 Days	40 Days 40 Days
Dioxins and Furans	8290 1613	OS/B NA	ON	4° C, store in the dark	30 Days	45 Days
1,2-Dibromoethane (EDB) 1,2-Dibromo-3-Chloropropane, 1,2,3-Trichloropropane	8011 504.1		VOA	4° C	W: 14 Days	Immediately
Nitrosamines	8270C	OS/B NA	BNA	pH 7-10 with H2SO4 and 10 N NaOH, store extracts in sealed vials, in dark at -10° C	W: 7 Days S: 14 Days	40 Days 40 Days
Chlorinated Pesticides [20]	8081A	OS/B NA	2 x ON See 23 [23]	pH 5-9 with H2SO4 and 10 N NaOH within 72 hours, 4°C, store extracts in dark.	W: 7 Days S: 14 Days	40 Days 40 Days
Organophosphorus Pesticides [21]	8141A	OS/B NA	ON	4° C Store samples and extracts in dark	W: 7 Days S: 14 Days	40 Days 40 Days
Polychlorinated biphenyls	8082	OS/B NA	2 x ON See 23 [23]	4° C Store extracts in dark	W: 7 Days S: 14 Days	40 Days 40 Days
Semivolatiles [22]	8270C	OS/B NA	2 x BNA See 23	Store extracts in sealed vials, in dark at -10° C	W: 7 Days S: 14 Days	40 Days 40 Days

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers	Preservation	Holding Time
Volatiles (waters)				**Collection To Analysis**
Fuel Oxygenates	8260B	2 x VOA	no headspace, TSP to pH > 11, 4° C	180 Days
Reactive compounds [24]	8260B	2 x VOA	no headspace, 4° C	ASAP [9]
Other Compounds	8260B	2 x VOA	pH < 2 using 1:1 HCl or solid NaHSO4, no headspace, 4° C	14 Days
Volatiles (soils) [25]				
Reactive Compounds Examples include styrene, 2-Chloroethylvinylether	Low Concentration	Sealed Vial	Use reagent water (no acid preservative), freeze > -20° C , < -7° C on site	ASAP [9]
		SCD	4° C or freeze > -20° C , < -7° C on site, extruded into sealed vial without acid preservative within 48 hours	ASAP [9]
Volatile Compounds	Methanol	2 x VOA	Preserve on site using ratio 1:1 methanol to soil, 4° C	14 Days
Volatile Compounds	Methanol	SCD	4° C or freeze > -20° C , < -7° C on site and extruded into sealed vial with methanol within 48 hours	14 Days

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Hazardous Waste Characterization Using Method 1312

Contaminants	Containers	Field Collection To TCLP Extraction	TCLP Extraction To Preparative Extraction	Preparative Extraction To Determinative Analysis	Total Elapsed Time
Volatiles	OX	14 Days	Not Applicable	14 Days	28 Days
Semivolatiles	MX	14 Days	7 Days	40 Days	61 Days
Mercury	MX	28 Days	Not Applicable	28 Days	56 Days
Metals	MX	180 Days	Not Applicable	180 Days	360 Days

Radiochemistry Contaminants

Radiochemistry Contaminant	Method	Containers Water	Preservation	Holding Time Collection To Analysis
Gross Alpha, and Gross Beta	9310	1 L HDP or Glass	pH to 2 1 N HNO3	6 Months
Alpha Emitting Radium Isotopes	9315	1 L HDP or Glass	pH to 2 1 N HNO3	6 Months
Radium 228	9320	1 L HDP or Glass	pH to 2 1 N HNO3	6 Months

Unpreserved samples for analysis of radiochemistry contaminants must be received at the laboratory within five days of collection.

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Wisconsin GRO/DRO Guidelines

Contaminants		Containers			Holding Times	
Organic Compounds	**Methods**	**Soil**	**Water**	**Preservation[26]**	**Collection To Preparation**	**Preparation To Analysis**
Gasoline Range Organics	8015-Wis					
Waters:			3 x VOA	0.5 ml 1:1 HCl to sample bottle first, no headspace, avoid agitation, 4° C	14 Days	14 Days
Carbonate aquifer waters:			3 x VOA	Preserved with Sodium Azide[27]	14 Days	14 Days
Carbonate aquifer waters:			3 x VOA	Without Sodum Azide[27]	2 Days	14 Days
Soils:		VOA		Preserve in field with MeOH, 4° C	21 Days	21 Days
		SCD		4° C, preserve with MeOH < 48 Hours	21 Days	21 Days
Diesel Range Organics	8015-Wis					
Waters:			BNA[28]	5 ml 1:1 HCL to sample bottle first, no headspace, 4° C	7 Days	47 Days
Carbonate aquifer waters:			BNA[28]	Preserved with Sodium Azide[27]	7 Days	47 Days
Carbonate aquifer waters:			BNA[28]	Without Sodium Azide[27]	2 Days	47 Days
Soils:		VOA SCD		4° C, preserve with MeOH 1:1 < 72 hours	47 Days	47 Days

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

For soils requiring leach tests to evaluate the mobility of non-volatile contaminants in soils [29]

Contaminants[31]	Methods	Containers	Preservations (sample and leachate)		Holding Times [30]			
			Sample	Leachate [32]	Collection To Leaching	Leaching To Preparation	Leaching To Analysis	Preparation To Analysis
Mercury	7470	MX	4° C	pH < 2 1:1 HNO3, 4° C	28 Days		28 Days	
Metals	6010B/6020	MX	4° C	pH < 2 1:1 HNO3, 4° C	180 Days		180 Days	
Semivolatiles	8270C	MX	4° C	4° C, Store extracts from the leachates in dark at -10 ° C	14 Days	7 Days		40 Days
Pesticides	8081A	MX	4° C	pH 5-9 10 N NaOH and H2SO4, 4° C	14 Days	7 Days		40 Days
PCBs	8082	MX	4° C	4° C, Store extracts from the leachate in dark	14 Days	7 Days		40 Days

For soils requiring leach tests to evaluate the mobility of volatile contaminants in soils

Contaminants	Methods	Containers	Preservations (sample and leachate)		Holding Times	
			Sample	Leachates	Collection To Leaching	Leaching To Analysis
Volatiles [33]	8260B	2 x SCD	< 4° C	pH < 2 1:1 HCl, 4° C	48 Hrs	14 Days

Table 3 Footnotes

1. The container sizes and types specific for the MDEQ Environmental Laboratory (MDEQ Lab) are listed in this table when applicable. Other laboratories may specify other sizes and types. Letters in parentheses () indicate that the included letter must be added to the prefix code on the bottle from the MDEQ Lab to indicate to the laboratory what process was used, if any, for preservation.
2. "Contaminants" refers to elements, individual compounds, groups of compounds, chemical or physical properties. Contaminant groups in Table 3 are underlined and are simply identified for convenience. These group names do not reflect any official or standardized groups used by other agencies. Italicized contaminant names indicates that the MDEQ Lab does not perform analysis for the contaminant.
3. Methods in the table are listed primarily to clarify the type of method routinely used for environmental samples and preservation used for associated contaminants. The methods listed are not the only methods acceptable. RRD Operational Memorandum No. 2, Attachment 1, TDLs and Available Methods lists the available analytical methods the MDEQ has determined capable of achieving theTDLs. When available methods are used, applicable sample preservation techniques within those methods must be used.
4. Abbreviations and terms used for preservation are as follows:

Abbreviation	**Meaning**	**Abbreviation**	**Meaning**
< - >	Less than - Greater than	HNO3	Nitric acid
M	Molar concentration	NaOH	Sodium hydroxide
N	Normal concentration	ZnAc	Zinc acetate
HCl	Hydrochloric acid	° C	Degrees centigrade
H2SO4	Sulfuric acid	In Situ	Measure in matrix
EDTA	Ethylenediamine,tetra,acetic acid		

ASAP – Make arrangements to deliver samples overnight and have laboratory analyze samples upon receipt.
Immediately - Transport samples to laboratory within 24 hours or overnight. Plans must be made in advance to have the laboratory analyze the samples upon receipt.
4° C – Store samples at about four degrees centigrade. Just above freezing up to six degrees C is acceptable. Ice is preferred to cool samples. If commercial ice packs are used, the bottom, walls, and top inside cover of the cooler must be lined with the packs so as to completely encapsulate the samples as much as possible. A temperature control sample should be included when blue ice packs are used.
De-chlorinate – Means that a portion of the sample should be separated and tested for residual chlorine. Diethyl-p-phenylenediamine (DPD) kits are commercially available to test for residual chlorine in the field. About 25 mg ascorbic acid powder per 40 ml sample, for each 5 mg/L of residual chlorine determined from the DPD kit, should be added to sample bottles testing positive that are to be used to analyze for volatile contaminants, prior to sampling. For non-volatile contaminants use 80 mg/L sodium thiosulfate per liter of sample for each 5 mg/L of residual chlorine found. If pH adjustment is necessary, perform pH adjustment after dechlorination. Do not mix dechlorination reagents with the preservatives used to adjust the pH. Treat the samples only if they contain free or combined chlorine. Most environmental samples are not chlorinated while tap water samples originating from a municipal water source usually are chlorinated.
pH – Indicates an estimated hydrogen ion measurement. Use only the specified chemicals to adjust pH. Do not add more than is needed to obtain the desired pH. If preservation using hydrochloric or sulfuric acids (HCl or H2SO4) is needed, two drops of 1:1 HCl, or H2SO4 for every 40 ml of sample, will lower the pH to less than two for most waters.

Table 3 Footnotes

5. "Holding Time" refers to the maximum time that a sample or sub-sample can be held before the next step in the analysis is performed. Samples may be held for other specified times if the laboratory has supporting data to demonstrate stability. Exceptions to times specified in the heading of this column are explained within the table for each applicable contaminant.
6. The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. Note: The addition of EDA has no effect on bromate or chlorate, so they can also be determined in a sample preserved with EDA. Residual chlorine dioxide should be removed from the sample. Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample must be purged with an inert gas (helium, argon, or nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to ethylenediamine preservation and at time of sample collection.
7. Limit compositing to less than 24 hours and then follow grab sample guideline of 24 hours after collection.
8. Several methods are available to measure TPH. Results are method dependent.
9. No hold time has been established. Samples should be analyzed as soon as possible.
10. The MDEQ Lab DO kit uses solutions designated as DO-1 (Manganese Sulfate) and DO-2 (alkaline Iodide-Azide).
11. Prior to collection, add to sample bottle 8 drops 1 M ZnAc per 100 ml sample to be collected and enough 10 N NaOH expected to make pH > 9. Collect sample with minimum of aeration, add more NaOH as needed to increase pH > 9. Fill bottle without headspace. If the sulfide concentration is expected to exceed 64 mg/L, increase the amount of ZnAc proportionally.
12. Disodium EDTA. Prepare using 2.5 g per 100 ml distilled water.
13. Applicable to mineral oils. Not appropriate for analysis of soils for gasoline and other light petroleum fractions.
14. Under the Federal Safe Drinking Water Act guidance, a 30-hour holding time for coliform samples mailed from water treatment systems is acceptable. Water samples for coliform analysis should have 1-2 inches of headspace in the sample container.
15. Aqueous samples should be tested for sulfides, oxidizing agents, and soluble aldehydes within 15 minutes of sampling to determine and preserve as appropriate. Alternatively, all samples may be preserved with NaOH to a pH>12 and sent to the lab for analysis within 24 hours.

    A. Test for Oxidizing Agents

    Test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment.

    To samples testing positive add 0.1N Sodium Arsenite solution a few ml at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 ml of Sodium Arsenite solution for each liter of sample.

    Ascorbic Acid can be used as an alternative although it is not as effective as Sodium Arsenite. Add a few crystals of Ascorbic Acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of Ascorbic Acid for each liter of sample volume.

Table 3 Footnotes

B. Test for Sulfides (Note that samples are always treated with Lead Carbonate or Cadmium Nitrate.)

Samples with visible particulates must be filtered.
Keep this filter (#1).
Treat samples with solid Lead Carbonate or Cadmium Nitrate powder and immediately filter.
Discard this filter.
Test filtrate for sulfides using Lead Acetate paper and further treat samples showing positive results with Lead Carbonate or Cadmium Nitrate powder and filter.
Discard this filter.
Continue testing until samples show a negative result for sulfides using Lead Acetate paper.

C. Soluble Aldehydes Test

Use a separate solution of the sample to test for aldehydes.
Treat samples showing a positive result with 20 ml of 3.5% Ethylenediamine solution per liter of sample.

D. Preservation

Reconstitute the sample by adding the sediment collected on filter #1 back into the filtrate.
Add NaOH until the sample pH > 12 and cool to 4°C.
Maximum holding time is now 14 days. Equipment blanks must be handled the same as real samples.

16. Buffer Solution. Dissolve 33 g of ammonium sulfate in 75 ml of reagent water and add 6.5 ml of ammonium hydroxide. Dilute to 100 ml with reagent water. Degas the solution with helium gas for 5-10 minutes prior to use. Add the buffer solution, drop wise, to the sample and check after addition with pH paper, or continuously with a pH meter.
17. Method 3060A must be used for preparation of soils. Barium chromate is only partially soluble using Method 3060A. This method may not be appropriate for investigations involving this contaminant when high levels of barium are found at sites.
18. White phosphorus from munitions is released into the environment in the form of small, discrete particles. These particles persist in soils, sediments, and may occur as suspended or colloidal particles in anoxic waters. Therefore, some samples or sample aliquots from a given location may contain P4 particles while others do not. The nature and distribution of P4 contamination from other, non-military, sources has not been studied, but sample collection procedures should address the likelihood that P4 is present in discrete particles, and must be designed to ensure that multiple representative samples of the matrix of interest are collected. In addition, soil and sediment samples must be carefully homogenized and sub-sampled.

    Aqueous samples should be poured gently into the sample container to minimize agitation which might drive off the volatile P4. If bubbling does occur while transferring the sample to the container, the sample should be discarded and another sample collected. Each container should be filled with sample until it overflows. Each container should be tightly sealed with a PTFE-lined cap. The container should then be inverted to check for air bubbles. If any air bubbles are present, a new sample must be collected.

19. If boron is a chemical of concern at a site, use a wide mouth plastic container for collection of soil samples.

Table 3 Footnotes

20. If analysis includes BHCs, cis, trans-Permethrin, or Trifluralin, samples should be extracted as soon as is practical. See requirements for specific pesticides, published under the Safe Drinking Water Act and applicable to drinking water samples.
21. If analysis includes Disulfoton Sulfoxide, Diazinon, Pronamide, or Terbufos, samples must be extracted as soon as is practical.
22. Includes groups referred to in other guidance as:
    Total Petroleum Hydrocarbons (TPH), Acid Extractables (Phenols), Chlorinated Hydrocarbons, Nitroaromatics and Isophorone, Nitrosoamines except Diphenylnitrosamine, Polynuclear Aromatics, Phthalate Esters, Haloethers, and Phenolics.
23. If samples are to be analyzed for semivolatiles and pesticides/PCBs, collect a total of three containers. For quality control purposes, collect an additional container for each contaminant group, for every 20 samples.
24. Reactive contaminants with cleanup criteria include 2-chloroethylvinyl ether and styrene. Contact the laboratory regarding other contaminants.
25. Preservation as provided in RRD Operational Memorandum No. 2, Attachment 6 is required for the collection of soils. The MDEQ Lab provides a sampling kit to collect soil samples using this procedure. Soils collected to determine volatiles leached from soils should be sampled with 25 gr syringe-type coring devices.

    The sonication time used to extract the volatile compounds from the soil is important and must be standardized for analysis of volatile organic compounds in soil and comparison of results with the cleanup criteria. Soils should be sonicated as soon as possible after receipt, and a 20-minute sonication time must be used as specified in the MDEQ Lab SOP #501, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).

26. Specifications must be followed from Modified DRO, Method for Determining Diesel Range Organics, Wisconsin DNR, September 1995 for DRO and Modified GRO, Method for Determining Gasoline Range Organics, Wisconsin DNR, September 1995, for GRO.
27. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If the pH is greater than two, the sample results must be flagged. Flagging is not required of samples collected from carbonate aquifers if preserved with sodium azide or extracted within 48 hours of collection.
28. The Wisconsin procedure requires a Teflon™ lined cap. The Teflon™ must be touching the sample.
29. The data in this table applies to soils to determine potential leaching of contaminants. See RRD Operational Memorandum No.2, Attachment 2, Soil Leaching Methods for applicable leaching tests.

    Each soil type tested should have associated quality control as provided in the leaching procedures. This requires spiking the leaching solution with the contaminants of concern at levels above the TDLs listed in RRD Operational Memorandum No.2, Attachment 1. When relevant pathways have been evaluated for response activity under Part 201 or Part 213, spiking the leaching solution may be appropriate at approximately one-half of the cleanup criteria for the appropriate pathway whenever possible. Duplicate samples should be collected to facilitate the spiking of samples.

Table 3 Footnotes

The crushing, cutting, grinding, sieving, and filtering, or other procedures used in leaching procedures may alter the physical characteristics of soils. As the physical characteristics of soils may affect the mobility of contaminants, such procedures are not appropriate for soils for the purposes of this test. Such procedures may be appropriate for other types of material such as brick and concrete.

Samples collected and stored using a syringe-type coring device (SCD), as specified in Method 5035 of SW-846, should be extruded directly into the leaching solution by the laboratory to minimize exposure to the atmosphere.

After completion of the leaching procedure for soils, aliquots taken for analysis of specific contaminants must be immediately collected and preserved as specified in Table 3 for aqueous solutions of the respective contaminants.

30. Other holding times, specific for compounds within the contaminant groups, may be more appropriate. If the compounds of concern at a site have been established, use specifications in this table specific for these compounds, or specifications as may be provided in the analytical method itself.
31. Contact the MDEQ Lab concerning the use of leaching procedures for other contaminants.
32. Extracts from leaching tests should be preserved immediately after leaching, according to the guidance given in the individual analysis methods for the contaminants being measured.
33. Sample collection procedures using a syringe-type coring device, as provided in Method 5035, are appropriate when leaching is used to evaluate the mobility of volatile components leached from soils. Extrusion of the soil sample into the leaching solution by the laboratory is required within 48 hours. After completion of the leaching procedure, an aliquot of leaching solution must be immediately collected and preserved as specified in Table 3 for associated contaminants in aqueous solutions. If larger sample sizes are required, multiple devices must be used.

SOP 8 – SOIL SAMPLING

Appendix 2

MDEQ/RRD Op Memo 2, Attachment 6
'Sampling Methods for Volatile Organic Compounds'

Remediation and Redevelopment Division

Michigan Department of Environmental Quality

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: **SAMPLING AND ANALYSIS – ATTACHMENT 6**
SAMPLING METHODS FOR VOLATILE ORGANIC COMPOUNDS

Key definitions for terms used in this document:

NREPA:	The Natural Resources and Environmental Protection Act, 1994 PA 451, as amended
Part 201:	Part 201, Environmental Remediation, of NREPA
Part 211:	Part 211, Underground Storage Tank Regulations, of NREPA
Part 213:	Part 213, Leaking Underground Storage Tanks, of NREPA
MDEQ:	Michigan Department of Environmental Quality
RRD:	Remediation and Redevelopment Division
U.S. EPA:	United States Environmental Protection Agency
Contact time:	The time from when the sample was preserved with methanol to the time the aliquot was taken for analysis, or the time the sample was in contact with the methanol prior to analysis.
Criteria or criterion:	Includes the cleanup criteria for Part 201 and the Risk-based Screening Levels as defined in Part 213 and R 299.5706a(4)
Facility:	Includes "facility" as defined by Part 201 and "site" as defined by Part 213
Method 5035A:	U.S.EPA Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatiles Organics in Soil and Waste Samples," Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, USEPA, Office of Solid Waste and Emergency Response, Dec 1996, Third Edition.
Method 5021A:	U.S.EPA Method 5021A, "Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis", Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, U.S.EPA, Office of Solid Waste and Emergency Response, Dec 1996, Third Edition.
Response Actions:	Includes "response activities" as defined by Part 201 and "corrective action" as defined by Part 213
Sonication:	The procedure for mixing the soil with methanol using sound waves.

PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides direction for the collection and preservation of soil samples using the procedures in U.S.EPA Methods 5035A and 5021A for analysis to determine concentrations volatile organic compounds (VOCs). This attachment is applicable for site assessments, site investigations, and response activities under Part 201, Part 211, and Part 213.

To produce reliable representative analytical results, the MDEQ implemented the use of the methanol preservation procedures for the preservation of soil samples collected for analysis to determine concentrations of VOCs on April 30, 1998.

INTRODUCTION

The requirements for collection and preservation of samples are based on the latest revisions of U.S. EPA Methods 5035A and 5021A. The applicable contaminants that can be measured are listed within the methods. Other contaminants may be included if method performance data exists for the contaminant that demonstrates the accuracy, precision and detection that can be measured.

Guidance on applicable target detection limits (TDLs) and available analytical methods are included in RRD Operational Memorandum No. 2, Attachment 1.

USE OF PROCEDURES WITHIN METHODS 5035A and 5021A

Method 5035A includes several procedures for the collection and preparation of soils for VOCs analysis. These include high concentration methods (methanol preservation), sealed samplers using soil coring devices, and the low concentration soil method using sealed containers for direct attachment to the analytical instrument. Method 5021A provides for the sample preparation of both waters and soils using sealed containers.

Method 5035A, High Concentration Method – Option 1, Methanol Preservation

The MDEQ accepts results generated using the high concentration soil method of Method 5035A for site assessment, site investigations, and response activities, provided the requirements listed below are followed and documented:

- Samples are preserved with methanol in the field using a procedure consistent with that provided in this document.
- At least ten grams of soil are collected.
- The ratio of methanol volume to soil weight is equal to or greater than one.
- Samples are sonicated for at least 20 minutes as soon as possible upon receipt at the lab.
- An aliquot of methanol is taken immediately after sonication, and stored for analysis.
- The sample with methanol is not used for analysis of volatiles once the aliquot of methanol is taken.
- The laboratory standard operating procedures provide the information listed within this document's section entitled Laboratory Related Procedures and Documentation.
- Operational Memorandum No. 2, Attachment 1, Target Detection Limits and Available Methods direction has been followed.

Method 5035A, High Concentration Method – Option 2, Bulk Sampling

The bulk sampling procedure in Method 5035A does not produce a reliable representative sample because it is susceptible to volatilization and biodegradation. Therefore, the MDEQ does not accept results generated using bulk sampling procedures, unless acceptable justification is provided that documents the nature of the sample prevents sampling by the procedures described as acceptable in this document.

Method 5035A, Low Concentration Method

The MDEQ accepts results generated using the low concentration soil method of Method 5035A, for site assessment, site investigations, and response activities, provided the requirements listed below are followed and documented:

- The sealed containers are attached directly to the instrumentation.
- The preservation is applied correctly to the various soil types.
- Information that validates the use of the method with the appropriate type of soil is provided.
- Information that demonstrates the effectiveness of the sealed containers ability to prevent the exposure of the sample to environmental conditions is provided.

The low concentration preservation procedure may not be appropriate for all soil types. For example, calcareous soils cannot be sampled by the low concentration method when sodium bisulfate is used because a chemical reaction occurs that adversely affects the results. Soil samples must be tested in the field prior to collecting the samples for analyses, as discussed in Method 5035A, to determine if the acidic preservation for the low concentration procedure can be used. If the acidic preservation cannot be used, alternate procedures for preservation in Method 5035A should be used. The preferable alternate procedure is to extrude the samples into empty sealed vials and freeze on site to < -7 C°. Care must be taken to not freeze the vials below -20 C° to avoid potential problems with vial seals.

Method 5021A, Headspace Analysis using Sealed Containers

The MDEQ accepts results generated using the sample collection and preservation methods of Method 5021A for site assessment, site investigations, and response activities, provided the same requirements for Method 5035A, Low Concentration Method are documented. The preferred analytical method is Method 8260B (see RRD Operational Memorandum No. 2, Attachment 1). This sample and collection procedure is highly recommended for the analyses of contaminants that are very soluble in water.

Method 5035A, Soil Coring Devices (used to transfer samples to the laboratory)

The MDEQ requires the use of soil coring devices to evaluate the leaching of volatiles from soils, as provided in Operational Memorandum No. 2, Attachment 2, Soil Leaching Methods. The requirements in Attachment 2 must be met.

The MDEQ does not recommend the use of soil coring devices for initial site characterization where the objectives include establishing the contaminants of concern; or for response activities where the objectives are to demonstrate final compliance with cleanup criteria. The MDEQ may accept results using the soil coring devices, providing the following requirements are documented:

- Scientific studies exist that demonstrate the device to be effective for the use intended. The manufacturer of the device should be contacted regarding studies that prove them effective.
- The party proposing the use of the soil coring devices must demonstrate the effectiveness of the devices to retain volatile chemicals, for the specific chemicals of concern at the facility. Demonstration of the effectiveness of the devices proposed to be used can be accomplished using duplicate sampling. The demonstration must include duplicate samples

collected using methanol preservation in the field. Duplicate samples must be collected for a minimum of one sample, or for at least one of every five samples collected.
- Written protocols must be established regarding the use of the devices to collect samples, and to preserve samples at the laboratory. These protocols must be provided to the MDEQ.
- Confirmation samples must be collected using methanol preservation in the field, equivalent to the standard operating procedure of this document. Confirmation samples must be collected for a minimum of two samples, or for at least two from every ten samples collected.
- All requirements of Method 5035A regarding the use of the samplers must have been met.

OXYGENATES

Oxygenates refer to methyl(tert)butylether (MTBE), t-Butyl alcohol (TBA), Di-isopropyl ether (DIPE), Ethyl(tert)butylether (ETBE), Ethyl alcohol, Methyl alcohol, and Tertiaryamylmethylether (TAME), and the oxygenated ethers refer to MTBE, DIPE, ETBE and TAME. When any of the oxygenated ethers are required for analysis, and high temperature purging is used in the analysis, samples collected must have the pH adjusted to > 10 in the field using Trisodium phosphate dodecahydrate (TSP), or two samples can be collected and the laboratory instructed to neutralize one prior to the analysis for oxygenated ethers. The laboratory should be contacted regarding its procedure for the analysis of oxygenated ethers to determine if high temperature purging is used. Methods 5035A and 5021A can be used for sampling for oxygenates, provided the requirements in this document are met. Method 5021A is highly recommended.

Questions concerning this document should be directed to Mr. A. Ralph Curtis, Toxicology Unit, RRD, at 517-373-8389, or email to curtisar@michigan.gov.

The following documents are rescinded with the issuance of this attachment:

- Environmental Response Division procedure for the Collection and Methanol Preservation of Soils for Volatile Organics, dated May 1, 2000.
- Storage Tank Division procedure for the Collection and Preservation of Soil Samples for Volatile Organic Analysis, dated May 18, 2000.
- Storage Tank Division Informational Memo No. 13 “Implementation of Environmental Protection Agency (EPA) SW-846 Method 5035 Closed-System Purge and Trap and Extraction for Volatile Organics in Soils and Waste Samples”, dated September 4, 1998.

APPENDAGE:

Standard Operating Procedure for Methanol Preservation in the Field

This memorandum and its attachments are intended to provide direction and guidance to foster consistent application of Part 201, Part 211, and Part 213 and the associated administrative rules. This document is not intended to convey any rights to any parties or create any duties or responsibilities under the law. This document and matters addressed herein are subject to revision.

STANDARD OPERATING PROCEDURE for METHANOL PRESERVATION IN THE FIELD

SUMMARY

Soil samples are collected using conventional procedures, including auger and split spoon techniques. Sub-samples are then taken using syringe-type coring devices and immediately transferred into pre-weighed VOC vials containing reagent grade methanol sufficient to obtain an estimated ratio of 1:1 with the soil. The samples are transferred to the laboratory. Upon receipt at the laboratory, the following steps are taken as soon as is practical:

An accurate sample weight is determined.
The sample container is swirled gently to break up soil clumps.
The sample is sonicated for 20 minutes.
An aliquot taken and stored for analyses using Method 8260B.

Method 5035A uses a 2:1 ratio of methanol volume to soil weight. This ratio is acceptable contingent that the requirements in Operational Memorandum No. 2, Attachment 1, Target Detection Limits and Available Methods, are met.

LABORATORY RELATED PROCEDURES AND DOCUMENTATION

Procedures - The laboratory selected should have written standard operating procedures that address the provision of sampling supplies intended for methanol preservation of samples, sample receipt checks, sample preparation steps and documentation, sample collection requirements, and analyses. The laboratory should first be contacted regarding specific requirements. The laboratory's standard operating procedure governing the sample preparation should specify the contact time routinely applied, and when this time period is not met, this must be narrated with the results. The following documentation must be included:

- Copies of the certifications of the methanol used.
- Percent moisture in the samples (determined using separate vial/container with just soil).
- Dates samples were collected, and preserved if not immediately performed upon collection.
- Dates samples were received at the laboratory.
- Sample weights.
- Sample moisture (soils and sediments).
- Actual ratios of methanol to soil.
- Sonication dates/times.
- Minutes of sonications if different from 20 minutes.
- Dates/times aliquots were taken for analysis, if not taken immediately after sonification.
- The dates of the analysis.

MDEQ LABORATORY SPECIFICATIONS FOR SAMPLE COLLECTION

The following specifications apply for sample collection kit provided by the MDEQ laboratory. Other laboratories may have similar kits with specifications. Contact the laboratory selected.

Target Soil Weight = 10 grams
Allowed Weight = 9 to11 grams
Size of VOC Sampling Vials = 40 ml

Methanol Volume (provided in tubes) = 10 ml
Soil Coring Device (Syringe Sampler) Size = 10 ml
Green Sticker to Warn of Hazardous Waste
Wide Mouth Jars (4 oz. and 8 oz.)

HEALTH AND SAFETY

Material Safety and Data Sheets (MSDSs) providing health and safety data, and emergency procedures should accompany staff in the field. Methanol ampoules, tubes, and vials must be provided to field staff inside protective containers to hold any spillage. Methanol is a toxic and flammable liquid. Handle with proper safety precautions. Wear safety glasses and protective gloves. Nitrile Rubber or Viton gloves are recommended. Avoid inhalation. Store and handle in a ventilated area, away from sources of ignition and extreme heat. Store methanol in a cool place, preferably in sample coolers on ice. This is especially important for methanol in tubes, where pressure buildup due to extreme heat may result in rupture. Vials should be opened and closed quickly during collection. In the event of eye contact, immediately flush with large amounts of water for at least 15 minutes, occasionally lifting upper and lower lids. Seek medical attention immediately.

SHIPPING

The shipping of methanol is regulated by the U.S. Department of Transportation (DOT), Title 49 of the Code of Federal Regulations. The DOT number is UN 1230. The amount of methanol used for sample preservation falls under the exemption for small quantities. Requirements for shipment of samples by common carrier are as follows:

Maximum volume of methanol in a sample container cannot exceed 30 ml.
The sample container cannot be full of methanol.
Sufficient absorbent material must be used in the container to completely absorb sample content.
Each cooler must have less than 500 ml of methanol.
The cooler or package weight must not exceed 64 pounds.
Each cooler must be identified as containing less than 500 ml methanol.

APPARATUS AND MATERIALS NEEDED FOR SAMPLE COLLECTION

Absorbent Material – If the samples are to be shipped by common carrier, vermiculite or similar material, sufficient to completely absorb the methanol for each sample.

Calibration Weight - Near or equal to the target sample weight.

Certified Methanol – Methanol certified for purge and trap gas chromatography is analytically verified prior to sampling (by lot). In this procedure the methanol is provided in sealed ampoules. Some labs may provide methanol in the sampling vial.

Field Balance - Capable of holding sampling vial and syringe on the wide mouth jar used to prevent balance contamination, and measurement within + 0.2 grams.

Hazardous Waste Warning Label - Suitable vial labels to warn personnel of the presence of methanol as a preservative.

Methanol Sampling Kit/Method 5035A Sampling Kit:

Protective Wear - Nitrile rubber or Viton gloves. Splash proof safety goggles.

Plastic Bags - Air tight seals, capable of holding three sample VOC vials, and sub-coring device.

Protocol to be used for the collection of samples.

Sub-Coring Device - A syringe type device, whose material has been tested and found free of contaminants,. This device is used to sub-sample the targeted amount of soil, for transfer into methanol in the field.

Wide Mouth Jar (for holding methanol tubes) - Of suitable size to allow temporary storage and shipment of the methanol tubes.

Wide Mouth Jar (for preventing balance contamination) - Of suitable size to allow temporary storage of the syringe type sampler and VOC sample vial on the field balance.

Volatile Organic Compound (VOC) Syringe Labels - Methanol resistant labels.

VOC Vials - Vials with Teflon™ lined septa, pre-weighed, with methanol resistant labels.

SAMPLE CONTAINERS, PRESERVATION AND HOLDING TIMES

Containers - Sample containers are VOC Vials with Teflon™ lined septa of suitable size to hold the soil plus methanol, supplied with methanol resistant labels.

Preservation – Samples are preserved in the field approximately one to one ratio of soil weight to methanol volume, using pre-weighed vials and a field balance. The exact sample weights and ratios are determined at the laboratory. More methanol is added to make the ratio one to one when possible. When weights are less than the specified minimum, the reporting limit is increased. The maximum and minimum limits for the weights of soils specified by the MDEQ laboratory are provided in the section of this document entitled “Specifications for the Collection of Samples Using Methanol Preservation.”

Holding Times - The maximum allowable holding time is 14 days from sample collection to analysis. If the maximum allowable holding time is exceeded, interpret the results as minimum concentrations of the measured compounds.

QUALITY CONTROL

Field Blanks

Use - Field blanks are used to determine sample contamination that may occur during the storage, transportation, sampling, and analysis of samples. A field blank is a sample vial containing a pre-measured quantity of VOC-free methanol, obtained from the laboratory or prepared in a contaminant free environment.

Frequency - The number of field blanks depends upon project objectives and the field activities being performed at specific locations. It is recommended that a field blank be created at each location where activities may result in significant VOCs released into the environment, or for every 20 samples, whichever is more.

Interpretation – Positive results may indicate contamination from the methanol, the sample container, from the air at the site, from diffusion of air containing volatiles into the blank during transport to the laboratory, or from the laboratory environment. Compare field blank results with trip blank results and laboratory method blanks to isolate the cause. Sample results that approach the field blank results may be unusable.

Trip Blanks

Use - Methanol trip blanks are used to determine if contamination is occurring from the methanol, storage, transportation, or the field.

Frequency - One trip blank should be used per cooler.

Interpretation – Positive trip blanks can be attributed to the methanol, sample vial material, and the environment in the cooler or sample transport container. Trip blanks should be prepared at, and provided by, the laboratory in order to make this interpretation. If consistent positive results are obtained, contact the laboratory and have a trip blank prepared at the laboratory and immediately analyzed to attempt isolation of the cause.

Methanol

Only purge and trap grade methanol verified to be suitable for methanol preservation should be used. Field staff should maintain documentation of the methanol lot numbers for all associated samples. If consistently high levels of compounds are measured in methanol field blanks associated with a specific lot number, request the laboratory to verify the quality of the methanol lot used to preserve the samples.

Contamination

Contamination by airborne VOCs in the air is possible by diffusion through the vial septum during shipment, storage, collection, and analysis. To control such contamination:

Use appropriate VOC sample vials.
Avoid sources that generate VOCs such as petroleum products, especially auto exhaust fumes.
Keep sample containers in coolers as much as possible.
Collect samples quickly.
Use methanol provided in sealed ampoules, tubes, or VOC vials.

Attempt to isolate the source of contamination and incorporate appropriate procedures to avoid similar circumstances.

FIELD BALANCE CALIBRATION CHECK

The field balance calibration should be checked prior to each sampling event, and whenever necessary because of handling in the field. Record this check in the field notebook.

CORRECTIONS FOR SAMPLES WITH HIGH WATER CONTENT

Concentrations of volatile compounds in soils must be reported on a dry weight basis, using the moisture content of the soil to adjust results. Routine procedures by the laboratories include this correction. Laboratories may not routinely correct results because of the effects due to the miscibility of the methanol with the water in the sample. The effects are to bias the results low, and if the moistures in the samples are high, these biases may be significant. The effects of this biases upon results should be considered when soils are sampled, and if necessary the laboratory instructed to correct results accordingly.

ELEVATED REPORTING LIMITS DUE TO HIGH MOISTURE

For samples with excess moisture, reporting limits may need to be elevated higher than levels routinely reported by the laboratory. Elevated reporting limits may be acceptable if they do not exceed applicable criteria. Historical site information and published information can be used to ascertain the range of moisture levels that can be expected. This can be used to determine if the biases are significant. Additional guidance regarding elevated reporting limits is available in RRD Operational Memorandum No. 2, Attachment 1.

OTHER METHANOL PRESERVATION PROCEDURES

Variations to the field procedure in this method may be used if approved in advance by the MDEQ. Important considerations are:

- Samples must be preserved in the field, a target ratio of 1:1 for the weight of the soil to the volume of methanol should be used.
- Samples must be sonicated for 20 minutes at the laboratory.
- A methanol aliquot must be taken and stored for analysis immediately after sonication that is sufficient for initial analysis, and analysis of any subsequent dilutions.
- Sufficient documentation to validate the data must be provided to the MDEQ.

FIELD SAMPLING PROCEDURE

1. Make arrangements with the laboratory to obtain appropriate Methanol Preservation Sampling Kits.
2. Record the tracking or lot number(s) for the methanol in the field notebook. If more than one lot is used, each lot must be associated with the samples for which it was used.
3. Prior to collection, check the calibration of the balance. See "Field Balance Calibration Check" on page 10 of this document.
4. Prior to collection prepare a temperature blank sample using tap water and a VOC vial.
5. Prior to collection prepare a sufficient quantity of methanol field blanks, i.e., at least one per cooler and one per methanol lot as follows:

   a) Select an area free of VOC sources.
   b) Remove a methanol tube from the wide mouth jar.
   c) Use scissors to cut off the top, and place the methanol into one of the pre-weighed sample vials.
   d) Place the cap on the vial and tighten it. Avoid over-tightening.
   e) Place a green sticker on the top of the cap.
   f) Record the identification of the vial as "Methanol Field Blank" on both the vial label and in the field notebook.

6. Calibrate the syringe to estimate the amount of soil needed to meet the target weight, and use that syringe as a comparison for how much sample is needed.

   Calibration is performed using steps 10 - 17 below, using the syringe only, and part of the soil that is to be collected. The soil used for calibration cannot be used as the sample. It must be extruded from the sampler and discarded at the site before collecting the sample. The sampler does not have to be cleaned between calibration using this step, and collection of the sample.

7. Place the wide mouth glass jar, used to prevent balance contamination, on the balance.
8. Record the location, date, and time of sampling in the field log book. Do not place any labels, stickers, tape, etc. on the pre-weighed sample vials.
9. For methanol field blanks, remove the cap from a methanol field blank which was prepared in Step 5 above, place the opened vial in the collection area for the approximate time it takes to collect a sample, and then cap the methanol field blank for storage and transport to the laboratory.
10. Place a pre-weighed VOC vial and syringe in the wide mouth jar on the balance.
11. Record the weight in the field log book. If the balance features re-zeroing, zero the balance.
12. Remove the syringe. If a cap is provided, remove the cap and place it in the jar.
13. Insert the open end of the syringe into a fresh face of undisturbed soil, and fill it as appropriate according to the calibration of the syringe (Step 6).
14. If necessary, use your gloved finger (decontaminate before next sample), or other appropriate instrument, and push the soil deeper into the syringe sampler.
15. If a cap was provided, immediately cap the end of the syringe.

16. Place the syringe in the jar on the balance. Read the weight, and if necessary, subtract the weight of the syringe, vial, and jar, as appropriate, to determine the weight of the soil.
17. If the weight of the sample is determined to be more than the maximum amount allowed, extrude enough soil to obtain the target amount within the specified tolerance, and re-weigh. See the table in this document, "Specifications for the Collection of Samples Using Methanol Preservation" for the applicable target sample size and tolerance.
18. If the weight of the sample is less than the minimum amount allowed, re-sample and repeat steps starting with Step 7.
19. Record the soil weight in the field notebook. DO NOT RECORD the weight on the sample vial label.
20. Remove the cap from the sample vial, and place it in the jar on the balance, with the septum upwards.
21. If the required amount of methanol is not included with the pre-weighed vial, immediately remove a methanol tube from the wide mouth glass storage jar, holding the tube upright use scissors to cut (plastic) off one end, and pour the methanol into the sample vial, taking care to avoid spillage.
22. Insert the open end of the syringe sampler into the mouth of the vial, and carefully extrude the soil, taking care to avoid spillage. Loss of several drops will not make a significant difference in the results. If a significant amount is spilled, a new sample must be collected, or the sample must be appropriately flagged to indicate estimated results.
23. Using a clean brush, paper towel, or other suitable material, thoroughly wipe excess soil particles from the threads and vial body. Particles left on the threads will prevent a good seal.
24. Place the VOC cap on the sample vial. The cap must be tight; however, over-tightening should be avoided.
25. Gently swirl the sample and methanol for about 10 seconds to break up the soil. DO NOT SHAKE.
26. Place the sample in a plastic bag on ice in a cooler.
27. Attach a green sticker on the plastic bag to indicate a hazardous waste.
28. Using the syringe sampler, take another sample from the soil.
29. Cap and label the syringe with the sample identification.
30. Place the syringe with the sample in the plastic bag. This sample is for dry weight determination.
31. Decontaminate the jar/balance using decontamination procedures appropriate for the type and level of contamination.
32. Unused methanol must be returned to the laboratory for disposal.

STANDARD OPERATING PROCEDURES 2010

Appendix A

Manta Operating Manual

Center for Toxicology and Environmental Health, L.L.C.

5120 N. Shore Drive, North Little Rock, AR 72118 Phone: 501.801.8500 www.cteh.com

STANDARD OPERATING PROCEDURES FOR:

MANTA 2 MULTIPROBE - OPERATING MANUAL

Prepared By

Center for Toxicology and Environmental Health, L.L.C.

For:

Internal Use Only

In Reference to:

Enbridge-Marshall Release

Sector Mobile

Valid until replaced by a global CTEH plan

August 14, 2010

Center for Toxicology and Environmental Health, L.L.C.
CTEH
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Manta 2 Multiprobe – Operating Manual

Manta 2 Multiprobe – Operating Manual

1.0 Introduction

The Manta 2 is a multi-parameter water sampling probe, composed of a transparent housing, communication circuitry, and multiple sensors such as; temperature, pH, dissolved oxygen, etc. Using the Manta 2 Control Software, the multiprobe interfaces with either the Amphibian Data Display (Microsoft Mobile Device) or a laptop computer.

1.2 Application

The Manta 2 is used in one of three different applications:

1.2.1 Manual Method

The Manta 2 connects to either the Amphibian (Field PC) or a laptop with the underwater cable. The user can then interface with the multiprobe and gather data over a short time period.

1.2.2 Unattended Sampling

The Manta 2 can be anchored and left unattended to gather data over an extended period. Data is downloaded from the multiprobe at the end of the sampling period.

1.2.3 Telemetry System

A modem, battery pack and data logger makes up the data telemetry system. This system transmits data gathered by the Manta to a secure website via a cellular or satellite system. The telemetry unit is a great application for unattended sampling.

2.0 Manta 2 Multiprobe

2.1 Sensors and Parameters

A sensor is composed of a sensing element and the necessary circuitry to communicate with the multiprobe. A parameter is a unit in which data is displayed. For example, the Optical DO Sensor provides data in one or more parameters such as, percent saturation or mg/L. You have the option of selecting which sensors (if equipped) and parameters are displayed. The program will only collect data from what you select. Following is a list of sensors and parameters.

2.1.1 Temperature

The temperature sensor is an electrical resistor (thermistor) that measures a change in resistance predictably with temperature. The thermistor does not require calibration.

Parameters: °C and °F

2.1.2 pH

The pH of water is measured by using a glass electrode and a reference electrode filled with a standard electrolyte (KCl) solution. The specially formulated glass on the pH electrode absorbs water, specifically the H^+ and OH^- ions. When these ions attract to the glass, they offset the ionic constituency of the KCl electrolyte. This offset results in a charge separation across the glass and the voltage is measured. The displayed pH measurement is compensated for temperature (corrected to 25°C).

Parameter: 0 -14 pH Units

2.1.3 Dissolved Oxygen (DO)

The DO sensor is an optical sensor comprised of a blue-light source, a sensing surface, and a red-light receiver. The sensing surface is an O_2 –active compound stabilized in an O_2 permeable polymer, typically silicone. The O_2 – active compound fluoresces, or absorbs energy in the form of blue light, then emits energy as red light. The red-light receiver measures the amount of emitted red light resulting from the blue-light's energy. The optical sensor has very little calibration drift and is not flow dependent (typical DO sensors consume oxygen requiring the use of a circulator).

Oxygen quenches fluorescence, meaning the amount of red light is reduced if O_2 molecules are present to interfere with the O_2 – active compound. An increase in oxygen results in a decrease of red light directly relatable to the amount of oxygen present. Sensor output is corrected for the temperature characteristics of the membrane, and for the temperature characteristics of the oxygen-saturated water.

Parameters: 0 -25 mg/L
0 – 200% Saturation

2.1.4 Conductivity / TDS / Salinity

The multiprobe uses a four electrode (two pairs situated in a stable geometry) method for determining water conductivity. Each electrode pair receives a constant voltage. Conductivity is measured as the current required to maintain that voltage. Therefore, an increase in water conductivity results in an increase in voltage.

The voltage is reported as specific conductance (conductivity corrected to 25°C). The multiprobe also reports Total Dissolved Solids (TDS) and Salinity. These two parameters are calculated from conductivity, not calibrated.

Parameters:	Conductivity	0 – 100 µS/cm
	Salinity	0 – 70 PSU (PPT)
	TDS	0 – 65 g/L

2.1.5 Turbidity

The optical turbidity sensor measures suspended solids in water using a beam of infrared light. The beam is scattered by particles in the water and measured as the fraction of light scattered 90° to that beam. An increase in particles equals an increase in turbidity. Although the sensor requires little maintenance, it should be checked periodically to ensure the optical window is free of accumulation. The sensor installed on the multiprobe has a small wiper that cleans the optical window. Occasionally inspect to ensure proper working order.

Parameter: 0 – 3000 NTU (Nephelometric Turbidity Units)

2.1.6 Fluorometer CDOM

The Manta 2 is equipped with a CDOM Fluorometer configured and scaled for the analysis of crude oil. CDOM stands for colored dissolved organic matter. The sensor measures the fluorescence of dissolved organic matter present in the water and delivers an output voltage proportional to the concentration. Fluorescence is temperature sensitive, meaning an increase in sample temperature will result in a decrease in fluorescence.

Parameter: ppm (range to follow)

2.2 Amphibian Data Display

The Amphibian Data Display (Archer Field PC) is a Microsoft based PDA. Calibration, data acquisition, and other various controls are performed using the Manta 2 Control Software. With the onboard GPS locator, the user can pair GPS coordinates with each sample point. Data collected and stored within the Amphibian can be transferred to a laptop computer.

2.3 Underwater Cable

The Underwater Cable is capable of deploying the multiprobe to a max depth of 200 ft. The cable connects the multiprobe to the Amphibian, a laptop computer or telemetry device.

2.4 Storage / Calibration Cup

The storage / calibration cup covers and protects the sensors when the probe is not in use. The cup should always contain a few ounces of tap water to keep the sensors moist. During calibration, hold the probe with the sensors pointing up. Remove the black lid from the calibration cup and pour in the solution standard. The lid is then replaced and the probe turned upright. This should fully immerse the sensors in the calibration standard, add solution if necessary.

2.5 Weighted Sensor Guard

The weighted sensor guard replaces the storage / calibration cup when sampling with the Manta 2. The sensor guard is vented allowing water to flow over the sensors.

2.6 Battery Pack

The battery pack provides power to the multiprobe. The underwater cable connects to the batteries 9-pin connector and the second cable (attached to batteries 9-pin connector) connects to the Amphibian (If using a laptop computer, use the 9-pin to USB converter cable).

2.7 LED Lights

The circuitry installed inside the Multiprobe is equipped with three LED lights. These lights are visible through the Manta's housing.

Green:	Blinks once every two (2) seconds to indicate the Manta 2 has adequate operating voltage.
Yellow:	Blinks briefly, when the Manta 2 receives RS-232 communication.
Red:	Blinks every two (2) seconds for ten (10) seconds upon each power up if logging is enabled.

2.8 Software

2.8.1 Eureka Manta2 Control Software – ver. 0.1.8.34

This software is loaded onto both the Amphibian and can be loaded on a laptop computer. The software interfaces with the communication circuitry inside the Manta 2, allowing the user to set-up, program, log data and calibrate the sensors.

2.8.2 Microsoft Mobile Device Manager – ver. 6.1

Installation of the Mobile Device Manager software is necessary in order to transfer files saved in the Amphibian to a computer. The software can be downloaded for free on Microsoft's website.

3.0 Calibration

3.1 Basics

Use the Amphibian hand held device (or PC) and start the Eureka Amphibian Software. Select Manta2 at the bottom of the screen to open the Menu (top of page if using a PC). A pop-up screen will appear listing parameters to calibrate. Next, click on the sensor / parameter you wish to calibrate. Another screen will appear with instructions for the specific parameter, current reading and a box for you to enter the value of the calibration standard. For most parameters, you enter the value of the standard and hit "enter". The Current Box will show the sensors reading. Hit "enter" to accept the value once the reading has stabilized. The value is accepted if the calibration returns an acceptable sensor response factor (SRF) value between 60% and 140%. However, if the SRF is not acceptable (outside the 60% -140% range), you are given the option to accept the calibration despite the deviant SRF, or you can return to the calibration steps and review instructions, calibration value, etc.

3.2 Barometric Pressure

You must enter the local Barometric Pressure (BP) before each calibration.

1. Open the Manta2 Menu and select Calibrate.
2. Select BP from the pop-up menu of calibration parameters.

   There are four options for entering BP. For the preferred method, Option 1, enter the BP value in mm Hg. If you are unable to look up the local BP, Option2 allows you enter the elevation. Elevation must be taken from an altimeter or GPS unit. Option 3 cannot be used since the multiprobe is not equipped with a depth sensor. Option 4 can be used (not preferred) if you are unable to look up the local BP or elevation.
3. Enter the value in the box and select "OK". You will be immediately returned to the main screen.

3.3 Date & Time

The date and time are currently set in the device, but if you need to make changes, open the calibration menu. Then select Date & Time from the pop-up screen, and follow the instructions.

3.4 General Calibration Procedure

1. Clean the sensor and perform any necessary sensor-specific maintenance.
2. Select a calibration standard with a value similar to the values you expect to see.
3. Rinse sensors thoroughly with de-ionized water by filling the calibration cup and shaking vigorously to remove traces of old calibration solutions. Repeat if necessary.
4. Rinse the sensors twice with a small amount of the calibration solution.

5. Fill the calibration cup with the solution and immerse the sensor. Most parameters are temperature compensated. The thermistor is the shortest sensor so be sure to immerse it in the solution. Typically, you need to fill the calibration cup entirely in order to immerse all the sensors during calibration.
6. Select the parameter to be calibrated from the menu describe above.
    a. Enter the calibration value and press enter to accept.
    b. Press enter again once the reading has stabilized to calibrate. The Manta 2 will report the resulting SRF, Press Y to accept, N to back up one step, or Exit to leave the sensor un-calibrated.

3.5 Sensor Specific Calibrations

3.5.1 pH

Use a (2)-point calibration using 2 buffers, 7.00 and 10.0.

1. Rinse the sensors in DI water, discarding rinse into the decon bucket.
2. Rinse the sensors with the first buffer (7.00).
3. Fill cup with the number 7.00 buffer and upright the probe to immerse the sensors.
4. Follow the calibration instructions and discard the used solution into the decon bucket.
5. Rinse the sensors with DI water. Discard rinse into decon bucket.
6. Rinse sensors with the second buffer (10.0).
7. Fill calibration cup with the number 10.0 buffer and upright probe to immerse the sensors.
8. Follow the calibration instructions and discard the used solution into the decon bucket.

3.5.2 Conductivity

Use a (1)-point calibration.

1. Rinse the sensors with DI water, discarding rinse into decon bucket.
2. Fill the calibration cup with the standard (appropriate to the sampled waters). Use the 12,586 μS/cm solution to calibrate for seawater.
3. Follow the calibration instructions and discard the used solution into the decon bucket.

3.5.3 Turbidity

Use a (2)-point calibration, a zero and an approximate standard dependent upon water(s) to be tested. For our purposes, we will use a standard solution of 400 NTU.

To Zero;

1. Rinse sensors twice with deionized water. Partially fill the calibrations cup with DI water, close and shake vigorously. Discard rinse into decon bucket.
2. Fill the calibration cup with the zero turbidity standard, replace lid and upright the multiprobe to immerse the sensor in the solution.
3. Follow the calibration instructions in the control software.

To set the second point, repeat the steps above using a 400 NTU standard solution. Discard used solutions into your decon bucket.

3.5.4 Dissolved Oxygen (DO)

Calibrate by setting the sensor's saturation point. Be sure to set the local Barometric Pressure before calibrating DO.

1. Take a 1-liter jar and fill halfway with distilled water, screw on cap, and shake vigorously for one minute.
2. Remove cap and let jar stand for one minute. This lets the tiny air bubbles float out of the top.
3. Completely immerse the sensor in the aerated water, cap and upright.
4. Wait a few minutes for the temperature and reading to equilibrate.
5. Follow the calibration instructions in the control software.

3.5.5 Fluorometer CDOM

Use a two-point calibration.

To Zero;

1. Rinse sensors twice with deionized water. Partially fill the calibrations cup with DI water, close and shake vigorously. Discard rinse into decon bucket.
2. Fill the calibration cup with the zero standard and upright the multiprobe to immerse the sensor in the solution.
3. Follow the calibration instructions in the control software.

To set the second point, repeat the steps above using a relative standard solution. Discard used solutions into your decon bucket.

3.6 Fluorometer CDOM Instrument Check Procedure (Pre and Post Sampling)

This procedure checks for instrument drift and is not a method of calibration. The check should determine if the instrument's response to a known quantity of fluorescing material is changing overtime. Anyone monitoring for a subsurface plume of oil resulting from MC 252 incident are requested to conduct this type of procedure before and after each sampling event.

1. Use a Glass Beaker for your water samples. (Avoid plastic beakers. Plastic fluoresces and will interfere with the sample fluorescence)
2. Place the glass beaker on a Non-Reflective Surface, preferably black.
3. Ensure that the sensor is more than 3 inches above the bottom of the glass beaker.
4. Ensure that the sensor is in the center of the glass beaker, and has more than 2 inches clearance between the circumference of the sensor and the inside surface of the beaker. Turner Designs recommends using a 1L Glass Beaker for measurements.
5. Check that the optical surface of the sensor is free of air bubbles.
6. Be sure your sensor is calibrated.
7. To maximize consistency between measurements, place sensor at exactly the same height for each sample. This is most easily done using a Lab Stand.

4.0 Data Management

4.1 Calibration Log

All calibrations are stored within the Manta 2 multiprobe in the cal.Log file. When performing calibrations, regardless of whether the Amphibian or PC is used, the calibrations are always appended to end of the cal.Log. You can choose to view this log with either the Amphibian or PC. You will need to use the PC to export, save and/or print a copy of the cal.Log file.

4.2 Logging vs. Snapshot

There are two methods in which to log and store data. Logging and Snapshot.

Logging: Unattended data capture and storage into the Manta 2.

Snapshot: Manual capture and storage of data in the PC or Amphibian.

4.3 Snapshot & Automatic Snapshot

Snapshot is a manual method of data collection but can be automated. There are two options to store data using Snapshot; first, a previously set snapshot location can be appended, or a new location can be created. Snapshot can be accessed by selecting "PDA" at the bottom of the Amphibian screen, or by selecting PC if using a laptop. From the pop-up menu, select Snapshot Locations. This will open the snapshot location menu where you can "Select to Use" a previously set-up location, or "Create New" to create a new location.

4.3.1 Snapshot

By clicking Snapshot at the top of the main screen, you record a single point of data for each parameter each time you click it.

4.3.2 Automatic Snapshot

This option sets the snapshot (manual) function into automatic and records a set of points according to the scrolling interval setting. This will continue for as long as data display is on. Automatic snapshot ends if you exit out of the program. To turn on Automatic Snapshot, click on the PDA or PC depending on what you are using to display the information. Select Automatic Snapshot to open up the next menu. From this menu, select "On" or "Off" to record data at the scrolling interval previously set.

4.3.3 SS & Annotate

This option is to the right of the Snapshot button and allows the user to add a note to the Snapshot. Not an option when Automatic Snapshot is on.

4.4 Scrolling Interval

Once the file you wish to use has been selected or created, you will need to set-up your scrolling interval. Click on PDA on the Amphibian or PC on the computer. From here, you can select from the list of intervals or enter a custom value, hit "OK". The program will always use this interval until changed.

4.5 Logging and Managing Data via the Amphibian or PC

4.5.1 Managing Logged Data

Logging is intended for gathering unattended data, as the data is stored within the Manta 2. This method could provide a backup data file to the snapshot method. Open up the Manta 2 Menu at the bottom of the data display and select "Manage Manta 2 Files". This will open another menu listing previously created .LOG files including the file's last modified date. From here, you can create a new .LOG file specific to a sampling event, or append data to an existing file. Once you are finished, click on the OK button in the upper right-hand corner of the display.

4.5.2 Logging Interval

To set the Logging Interval, open the Manta 2 Menu and select the "Logging Interval" option. This will open a menu listing intervals from one to 360 minutes. There is also an option to enter a custom interval. Select your interval and click "OK" to return to the main menu.

4.5.3 Log On or Log Off

To ensure you are logging and storing data in the Manta 2 multiprobe, make sure you read "Log On" at the bottom of the main data display screen for the Amphibian, or the logging button on the PC screen reads Manta 2 is Logging. If "Log Off" or "Not Logging" is displayed, then click the button on the Amphibian or PC to activate data logging.

4.5.4 Accessing Logged Data File

In order to access the logged data, you will need to set-up the equipment and access via a laptop. Remember the .LOG file is stored in the Manta 2 multiprobe and not the Amphibian. To access the logged data file you must first connect the multiprobe to the battery, and then connect the USB to 9-pin serial connector to your PC. Make sure the Green LED light is blinking letting you know the Probe has sufficient power. Once the multiprobe is set-up and connected to the PC, you may open up the Manta2 Control Software. It is important to open the Manta 2 Control Software AFTER the multiprobe is connected and turned on. The menus in the Manta 2 Control Software are set up the same as the Amphibian.

1. Open the Manta2 Menu
2. Select the Manage Manta 2 Files option
3. Select the .LOG file you wish to transfer
4. Select Export Data to upload data and save onto your PC

If the PC and Control Software was being used to Log Data then several options are available. You can periodically export and save the log file during sampling, or export one time when the sampling event is over (recommended).

4.5.5 GPS Coordinates

The Amphibian Data Display is equipped with a GPS locating device. Enable GPS in order to log coordinates for each data point. To enable, click on the PDA menu and select Enable GPS from the pop-up menu.

4.5.6 Telemetry Unit

A Telemetry Unit is the best choice for acquiring unattended data. The unit collects data automatically (at set intervals) and transmits the data via cellular or satellite communication systems. The data is uploaded to a secure website where it can be managed and displayed. A modem, battery pack and data logger makes up the data telemetry system.

5.0 Summary

The Manta 2 multiprobe and software are easy to use and maintain. Calibration is straightforward, and accurate SRF values can be acquired if the calibration instructions are followed. People using the multiprobe for the first time should take the necessary time to familiarize themselves with the unit before conducting any field sampling.