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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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
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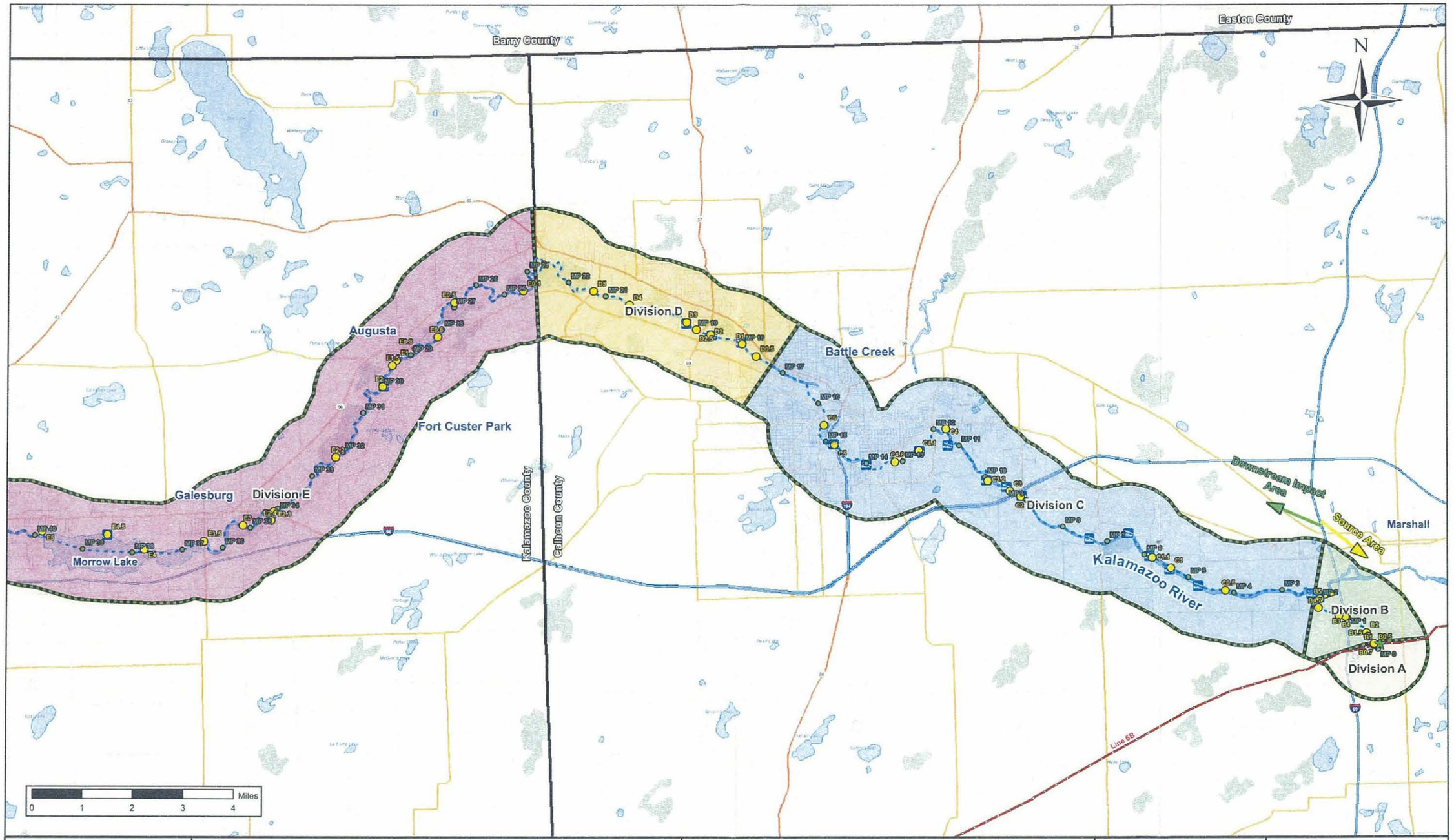

Legend

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

ENBRIDGE

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

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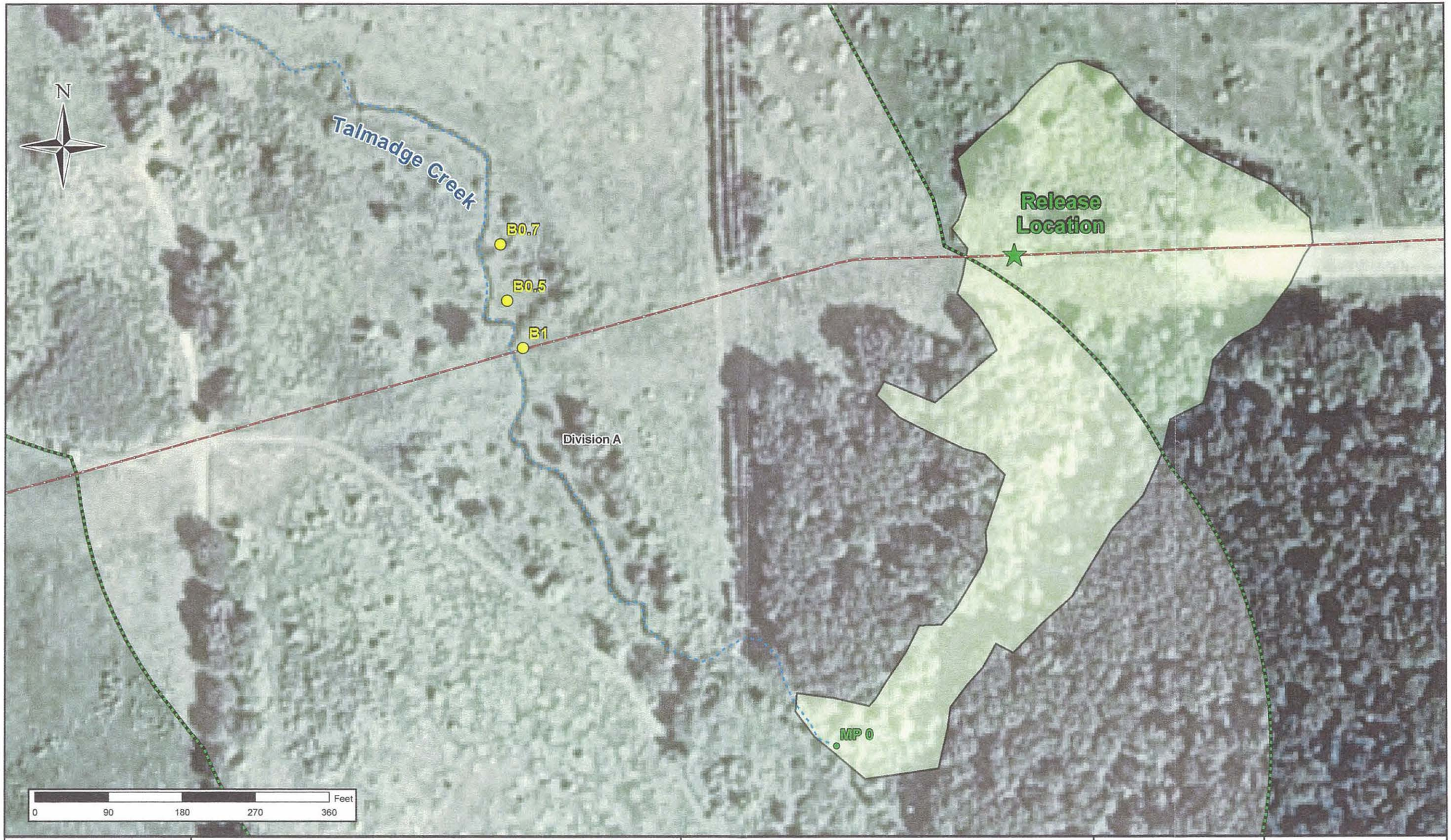

Legend

- 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 3: Division A - Multiple Media Sampling Locations

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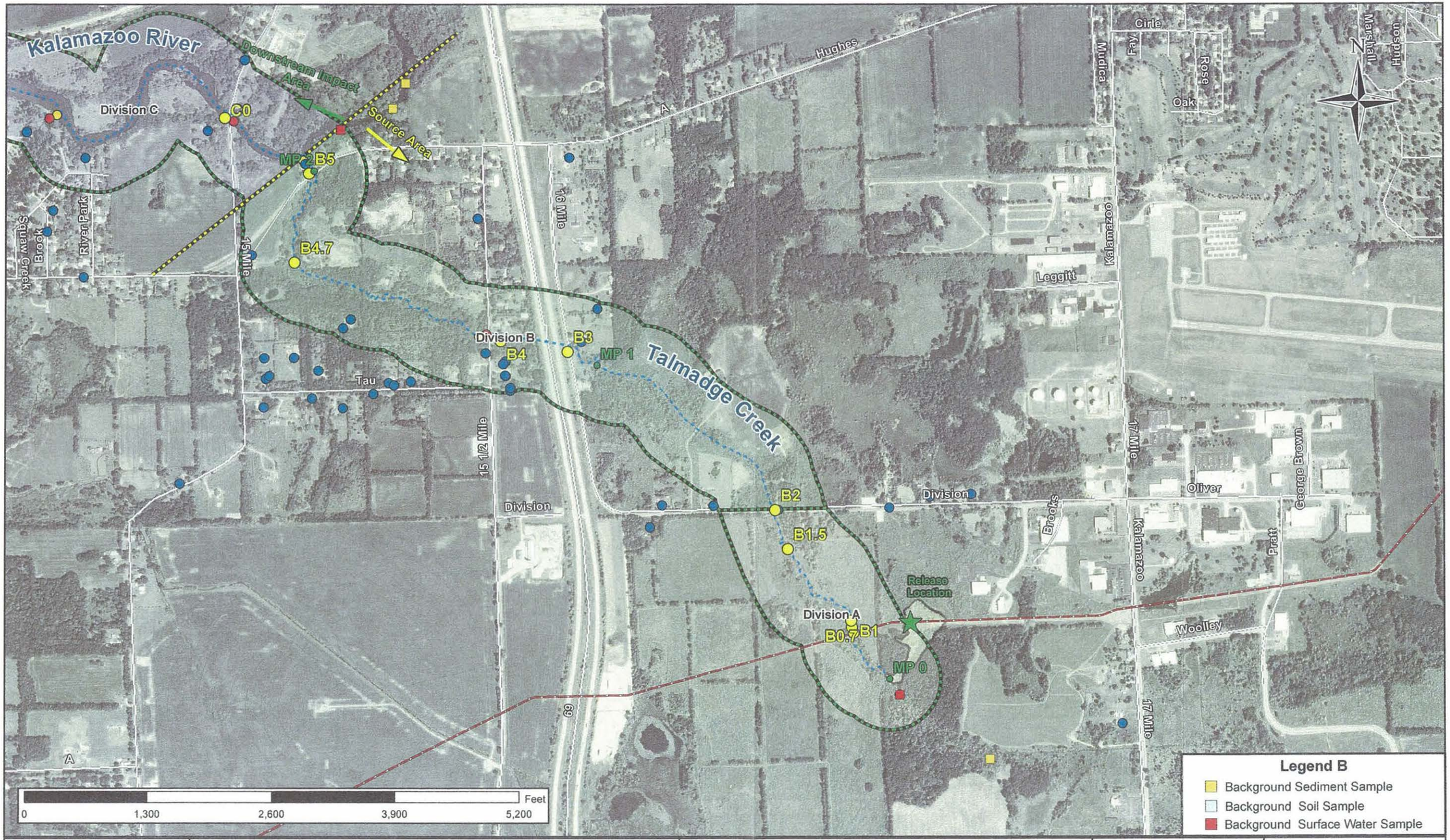

Legend A

- 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 4: Division B - Multiple Media Sampling Locations

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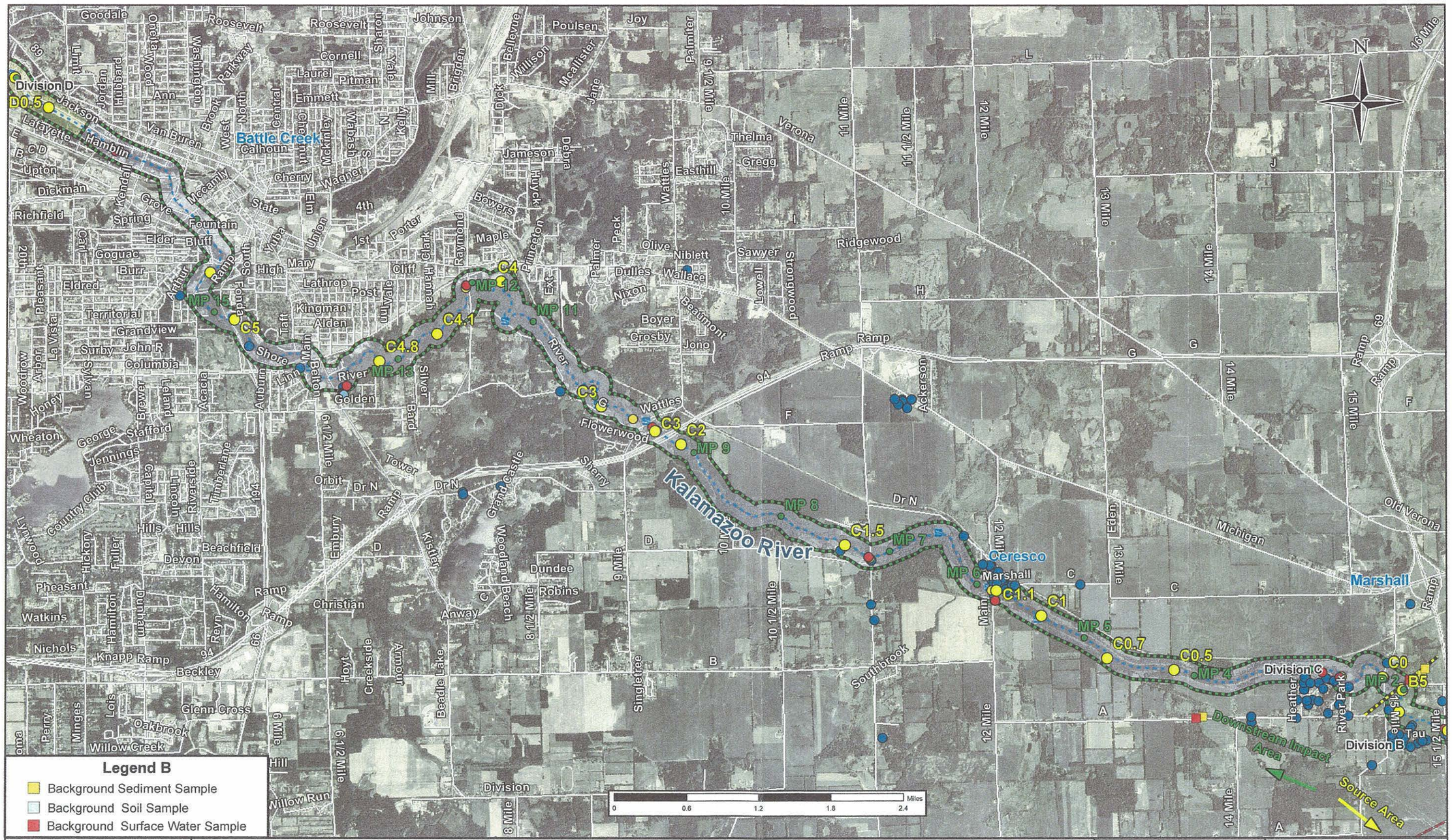
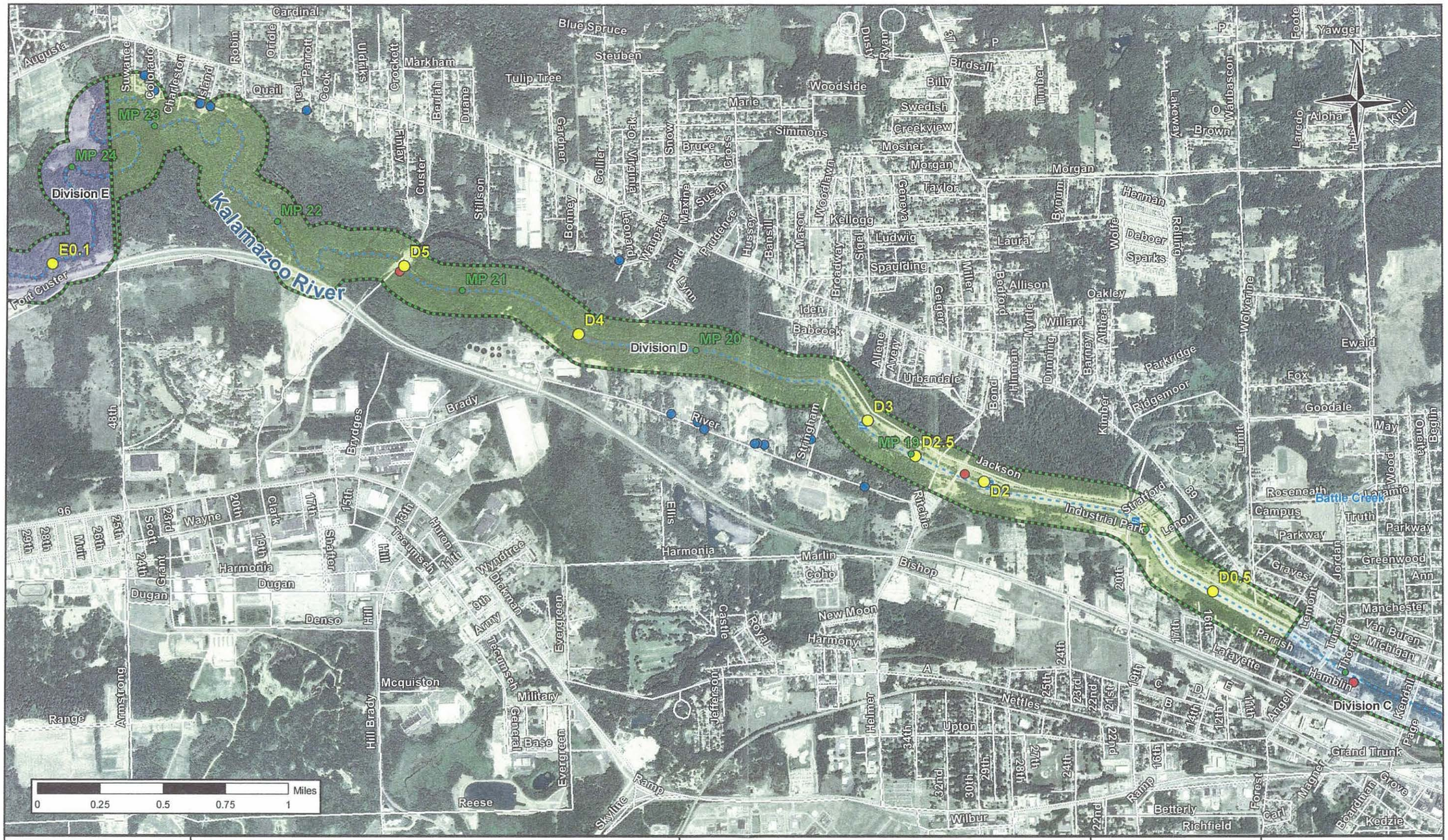

Division D
D0.5
Battle Creek
Calhoun
Jameson
Bowers
Maple
Olive
Niblett
Sawyer
Ridgewood
Thelma
Gregg
Easthill
Verona
Jackson
Lafayette
Hamblin
Upton
Dickman
Richfield
Spring
Grove
Fountain
Bluff
Elder
Goguac
Burr
Eldred
Territorial
Grandview
Surrey
Columbia
Sylvan
Honey
Wheaton
George
Stafford
Jennings
Country Club
Hickory
Fuller
Hills
Devon
Beachfield
Pheasant
Watkins
Nichols
Knapp
Beckley
Glenn Cross
Oakbrook
Willow Creek
Perry
Minges
Lois
Hamilton
Dunham
Christian
Orbit
Dr N
Ramp
Emory
Kistler
Grand Cassie
Woodland Beach
Dundee
Robins
Anway
Hoyt
Creekside
Amount
Beadle Lake
Singletree
Southbrook
Division
Willow Run
Hill
Tower
Sherry
Michigan
Old Verona
Eden
Ceresco
Marshall
Division C
Division B
Heather
River Park
Tau
Ackerson
Lyndon
Cornell
Laurel
Emmett
Pitman
Sharon
Johnson
Roosevelt
Goodale
Poulsen
Joy
Palmer
Dulles
Nixon
Wallace
Beaumont
Boyer
Crosby
Jono
Lowell
Strongwood
Arthur
Ramp
South
High
Mary
Cliff
Lathrop
Post
Kingman
Alden
Tiaft
Livale
Hannah
Clark
Raymond
Princeton
Ext
Pack
Wattles
Flowerwood
Shore
Main
Baton
River
Golden
Silver
Bard
Auburn
Lima
Acacia
Lelanet
Broadway
Woodlawn
Lavista
Parkway
Wesleyan
Timberlane
Lincoln Hills
Riverside
Capital
Hamilton
Reyn
Ramp
Ramp
Ramp



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

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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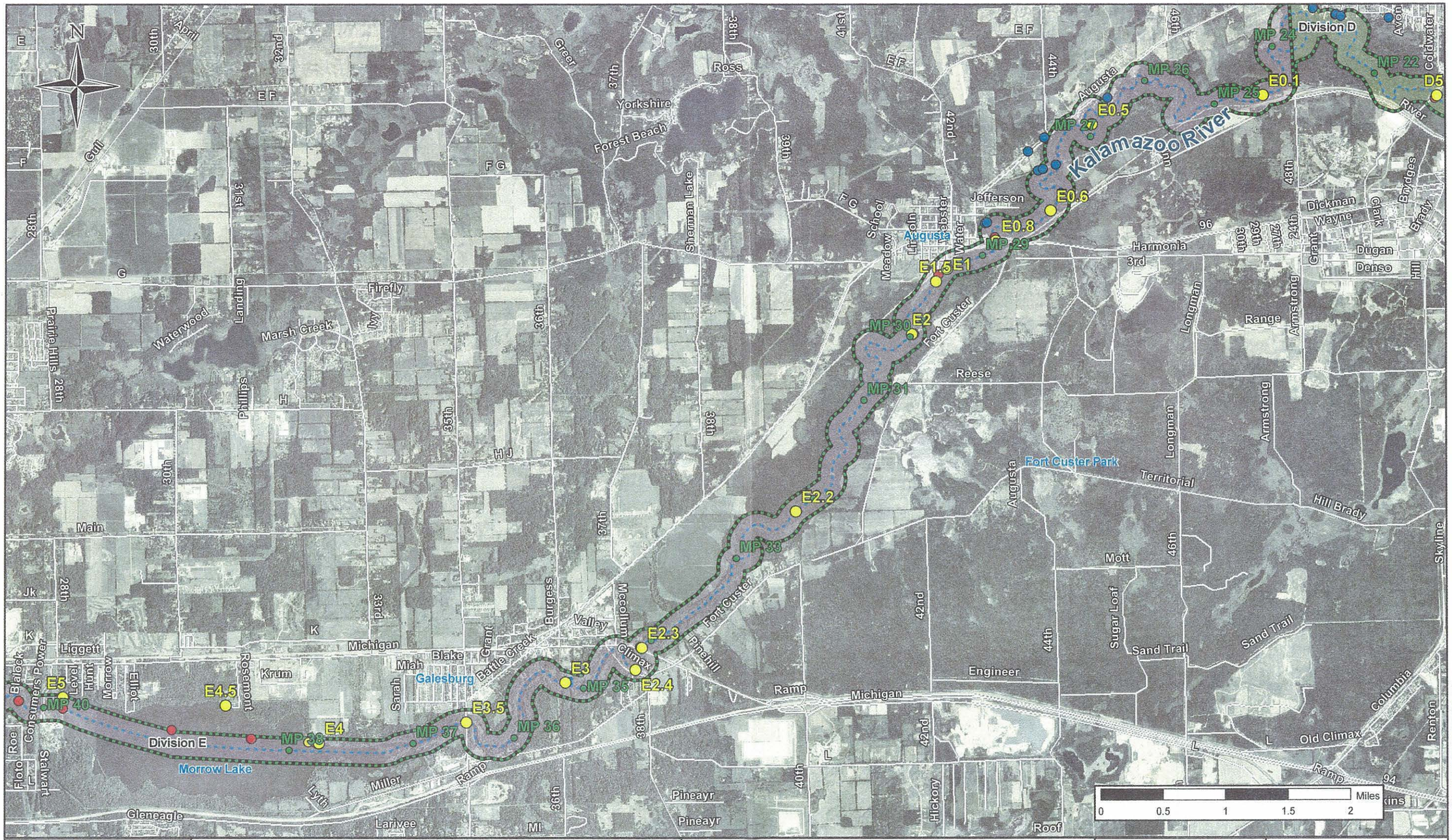

Legend

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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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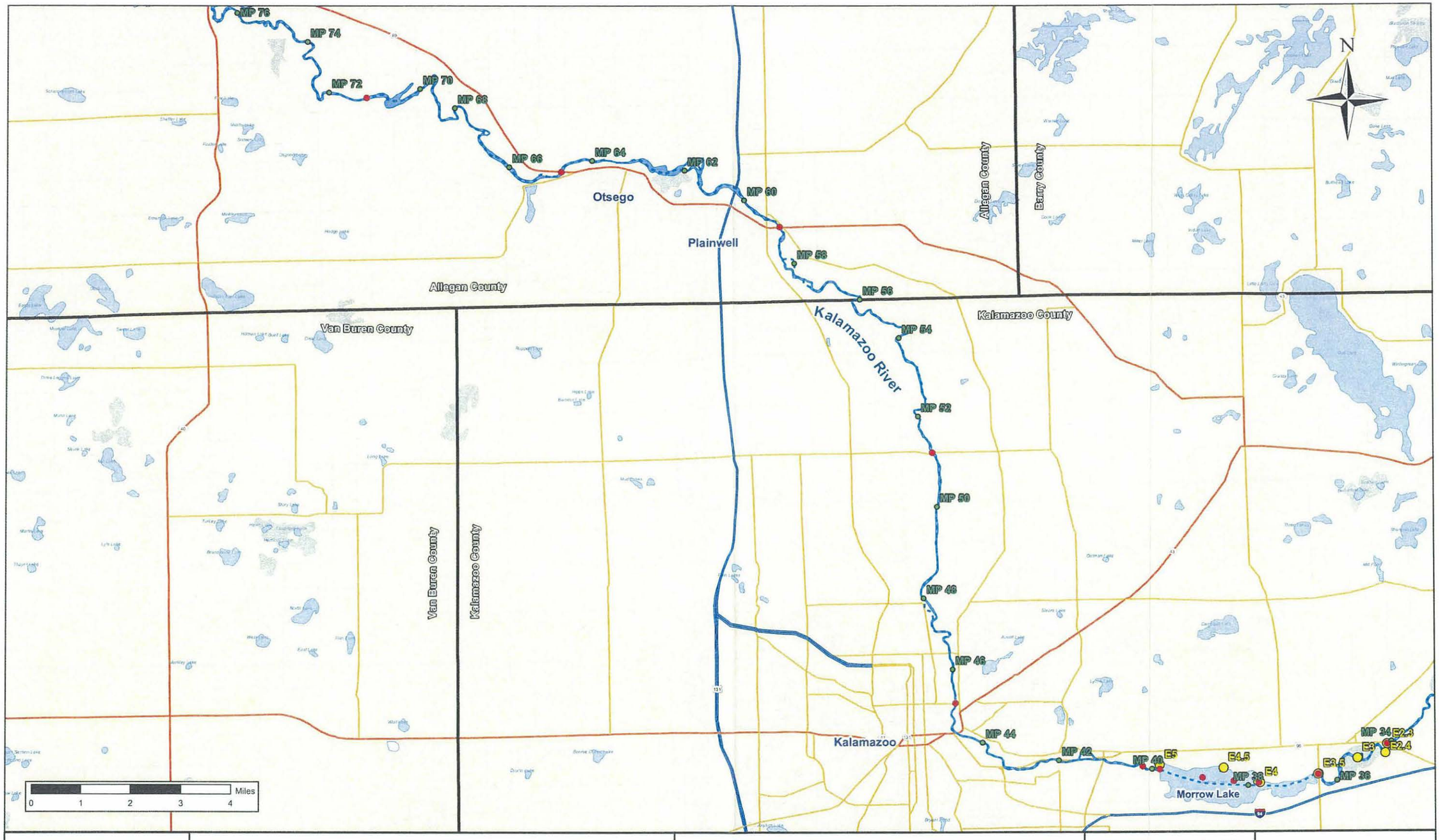

Legend

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

ENBRIDGE

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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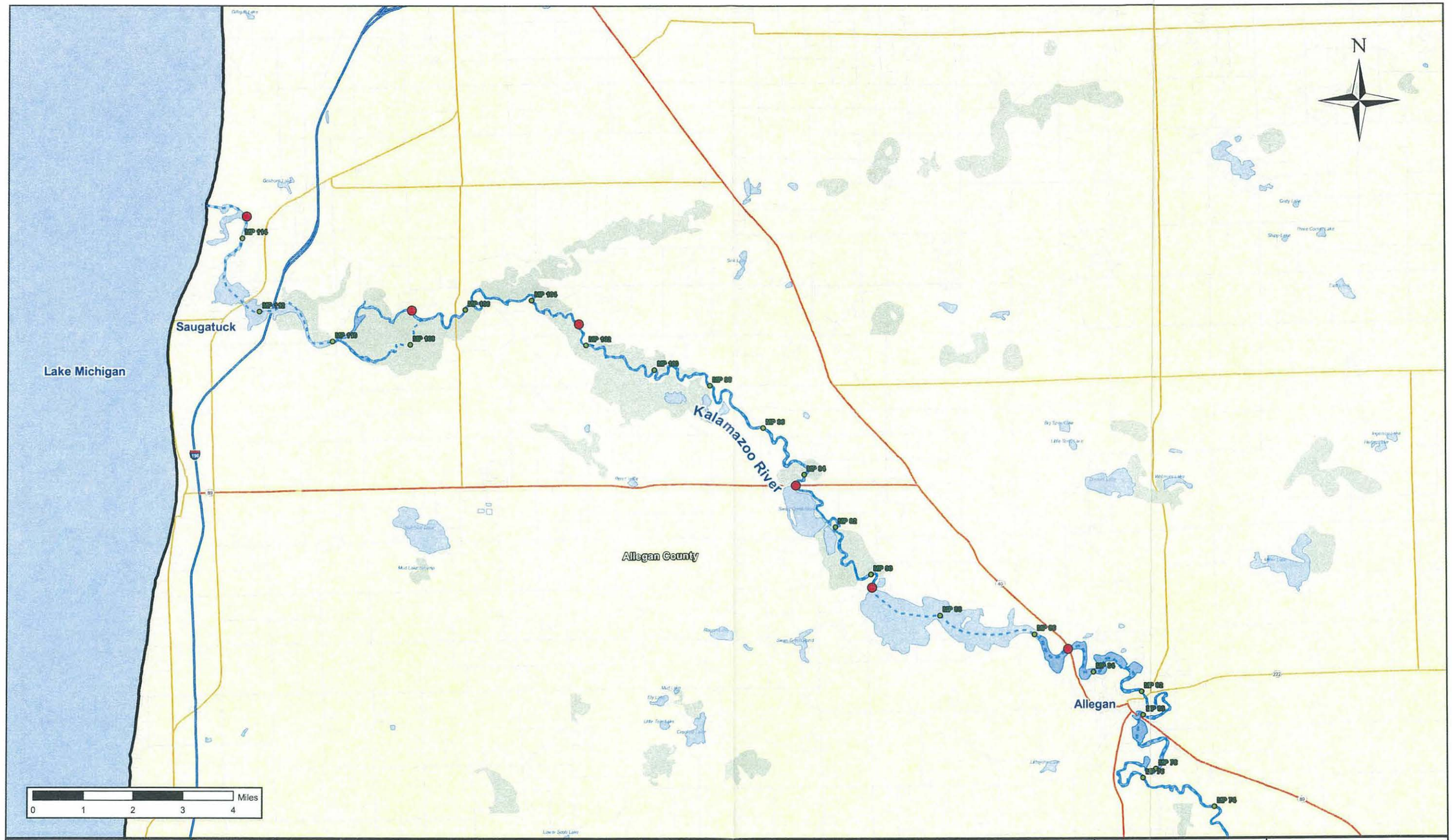

Legend

River Centerline | Downstream Milepost | Major Road | Surface Water Sample | Water Access

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Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 9: Downstream Surface Water Sampling Locations
MP 74 to Lake Michigan

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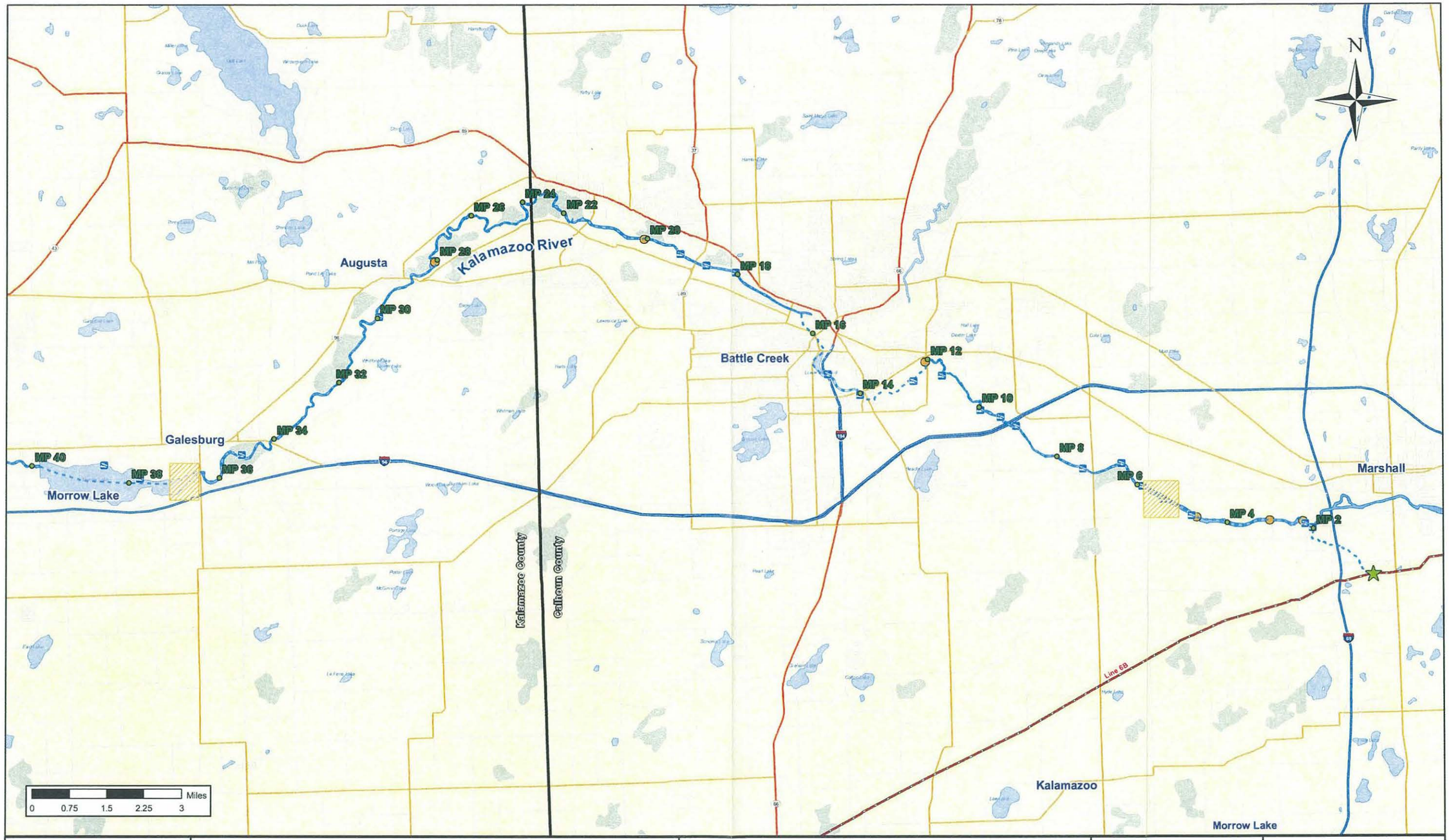

Legend

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

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Enbridge Energy, Limited Partnership
Enbridge Line 6B MP 608 - Marshall, MI
Sampling and Analysis Plan
Figure 10: Proposed Sediment Sample Locations

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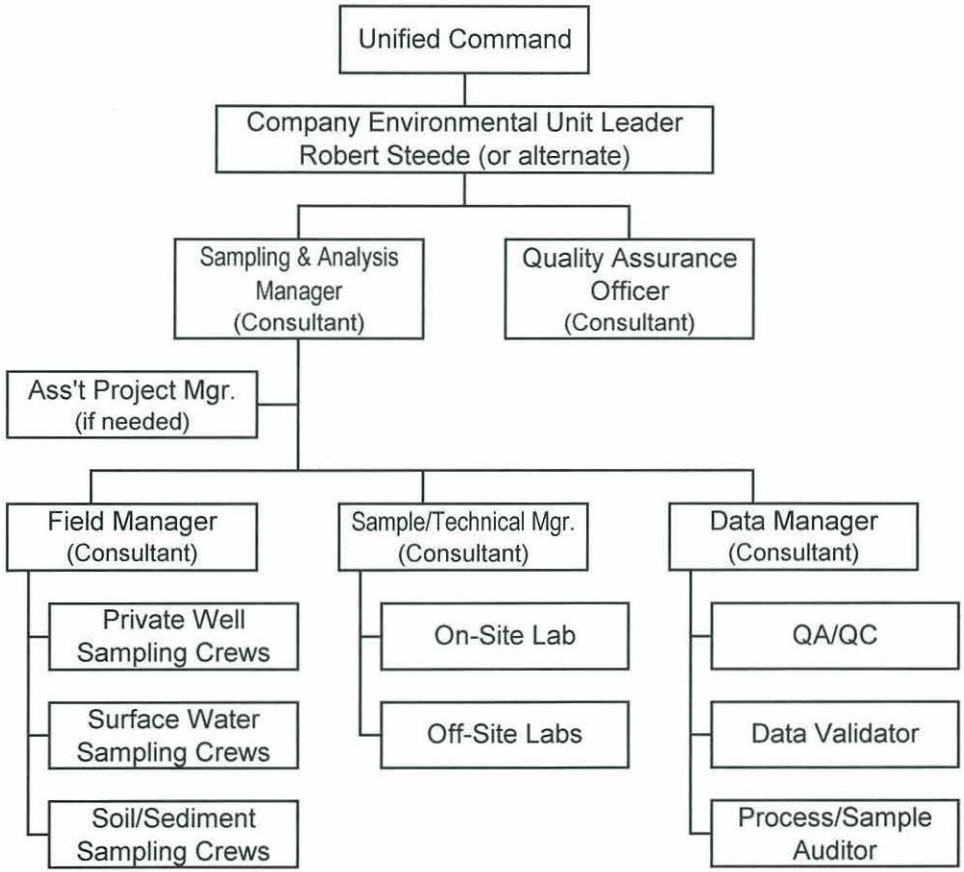
Figure 11

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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NORTH LITTLE ROCK, AR 72118
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Appendix D - Equipment SOPs

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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

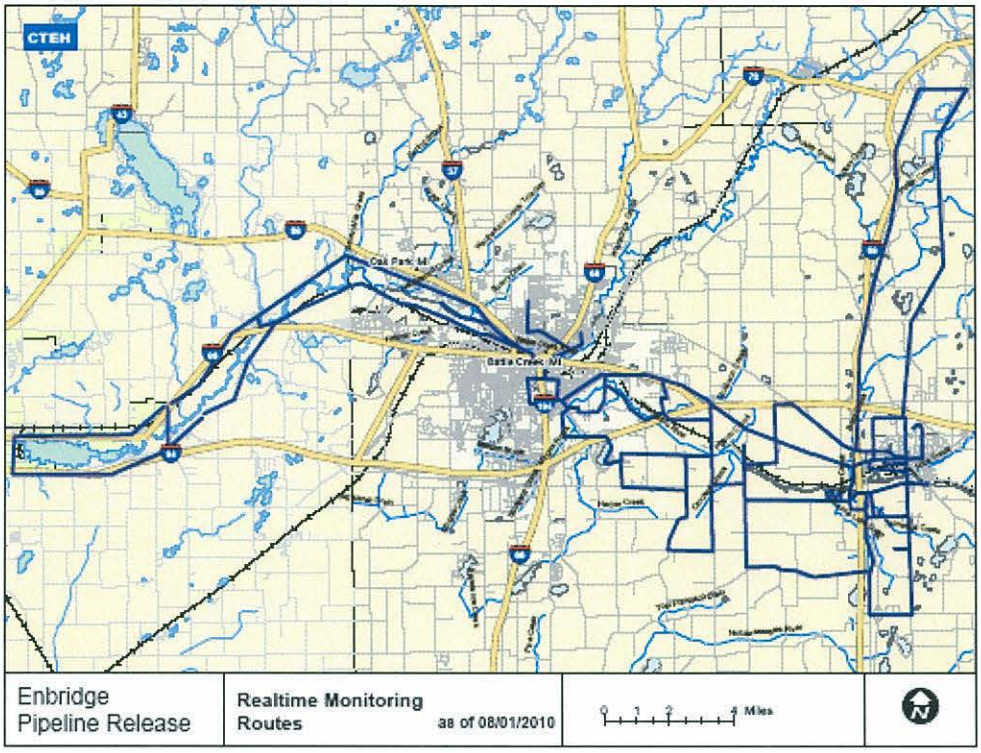


Table 1
Real-Time Air Monitoring Equipment

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

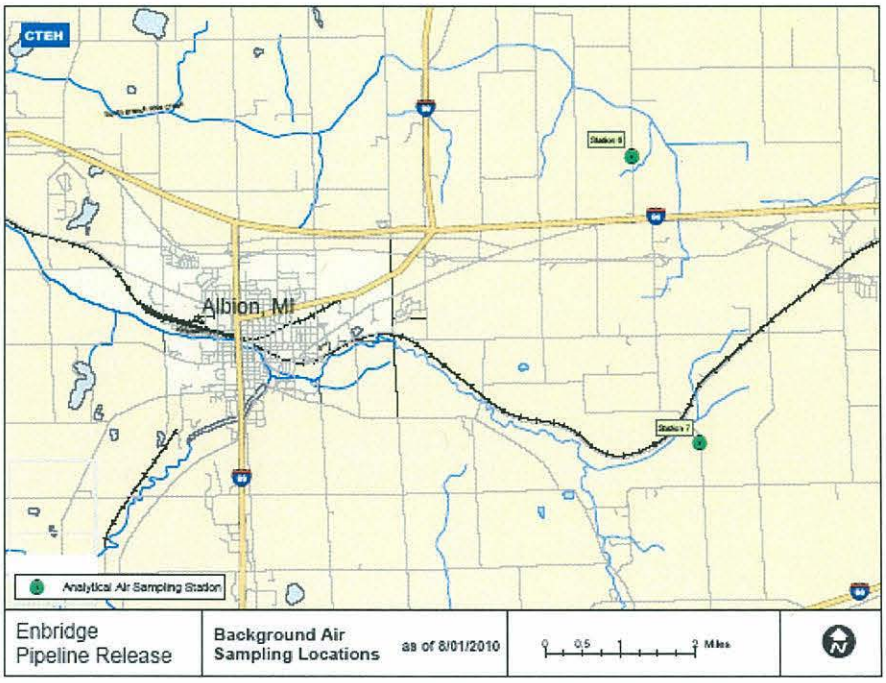
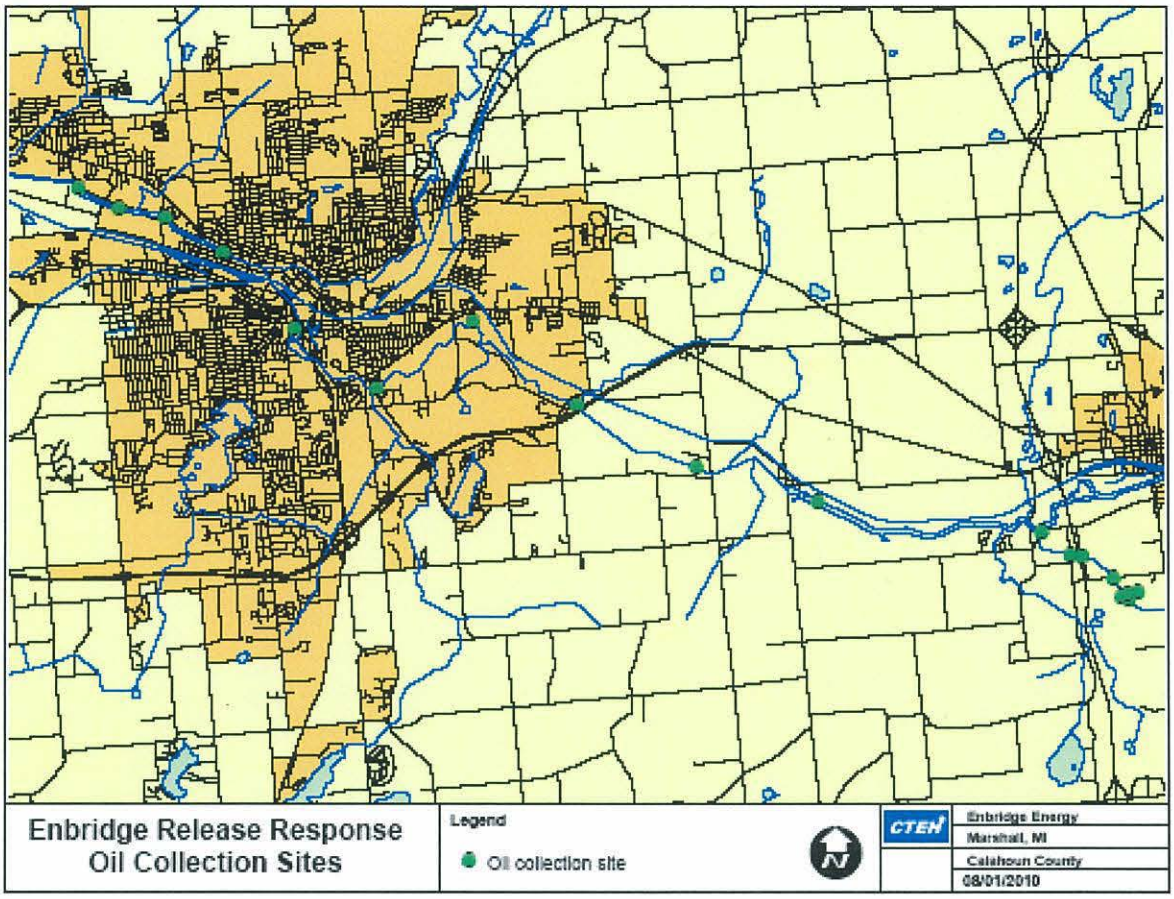


Figure 4
Location of Oil Collection Sites



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.

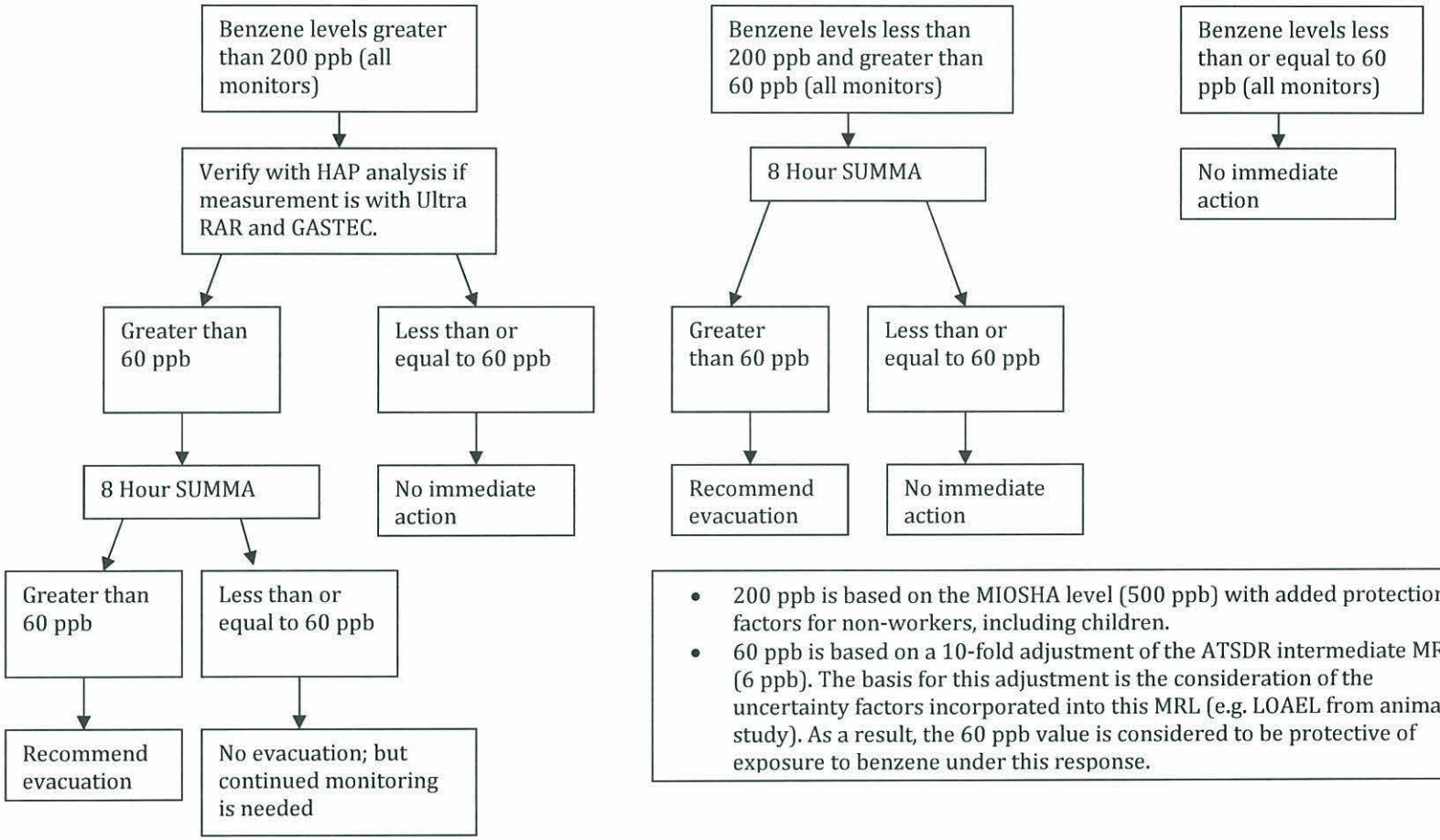
7. Data Quality and Management

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)



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.

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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

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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

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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 Colormetric 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

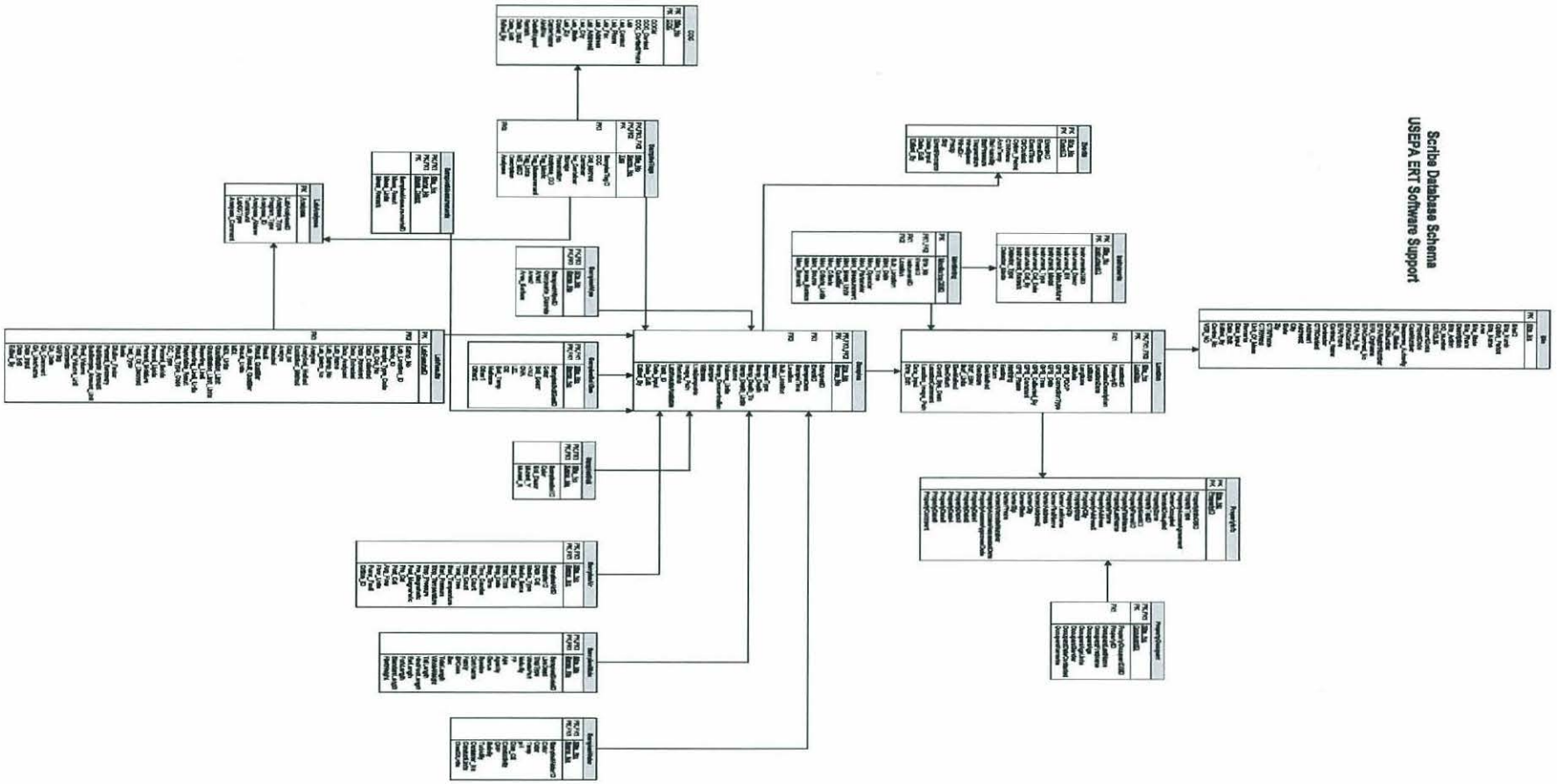
Global Lab EDD to Scribe Data Mapping

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.

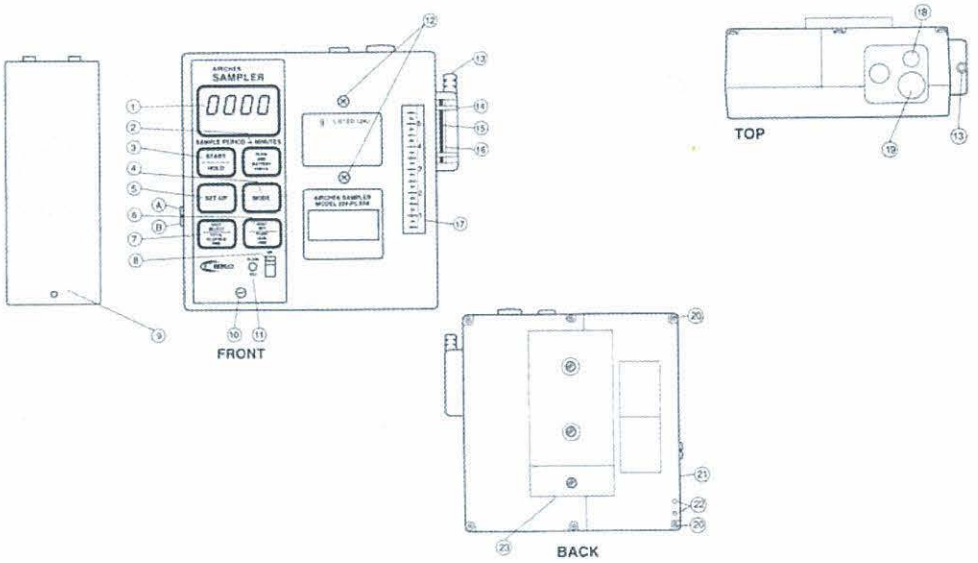
NOTE: The sample period is the *total* time of the sampling event.

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.

NOTE: 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

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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):

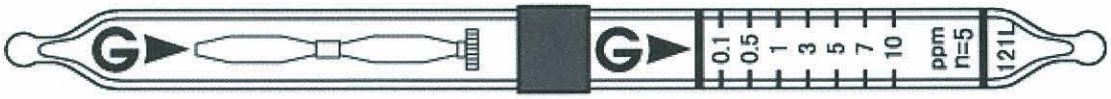
1. Determine your analyte of concern.
2. Pick out a box of detector tubes and insure the following items (The following instructions assume you have picked out a previously un-opened box):
   a) The box of detector tubes is not expired (Expiration date is printed on the top of the box).
   b) The measuring 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

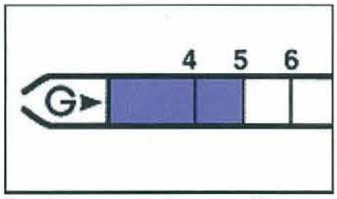
detector tube. If you pull more or less than this number, you must apply a correction factor that you will find in the instructions.

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).

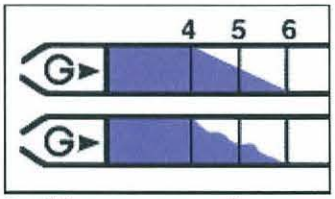
Tips for detector tube reading

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



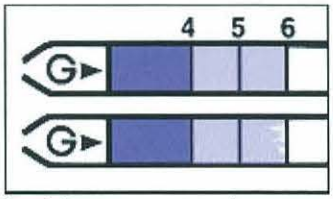
In this case, the reading would be 5%.

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.

CTEH

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 Ingredients	Approximate Concentrations (%)	C.A.S. Nos.	LD50/LC50 Specify Species & Route	Exposure Limits
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 LC50,rat,4 hr,13200 ppm	1 ppm (OEL), 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

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

SOP-1 – Multi-Media Sampling
SOP-2 – Sample Identification
SOP-3 – Field Documentation
SOP-4 – Water/Sediment Sampling
SOP-5 – Decontamination
SOP-6 – Equipment Calibration
SOP-7 – Potable Well Sampling
SOP-8 – Soil Sampling
Appendix A – Manta Operating Manual

STANDARD OPERATING PROCEDURES 2010 - 1

Multi-Media Sampling

Contents

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3.0 Deployment Protocol	3
4.0 Sampling Methods	3
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4.4 Sample Collection	4
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4.6 Important Sampling Notes	5
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Attachment 3	8

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

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Secretary, U.S. Department of Commerce

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Under Secretary for Oceans and Atmosphere and NOAA Administrator

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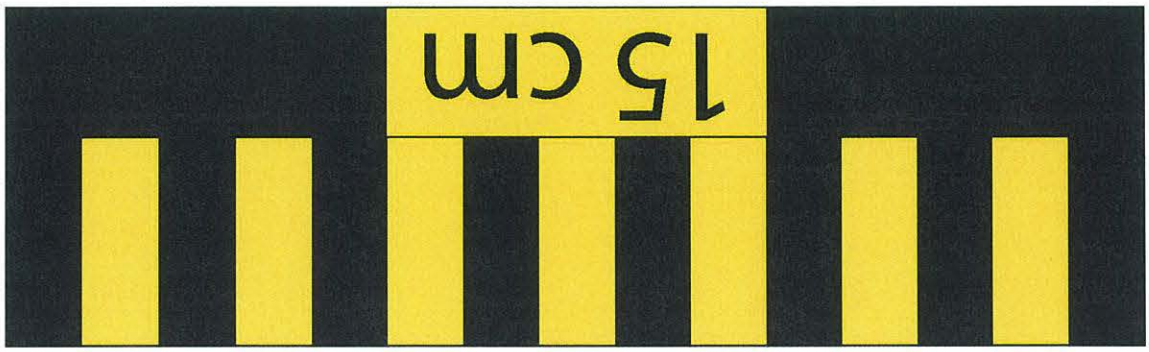
NOAA Ocean Service

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

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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

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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'

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
DO	250	Glass, glass stopper
GN	500	Plastic
GA	500	Plastic
GG	250	Glass, screw cap
GB	500 250	Plastic Plastic
S	250	Plastic
MA	500	Plastic
MAD	500	Plastic
MD	500	Plastic
MN	500	Plastic
OG	250	Glass, wide mouth
VOA	40	Glass Septum vial
ON	1000	Glass, amber
Sealed Vial	Varies	Laboratory Specific

Container Code	Size ml	Bottle Type
BNA	1000	Glass, amber
MS	250	Glass, wide mouth
GS	250	Glass, wide mouth
OS/BNA	250	Glass, wide mouth
VOA	40	Glass, septum vial (soils require MeOH kit)
SCD	NA	Soil coring device [1,2]
MO	250	Glass, wide mouth
OL	250	Glass, wide mouth
HW	250	Glass, wide mouth
MX	250	Glass, wide mouth
OX	250	Glass septum jar
L	500	Fluoropolymer [1,3]
M	250	Glass or HDP[1]
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 H2SO4 / HCl/NaHSO4, 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 H2SO4, 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 H2SO4, 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 HNO_3 , 4° C	28	Days		
Mercury, Low Level	1669/1631	MS	L	10 ml 1:1 Hg-free HNO_3 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 Organic Compounds	Methods	Containers		Preservation [26]	Holding Times	
		Soil	Water		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'

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

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

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

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Manta 2 Multiprobe – Operating Manual

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5.0 Summary

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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.

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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.

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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.

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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.

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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.

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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;

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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.

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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.

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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

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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.

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Approved

Enbridge Line 6B MP 608

Marshall, MI Pipeline Release

2011 Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan

Prepared for United States Environmental Protection Agency

Enbridge Energy, Limited Partnership

Submitted: June 15, 2011

Approved: June 21, 2011

Approved

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Attachment B Enbridge Oil Spill Human Health Screening Levels

Attachment C Meteorological Station Specifications

Attachment D Field Standard Operating Procedures

Attachment E Galson Laboratories SOP for VOCs by OSHA PV-2120 & EPA TO-15

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LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
COC	Chain of Custody
COPC	Contaminate of Potential Concern
Enbridge	Enbridge Energy, Limited Partnership
D/T	dilution-to-threshold
GPS	global positioning system
Line 6B	The pipeline owned by Enbridge Energy, Limited Partnership that runs just south of Marshall, Michigan
MIOSHA	Michigan Occupational Safety and Health Administration
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
OSHA	Occupational Safety and Health Administration
OVM	Organic Vapor Monitoring
PEL	Permissible Exposure Limit
ppm	parts per million
ppmv	Parts per million by volume
QAPP	Quality Assurance Project Plan
SEG	Similar Exposure Group
STEL	Short Term Exposure Limit
Supplemental Order	Supplement to Order for Compliance Under Section 311(c) of the Clean Water Act, issued by U.S. EPA Region 5 on September 23, 2010 to Enbridge Energy Partners, L.P. *et al*., Respondents, Docket No: CWA 1321-5-10-001
U.S. EPA	United States Environmental Protection Agency
U.S. EPA Order	U.S. EPA Removal Administrative Order Under Section 311(c) of the Clean Water Act, issued on July 27, 2010 to Enbridge Energy Partners, L.P., Docket Number: CWA 1321-5-10-001
TICs	Tentatively Identified Compounds
TWA	Time Weighted Average
VOCs	Volatile Organic Compounds

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1.0 INTRODUCTION AND PURPOSE

Enbridge will conduct air sampling and air monitoring to protect worker safety and public health during assessment and recovery operations. Enbridge has been directed to conduct real-time air monitoring and air sampling in the following areas:

- Surrounding communities including Baker Estates and Ceresco;
- Work areas where impacted soil and/or sediment is being disturbed from removal activities,
- Work areas where submerged oil is being removed,
- Other areas in response to odor concerns, and
- Real-time monitoring in Communities along impacted shorelines.

The air monitoring will include volatile organic compounds (VOCs), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and benzene. Air sampling will only be conducted for VOCs.

Data gathered in the above mentioned areas will be used to assess the potential for community and worker exposures. All field work and data collection will be conducted in accordance with approved work plans and standard operating procedures (SOPs). More detailed discussions of air sampling and real-time air monitoring can be found in the following sections.

2.0 AIR SAMPLING METHODS

Air samples for VOCs will be collected by subatmospheric sampling using evacuated canisters. The collected whole-air samples will be analyzed according to modified U.S. EPA Method TO-15 and OSHA PV-2120. Attachment E presents the laboratory SOP for this sampling. The list of target compounds (with detection limits) is presented in Attachment A . The laboratory will also provide a report of all Tentatively Identified Compounds (TICs) detected in each canister sample.

Canister samples will consist of either grab (instantaneous), 8-hour, or 24-hour collections. The collection time will be based on monitoring objectives. For instance, a grab sample will be collected in response to odor reports, 8-hour collection for work shift related monitoring, and 24-hour sampling for evaluating the potential for long-term exposure at community and/or residential sites. All extended duration samples will be collected using critical flow

orifices calibrated by the laboratory to collect a specified target volume into the canister over the desired period. Details of the flow rate settings and pressure limits of the flow controllers are contained in the applicable SOP.

All air samples will be sent to Galson Laboratories, an American Industrial Hygiene Association (AIHA) accredited laboratory, in Syracuse, NY. Samples will be expedited for shipping and analysis. Initial samples will be on a one-day turnaround time for sample results. If approved by U.S. EPA, the turnaround time may be extended to a three to 10 day period.

3.0 METEOROLOGICAL DATA

Meteorological data is an important consideration for deploying canisters and for interpreting air sampling results. A combination of portable meteorological stations and National Weather Service (NWS) data will be used to support air sampling and monitoring.

Two portable meteorological stations will be deployed to provide more time-resolved meteorological data than the once-hourly NWS observations. The stations will include sensors for wind speed, wind direction, air temperature, relative humidity, barometric pressure, and precipitation (precipitation gauge). The meteorological station clocks (or SAFER computer, if it assigns the 5-minute data timestamp) should be maintained in reference to a National Institute of Standards and Technology (NIST) clock source. The stations will be mounted on tripod-based masts. The stations will operate on battery power. Specifications for the meteorological stations are presented in Attachment C.

Specific station locations will be determined to the extent possible based on U.S. EPA guidance for instrument exposure. Primary consideration will be placing the stations in open areas with unobstructed wind flow. The wind direction sensors will be aligned to within 5 degrees of true north, and have a measurement accuracy of 5 degrees or better. Data will be recorded, and downloaded from the stations on a daily basis. The station clocks will be set to Eastern Standard Time. Station locations will be documented with global positioning system (GPS) devices.

One meteorological station will be set up near Ceresco Dam, and the other will be placed near Baker Estates (MP 12.1). Data from these two sources will be used to create daily

wind roses for the areas of concern, and identify samples collected as being upwind or downwind of the contaminated areas.

In other areas potentially impacted by the removal, NWS data from Battle Creek (call sign KBTL) or Kalamazoo (call sign KAZO) will be used to produce wind roses and classify upwind/downwind samples. The observations will be downloaded from the internet daily, and placed into a database. In the event portable weather station data are not available for a period, representative NWS data will be used in its place.

Forecasts issued by the NWS, accessed via the NWS web site, will be used to plan sampler deployment. Samplers will be placed in patterns so as to capture (as best possible) conditions both upwind and downwind of a contaminated area based on these forecasts. Predicted shifts in winds due to frontal passages will be taken into consideration in sample placement.

4.0 COMMUNITY EVALUATIONS

Community evaluations will initially be conducted in the Baker Estates and Village of Ceresco communities. U.S. EPA may request evaluation of these or other communities in the future, if changing removal conditions warrant. The evaluations will be performed using both sampling and real-time monitoring.

Real-time air monitors will collect data for total VOCs, H_2S, SO_2, and benzene using the equipment listed in Table 1.

Table 1 Summary of Real-Time Air Monitoring Equipment

Instrument	Analyte	Detection Limit
MultiRAE PID	Total VOCs	0.1 ppm
MultiRAE H_2S electrochemical sensor	H_2S	1 ppm
MultiRAE SO_2 electrochemical sensor	SO_2	0.1 ppm
UltraRAE PID with benzene sep filters	Benzene	0.05 ppm
Gastec Pump w/Benzene Colorimetric Tubes	Benzene	0.05 ppm

One MultiRAE (5 gas instrument) and one UltraRAE benzene monitor will be utilized to take snapshot readings of air quality in the vicinity of the community, during work activity periods each day. The instruments will be used in a mobile mode, covering areas between the contaminated areas and the community (or within the community), based on forecasted prevailing wind directions. Each monitoring location will be documented with GPS equipment, along with the time of the reading.

In addition to real-time air monitoring, analytical air samples will also be collected in or adjacent to select community areas. Three canister samples will be collected simultaneously over contiguous 24-hour periods in the vicinity of the communities being evaluated. The target compound list for community sampling is the same as the list presented in Attachment A. Multiple canisters in each community area allow for better evaluation of the presence or absence of crude oil related chemicals and can capture vapors as changes in wind direction occur. The samplers will be deployed based on forecast wind directions, so as to capture a representative sample of air flowing from contaminated areas into the community. All sampling locations will be documented with GPS devices.

Air monitoring and sampling will be conducted for a minimum period of 14 24-hour periods. Based on the review of the data collected during the initial period, sampling and/or monitoring may be reduced in frequency or discontinued at the discretion of U.S. EPA.

Results from the initial 14-day period will be compared to the screening concentrations found in Attachment B. Enbridge and U.S. EPA will evaluate this comparison to determine the need for ongoing sampling and/or monitoring. If results from the initial 14-day time period yield no detections above applicable screening values, then sampling operations may be reduced or discontinued. In the event that results should exceed a screening level, additional sampling, monitoring, or protective measures may be required.

5.0 WORK AREA PERIMETER EVALUATIONS

5.1 Work Zone Perimeter Sampling

Perimeter samples will be collected at all work sites involving the submerged oil, dredged sediment, and overbank excavation. Three canister samples will be collected simultaneously over an 8-hour period along the perimeter work areas, coinciding with work activity. Sample locations will be selected based on anticipated activities and forecast wind

directions. The purpose is to select locations with the greatest opportunity to detect volatile organic compounds, if any, that are released during recovery activities. Work area samples will be positioned to ensure both upwind (1 sample) and downwind (2 samples) capture zones from work operations to evaluate VOC vapors on-site and as background. Sample canisters will be placed as close as practical to the actual removal activities, without compromising site safety or work efforts. All sample locations will be documented using GPS devices.

Perimeter sampling will be conducted at all work locations for a minimum period of 14 days, or until results can be evaluated for that time period. Enbridge and U.S. EPA will review all sampling results from the initial 14-day period, and determine the perimeter sampling frequency and strategy needed for ongoing operations.

5.2 Work Zone Real-time Monitoring

Real-time air monitoring for VOCs, H_2S, SO_2, and benzene, will be conducted using a MultiRAE and UltraRAE/Gastec Pump with benzene colorimetric tubes (Table 1) by Health and Safety (H&S) personnel within and along the perimeter of all the work zones, including the tar patty recovery work zones. If the H&S monitoring indicates a VOC alarm above applicable action levels, benzene checks will be initiated with a real-time benzene monitor along with appropriate protective action as described in the HASP. The benzene checks will be recorded in air monitoring log books or by entry into a handheld data collection device.

6.0 WORKER EXPOSURE MONITORING

Enbridge will evaluate worker exposure to benzene, toluene, ethylbenzene, xylenes, and n-haxane(COPCs) by collecting breathing zone samples representative of each worker population associated with the oil recovery operations. Each oil recovery workgroup consist of two to four workers conducting similar tasks within close proximity to one another and at similar distances to potentially contaminated sediment for the duration of their respective work shifts. Each workgroup will be evaluated to identify the “maximum risk employee” based on the work task and their proximity to contaminated material. The maximum risk employee(s) from each work group, collectively, will represent the sample population from which exposure samples should be collected.

Worker exposure monitoring for the COPCs will be conducted using both real-time and analytical methods. Worker exposure real-time data for VOCs will be collected using a data-logging MultiRAE PID equipped with a Teflon tubing inlet positioned in the worker's breathing zone. Prior to each work shift, the MultiRAE plus PID will be calibrated using 100 ppm isobutylene calibration gas. The real-time data collected form the data-logging MultiRAE will be downloaded at the conclusion of the work shift. The data will be downloaded via ProRAE Suite software and incorporated into the air monitoring database. The worker's TWA concentration for VOCs will be calculated for each sampled worker.

In addition to the MultiRAE plus PID personal monitor, Enbridge may elect to co-locate an organic vapor monitor (OVM) badge in the worker's breathing zone. These analytical samples will be collected on the 3M 3500/3520 organic vapor monitor (OVM) badge and analyzed for benzene, ethyl benzene, n-hexane, toluene, and xylene using gas chromatography flame ionizing detection (GC/FID) in accordance with the National Institute for Occupational Safety and Health (NIOSH) air sampling method 1500/1501. The OVM badge is a passive dosimeter, composed of a permeation membrane and activated charcoal which collects air samples at a flow rate controlled by the physical process of diffusion. Collected samples will be properly logged and shipped to an AIHA accredited laboratory for subsequent analysis. Table 2 summarizes the analytical detection levels for the OVM badges.

Table 2 OVM badge limit of detection (LOD) for COPCs.

COPCs	Collection Media	Flow Rate (cc/min)	Sample Duration* (min)	Laboratory LOQ (ug)	Limit of Detection (ppm)
Benzene	3M 3520	35.5	600	2.0	0.029
Ethyl benzene	3M 3520	27.3	600	5.0	0.070
n-Hexane	3M 3520	32.0	600	5.0	0.074
Toluene	3M 3520	31.4	600	5.0	0.070
Xylene	3M 3520	27.3	600	15.0	0.211

*Sample duration may vary

Once analyzed, a time-weighted average (TWA) concentration will be calculated to determine if the worker's exposure meets or exceeds the COPC's site action levels referenced in the Enbridge Health and Safety Plan and/or applicable occupational exposure limits (OELs). Table 3 displays the applicable OELs including standards established by OSHA. The Michigan Department of Labor and Economic Growth Director's Office Occupational Health Standards for benzene are also referenced in Table 3.

Table 3 Occupational Exposure Limits

COPCs	OSHA PEL-TWA(a)	OSHA PEL-STEL(b)	OSHA PEL-Ceiling(c)	ACGIH TLV-TWA(d)	ACGIH TLV-STEL(e)	MIOSHA PEL-TWA(f)	MIOSHA PEL-STEL(g)
Benzene	1	5	NE(h)	0.5	2.5	1	5
Ethyl Benzene	100	NE	NE	20	125	NE	NE
n-Hexane	500	NE	NE	50	NE	NE	NE
Toluene	200	NE	300	20	NE	NE	NE
Xylene	100	NE	NE	100	NE	NE	NE

a. OSHA PEL-TWA = The permissible concentration in air of a substance that shall not be exceeded in an 8-hour work shift or a 40-hour work week (OSHA, 1989).

b. OSHA PEL-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (OSHA, 1989).

c. OSHA PEL-Ceiling = The exposure limit that shall at no time be exceeded. If instantaneous monitoring is not feasible, then the ceiling shall be assessed as a 15-minute timw-weighted average exposure, which shall not be exceeded at any time during the work day (OSHA, 1989).

d. ACGIH TLV-TWA = The Threshold Limit Value-TWA is the concentration for a normal 8-hour workday and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (ACGIH, 2011).

e. ACGIH TLV-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (ACGIH, 2011).

f. MIOSHA PEL-TWA = The permissible concentration in air of a substance that shall not be exceeded in an 8-hour work shift or a 40-hour work week (R 325.77103 Rule 3 (1) MIOSHA Reference of OSHA Permissible Exposure Limits).

g. MIOSHA PEL-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (R 325.77103 Rule 3 (2) MIOSHA Reference of OSHA Permissible Exposure Limits).

h. NE = Not Established.

If sample results indicate an exceedance of the site action level and/or OELs for the COPCs, additional measures will be taken to protect worker health. If the monitoring required by paragraph (e)(2)(i) of the OSHA benzene standard 1910.1028 and R 325.77102 (B) of the MIOSHA benzene standard R 325.77102 section reveals employee exposure at or above the action level of 0.5 ppm but at or below the TWA, the employer shall repeat such monitoring for each such employee at least every year. Specifically, if OVM sample results indicate a benzene exceedance in excess of the OSHA Permissible Exposure Limit (PEL-TWA), a regulated area will be established wherever the airborne concentration of benzene exceeds or can reasonably be expected to exceed the permissible exposure limits (1910.1028(d)(1)) (MIOSHA R 325.77104 Rule 4). If a regulated area is established based on detections of elevated benzene , access will be limited to authorized persons with appropriate personal protective equipment (PPE) (1910.1028(d)(2).

7.0 ODOR INVESTIGATIONS

Enbridge will provide an Odor Response Team. The Odor Response Team will be deployed within 30 minutes (maximum) after receiving odor complaints/concerns. Responses will be conducted 24 hours a day, 7 days a week. Enbridge will immediately relay all initial odor reports to U.S. EPA Air Monitoring Operations Section and MDEQ. The MDEQ will notify Michigan Department of Public Health staff of the odor complaints.

Personnel responding to the odor event will travel to the location where the report originated. Real-time air monitoring data and analytical “grab” canister sample data will be collected at the reported location. Short-term real-time readings will be taken for VOCs, H_2S, and SO2

using a MultiRAE monitor and benzene using an UltraRAE monitor or Gastec pump with benzene specific colorimetric tubes. These readings will be reported to the complainant immediately, and recorded in log books. At least one canister sample will be obtained, with additional canisters possible depending on the situation encountered. The canister samples will be analyzed using the same analytical approach and target compound list as routine samples (Attachment A). In addition, at the time of sampling, the Odor Response Team will document the presence or absence of odors and the subjective quality of the odors. The odor event location will also be documented using GPS.

After completion of the field visit, the Odor Response Team will relay the collected information to Enbridge. Enbridge will provide U.S. EPA with daily summaries of all Odor Response Team activities. Upon receipt of canister sampling results, Enbridge contractor will prepare a follow-up letter report, to be transmitted to Enbridge Safety, the complainant, and U.S. EPA.

8.0 TAR PATTY STUDY

The potential for fugitive VOCs from tar patties will be evaluated using a bagging technique. Several tar patties will be enclosed in a mylar or equivalent bag, and allow to warm in direct sunlight. The air inside the bag (headspace) will then be sampled and analyzed.

At 10% of the tar patty removal sites, headspace samples will be collected. At all of the selected sites, one bag of material will be sampled by directly pulling headspace air into a MultiRAE instrument and an UltraRAE benzene-specific monitor. At half of the selected sites, an additional bag of material will be collected and the headspace air sampled by extracting to a Tedlar bag for TO-15 analysis (Attachment A).

The results of these results will be obtained on rapid turnaround from the laboratory, and submitted by Enbridge to U.S.EPA. Enbridge and U.S. EPA will determine the need for monitoring and/or sampling during tar patty removals based on the results.

9.0 DATA QUALITY AND MANAGEMENT

Air samples will be sent to Galson Laboratories located in Syracuse, N.Y or other approved laboratory. Preliminary results will be provided to Enbridge Energy's designated representative and to any other designated representative or organization within one to two

days of receipt by the laboratory. Analytical results will be flagged in instances where the contaminant is also detected in the laboratory blanks. The expedited turnaround time for Galson can be as little as one business day, upon laboratory receipt. All data will be submitted to the U.S. EPA Scribe database through Enbridge data management system. In addition, Enbridge will provide daily monitoring summary reports to U.S. EPA (by end of following day).

Collocated duplicate samples will be collected at a frequency of 1 per 10 (10%). Trip blank analysis will be conducted once per week as directed by U.S. EPA.

10.0 AIR SAMPLING AND MONITORING REPORTING

Enbridge will provide on a daily basis the following deliverables:

An overview of air sampling and monitoring activities conducted the previous day. The overview will consist of a map of the area between the spill site and Morrow Lake, or the geographical extent of air sampling and monitoring activities, whichever is smaller. The map will include the following layers:

- Locations of discrete analytical samples collected the previous day. Labels will include a common name (e.g. Ceresco) or project marker name (e.g. MP 24.75), count of discrete sampling locations, and count of samples collected.
- Locations of instantaneous readings collected the previous day. The symbols will be color-coded by analyte. Benzene readings will be colored differently from the other analytes.
- Summary table of instantaneous readings collected the previous day. The table will list counts of readings collected by location category (e.g. Work Area, Community), as well as counts of any detections.
- Windrose(s) generated from meteorological data collected the previous day.

An overview of the latest full day of air sampling laboratory analysis results received. The overview will consist of one or more maps of the area(s) encompassing all locations where any compounds were detected. The map(s) will include the following layers:

- Locations of all discrete analytical samples. Labels will include a unique location code for each symbol, as well as common name or project marker name.

- Chart listing concentrations and applicable screening levels of all analytes detected in the locations included in the extent of the map.
- Windrose(s) generated from meteorological data collected the day of sampling.

- The daily report package will also contain tabular summaries of hourly meteorological data. This shall be a set of tables that show air monitoring parameters for each day (by hour), as recorded from each portable weather and NWS station. The summaries shall also include a daily average for each parameter.

These deliverables are provided following an internal QA/QC process. The analytical data is received and reviewed by a qualified individual (project manager/industrial hygienist and/or toxicologist). The data will be reviewed on a daily basis to ensure that necessary actions are implemented if required (such as additional canister placement and/or real-time monitoring). Data is then uploaded to the Sharefile site for dissemination. An email notice will be sent informing participating regulatory agencies that the information for that day is available for viewing or download.

The final report will be produced upon completion of air monitoring/sampling activities detailed in this plan. The final report will consist of a compilation of real-time and analytical data, physical parameters such as wind direction, and geographical area. An evaluation of the results will be conducted to determine if COPCs were present during the oil recovery operations and if those COPC concentrations exceeded applicable human health air screening levels.

11.0 PROJECT ORGANIZATION

Enbridge Consultants will be responsible for the following:

- Toxicological support;
- Air monitoring;
- Air sampling;
- Air data quality assurance/quality control, and
- Data evaluation and reporting

Mr. Chase Selby, Environmental Scientist Project Manager, will serve as the Project Manager and Dr. Phillip T. Goad (Principal Toxicologist) will serve as the Project Director

and Mr. Brett Yokom, Project Engineer, will serve as Enbridge's Task Manager for this scope of work.

12.0 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 Enbridge's Consultant calibration logs.

13.0 CHAIN OF CUSTODY (COC)

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

14.0 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 the sample was collected, and
- Unique identifier.

15.0 PACKAGING AND SHIPPING

Packaging and shipping of air samples will be conducted following method recommendations. Canisters will be shipped in a box via carrier service (ex. FedEx). Air samples do not require sample preservation in the field. However, caps will be placed on canisters and regulators or critical orifices will be detached during shipment. The person packaging the samples is responsible to ensure that the sample packaging is in suitable condition for shipping.

Attachment A
Compounds Detected by TO-15 Analysis

Attachment A

Table 1 Predominant Crude Oil VOCs Detect by TO-15 Analysis[1]

Analyte	Laboratory LOQ	Analyte	Laboratory LOQ
Benzene	5.0	Heptane, n-	5.0
Butane, 2-methyl-*		Hexane, n-	5.0
Cyclohexane	5.0	Naphthalene	5.0
Cyclohexane, 1,3-dimethyl-*		Nonane*	
Cyclopentane, methyl-*		Hexane, 2-methyl*	
Cyclohexane, 1,3-dimethyl-, cis-*		Octane*	
Cyclohexane, butyl-*		Octane, 3-methyl-*	
Cyclohexane, ethyl-*		Pentane, 2-methyl-*	
Cyclohexane, methyl-*		Toluene	5.0
Cyclohexane, propyl-*		Benzene, 1,2,4-trimethyl	5.0
Cyclopentane, 1,1 -dimethyl*		Hexane, 3-methyl*	
Cyclopentane, 1,3-dimethyl-, trans *		Hexane, 3-methyl*	
Cyclopentane, 1,2-dimethyl-, trans *		Heptane, 2-methyl-*	
Heptane, 3-methyl-*		Cyclohexane- 1,1,3-trimethyl*	
2-Octene, 2,6-dimethyl-*		Benzene, 1,3,5-trimethyl	5.0
Decane*		Undecane*	
Dodecane*		Xylene, m&p-	10
Ethylbenzene	5.0	Xylene, o-	5.0
Ethyltoluene, 4-	5.0		

1 – The laboratory will also be asked to report on all analytes included in their TO-15 method standard analyte list.

*- Tentatively identified compound (TIC)

Attachment B

Enbridge Oil Spill Human Health Screening Levels

Attachment B

Enbridge Oil Spill Human Health Air Screening Levels August 13, 2010			
Chemical Name	**Chemical Abstract Service Number**	**Screening Level in parts per billion by volume (ppbv)**	**Source of Screening Level**
1,1,1-trichloroethane	71-55-6	700	ATSDR Int. MRL
1,1,2,2-Tetrachloroethane	79-34-5	0.006	EPA RSL
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4,000	EPA RSL
1,1,2-Trichloroethane	79-00-5	100	Chronic MRL or RfC
1,1-Dichloroethane	75-34-3	100	Chronic MRL or RfC
1,1-Dichloroethene	75-35-4	20	ATSDR Int. MRL
1,2,4-Trichlorobenzene	120-82-1	30	Chronic MRL or RfC
1,2,4-Trimethylbenzene	95-63-6	1.5	EPA RSL
1,2-Dibromoethane	106-93-4	1	Chronic MRL or RfC
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9,900	EPA RSL
1,2-Dichlorobenzene	95-50-1	30	Chronic MRL or RfC
1,2-Dichloroethane	107-06-2	1,000	Chronic MRL or RfC
1,2-Dichloropropane	78-87-5	7	ATSDR Int. MRL
1,3-Butadiene	106-99-0	1	Chronic MRL or RfC
1,3,5-Trimethylbenzene	108-67-8	45	MDNRE
1,3-Dichlorobenzene	541-73-1	0.5	MDNRE
1,4-Dichlorobenzene	106-46-7	200	ATSDR Int. MRL
1,4-Dioxane	123-91-1	1,000	ATSDR Int. MRL
2,2,4-Trimethylpentane	540-84-1	750	MDNRE
2-Chloro-1,3-butadiene	126-99-8	2.1	EPA RSL
2-Propanol	67-63-0	3,000	EPA RSL
3-Chloropropene	107-05-1	0.3	Chronic MRL or RfC
Acetone	67-64-1	13,000	ATSDR Int. MRL
Acetonitrile	75-05-8	38	EPA RSL
Acrylonitrile	107-13-1	1	Chronic MRL or RfC
Benzene	71-43-2	6	ATSDR Int. MRL
Benzyl chloride	100-44-7	0.01	EPA RSL
Bromodichloromethane	75-27-4	0.01	EPA RSL
Bromoform	75-25-2	0.21	EPA RSL
Bromomethane	74-83-9	50	ATSDR Int. MRL
Butane	106-97-8	10,000	MDNRE
Carbon disulfide	75-15-0	200	Chronic MRL or RfC
Carbon tetrachloride	56-23-5	30	ATSDR Int. MRL
Chlorobenzene	108-90-7	200	Chronic MRL or RfC
Chloroethane	75-00-3	4,000	Chronic MRL or RfC
Chloroform	67-66-3	50	ATSDR Int. MRL
Chloromethane	74-87-3	200	ATSDR Int. MRL
cis-1,2-dichloroethene	156-59-2	8.6	MDNRE
cis-1,3-Dichloropropene*	10061-02-6	4.4	MDNRE
Cumene	98-82-8	100	Chronic MRL or RfC
Cyclohexane	110-82-7	2,000	Chronic MRL or RfC

Cyclohexane,methyl	108-87-2	4,000	MDNRE
Chemical Name	**Chemical Abstract Service Number**	**Screening Level in parts per billion by volume (ppbv)**	**Source of Screening Level**
Cyclopentane	287-92-3	6,000	MDNRE
Dibromochloromethane	124-48-1	0.01	EPA RSL
Dichlorodifluoromethane	75-71-8	42	EPA RSL
Ethyl Acetate	141-78-6	890	MDNRE
Ethyl benzene	100-41-4	700	ATSDR Int. MRL
Heptane	142-82-5	850	MDNRE
Hexachlorobutadiene	87-68-3	10	Chronic MRL or RfC
Hexane	110-54-3	200	Chronic MRL or RfC
Isobutane	75-28-5	10,000	MDNRE
Methyl butyl ketone	591-78-6	10	Chronic MRL or RfC
Methyl ethyl ketone	78-93-3	2,000	Chronic MRL or RfC
Methyl isobutyl ketone	108-10-1	700	Chronic MRL or RfC
Methyl tert-butyl ether	1634-04-4	700	ATSDR Int. MRL
Methylene chloride	75-09-2	300	ATSDR Int. MRL
Napthalene	91-20-3	1	Chronic MRL or RfC
Nonane	111-84-2	100	MDNRE
Pentane	109-66-0	6,000	MDNRE
Propene	115-07-1	2,000	Chronic MRL or RfC
Styrene	100-42-5	200	Chronic MRL or RfC
Tetrachloroethene	127-18-4	40	Chronic MRL or RfC
Tetrahydrofuran	109-99-9	6.1	MDNRE
Toluene	108-88-3	1,000	Chronic MRL or RfC
trans-1,2-Dichloroethene	156-60-5	200	ATSDR Int. MRL
trans-1,3-Dichloropropene*	10061-01-5	0.5	MDNRE
Trichloroethene	79-01-6	100	ATSDR Int. MRL
Trichlorofluoromethane	75-69-4	130	EPA RSL
Vinyl acetate	108-05-4	10	ATSDR Int. MRL
Vinyl bromide	593-60-2	1	Chronic MRL or RfC
Vinyl chloride	75-01-4	30	ATSDR Int. MRL
Xylenes	1330-20-7	2,000	ATSDR Int. MRL

* MDNRE provisional screening value for Dichloropropene based on a 1 in 100,000 cancer risk

ATSDR Int. MRL - The Agency for Toxic Substances and Disease Registry Intermediate Minimal Risk Level (MRL) is the preferred screening level. The MRL is protective of daily human inhalation exposure for up to a year, including sensitive individuals such as children, the elderly, and those with pre-existing illnesses.

ATSDR Chronic MRL or EPA RfC - If no Intermediate MRL is available, the screening level is the ATSDR Chronic MRL or the EPA Reference Concentration (RfC). The chronic MRL and the RfC are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

EPA RSL - If none of the above are available, the EPA Regional Screening Level (RSL) is the screening level. The RSLs are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

MDNRE - If none of the above are available, the Michigan DNRE Air Quality Division, Air Toxics Screening Level is the screening level. The MDNRE screening levels are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

Attachment C

Meteorological Station Specifications

SAFER SYSTEMS The right response to a chemical emergency.

Datalogging Specs:

The Coastal WeatherPak outputs data every 30 seconds. SAFER reads this stream as the data comes in and compiles 5 five minute average of the data for use with its model. The data is logged internally to the computer in the SAFER STAR file structure and can be accessed through dbf format by opening the file in Excel. It can also be accessed for further analysis by using the Meteorological analysis application that is a part of the SAFER STAR program suite. Because the data is stored on the hard drive, it is never deleted (no FIFO buffer) and the only way the data can be erased is by manually deleting the files or a hard drive crash.

Technical specs of the instruments:

Wind Speed:
Range: 0 to 60 m/s (130 mph)
Survival: 100 m/s (220 mph)
Threshold: 1.0 m/s (2.2 mph)

Wind Direction
Range: 360° mechanical, 355° electrical
Survival: 100 m/s (220 mph)
Threshold: 0.9 m/s (2.0 mph)

Temperature
Operational Range: -40°C to 50°C (-40°F to 122°F)
Accuracy: ±0.2°C over full range (0.36°F)
Resolution: 0.5°C (1.0°F)

Humidity
Operating Temperature Range: -40°C to +80°C
Measuring Range: 0 to 100% RH
Accuracy at +20°C: +/- 2% RH (0 to 90% RH)
+/- 3% RH (90 to 100% RH)
Temperature Dependence: +/- 0.05% RH/°C

Compass
Accuracy: ±1.0°
Resolution: 1°
Tilt Limit: ±45°

Mechanical Specs

Size: 4" x 22.5" (10.3 cm x 57.2 cm) (base unit without wind monitor)
Weight: 8 lbs (3.6 kg) (base unit without wind monitor)
Carry Weight: ABS Carry Case w/WEATHERPAK® 24 lbs. (10.9 Kg)
Canvas Tripod Bag 30 lbs. (13.6 Kg)
Material: 6061-T6 aluminum, 316SS hardware, O-Ring sealed Mil-Spec connector,thermoplastic resin coated
Set-up Time: 60 seconds, from carry case to full operation

Operating Specs

Temperature: Operation from -40°C to 70°C (-40°F to 160°F)
Pressure: Operation from 800 to 1100 mBar
Humidity: 10 day exposure with 100% RH
Rain: 20 in/hr
Shock/Vibration: Survival of 6 ft drop

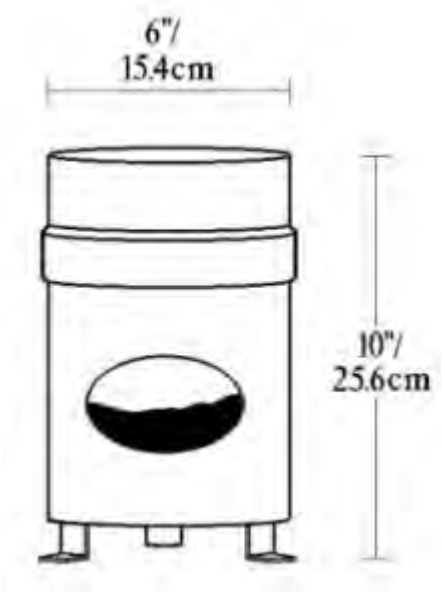
Tipping Bucket / Rain Gauge

S1068W / S1068Z

- **Rugged aluminum housing**
- **Completely automatic**
- **0.01” Accuracy**

This sensor consists of a gold anodized aluminum collector funnel with a knife edge that diverts the water to a tipping bucket mechanism. The mechanism is so designed that one alternate tip of the bucket occurs for each 0.01 inch of rainfall. Connecting the sensor to the ZENO® 3200 data logger, or to the WEATHERPAK® will allow record keeping of accumulated rainfall.

The spent water drains out of the bottom of the housing, so the sensor requires no attention or servicing of any kind. The aluminum housing is covered with a white baked enamel surface to withstand years of exposure to the environment. This sensor is factory calibrated, and due to the nature of its operation, should not require field calibration. Occasional cleaning of debris from the filter screen may be required.



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(800) 488-8291 / (206) 682-6048 / Fax: (206) 682-5658 www.CoastalEnvironmental.com

Rev 06/24/09

Technical Specifications

S1068W / S1068Z

Resolution:	0.01” (0.25 mm)
Accuracy:	1.0% at 2”/hr. or less
Average Switch Closure Time:	135 ms
Maximum Bounce Settling Time:	0.75 ms
Maximum Bounce Closure Time:	0.25 ms
Maximum Switch Rating:	30 VDC @ 2 A, 115 VAC @ 1 A
Temperature Limits:	0°C to +52°C (+32°F to +125°F)
Humidity Limits:	0 to 100%

PHYSICAL

Height:	10” (25.6 cm)
Weight:	2.5 lbs (1.13 kg)
Receiving Orifice Diameter:	6” (15.4 cm)
Cable:	15 ft, 2-conductor

Attachment D
Field Standard Operating Procedures

CTEH QA/QC and Data Validation Procedures for Real-Time Air Monitoring and Air Sampling

Quality Assurance and Quality Control

Quality assurance and quality control (QA/QC) measures are conducted following the collection of real-time air monitoring and analytical sampling to ensure that air monitoring and sampling results are defensible. Analytical sampling can be performed to verify real-time air monitoring results or to provide quantifiable data. The following sections describe QA/QC actions taken to ensure completeness and correctness of data.

1.0 Real-Time Air Monitoring

The term “real–time” refers to data collected using direct reading instruments that allow nearly instantaneous determinations of airborne chemical concentrations. Real-time measurements provide immediate information for worker and community exposure scenarios and, with the use of appropriate site safety measures, help prevent overexposures. Real-time air monitoring follows methods and procedures that are similar to analytical sampling. The following sections describes these actions.

1.1 Field Calibration

All field real-time air monitoring instruments or equipment will be calibrated prior to use in the field. Real-time instruments will be calibrated daily or as needed, according to manufacturer recommendations. Specifically, photo ionization detectors (PIDs) will be calibrated with a known concentration of isobutylene gas or zeroed using zero-grade air or at background site locations. Particulate matter monitors will be zeroed using manufacturer supplied zero filters. Gastec chemical specific colorimetric detector tubes are hermetically sealed and are calibrated by the manufacturer, and therefore, do not require field calibration.

1.2 Field Documentation

During the sampling events, all applicable notes, calibrations, sample locations, and sampling periods will be maintained in either various field books, portable handheld devices, or site logs. All instrument calibrations are to be documented on the field calibration log. The serial number of the instrument, gas applied, concentration, lot number of the gas, and expiration date of the gas are all documented.

All real-time readings will be documented either in bound notebooks, on CTEH field forms, in portable handheld devices, or by using radio telemetry systems combined with computer databasing capabilities. Each real-time record will have a description of the

location, global positioning system (GPS) data, sampling date and time, sampler's initials, concentration, analyte, and proper unit of measurement.

1.3 Verification of Real-Time Readings

Direct reading instruments perform sampling and analyses within the instrument and concentration readings can usually be obtained immediately. These instruments have fast response times and can follow rapid changes in concentration. Many are capable of storing continuous readings and displaying averages for selected time intervals. However, the presence of humidity, temperature extremes, and other atmospheric conditions may produce a phenomenon known as instrument drift. A second real-time instrument is often used to verify readings when drift is suspected or to confirm detections.

1.4 Data Management

All real-time data will be entered manually into a database or downloaded from the instrument source and imported into a database. This includes air data that were collected utilizing RAE System's Inc.'s instruments (AreaRAE, MultiRAE, ppbRAE, UltraRAE, MiniRAE), Lumex mercury monitor, Gastec colorimetric tubes, and TSI's aerosol monitors. All real-time manually-logged readings will undergo 100 percent QA/QC by field personnel. Data entered into databases will be reviewed electronically and manually by personnel.

2.0 Analytical Sampling

Steps are performed to ensure analytical samples are identified and handled properly in the field. The following sections describe these steps.

2.1 Sample Media Inspection

Analytical sampling media is shipped by a vendor and are prepared by the manufacturer. Upon receipt by CTEH, sampling media are inspected prior to use in the field and during time of preparation by field personnel. If sampling media appear to be damaged, broken, or incorrectly labeled, the media is discarded. Field personnel inspect to ensure media has not expired. Furthermore, field personnel inspect media to ensure that sample integrity will not be compromised prior to the sampling event. When samples are collected after a sampling event, they are inspected again before shipment to the analytical laboratory.

2.2 Integrated Sample Flow Rate Calibration

Integrated air sampling will be conducted utilizing a sample collection device that that pulls air across a medium and stabilizes chemicals for subsequent laboratory analysis. Sampling devices will be calibrated with a DryCal primary flow meter before and after each use. Pre-calibration and post-calibration of devices are recorded on CTEH field forms.

2.3 Sample Documentation

During the sampling events, all applicable notes, calibrations, sample locations, and sampling periods will be maintained in either field books, handheld devices, or site logs. All analytical sample documentation for samples collected in the field will be in compliance with the procedures outlined in this section, regardless of the sample media.

2.4 Sample Identification and Labels

Each analytical sample prepared and collected will be allocated a unique CTEH identifier (sample ID). This sample ID will be labeled on its assigned sample. All sample labels used on sample containers will include, at a minimum, a sample identification code, the date of the sample, site name, and an indication of the chemical sampled. The label will adhere to the media and the writing on it will be in indelible ink. The label will be secondarily affixed to the media with clear adhesive tape completely covering the label.

2.5 Field Blanks

Field blanks are designed to determine whether samples have been contaminated prior to or during the sampling event. The blank media are submitted to the laboratory without having air pulled through them. At least one field blank will be collected, for each different method, for each set of samples. The number of field blanks collected will be dependent upon method recommendations. If field blanks are not sent with analytical samples, the laboratory will prepare a method blank per QC batch and analyzed with samples. All samples analyzed at the laboratory will have a method blank prepared and analyzed with samples.

2.6 Field QA/QC Samples

Field blank samples will be collected as field QC checks for the samples. There are no known sources of QC samples for industrial hygiene sampling. Therefore, duplicates and matrix spike samples cannot be collected and sent to the laboratory for analysis. Laboratory QC samples will be analyzed concurrently with the analytical batch to which they are assigned.

2.7 Packaging and Shipping

Packaging and shipping of samples will vary depending upon sample media, contaminant concentration, preservation technique, and sample container. Packing and shipping samples should follow recommendations or requirements of analytical method. The person packaging the samples is responsible to ensure that the sample packaging is in suitable condition for shipping.

2.8 Chain of Custody

Chain of Custody (COC) is a legal term (a concept in jurisprudence) that refers to the ability to guarantee the identity and integrity of the sample and provides a chronological history of the sample from the time of collection through to reporting of the test results for the production of legally defensible data. Each sample will be identified on a COC record. Information recorded will include, at a minimum, sample collection date, time, sampler's initials, identification of sample matrix, sample volume, number of containers, analyses requested, preservation method, and signature blocks for each individual who has custody for the sample(s).

2.9 Custody Seals

Custody seals are placed on either the sample container or the sample or both. Custody seals are signed by the sampler with date and time. This is done to ensure that samples are not tampered with until received by the laboratory.

3.0 Laboratory Analytical Procedures

The most current versions of NIOSH, OSHA, or EPA methods will be used by the contract laboratory for the analyses of chemicals sampled for. Each contract laboratory is selected to comply with local, state, or federal regulations. Laboratories are either dictated by governing agency, by accreditation, or due to limitations on who can perform prescribed analysis. When options are available, CTEH chooses AIHA accredited laboratories who are also certified locally for analytical method. The following sections describe procedures to ensure data quality and usability.

3.1 Sample Containers, Preservation, and Holding Times

All sample media will be provided by the analytical laboratories or media manufacturers. Sample preservation and temperature, if necessary, shall be checked immediately upon receipt of samples at the laboratory. The results of these checks will be recorded on the

chain-of-custody form submitted with the sample. This is performed to ensure sample integrity.

3.2 Sample Handling in the Laboratory

Upon receipt, all samples will proceed through an orderly processing sequence (as defined in the laboratory QA/QC Plan) specifically designed to ensure continuous integrity of both the sample and other pertinent information to the analysis. All samples will be carefully checked and verified for proper chain-of-custody (COC) records, proper label identification, and any associated discrepancies. These items will be documented by use of a laboratory receipt form.

If no discrepancies are identified, the sample COC record will be signed, and the samples will subsequently be assigned a unique laboratory identification number by the laboratory for tracking and filing. The laboratory QA system and the use of an internal COC procedure will ensure that the samples are appropriately tracked from storage through the laboratory until the analytical process is complete.

Analytical and procedural information and activities will be documented with the use of Standard Operating Procedures (SOPs), a laboratory data management system, laboratory bench sheets, laboratory notebooks, and orderly project files containing any information pertinent to the analysis or integrity of the results.

The contracted laboratory will provide a written QA/QC program that discusses rules and guidelines to ensure the reliability and validity of all analytical work conducted in their laboratory. Compliance with the QA/QC program is coordinated and monitored by designated laboratory quality assurance personnel.

The laboratory will document, in each data package provided, that both initial and ongoing instrument and analytical QC functions have been met. Corrective action will be initiated on any samples analyzed in non-conformance with the QC criteria.

3.3 QA/QC Samples Prepared at the Laboratory

Method quality control checks will be analyzed as outlined in the individual method for each analysis performed. Furthermore, laboratories will prepare at minimum, one method blank per analytical batch. The method blank is carried through each step of the analytical method to examine the potential for cross-contamination. In addition or at the request of clients, laboratories will prepare a laboratory control sample (LCS). The primary purpose of the LCS is to demonstrate that the laboratory can perform the overall analytical approach in a matrix free of interferences (e.g, in reagent water, clean sand, or

another suitable reference matrix). The LCS is a blank sample that is spiked with a known concentration of analyte. The LCS is prepared and analyzed with samples. Since there are no known sources for duplicate or matrix spike samples, a laboratory control sample duplicate (LCSD) is often prepared and analyzed. This should be accomplished at a frequency of 1 in every 20 samples analyzed or as necessary, whichever is more frequent.

3.4 Data Reduction

The laboratory will perform in-house analytical data reduction and review of chemical analyses under the direction of the laboratory's technical staff, QA Officer, and Project Manager for this project. These individuals are responsible for evaluating the quality of the data and indicating which, if any, data may be listed as "unacceptable" and/or which should be considered potentially unreliable. A report by the personnel assessing data quality will be submitted to the Laboratory Project Manager or designee with every data package prior to transmittal to the client.

Data reduction, review, and reporting by the laboratory will be conducted as detailed as necessary in the laboratory Quality Assurance Project Plan (QAPP).

3.5 Data Reporting

The specific data items in each analytical data set submitted to CTEH will include, but will not be limited to, the following items:

- Cover sheet listing the samples included in the report and narrative comments describing problems encountered during analysis;
- Copies of signed COC records;
- Tabulated results of the compounds identified and quantified;
- Analytical results for QC field blanks;
- Calculations of detection (reporting) limits;
- Raw electronic data files

3.6 Preventive Maintenance and Calibration

The approved laboratory will be responsible for the maintenance of laboratory instruments and equipment. Instruments and measurements made as part of the analytical methodology will be as specified in the method, without modification. The laboratory's QA program ensures that only trained personnel perform routine maintenance on all major instruments and that repairs are performed by trained laboratory personnel or service technicians employed by the instrument manufacturer or

representative. Instrument maintenance will be appropriately documented through the use of instrument logs that will be included in the laboratory project file.

3.7 Corrective Measures

When errors, deficiencies, or out-of-control situations exist, the laboratory QA program provides systematic procedures, called corrective actions, to resolve problems and restore proper functioning to the analytical system.

3.8 Laboratory Data Report

Laboratory data reports will be issued for each work order generated by the laboratory. A work order is generated for a single client's samples, received by the laboratory on the same day. The deliverable components of the data report are listed below:

- Data Report (analyte, method, detection limit, date and time of analysis and results for each sample)
- Field and Laboratory Blank Summaries
- Dilution Factors
- Chain-of-Custody Records
- Cooler Receipt Forms
- Laboratory Sample Preparation Data Sheets
- Extraction/Digestion Logs

As appropriate, each of these deliverable components is given for each of the types of analyses that are conducted.

4.0 Data Validation/Verification

Prior to reporting and submittal to client, CTEH conducts data verification or data validation procedures on analytical data. A CTEH Environmental Chemist will conduct data verification on the analytical data at the request of the client. Frequency and methods are chosen to best represent the intended use of the data. Data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements. The analytical data will be evaluated to determine whether the reported laboratory results are compliant with the requirements of the sampling and analysis methods and procedures used to generate results.

The following parameters will be evaluated:

- Data Completeness

- Holding Times
- Sample Preservation
- Sample Receipt
- Sample Analysis

At the completion of the data verification process, the reviewer will prepare a summary of the results and note data usability.

Furthermore, data validation is a systematic procedure of reviewing a body of data against a set of established criteria to provide a specified level of assurance of its validity prior to use. The validation process will include checks for internal consistency, checks for transmittal errors, and checks for verification of laboratory capability. Evaluation of these criteria will involve review of parameters listed above and:

- Evaluation of Holding Times
- Review of Surrogate Recoveries
- A review of all QA/QC samples
- Detection limit records
- Instrument calibration records
- Continuing calibration records
- Internal standard records
- Target compound results
- Sample results

At the completion of the data validation process, the reviewer will prepare a summary of the results, validate sampling results, and specify the uses for which the data are suitable.

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

Toxicology Emergency Response Program (6/3/2008)
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.**

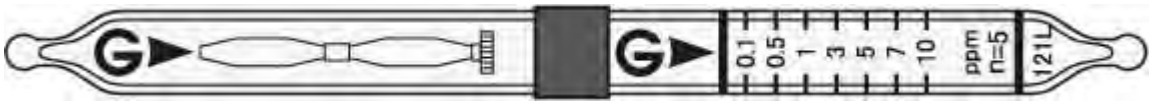
Equipment Use Instructions (step by step)

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 are 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

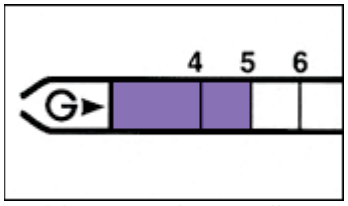
this number, you must apply a correction factor that you will find in the instructions.

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).

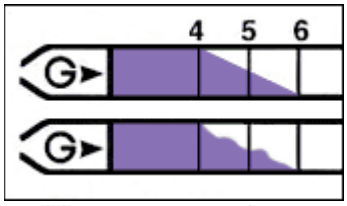
Tips for detector tube reading

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



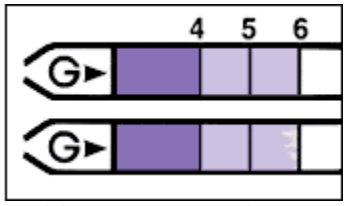
In this case, the reading would be 5%.

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: Equipment Room Manager

***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*:**

Nathan Williams 4_12_2011

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

Toxicology Emergency Response Program 04-19-2011
STANDARD OPERATING PROCEDURE NO. (Version 1.0)

SUBJECT: ***Motorola MC-55 Handheld***

Description of the SOP. The purpose of this document is to provide the reader with a thorough understanding of the general capabilities, proper usage and maintenance, and field data collection procedures with the Motorola MC-55.

Motorola MC 55 EPA (PDA/Handheld)

General notes
The Motorola MC 55 is an Enterprise Personal Assistant (EPA) device that runs Windows Mobile 6 operating system. The models that CTEH owns have the following amenities:

Touch screen	**Blue Tooth**	**Mobile Broadband**	**Barcode Scanner**
Barcode Scanner	**Camera**	**Key pad**	**Phone/Text**

**Note: as of this writing we do not have a means to have the barcode scanner and the camera enabled at the same time.

Proper usage

- The elastic strap on the back is there for you to put your off hand through while using the device. It makes holding the device easier.
- The stylus on the right side of the device is for use with the touch screen. While not *required* to use the touch screen, the stylus provides greater control and precision.
- If you take good care of your unit it will be more reliable than one that is mishandled or used improperly. Taking the battery out is the only way to turn the unit off. Even if the red power button is pressed and the screen goes black the unit is still on.

Section 1 Battery

The charge of one battery on a MC 55 will last 100 hours in standby mode and 6 hours of talk time (most units won't have phone feature on). For data entry purposes this translates to a couple of days. In the case of a failing or worn out battery it may not last a whole day of regular data entry. As is the case with any rechargeable battery, life and function will be optimized if the following is done:

- The battery is charged only if it is very low and not left charging after the battery has been fully charged.
- Extreme heat and cold temperatures are avoided. Battery is kept in a dry environment and not submerged in water. If the battery or the unit manages to get wet remove the battery immediately and allow the unit and the battery to dry separately. If the battery gets wet and the small white rectangle (on the right) turns pink or red, discontinue use of battery and dispose of it at a facility that recycles batteries.

- **Note:** The battery will not work as well if the battery gets excessively hot; which can happen if the unit is charged and used non-stop, is used intensely or is left in the sun. If the performance has degraded significantly due to overheating it might be beneficial to take the battery out and let the battery cool off.
- **Removing or replacing battery:** Figures 1.1 and 1.2 demonstrate the proper procedures for removing and replacing the unit's battery.

Figure 1.1: Procedure for removing battery from unit.

<table>
<tr>
<td>STEP 1
Flip the unit over so that the screen is facing down.
 </td>
<td>STEP 2
Pull up on the strap to let the strap down.
 </td>
</tr>
<tr>
<td>STEP 3
On the gray metal piece there is a black battery lock. Slide the lock to the Right (it will take some oompf). The battery should pop up a little but it might not.
 </td>
<td>STEP 4
Pull the battery off of the unit.
 </td>
</tr>
</table>

Figure 1.2: Procedure for replacing battery in unit.

STEP 1

(If the elastic band has already been taken down then continue to step one otherwise do step three from Figure 1.1 first)

Slide the bottom of the battery into the back of the unit.

STEPS 2 & 3

Hold the unit with both hands so your fingers are on the battery and your palms are on the sides of the screen.

STEP 4

Reattach the elastic band by sliding the metal clip on the end of the band onto the top of the unit. The unit should come on as soon as the battery is installed. If not you may need to press the red power button once to turn it on.

Section 2 General Hand Held Unit Practices and Guidelines

Following is a list of best practices and guidelines which should ensure optimal usage of the MC 55 unit.

- Do not drop or subject unit to sudden impacts.
- Avoid getting the unit wet. If the unit does get wet remove the battery immediately.
- For general transport, make sure that the unit is secured in a closeable pouch or container when not in use. Failure to secure the unit in a closable pouch or container may result in the unit getting dropped or left behind.
- This MC 55 has **not** been certified for usage in volatile or flammable environments. Make sure the unit is off if before entering a flammable or volatile environment.
- Do not use a writing pen or sharp objects on the touchscreen.

Section 3 Windows Mobile 6 OS Basics

3.1 Resetting the device:

A lot of the problems that you might encounter with your device can be solved by resetting the device. This is done by pressing and holding the red power button until the screen goes white or about 5 seconds.

3.2 Volume

The rocker arm on the left of the unit is the volume control

3.3 Keyboards

Some units have a full QWERTY keyboard below the screen while some have a numerical keypad that is similar to a cell phone. The shift, orange and blue button have two modes: single and lock. Pressing the shift key ⇧ once will only capitalize the very

ut e 12 key style

next letter pressed, while pressing shift ⇧ twice will essentially turn caps lock on. Inputting text with the numerical pad is similar to texting with a phone. With the orange button enabled press the number that has the letter you want until the letter you want

appears. For the letter C this means pressing the 2 button three times. After a brief pause pressing 2 again (with orange locked) will result in an ‘a’ (or ‘A’).

3.3.1 On Screen Keyboard

Of course all devices have an onscreen keyboard that is fairly easy to use.
When you are at a point that you can input text on the device, press the keyboard button to bring up the onscreen keyboard.

The stylus will be very helpful in typing the correct keys. However, the screen can occasionally get out of line making using the onscreen keyboard very difficult. In the case of bad screen alignment follow the **Screen Alignment** section.

3.3.2 Other input modes

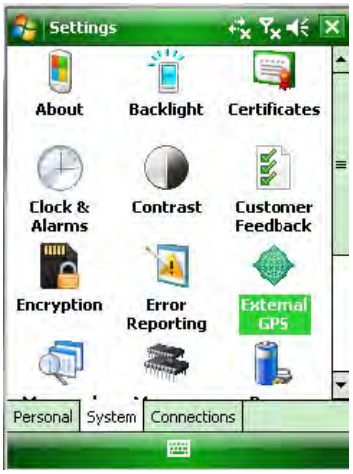
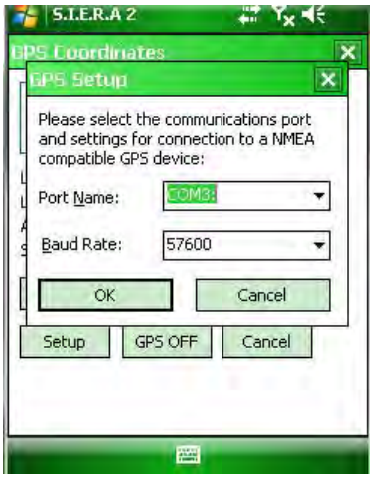
There are other ways to input characters into the device, which you can see if you press the up arrow next to the keyboard. You might find that your keyboard is gone in place of something else, in which case use the up arrow and select Keyboard.

3.4 GPS:

Figure 3.1 shows the steps for setting up the GPS on the MC-55.

- You should only manipulate the settings of the GPS after you have tried troubleshooting the problem. Your handheld shouldbe set up for GPS by the time you get it. However, in some rare cases it seems that the device loses the saved values for the GPS settings. There is also a different setup that works that your unit might be set up with, where the Pocket PC GPS settings uses COM:8 instead of COM:3.
- The GPS locator works off of satellites, which means that a clear line of sight with the sky is critical. Being indoors or under large structures will block the GPS signal.
- The first satellite synch can take 10-20 minutes or longer on occasion. Staying in one place will help your device find its location during this period. After the first synch the GPS location should be more responsive.

Figure 3.1: Steps for setting up GPS on the MC-55

<table>
<tr><th>STEP 1</th><th>STEP 2</th><th>STEP 3</th></tr>
<tr><td>
</td><td> 
</td><td> 
</td></tr>
<tr><th>STEP 4</th><th>STEP 5</th><th>STEP 6</th></tr>
<tr><td>
</td><td>
</td><td>
</td></tr>
</table>

In my personal experience (Matt Reed) I have seen very few GPS radios fail in the MC55. However, if after thoroughly troubleshooting your GPS issues without success call your equipment or IT tech for help.

1. Press |Start| -> |Settings|
2. Click the |System| tab on the bottom and select External GPS
3. In the Programs tab the GPS program port should be COM3
4. In the Hardware tab the GPS Hardware Port should be COM8 and the baud rate set to 57600
5. In the Access tab Check the box Manage GPS Automatically
6. When you are getting your latitude and longitude for a data point in a Pocket PC Creations app (like S.I.E.R.A. 2, Personnel Sampling, Real Time 2.2 etc.) and you choose automatic, a window should pop up saying "Connecting to GPS…" from there click "Setup". The Port Name should be COM3 (the same as the GPS program port) and the Baud Rate should be 57600.

Section 4 Screen Alignment

The MC55 touch screen translates where you press the screen with your finger or stylus into coordinates in the operating system. Sometimes the translation is off. Pressing on top of the item that you want to press translate to a different spot in the OS.

For example: If you press the 'g' on the onscreen keyboard and the 'x' is what gets highlighted then the translation is off and you have a screen alignment problem.

You can fix this by

1. Pressing the blue button followed by
2. Pressing the backspace button.

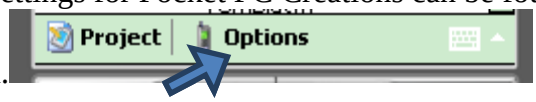
Then follow the onscreen directions. There has been one instance (out of 200 +) that I am aware of where the screen would not stay aligned after doing a software screen alignment. In these cases report the problem and get a replacement.

Section 5 Pocket PC Creations (PPCC)

Each application in Pocket PC Creations is project specific. If you have questions regarding how to use it or what to put into a certain app ask your supervisor or site lead.

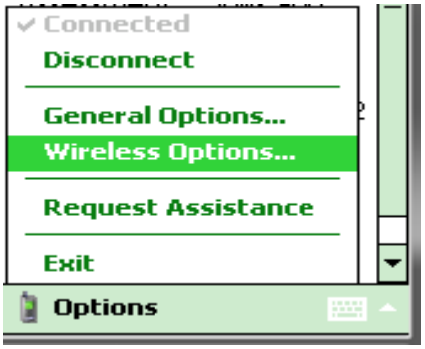
If you don't have the Pocket PC Apps that you need to do your function you will need to call your site lead or IT tech to get it.

The settings for Pocket PC Creations can be found under the "Options" menu.



5.1 Wireless Options

First let's go over the Wireless Options.



[✓] (checked) Connect to a PPCC server:
The top check box often gets unchecked if a recent connection attempt was unsuccessful (more on this later)
The Address: is |samples.cteh.com:4001|
note the colon between "com" and "4001"
There isn't a password.
[✓] (checked) Automatically connect to: |Internet|.
[✓] (checked) Maintain a continuous connection,
[ ] (unchecked) Require and use AES-256 encryption.
[ ] (unchecked) Auto submit sessions:
[✓] (checked) Receive new sessions upon connect.
[✓] (checked) Allow remote assistance

If your unit is having trouble connecting contact Matt Reed, Brady Davis, or Anton Avguchenko at 501-801-8500.

Section 6 Real-time Readings

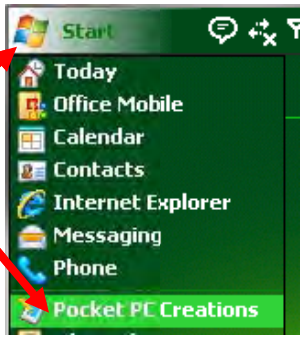
Basic:
Use the stylus to enter data for each required field. Navigate through the pages by using "Next" at the bottom and the scroll bar on the right side of the screen.

A good rule-of-thumb is to think about what information would be helpful to someone looking at this data several months/years from now if they were trying to get a good idea of what happened and where you were.

You can navigate between different Pocket PC Creations using the **"Back"** button inside each program.

Detailed:

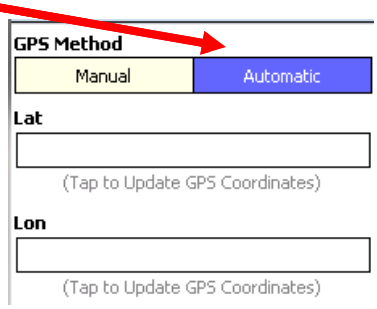
1) Turn on the hand held unit by pushing the small **red** button at the bottom front of the handheld. Handhelds are notoriously hard to actually turn off, so you may also be able to just tap the screen.
2) After a couple of minutes it will come to a **green** screen with start at the top left corner of the screen. Press Start.
3) The next screen will be **a green** screen. Go to **Pocket PC Creations**.
4) The next screen will be white with several files. Pick **RealTime 2.2.** (or the most recent version of RealTime)



5) Your next screen will be a white screen, go to the bottom and pick **new.**

6) You can enter text and numbers using the physical keys on the handheld or by tapping the small keyboard icon in the bottom right of the screen with the stylus. This will bring a keyboard up on the screen that you can type with using the stylus.
7) Fill in the correct **date** (this should be automatically filled in when you start a new reading), **project number**, and **region**.
8) Next enter your name, choose indoor or outdoor sampling, and select the appropriate **"Location Category"**.
9) Hit **"Next"** to move on to the next page when you've completed the current one.

10) Make sure you enter coordinates whenever possible. If outside, you should be able to choose "Automatic" and just tap the box(es) for Latitude/Longitude. It can take several minutes to acquire satellites and provide a reading the first time you do this after powering on the MC55, but after that it should be fairly instantaneous. If the GPS isn't working, you can often get coordinates from your cellphone or Google Earth, Google Maps, etc. and enter them by choosing "Manual".

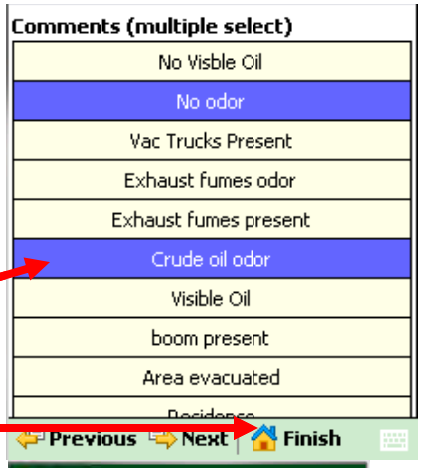


11) Enter the address if known and be concise, specific, but also detailed in the **"Location Description"** and later **"Additional Comments"**.

12) Next enter the matrix (what you measured for: air, water surface, soil), the instrument used, its barcode number, the analyte that you measured for (H2S, LEL, O2, SO2, VOC, etc), result flag either non-detect or detect, reading that your instrument gave you, detection limit of the analyte, units measured (%, ppm), instrument details (was there fog, rain, elevated humidity, moisture interferer, drift of areaRAE, battery low, 100ml, 200ml, 300ml).

   a. ***NOTE** If entering a Gastec reading, indicate how many pump strokes here by choosing the volume of air pumped. Be sure to enter the Gastec Tube Number in the "Additional Comments" field.

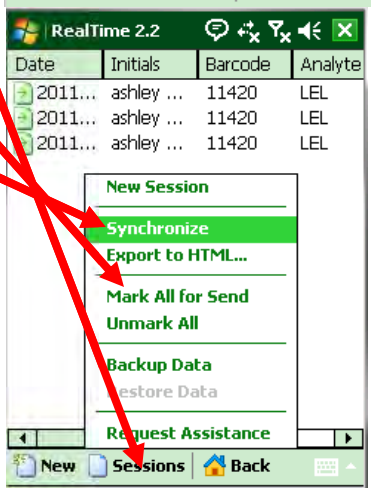
13) On the next two screens, choose any comments that apply, and concisely provide any other details that might be useful in **"Additional Comments"**



14) Then hit "**Finish".**

15) To synchronize and send data to main computer on site, tap "**Sessions"** at the bottom of the screen, touch **"Mark All for Send"**, touch **"Synchronize"**.

16) You should synchronize your data regularly. Don't use the "duplicate" feature unless expressly told you can do so. This often leads to errors that invalidate the data you are collecting and costs CTEH more time than you will save.



Section 7 SIERA Points

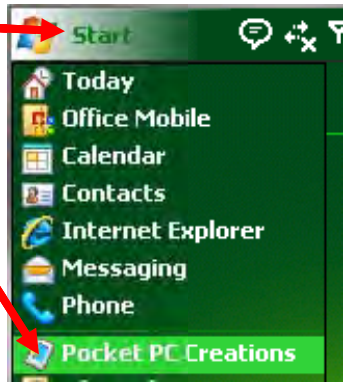
Basics:

SIERA Points are used to record samples, monitoring stations, and events. The SIERA2 program works a lot like RealTime described above. Navigate through the pages using **"Next"** and the scroll bar on the right of the screen.

Details:

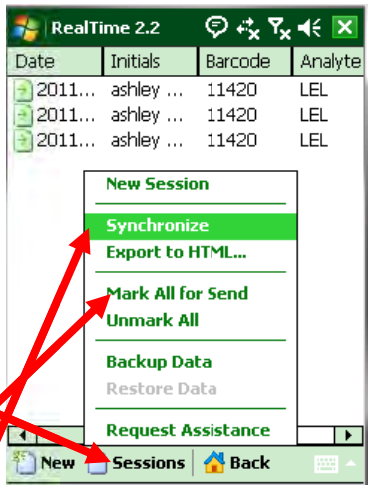
1) Turn on the hand held unit by pushing the small **red** button at the bottom front of the handheld.

2) After a couple of minutes it will come to a **green** screen with start at the top left corner of the screen. Press **"Start"**.



3) The next screen will be a **green** screen. Go to "P**ocket PC Creations"** and press it.
4) The next screen will be white with several files. Pick "**SIERA 2"**.
5) Your next screen will be a white screen, go to the bottom and pick "N**ew"**.

6) Fill in the **Project**, **DateTime** (should be automatic), GPS method (pick automatic if outside), **region** or state that you are in, **Location Description**, your **initials**, **SIERA Type** (sample, survey, tar ball, safety, source, instrument, event, receptor), **SIERA subtype**, **Primary identifier** (the Sample ID), **Other identifier** (Station Name), comments, touch "tap to attach image", push **yellow** button on front of handheld (or tap the screen) to take picture, back out of screen by pushing "B**ack"** at bottom of screen, touch "**Finish"**.
7) To synchronize and send data to main computer on site, tap **sessions** at the bottom of the screen, touch "**Mark all for send"**, hit **"Sessions"** again, touch "**Synchronize"**.



Additional media needed for this equipment:

A/C adapter (necessary for charging battery)

Car charger (necessary for charging battery in the field)

Docking station (for both charging and synchronizing directly to computer)

SIM Card

Notification Procedures for Equipment Failure:

CTEH-Matthias “Papa Lemur Finkelstein” Reed – (501) 801-8652

References and Further Assistance

Motorola MC-55 User’s Guide

Call Anton Avguchenko, Matt Reed, or Brady Davis if you need help.

CTEH Main Number: 501-801-8500

Created by

Matthias Reed April 19, 2011
David Quibell April 25, 2011
Johnnie Chamberlin April 27, 2011

Attachments:
none

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

Nathan Williams 4_12_2011

UltraRAE 3000
User's Guide

RAE SYSTEMS

Rev. A
May 2008
P/N 059-4023-000

FCC Information

Contains FCC ID: S22BTMODULE-CL2

The enclosed device complies with part 15 of the FCC rules. Operation is subject to the following conditions: (1) This device may not cause harmful interference, and (2) This device must accept any interference received, including interference that may cause undesired operation.

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Read Before Operating

This manual must be carefully read by all individuals who have or will have the responsibility of using, maintaining, or servicing this product. The product will perform as designed only if it is used, maintained, and serviced in accordance with the manufacturer's instructions. The user should understand how to set the correct parameters and interpret the obtained results.

CAUTION!

To reduce the risk of electric shock, turn the power off before removing the instrument cover. Disconnect the battery before removing sensor module for service. Never operate the instrument when the cover is removed. Remove instrument cover and sensor module only in an area known to be non-hazardous.

ATEX WARNING!

To reduce the risk of electrostatic ignition, do not use the instrument without the rubber boot in place.

The instrument is classified as to intrinsic safety for use in Class I, Division 1, groups A, B, C, D, and ATEX II 2G EEx ia IIC T4, or non-hazardous locations.

Special Notes

When the instrument is taken out of the transport case and turned on for the first time, there may be some residual organic or inorganic vapor trapped inside the detector chamber. The initial PID sensor reading may indicate a few ppm. Enter an area known to be free of any organic vapor and turn on the instrument. After running for several minutes, the residual vapor in the detector chamber will be cleared and the reading should return to zero.

The battery of the instrument discharges slowly even if it is turned off. If the instrument has not been charged for 5 to 7 days, the battery voltage will be low. Therefore, it is a good practice to always charge the instrument before using it. It is also recommended to fully charge the instrument for *at least 10 hours* before first use. Refer to this User Guide's section on battery charging for more information on battery charging and replacement.

WARNINGS

STATIC HAZARD: Clean only with damp cloth.

For safety reasons, this equipment must be operated and serviced by qualified personnel only. Read and understand the instruction manual completely before operating or servicing. Use only RAE Systems battery packs, part numbers 059-3051-000 and 059-3052-000. This instrument has not been tested in an explosive gas/air atmosphere having an oxygen concentration greater than 21%. Substitution of components may impair intrinsic safety. Recharge batteries only in non-hazardous locations.

Do not mix old and new batteries or batteries from different manufacturers.

The calibration of all newly purchased RAE Systems instruments should be tested by exposing the sensor(s) to known concentration calibration gas before the instrument is put into service.

For maximum safety, the accuracy of the instrument should be checked by exposing it to a known concentration calibration gas before each day's use.

Do not use USB/PC communication in hazardous locations.

AVERTISSEMENT

DANGER

RISQUE D'ORIGINE ELECTROSTATIQUE: Nettoyer uniquement avec un chiffon humide.

Pour des raisons de sécurité, cet équipement doit être utilisé, entretenu et réparé uniquement par un personnel qualifié. Étudier le manuel d'instructions en entier avant d'utiliser, d'entretenir ou de réparer l'équipement.

Utiliser seulement l'ensemble de batterie RAE Systems, référence 059-3051-000 ou 059-3052-000. Cet instrument n'a pas été testé dans une atmosphère de gaz/air explosive ayant une concentration d'oxygène plus élevée que 21%. La substitution de composants peut compromettre la sécurité intrinsèque. Ne charger les batteries que dans des emplacements désignés non-dangereux.

Ne pas mélanger les anciennes et les nouvelles batteries, ou bien encore les batteries de différents fabricants.

L'étalonnage de tout instrument de RAE Systems doit être testé en exposant l'instrument à une concentration de gaz connue avant de mettre en service l'instrument pour la première fois.

Pour une sécurité maximale, la sensibilité de l'instrument doit être vérifiée en exposant l'instrument à une concentration de gaz connue avant chaque utilisation journalière.

Ne pas utiliser de connexion USB/PC en zone dangereuse.

1 Standard Contents

Instrument
Calibration Kit
Charging Cradle
AC/DC Adapter
Alkaline Battery Adapter
Data Cable
CD-ROM With User's Guide, Quick Start Guide, and related materials

2 General Information

The UltraRAE 3000 is a hand-held, programmable compound specific PID monitor designed to provide instantaneous exposure monitoring of a specific organic gas. It monitors a specific gas by utilizing a gas separation tube and the photoionization detector (PID) with a 9.8 eV gas discharge lamp. It also can be used to measure total volatile organic compound (VOC) as a broadband monitor by utilizing the PID with a 9.8 eV, 10.6 eV, or 11.7 eV lamp.

Features include:

Lightweight and Compact

- Compact, lightweight, rugged design
- Built-in sample draw pump

Dependable and Accurate

- Up to 16 hours of continuous monitoring with rechargeable battery pack
- Designed to continuously monitor VOC vapor at parts-per-million (ppm) levels

User-friendly

- Preset alarm thresholds for STEL, TWA, low- and high-level peak values.
- Audio buzzer and flashing LED display are activated when the limits are exceeded.

Datalogging Capabilities

- 260,000-point datalogging storage capacity for data download to PC

The UltraRAE 3000 consists of a PID with associated microcomputer and electronic circuit. The unit is housed in a rugged case with a backlit LCD and 3 keys to provide easy user interface. It also has a built-in flashlight for operational ease in dark locations.

3 Physical Description

The main components of the portable compound-specific and VOC monitoring instrument include:

- Three operation/programming keys for normal operation or programming
- LCD display with back light for direct readout and calculated measurements
- Built-in flashlight for illuminating testing points in dark environments
- Buzzer and red LEDs for alarm signaling whenever exposures exceed preset limits
- Charge contacts for plugging directly to its charging station
- Easy-to-use separation tube holder
- USB communication port for PC interface
- Protective rubber cover

4 Specifications

Size:	10" L x 3" W x 2.5" H (25.5 cm x 7.6 cm x 6.4 cm)
Weight:	26 oz (738 g) with battery pack
Detector:	Photoionization sensor with 9.8, 10.6, or 11.7 eV UV lamp
Battery:	A 4.2V/3300mAH rechargeable Lithium-Ion battery pack (snap in, field replaceable, at non-hazardous location only)
	Alkaline battery holder (for 4 AA batteries)
Battery Charging:	Less than 8 hours to full charge
Operating Hours:	Up to16 hours continuous operation
Display:	Large dot matrix screen with backlight

Measurement range & resolution

Lamp	Range	Resolution
10.6 eV	50 ppb to 10,000 ppm (VOC mode)	50 ppb
9.8 eV	50 ppb to 200 ppm, for benzene and butadiene; 50 ppb to 5,000 ppm (VOC mode)	50 ppb
11.7 eV	50 ppb to 2,000 ppm (VOC mode)	50 ppb

Response time (T_{90}):	2 seconds
Accuracy (Isobutylene):	3% at calibration point
PID Detector:	Easy access to lamp and sensor for cleaning and replacement
Correction Factors:	Over 200 VOC gases built in (based on RAE Systems Technical Note TN-106)
Calibration:	Two-point field calibration of zero and standard reference gases
Calibration Reference:	Store up to 8 sets of calibration data, alarm limits and span values
Inlet Probe:	Flexible 5" tubing (a short tube is also available) Separation tube housing with permanent VOC tube
Radio module:	Bluetooth (2.4GHz)
Keypad:	1 operation key and 2 programming keys; 1 flashlight switch
Direct Readout:	Instantaneous, average, STEL, TWA and peak value, and battery voltage

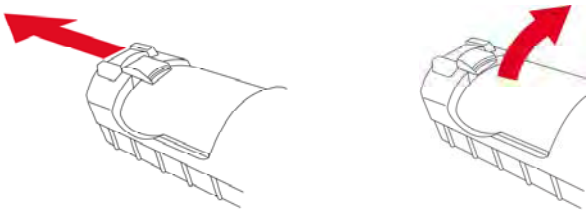
Intrinsic Safety:	US and Canada: Class I, Division 1, Group A, B, C, D Europe: ATEX (II 2G EEx ia IIC T4)
EM Interference:	Highly resistant to EMI/RFI. Compliant with EMC R&TTE (RF Modules)
Alarm Setting:	Separate alarm limit settings for Low, High, STEL and TWA alarm
Operating Mode:	Hygiene or Search mode
Alarm:	Buzzer 95dB at 12″ (30cm) and flashing red LEDs to indicate exceeded preset limits, low battery voltage, or sensor failure
Alarm Type:	Latching or automatic reset
Real-time Clock:	Automatic date and time stamps on datalogged information
Datalogging:	260,000 points with time stamp, serial number, user ID, site ID, etc.
Communication:	Upload data to PC and download instrument setup from PC via USB on charging station.
Sampling Pump:	Internally integrated. Flow rate: 450 to 550 cc/min.
Temperature:	-20º C to 50º C (-4º to 122º F)
Humidity:	0% to 95% relative humidity (non-condensing)
Housing (including rubber boot):	Polycarbonate, splashproof and dustproof Battery can be changed without removing rubber boot.

5 Replacing Alkaline Batteries

An alkaline battery adapter is supplied with each instrument. The adapter (part number 059-3052-000) accepts four AA alkaline batteries (use only Duracell MN1500 or Energizer E91) and provides approximately 12 hours of operation. (An optional rechargeable lithium-ion battery pack, part number 059-3051-000, is also available.)

To install the adapter in the instrument:

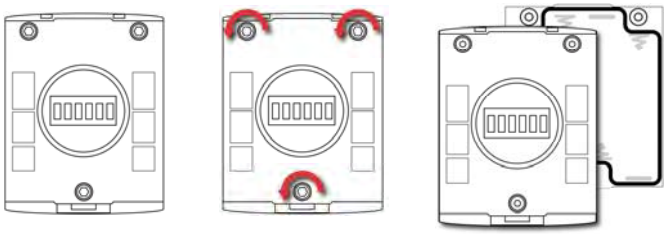
1. Remove the alkaline battery adapter from the instrument by sliding the tab and tilting out the adapter.



2. Replace the batteries (follow the procedure below).
3. Tilt the alkaline battery adapter and put it into the instrument.
4. Slide the tab back into place to secure the battery adapter.

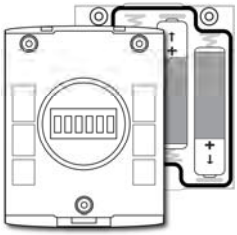
To insert batteries into the adapter:

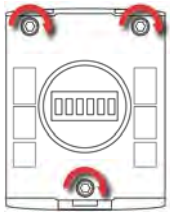
1. Remove the three hex-socket screws to open the compartment in the adapter.



2. Insert four fresh AA batteries as indicated by the polarity (+/-) markings.

3. Replace the cover. Replace the three screws.





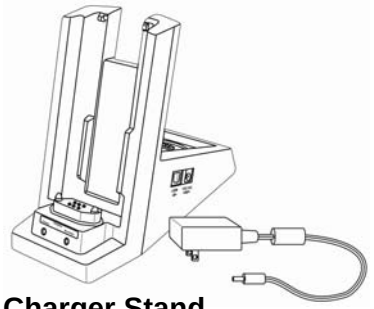
IMPORTANT!

Alkaline batteries cannot be recharged. The instrument's internal circuit detects alkaline batteries and will not allow recharging. If you place the instrument in its Travel Charger or Charger Stand, the alkaline battery will not be recharged. The internal charging circuit is designed to prevent damage to alkaline batteries and the charging circuit when alkaline batteries are installed inside the instrument. If you try to charge an alkaline batteries installed in the instrument, the Charging Cradle or Travel Charger's charging LED does not glow, indicating that it will not charge the alkaline batteries.

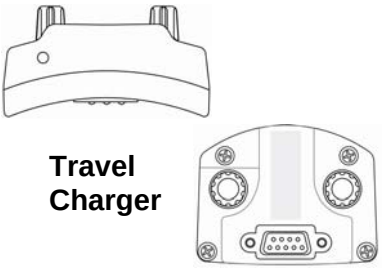
Note: When replacing alkaline batteries, dispose of old ones properly.

6 Charging A Lithium-Ion Battery

Always fully charge the battery before using the instrument. The instrument's Li-ion battery is charged by attaching the instrument to the Travel Charger (or by placing the instrument in the optional Charger Stand). Contacts on the bottom of the instrument meet the Travel Charger's (or Charger Stand's) contacts, transferring power without other connections.



Charger Stand

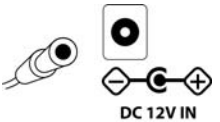


Travel Charger

Note: Before connecting the charger to the instrument, visually inspect the contacts to make sure they are clean. If they are not, wipe them with a soft cloth. Do not use solvents or cleaners.

Follow this procedure to charge the instrument:

1. Plug the AC/DC adapter's barrel connector into the instrument's Charger Stand or Travel Charger.



2. Plug the AC/DC adapter into the wall outlet.
3. Connect the AC/DC adapter to the Travel Charger (or Charger Stand).

4. Place the instrument into the Travel Charger or Charger Stand. The LED in the Travel Charger (or Charger Stand) should glow.

The instrument begins charging automatically. (If the optional Charger Stand is used, the "Primary" LED blinks green to indicate charging.) During charging, the diagonal lines in the battery icon on the instrument's display are animated and you see the message "Charging..."

Note: If the Li-ion battery has been discharged below a certain threshold, the "Charging..." message does not display immediately. The charging LED blinks to indicate that it is charging, and after it has been charging for a while, the "Charging..." message appears.

When the instrument's battery is fully charged, the battery icon is no longer animated and shows a full battery. The message "Fully charged!" is shown. (If the Charger Stand or Travel Charger is used, its LED glows continuously green.)

Note: If you see the "Battery Charging Error" icon (a battery outline with an exclamation mark inside), check that the instrument or rechargeable battery has been properly set into the Travel Charger (or Charger Stand). If you still receive the message, check the Troubleshooting section of this guide.

Note: If the instrument or battery has been charging for more than 10 hours and you see the "Battery Charging Error" icon and a message that says, "Charging Too Long," this indicates that the battery is not reaching a full charge. Try changing the battery and make sure the contacts on the instrument are meeting the Travel Charger's (or Charger Stand's) contacts. If the message is still shown, consult your distributor or RAE Systems Technical Services.

6.1 Charging A Spare Rechargeable Battery (Optional Charger Stand Only)

A rechargeable Li-ion battery can be charged when it is not inside the monitor. The Charger Stand is designed to accommodate both types of charging. Contacts on the bottom of the battery meet the contacts on the Charger Stand, transferring power without other connections, and a spring-loaded capture holds the battery in place during charging.

1. Plug the AC/DC adapter into the Charger Stand.
2. Place the battery into the Charger Stand, with the gold-plated contacts on top of the six matching charging pins.
3. Plug the AC/DC adapter into the wall outlet.

The battery begins charging automatically. During charging, the Secondary LED in the Charger Stand blinks green. When charging is complete, it glows steady green.

Release the battery from the Charger Stand by pulling it back toward the rear of the Charger Stand and tilting it out of its slot.

Note: If you need to replace the Li-ion battery pack, replacements are available from RAE Systems. The part number is 059-3051-000.

WARNING!

To reduce the risk of ignition of hazardous atmospheres, recharge and replace batteries only in areas known to be non-hazardous.

6.2 Low Voltage Warning

When the battery's charge falls below a preset voltage, the instrument warns you by beeping once and flashing once every minute, and the "empty battery" icon blinks on and off once per second. You should turn off the instrument within 10 minutes and either recharge the battery by placing the

instrument in its cradle, or replace the battery with a fresh one with a full charge.

6.3 Clock Battery

An internal clock battery is mounted on one of the instrument's printed circuit boards. This long-life battery keeps settings in memory from being lost whenever the Li-ion battery or alkaline batteries are removed. This backup battery should last approximately five years, and must be replaced by an authorized RAE Systems service technician. It is not user-replaceable.

6.4 Data Protection While Power Is Off

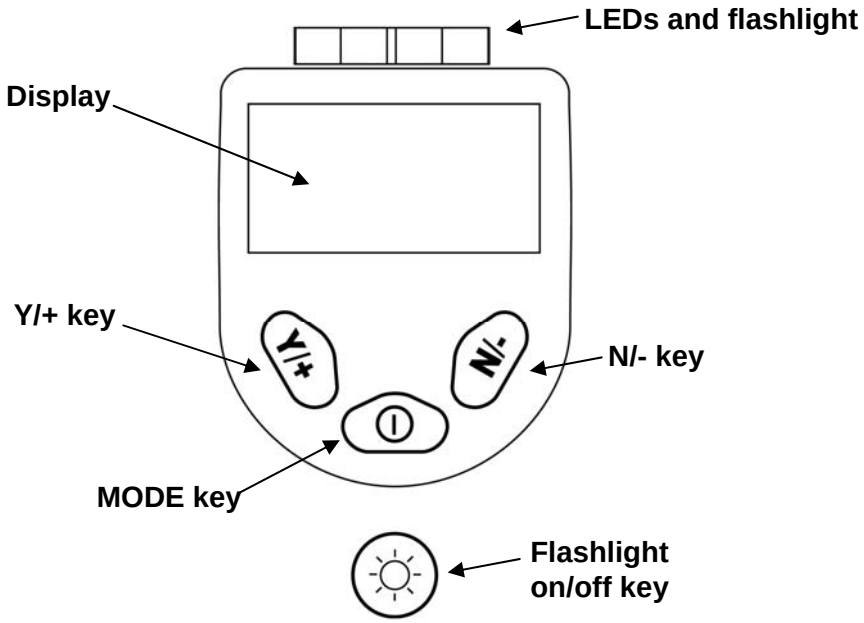
When the instrument is turned off, all the current real-time data including last measured values are erased. However, the datalog data is preserved in non-volatile memory. Even if the battery is disconnected, the datalog data will not be lost.

7 User Interface

The instrument's user interface consists of the display, LEDs, an alarm transducer, and four keys. The keys are:

Y/+
MODE
N/-
Flashlight on/off

The LCD display provides visual feedback that includes the reading, time, battery condition, and other functions.

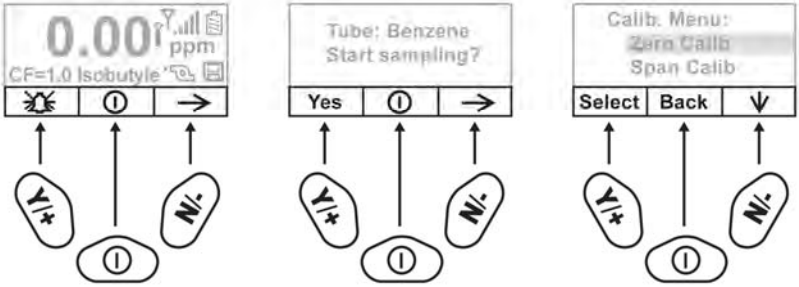


In addition to their labeled functions, the keys labeled Y/+, MODE, and N/- act as "soft keys" that control different parameters and make different selections within the instrument's menus. From menu to

menu, each key controls a different parameter or makes a different selection.

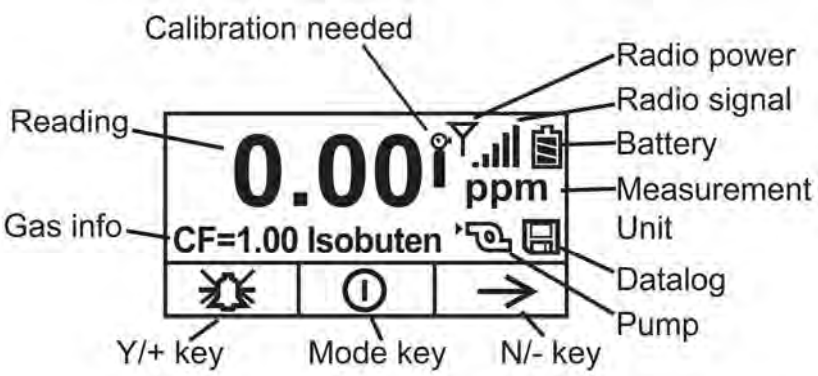
Three panes along the bottom of the display are "mapped" to the keys. These change as menus change, but at all times the left pane corresponds to the [Y/+] key, the center pane corresponds to the [MODE] key, and the right pane corresponds to the [N/-] key. Here are three examples of different menus with the relationships of the keys clearly shown:

RELATIONSHIP OF BUTTONS TO CONTROL FUNCTIONS



7.1 Display

The display shows the following information:



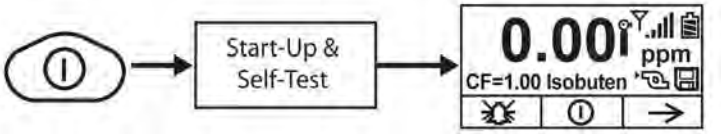
Gas info	Tells the Correction Factor and type of calibration gas
Reading	Concentration of gas as measured by the instrument
Calibration needed	Indicates that calibration should be performed
Radio power	Indicates whether radio connection is on or off
Radio signal	Indicates signal strength in 5-bar bargraph
Battery	Indicates battery level in 3 bars
Pump	Indicates that pump is working
Datalog	Indicates whether datalog is on or off
Y/+	Y/+ key's function for this screen
MODE	MODE key's function for this screen
N/-	N/- key's function for this screen

8 Operating The Instrument

The instrument is designed as a broadband VOC gas monitor and datalogger for work in hazardous environments. It gives real-time measurements and activates alarm signals whenever the exposure exceeds preset limits. Prior to factory shipment, the instrument is preset with default alarm limits and the sensor is pre-calibrated with standard calibration gas. However, you should test the instrument and verify the calibration before the first use. After the instrument is fully charged and calibrated, it is ready for immediate operation.

8.1 Turning The Instrument On (Simple)

1. With the instrument turned off, press and hold [MODE].
2. When the display turns on, release the [MODE] key.

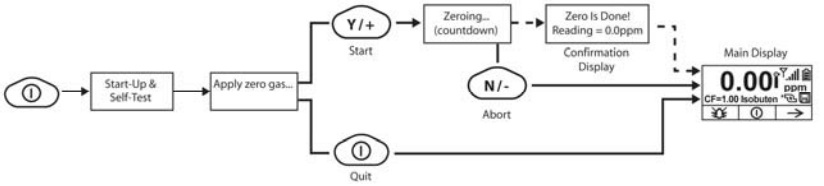


The RAE Systems logo should appear first. (If the logo does not appear, there is likely a problem and you should contact your distributor or RAE Systems Technical Support.) The instrument is now operating and performs self tests. If any tests (including sensor and memory tests) fail, refer to the Troubleshooting section of this guide.

Once the startup procedure is complete, the instrument shows a numerical reading screen with icons. This indicates that the instrument is fully functional and ready to use.

8.2 Turning The Instrument On (Power On Zero)

If your UltraRAE 3000 has been configured to perform a zero (fresh air) calibration upon startup, called Power On Zero, then the startup routine is interrupted so that you can perform a fresh air calibration. (See page 85 for details on turning this feature on or off.)



If you do not want to perform a zero calibration, press [MODE] to bypass it. If you start a zero calibration and want to abort it, press [N/-], and the calibration stops and the main display is shown.

8.3 Turning The Instrument Off

1. Press and hold the Mode key for 3 seconds. A 5-second countdown to shutoff begins.
2. When you see "Unit off..." release your finger from the [MODE] key. The instrument is now off.

Note: You must hold your finger on the key for the entire shutoff process. If you remove your finger from the key during the countdown, the shutoff operation is canceled and the instrument continues normal operation.

8.4 Operating The Built-In Flashlight

The instrument has a built-in flashlight that helps you point the probe in dark places. Press the flashlight key to turn it on. Press it again to turn it off.

Note: Using the flashlight for extended periods shortens the battery's operating time before it needs recharging.

8.5 Pump Status

IMPORTANT!

During operation, make sure the probe inlet and the gas outlet are free of obstructions. Obstructions can cause premature wear on the pump, false readings, or pump stalling. During normal operation, the pump icon alternately shows inflow and outflow as shown here:

During duty cycling (PID lamp cleaning), the display shows these icons in alternation:

If there is a pump failure or obstruction that disrupts the pump, the alarm sounds and you see this icon blinking on and off:

If you see this blinking icon, consult the Troubleshooting section of this guide.

8.6 Calibration Status

The instrument displays this icon if it requires calibration:

Calibration is required (and indicated by this icon) if:

- The lamp type has been changed (for example, from 10.6 eV to 9.8 eV).
- The sensor module has been replaced.
- It has been 30 days or more since the instrument was last calibrated.
- If you have changed the calibration gas type without recalibrating the instrument.

9 Operating Modes

The UltraRAE is actually two monitors in one:

- Compound-specific monitor
- VOC monitor

As a compound-specific monitor, it takes timed measurements and uses a separation tube in conjunction with software that enables the UltraRAE 3000 to give specific readings on one particular type of compound, such as benzene or butadiene.

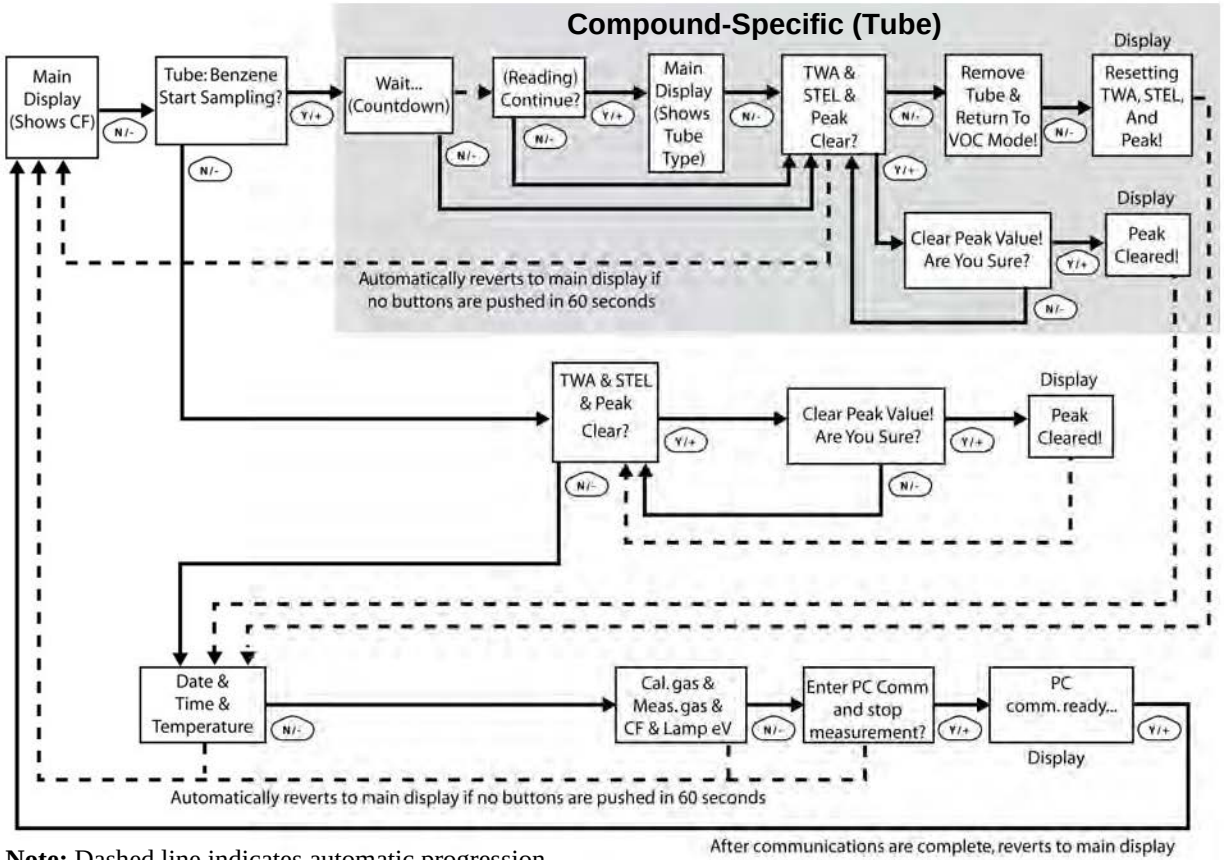
As a VOC monitor, the UltraRAE 3000 operates in different modes. In some cases, you can change modes using a password and using the instrument's navigation. In other cases, you must use ProRAE Studio software.

The following two sections cover operation in the two modes.

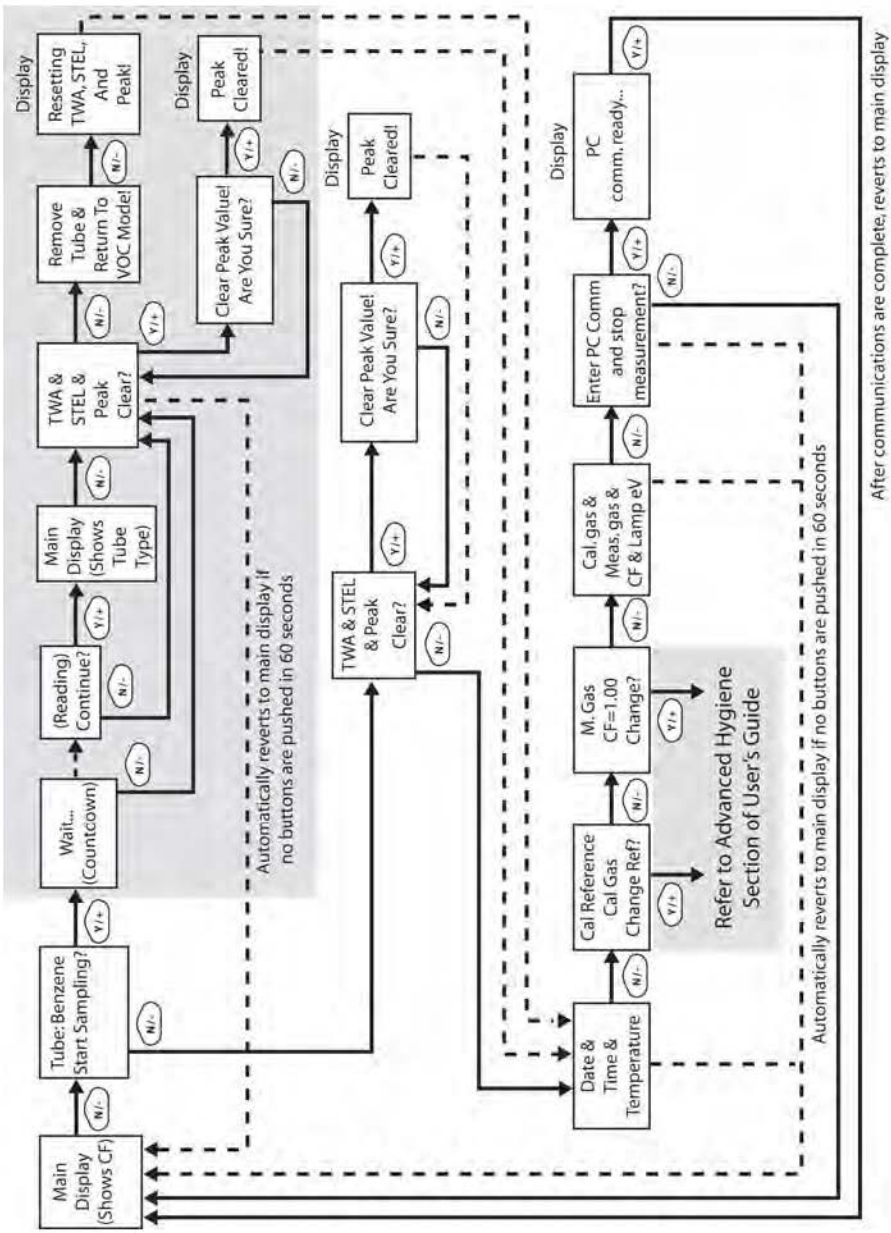
- Compound Specific, 31.
- VOC, page 38.

The diagram on the next page shows the basic flow of the UltraRAE 3000's functions. The area with the gray field is the compound-specific (tube) mode, while the rest shows VOC mode. Navigate through the steps by using the [Y/+] and [N/-] keys as shown in the diagram.

Note: If you use a password to access Programming Mode (see page 60), then the navigation changes slightly, entering part of Advanced Hygiene Mode's settings, as shown on page 29.



Note: Dashed line indicates automatic progression.


Main Display (Shows CF)
Tube: Benzene Start Sampling?
Wait... (Countdown)
(Reading) Continue?
Main Display (Shows Tube Type)
TWA & STEL & Peak Clear?
Remove Tube & Return To VOC Mode!
Display
Resetting TWA, STEL, And Peak!
Clear Peak Value! Are You Sure?
Display
Peak Cleared!
Automatically reverts to main display if no buttons are pushed in 60 seconds
TWA & STEL & Peak Clear?
Clear Peak Value! Are You Sure?
Display
Peak Cleared!
Date & Time & Temperature
Cal Reference Cal Gas Change Ref?
M. Gas CF=1.00 Change?
Cal. gas & Meas. gas & CF & Lamp eV
Enter PC Comm and stop measurement?
Display
PC comm. ready...
Refer to Advanced Hygiene Section of User's Guide
Automatically reverts to main display if no buttons are pushed in 60 seconds
After communications are complete, reverts to main display
Y/+
N/-

The default setting for your instrument is:

User Mode: Basic
Operation Mode: Hygiene

This is outlined in detail on page 88.

The other options, covered later in this guide, are:

User Mode: Advanced (page 92)
Operation Mode: Hygiene

User Mode: Advanced (page 96)
Operation Mode: Search

Using ProRAE Studio allows access to other options. In addition, Diagnostic Mode (page 97) is available for service technicians.

10 Compound-Specific Operation

10.1 Compound-Specific Measurement

The UltraRAE 3000 can perform compound-specific measurement in addition to general VOC measurement. This requires using a RAE-Sep separation tube (butadiene or benzene) and having the UltraRAE 3000 in Tube Mode, operating with a 9.8eV lamp.

10.2 Measurement Phases

To perform a compound-specific measurement, follow this order:

1. UltraRAE 3000 is ready for sampling
2. Prepare the separation tube
3. Insert the separation tube
4. Start measurement
5. UltraRAE 3000 displays and logs measurement
6. Remove the separation tube

10.3 Performing A Measurement

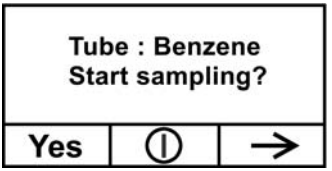
Before performing a compound-specific measurement for Benzene or Butadiene using a RAE-Sep separation tube, make sure the UltraRAE 3000 is in Tube Mode and that the appropriate tube type is selected. The UltraRAE 3000 only acts as a compound-specific measurement device when it is equipped with a 9.8eV lamp. The UltraRAE 3000 is designed to auto-sense the lamp type. It can also be manually set to default to a 9.8eV lamp type.

Make sure the UltraRAE 3000 is set to operate with your selected tube:

1. Enter Programming Mode.
2. Select Measurement.
3. Select Tube Selection.
4. Make a choice of Benzene or Butadiene.
5. Save your choice.

To begin measuring, turn on the UltraRAE 3000. This screen is shown, which includes the CF (correction factor) and measurement gas type for calibration reference:

Press [N/-] to advance. You will see this screen:



Do not begin sampling yet!

Before you start sampling, you must insert a RAE-Sep separation tube into the inlet/holder. Follow the Separation Tube Preparation and Placing A Tube Into The UltraRAE 3000 instructions before pressing any buttons on the UltraRAE 3000. Once the tube is in place, then proceed to measuring.

IMPORTANT!

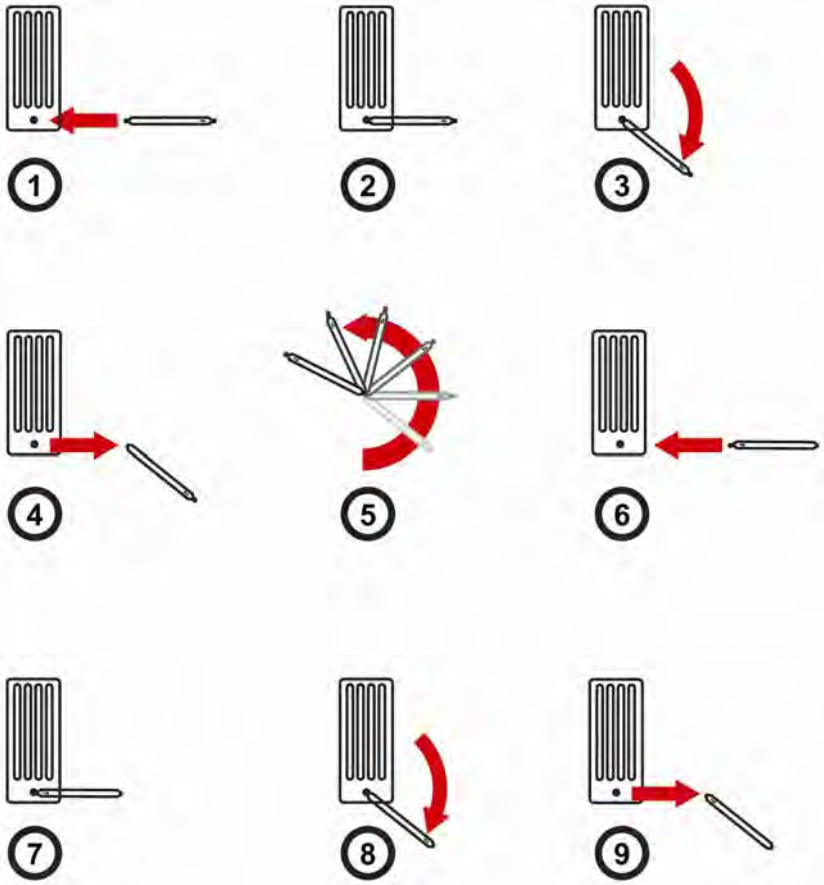
Once a tube's ends are broken off, the material inside is exposed. Therefore, use the tube for sampling as soon as possible.

10.4 Separation Tube Preparation

CAUTION!

Wear hand and eye protection when breaking tube tips. Use caution in handling tubes with broken ends. Keep away from children. RAE-Sep tubes should be disposed of according to local regulations. See footnotes of data sheets for disposal information.

1. Open a package of RAE-Sep separation tubes and remove one.
2. Place the tip in the package's tube tip breaker (the small hole on the front) and snap off the tip.
3. Turn the tube around and snap off the other end.

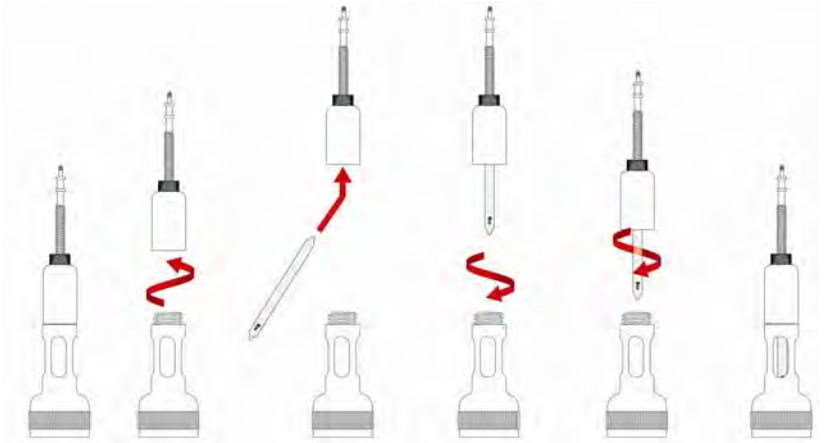


CAUTION!

Handle tubes with care. Tube ends are sharp after ends are broken off.

10.5 Inserting The Separation Tube

1. Unscrew the front of the sampling probe from the base.
2. Slip the tube into the rubber holder in the front portion. Make sure the arrow on the side of the tube points toward the instrument.
3. Insert the other end of the tube into the middle of the base while turning the front portion to tighten it onto the base's threads.



IMPORTANT!

Do not overtighten any portion of the sampling assembly.

Note: When the UltraRAE 3000 is used for VOC monitoring, no tube is inserted.

IMPORTANT!

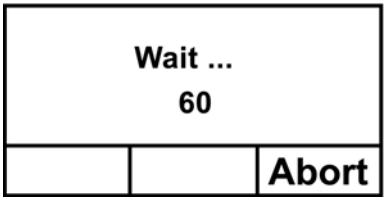
To ensure that there are no leaks, periodically test the seals:

With the UltraRAE 3000 running, place your finger over the end of the inlet probe. The alarm should sound and the pump-stall icon should flash on the display. This indicates that all seals are good. Stop the alarm by pressing [Y/+]. If the pump does not alarm or show the stalled-pump icon, then check that all inlet parts are tight and inspect the O-ring for damage (replace it if necessary).

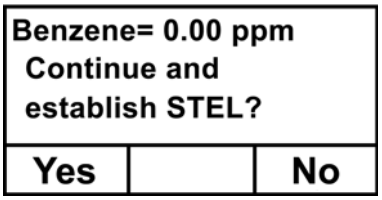
10.6 Measuring

Once the tube is in place, begin measuring by pressing [Y/+].

The display shows a countdown (60 seconds is shown here, but sampling time depends on the type of separation tube selected and the temperature):



Note: You can abort the sampling by pressing [N/-] at any time. Once the countdown is complete, the reading is shown:

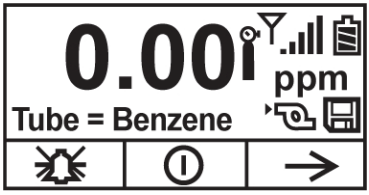


Press [Y/+] to continue sampling with the tube for 15 minutes to establish a STEL reading, or press [N/-] to return to the main menu.

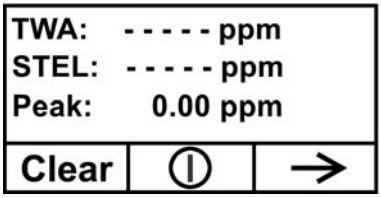
WARNING!

At least 1/4 of the tube should still be yellow-orange at the bottom. If not, the STEL value is not valid. Abort the measurement and change the tube. Then do a snapshot test instead of a STEL test. **Note:** If the STEL is exceeded, the UltraRAE 3000 goes into alarm.

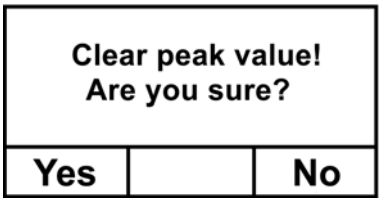
If you press [N/-] to return to the main menu, which shows the tube type instead of the CF (correction factor):



Press [N/-] to advance to this screen:

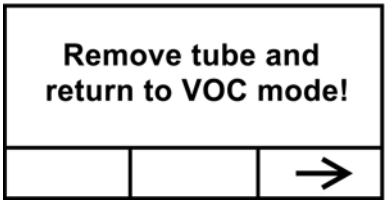


If you press [Y/+], you are asked, "Clear peak value! Are You Sure?" to confirm:

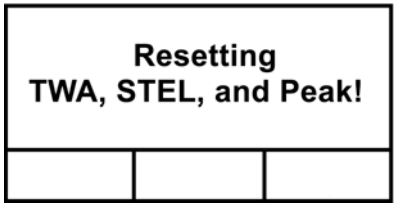


Press [Y/+] to clear the Peak value and exit to VOC operation.

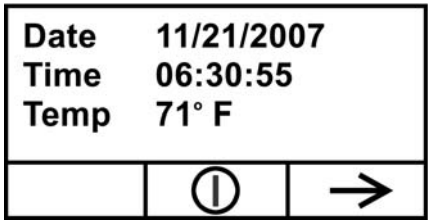
If you press [N/-], this display is shown:



Remove the tube and put the inlet back together. Then press [N/-]. This display is shown:



After a few seconds, the UltraRAE 3000 enters VOC mode and shows this display:



You can step through the rest of the steps by pressing [N/-] repeatedly until you reach the main menu again.

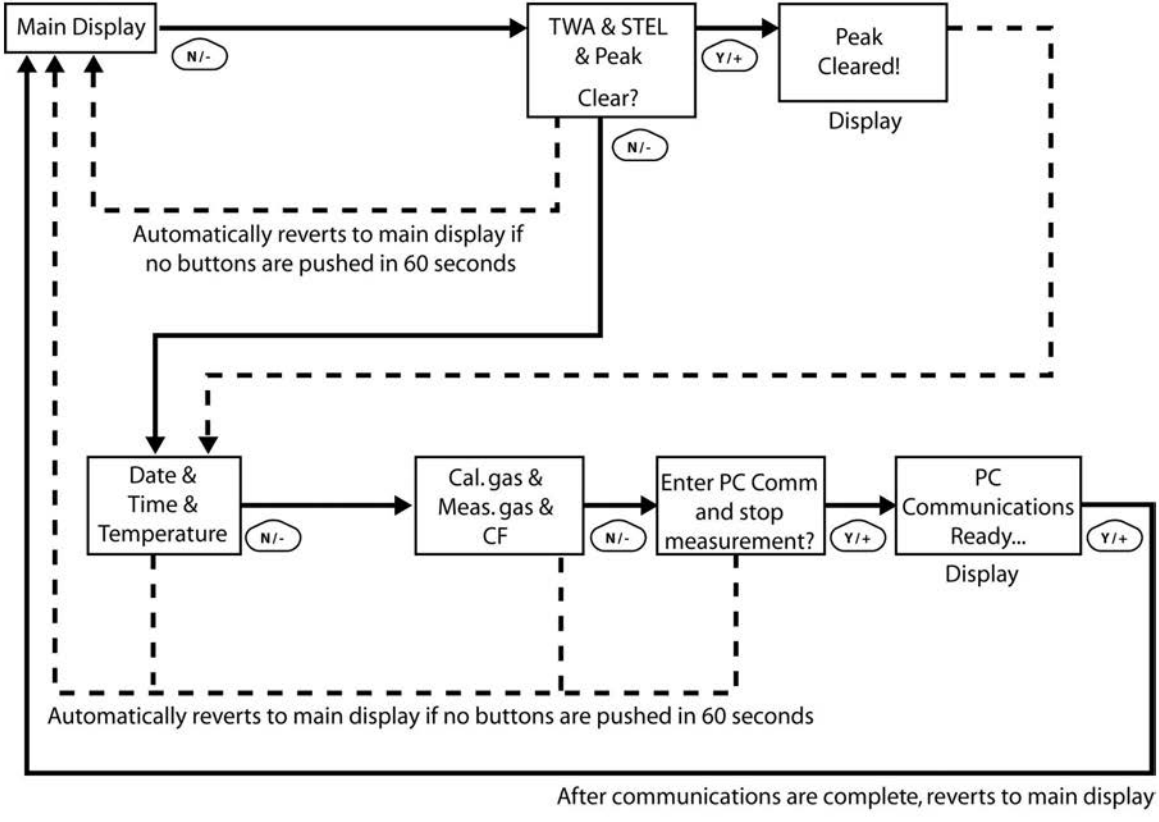
11 VOC Operation

11.1 Basic User Level/Hygiene Mode (Default Settings)

The instrument is programmed to operate in Basic User Level/Hygiene Mode as its default. This gives you the most commonly needed features while requiring the fewest parameter adjustments.

Pressing [N/-] steps you from one screen to the next, and eventually return to the main display. If you do not press a key within 60 seconds after entering a display, the instrument reverts to its main display.

Note: While viewing any of these screens, you can shut off your instrument by pressing [MODE].



Note: Dashed line indicates automatic progression.

After the instrument is turned on, it runs through the start-up menu. If the UltraRAE 3000 is set for "Power On Zero," then the message "**Apply zero gas…**" is displayed.

At this point, you can perform a zero air (fresh air) calibration. If the ambient air is clean, you can use that. Otherwise, use a cylinder of zero air. Refer to Zero Calibration on page 51 for a more detailed description of zero calibration.

Start zero calibration by pressing Start [Y/+]. You see the message "Zeroing…" followed by a 30-second countdown.

Note: You can press [MODE] to quit, bypassing the zero air calibration.

When zero calibration is complete, you see the message:

Zeroing is done!

Reading = 0.0 ppm

The instrument is now sampling and collecting data.

Note: At the Average & Peak, Date & Time & Temperature, Calibration Gas & Measurement Gas & Correction Factor, and PC Communications screens, the instrument automatically goes to the main display after 60 seconds if you do not push a key to make a selection.

12 Alarm Signals

During each measurement period, the gas concentration is compared with the programmed alarm limits (gas concentration alarm limit settings). If the concentration exceeds any of the preset limits, the loud buzzer and red flashing LED are activated immediately to warn you of the alarm condition.

In addition, the instrument alarms if one of the following conditions occurs: battery voltage falls below a preset voltage level, failure of the UV lamp, or pump stall.

12.1 Alarm Signal Summary

Message	Condition	Alarm Signal
HIGH	Gas exceeds "High Alarm" limit	3 beeps/flashes per second*
OVR	Gas exceeds measurement range	3 beeps/flashes per second*
MAX	Gas exceeds electronics' maximum range	3 beeps/flashes per second*
LOW	Gas exceeds "Low Alarm" limit	2 beeps/flashes per second*
TWA	Gas exceeds "TWA" limit	1 Beep/flash per second*
STEL	Gas exceeds "STEL" limit	1 Beep/flash per second*
Pump icon flashes	Pump failure	3 beeps/flashes per second
Lamp	PID lamp failure	3 beeps/flashes per second plus "Lamp" message on display
Battery icon flashes	Low battery	1 flash, 1 beep per minute plus battery icon flashes on display
CAL	Calibration failed, or needs calibration	1 beep/flash per second
NEG	Gas reading measures less than number stored in calibration	1 beep/flash per second

* Hygiene mode only. In Search mode, the number of beeps per second (1 to 7) depends upon the concentration of the sampled gas. Faster rates indicate higher concentrations.

12.2 Preset Alarm Limits & Calibration

The instrument is factory calibrated with standard calibration gas, and is programmed with default alarm limits.

Cal Gas	Cal Span	unit	Low	High	TWA	STEL
Isobutylene	100	ppm	50	100	10	25
Benzene	5	ppm	2	5	0.5	2.5
Butadiene	10	ppm	10	5	2	5

12.3 Testing The Alarm

You can test the alarm whenever the main (Reading) display is shown. Press [Y/+], and the audible and visible alarms are tested.

13 Integrated Sampling Pump

The instrument includes an integrated sampling pump. This diaphragm-type pump that provides a 450 to 550 cc per minute flow rate. Connecting a Teflon or metal tubing with 1/8" inside diameter to the gas inlet port of the instrument, this pump can pull in air samples from 200' (61 m) away horizontally, or 90' (27.5 m) vertically, at about 3' (0.9 m) per second flow speed.

Note: In Search Mode, the pump turns on when a sample measurement is started, and turns off when the sample is manually stopped.

If liquid or other objects are pulled into the inlet port filter, the instrument detects the obstruction and immediately shuts down the pump. The alarm is activated and a flashing pump icon is displayed.

You should acknowledge the pump shutoff condition by clearing the obstruction and pressing the [Y/+] key while in the main reading display to restart the pump.

14 Backlight

The LCD display is equipped with an LED backlight to assist in reading the display under poor lighting conditions.

15 Datalogging

During datalogging, the instrument displays a disk icon to indicate that datalogging is enabled. The instrument stores the measured gas concentration at the end of every sample period (when data logging is enabled). In addition, the following information is stored: user ID, site ID, serial number, last calibration date, and alarm limits. All data are retained (even after the unit is turned off) in non-volatile memory so that it can be down- loaded at a later time to a PC.

15.1 Datalogging Event

When Datalogging is enabled, measurement readings are being saved. These data are stored in "groups" or "events." A new event is created and stored each time the instrument is turned on and is set to automatic datalogging, or a configuration parameter is changed, or datalogging is interrupted. The maximum time for one event is 24 hours or 28,800 points. If an event exceeds 24 hours, a new event is automatically created. Information, such as start time, user ID, site ID, gas name, serial number, last calibration date, and alarm limits are recorded.

15.2 Datalogging Sample

After an event is recorded, the unit records a shorter form of the data. When transferred to a PC running ProRAE Studio, this data is arranged with a sample number, time, date, gas concentration, and other related information.

15.3 Auto/Manual/Snapshot Datalogging

The instrument has three datalog types:

Auto	Default mode. Collects datalog information when the instrument is sampling.
Manual	Datalogging occurs only when the instrument's datalogging is manually started (see page 63 for details).
Snapshot	Datalogs only during snapshot (single-event capture, initiated by pressing [MODE]) sampling. See page 65 for details.

Note: You can only choose one datalog type to be active at a time.

16 Accessories

The following accessories are included with the instrument:

- AC Adapter (Battery Charger)
- Travel Charger
- Alkaline battery adapter
- External Filter
- Organic Vapor Zeroing kit

Hard-case kits also include these accessories:

- Calibration gas, if specified
- Calibration adapter
- Calibration regulator and flow controller
- Charging Cradle (instead of Travel Charger)

17 Standard Kit & Accessories

17.1 AC Adapter (Battery Charger)

WARNING

To reduce the risk of ignition of hazardous atmospheres, recharge battery only in area known to be non-hazardous. Remove and replace battery only in area known to be non-hazardous.

Ne charger les batteries que dans emplacements designés non-dangereuses.

A battery charging circuit is built into the instrument cradle. It only needs a regular AC to 12 VDC adapter (wall-mount transformer, part number 500-0114-000) to charge the instrument.

To charge the battery inside the instrument:

1. Power off the instrument.
2. Connect the AC adapter to the DC jack on the instrument's cradle. If the instrument is off, it automatically turns on.
3. While charging, the display message shows "Charging." The Primary LED on the cradle flashes green when charging.
4. When the battery is fully charged, the LED changes to glowing green continuously, and the message "Fully charged" appears on the display. If there is a charging error, the LED glows red continuously.

A completely discharged instrument can be charged to full capacity within 8 hours. Batteries drain slowly even if an instrument is off. Therefore, if the instrument has been in storage or has not been charged for several days or longer, check the charge before using it.

The factory-supplied battery is designed to last for 16 hours of normal operation (no alarm), for a new battery under the optimum circumstances. As the battery becomes older or is subject to adverse conditions (such as cold ambient temperature), its capacity will be significantly reduced.

17.2 External Filter

The external filter is made of PTFE (Teflon®) membrane with a 0.45 micron pore size to prevent dust or other particles from being sucked into the sensor manifold, which would cause extensive damage to the instrument. It prolongs the operating life of the sensor. To install the external filter, simply connect it to the instrument's inlet probe.

18 Optional Accessories

18.1 Calibration Adapter

The calibration adapter for the instrument is a simple 6-inch Tygon tubing with a metal adapter on one end. During calibration, simply insert the metal adapter into the regular gas inlet probe of the instrument and the tubing to the gas regulator on the gas bottle.

18.2 Calibration Regulator

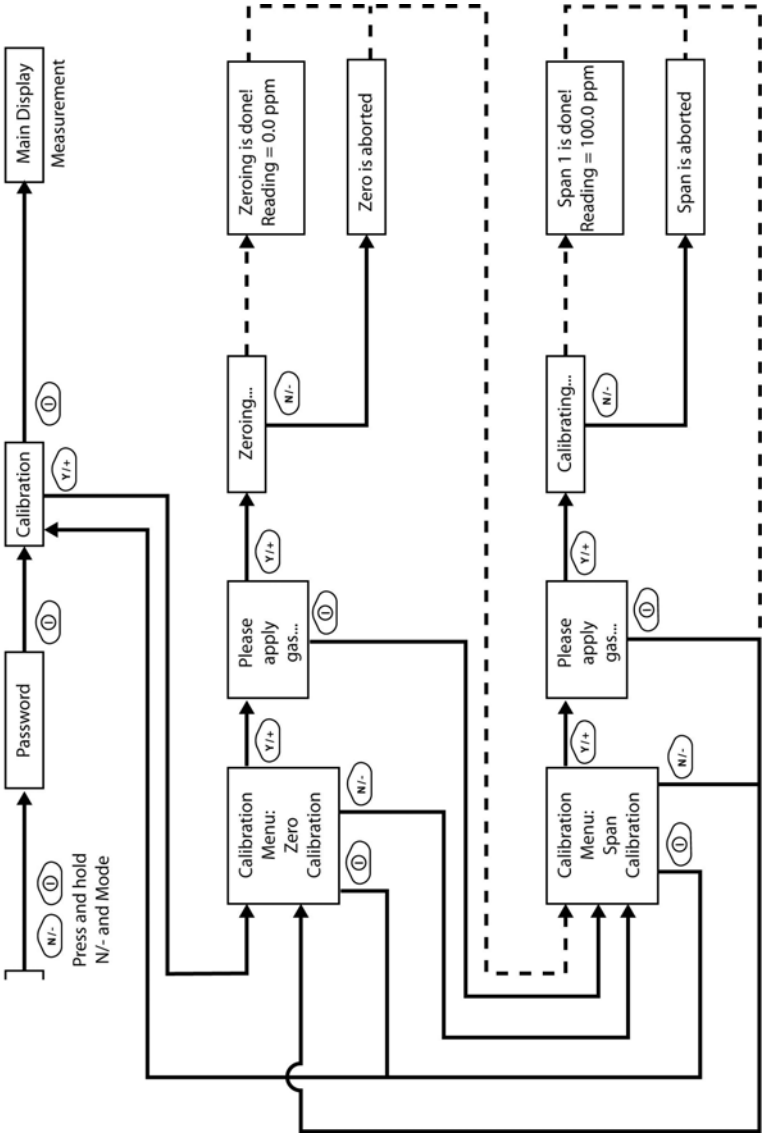
The Calibration Regulator is used in the calibration process. It regulates the gas flow rate from the Span gas cylinder into the gas inlet of the instrument during calibration process. The maximum flow rate allowed by the flow controller is about 0.5L/min (500 cc per min.). Alternatively, a demand-flow regulator or a Tedlar gas bag may be used to match the pump flow precisely.

18.3 Organic Vapor Zeroing Kit

The Organic Vapor Zeroing Kit is used for filtering organic air contaminants that may affect the zero calibration reading. To use the Organic Vapor Zeroing Kit, simply connect the filter to the inlet port of the instrument.

19 Standard Two-Point Calibration (Zero & Span)

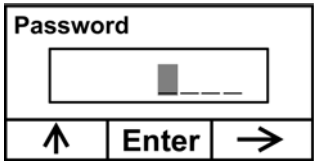
The following diagram shows the instrument's calibrations in Basic/Hygiene mode.



Note: Dashed line indicates automatic progression.

19.1 Entering Calibration

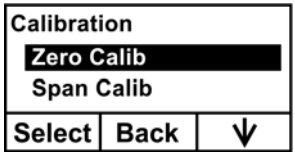
1. Press and hold [MODE] and [N/-] until you see the Password screen.



2. In Basic User Level, you do not need a password to perform calibrations. Instead of inputting a password, enter calibration by pressing [MODE].

   Note: If you inadvertently press [Y/+] and change any of the numbers, simply press [MODE] and you will be directed to the calibration menu.

The Calibration screen is now visible with Zero Calibration highlighted.



These are your options:

- Press [Y/+] to select the highlighted calibration (Zero Calib or Span Calib).
- Press [MODE] to exit calibration and return to the main display and resume measurement.
- Press [N/-] to toggle the highlighted calibration type.

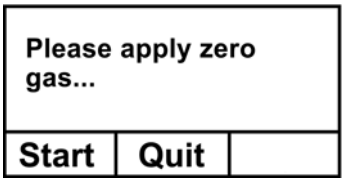
19.2 Zero (Fresh Air) Calibration

This procedure determines the zero point of the sensor calibration curve. To perform a fresh air calibration, use the calibration adapter to connect the instrument to a "fresh" air source such as from a cylinder or Tedlar bag (optional accessory). The "fresh" air is clean, dry air without organic impurities and an oxygen value of 20.9%. If such an air cylinder is not available, any clean ambient air without detectable contaminants or a charcoal filter can be used.

At the Zero Calibration menu, you can proceed to perform a Zero calibration or bypass Zero calibration and perform a Span calibration. You may also go back to the initial Calibration menu if you want to exit calibration.

- Press [Y/+] to start calibration.
- Press [MODE] to quit and return to the main calibration display.

If you have pressed [Y/+] to enter Zero calibration, then you will see this message:



1. Turn on your Zero calibration gas.
2. Press [Y/+] to start calibration.

   Note: At this point, you may press [MODE] if you decide that you do not want to initiate calibration. This will take you directly to the Calibration menu, highlighted for Span calibration.

3. Zero calibration starts a 30-second countdown and displays this message:

   Zeroing...

During the zeroing process, the instrument performs the Zero calibration automatically and does not require any action on your part.

Note: To abort the zeroing process at any time and proceed to Span calibration, press [N/-] at any time while zeroing is being performed. You will see a confirmation message that says "Zero aborted!" and then the Span calibration menu appears.

When Zero calibration is complete, you see this message:

Zeroing is done!
Reading = 0.0 ppm

The instrument will then show the Calibration menu on its display, with Span Calib highlighted.

19.3 Span Calibration

This procedure determines the second point of the sensor calibration curve for the sensor. A cylinder of standard reference gas (span gas) fitted with a 500 cc/min. flow-limiting regulator or a flow-matching regulator is the simplest way to perform this procedure. Choose the 500 cc/min. regulator only if the flow rate matches or slightly exceeds the flow rate of the instrument pump. Alternatively, the span gas can first be filled into a Tedlar bag or delivered through a demand-flow regulator. Connect the calibration adapter to the inlet port of the instrument, and connect the tubing to the regulator or Tedlar bag.

Another alternative is to use a regulator with >500 cc/min flow but allow the excess flow to escape through a T or an open tube. In the latter method, the span gas flows out through an open tube slightly wider than the probe, and the probe is inserted into the calibration tube.

At the Span Calibration menu, you perform a Span calibration. You may also go back to the Zero calibration menu or to the initial Calibration menu if you want to exit calibration.

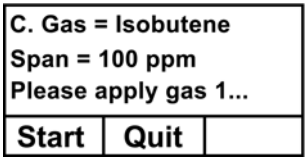
- Press [Y/+] to enter Span calibration.
- Press [N/-] to skip Span calibration and return to Zero calibration.
- Press [MODE] to exit Span calibration and return to the top calibration menu.

If you have pressed [Y/+] to enter Span calibration, then you will see the name of your Span gas (the default is isobutylene) and the span value in parts per million (ppm).

IMPORTANT!

If you are using the UltraRAE 3000 to test for benzene, it is recommended that you calibrate with 5 ppm benzene calibration gas from RAE Systems.

You will also see this message that prompts you:



1. Turn on your span calibration gas.
2. Press [Y/+] to initiate calibration.

   Note: You may press [MODE] if you decide that you do not want to initiate calibration. This will abort the span calibration and take you directly to the Calibration menu for Zero calibration.

3. Span calibration starts and displays this message:

   Calibrating...

During the Span calibration process, there is a 30-second countdown and the instrument performs the Span calibration automatically. It requires no actions on your part.

Note: If you want to abort the Span calibration process, press [N/-] at any time during the process. You will see a confirmation message that says "Span is aborted!" and then the Zero calibration menu appears. You can then proceed to perform a Zero calibration, perform a Span calibration, or exit to the topmost Calibration menu.

When Span calibration is complete, you see a message similar to this (the value is an example only):

Span 1 is done!
Reading = 100.0 ppm

The instrument then exits Span calibration and shows the Zero calibration menu on its display.

Note: The reading should be very close to the span gas value.

19.4 Exiting Two-Point Calibration In Basic User Level

When you are done performing calibrations, press [MODE], which corresponds with "Back" on the display. You will see the following message:

Updating settings…

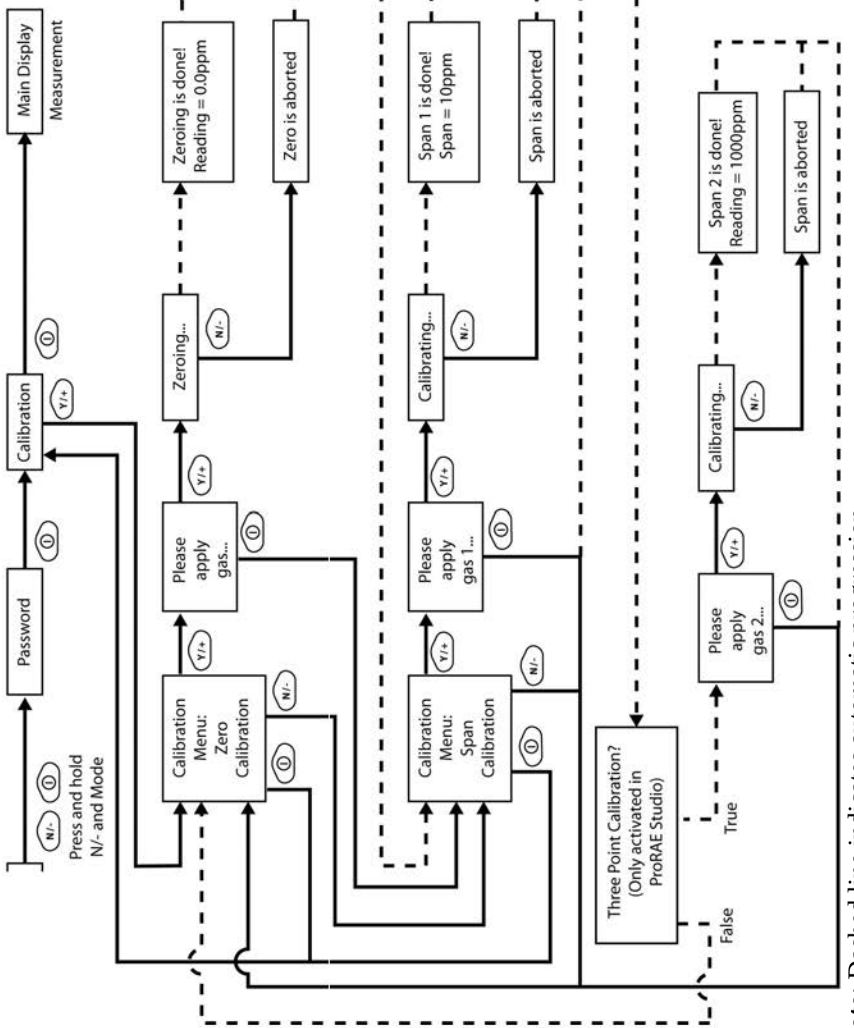
The instrument updates its settings and then returns to the main display. It begins or resumes monitoring.

20 Three-Point Calibration

For enhanced accuracy, it is possible to perform a second Span calibration in addition to the Zero and Span calibrations outlined in the previous section. Your instrument first must be set to allow this third calibration. This requires using ProRAE Studio software and a PC, as well as a higher concentration of calibration gas.

Note: Once the third calibration is set, you do not need to use ProRAE Studio to allow future 3-point calibrations. Also, you can only disable 3-point calibration capability by using ProRAE Studio again.

Perform the Zero and Span calibrations. After the first Span calibration (Span 1) is completed, the display a second Span calibration (Span 2) can be performed. The process is identical to the first calibration. As in the Span 1 calibration, you may exit and return to the Zero calibration screen if you choose not to perform this calibration or to abort it.



Note: Dashed line indicates automatic progression.

20.1 Span 2 Calibration

A cylinder of standard reference gas (span gas) fitted with a 500 cc/min. flow-limiting regulator or a flow-matching regulator is the simplest way to perform this procedure.

Note: This gas should be of a higher concentration than the gas used for Span 1 calibration.

Choose the 500 cc/min. regulator only if the flow rate matches or slightly exceeds the flow rate of the instrument pump. Alternatively, the span gas can first be filled into a Tedlar bag or delivered through a demand-flow regulator. Connect the calibration adapter to the inlet port of the instrument, and connect the tubing to the regulator or Tedlar bag.

Another alternative is to use a regulator with >500 cc/min flow but allow the excess flow to escape through a T or an open tube. In the latter method, the span gas flows out through an open tube slightly wider than the probe, and the probe is inserted into the calibration tube.

At the Span Calibration menu, you perform a Span calibration. You may also go back to the Zero calibration menu or to the initial Calibration menu if you want to exit calibration.

- Press [Y/+] to enter Span 2 calibration.
- Press [N/-] to skip Span calibration and return to Zero calibration.
- Press [MODE] to exit Span calibration and return to the top calibration menu.

If you have pressed [Y/+] to enter Span calibration, then you will see the name of your Span gas (the default is isobutylene) and the span value in parts per million (ppm). You will also see this message that prompts you:

Please apply gas...

4. Turn on your span calibration gas.

5. Press [Y/+] to initiate calibration.

   Note: You may press [MODE] if you decide that you do not want to initiate calibration. This will take you directly to the Calibration menu for Zero calibration.

6. Span calibration starts a 30-second countdown and displays this message:

   Calibrating...

During the Span calibration process, the instrument performs the Span calibration automatically and does not require any action on your part.

Note: If you want to abort the Span calibration process, press [N/-] at any time during the process. You will see a confirmation message that says "Span is aborted!" and then the Zero calibration menu will appear. You can then proceed to perform a Zero calibration, perform a Span calibration, or exit to the topmost Calibration menu.

When Span calibration is complete, you will see a message similar to this (the value shown here is for example only):

Span 2 is done!
Reading = 1000 ppm

The instrument then exits Span calibration and shows the Zero calibration menu on its display.

Note: The reading should be very close to the span gas value.

20.2 Exiting Three-Point Calibration

When you are done performing calibrations, press [MODE], which corresponds with "Back" on the display. You will see the following message:

Updating settings…

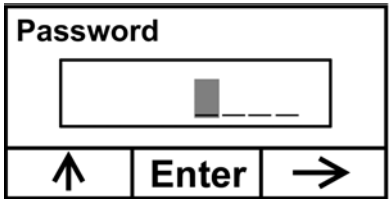
The instrument updates its settings and then returns to the main display. It begins or resumes monitoring.

21 Programming Mode

Programming Mode can be entered from either Hygiene Mode or Search Mode. If the current user mode is Basic, you must provide a 4-digit password to enter.

21.1 Entering Programming Mode

1. Press and hold [MODE] and [N/-] until you see the Password screen.



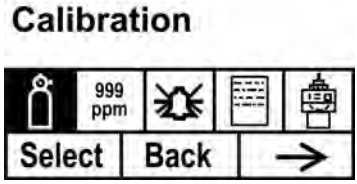
2. Input the 4-digit password:

- Increase the number from 0 through 9 by pressing [Y/+].
- Step from digit to digit using [N/-].
- Press [MODE] when you are done.

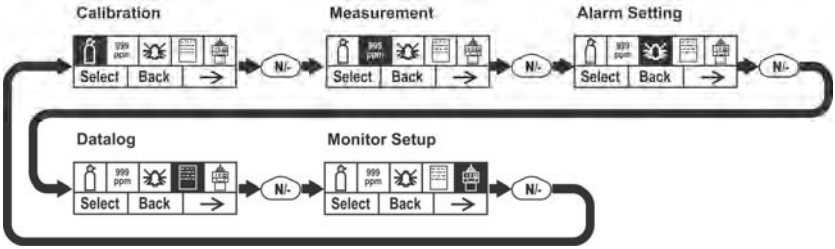
If you make a mistake, you can cycle through the digits by pressing [N/-] and then using [Y/+] to change the number in each position.

Note: The default password is 0000.

When you have successfully entered Programming Mode, you see this screen:



Note: The password can only be changed by connecting the instrument to a PC running ProRAE Studio software. Follow the instructions in ProRAE Studio to change it.The Calibration label is shown and its icon is highlighted, but you can press [N/-] to step from one programming menu to the next, with the name of the menu shown at the top of the display and the corresponding icon highlighted. As you repeatedly press [N/-], the selection moves from left to right, and you see these screens:



Note: When you reach Monitor Setup and press [N/-], the menu cycles back to Calibration.

22 Programming Mode Menus

The Programming Mode allows anyone with the password to change the instrument's settings, calibrate the instrument, modify the sensor configuration, enter user information, etc. Programming Mode has five menus. Each menu includes several sub-menus to perform additional programming functions.

This table shows the menus and sub-menus:

Calibration	**Measurement**	**Alarm Setting**	**Datalog**	**Monitor Setup**
Zero Calibration	Meas. Gas	High Alarm	Clear Datalog	Radio Power
Span Calibration	Meas. Unit	Low Alarm	Interval	Op Mode
	Tube Selection	STEL Alarm	Data Selection	Site ID
		TWA Alarm	Datalog Type	User ID
		Alarm Mode		User Mode
		Buzzer & Light		Date
				Time
				Pump Duty Cycle
				Pump Speed
				Temperature Unit
				Language
				Real Time Protocol
				Power On Zero
				Unit ID
				LCD Contrast
				Lamp ID

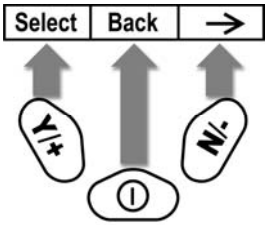
Once you enter Programming Mode, the LCD displays the first menu, Calibration. Each subsequent menu is accessed by pressing [N/-] repeatedly until the desired menu is displayed. To enter a sub-menu of a menu, press [Y/+].

22.1 Exiting Programming Mode

To exit Programming Mode and return to normal operation, press [MODE] once at any of the programming menu displays. You will see "Updating Settings…" as changes are registered and the mode changes.

22.2 Navigating Programming Mode Menus

Navigating through the Programming Mode menus is easy and consistent, using a single interface format of "Select," "Back" and "Next" at the top level. The three control buttons correspond to these choices as shown:



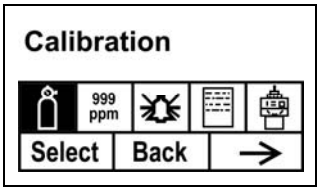
Note: Pressing [MODE] in the Programming Mode's top level causes the instrument to exit Programming Mode and return to monitoring.

The three keys perform the following functions in Programming Mode:

Key	Function in Programming Mode
[MODE]:	Exit menu when pressed momentarily or exit data entry mode
[Y/+]:	Increase alphanumerical value for data entry or confirm (yes) for a question
[N/-]:	Provides a "no" response to a question

22.3 Calibration

Two types of calibration are available: Zero (fresh air) and Span.



Select Zero or Span Calibration by pressing [N/+]. Once your choice is highlighted, press [Y/+].

22.3.1 Zero Calibration

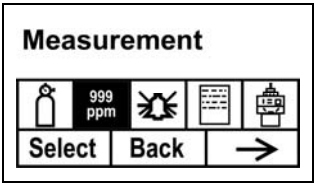
The procedure for performing a zero calibration is covered on page 49.

22.3.2 Span Calibration

The procedure for performing a basic span calibration is covered on page 49.

22.4 Measurement

The sub-menus for Measurement are Measurement Gas and Measurement Unit.



22.4.1 Meas. Gas

Measurement gases are organized in four lists:

- My List is a customized list of gases that you create. It contains a maximum of 10 gases and can only be built in ProRAE Studio on a PC and transferred to the instrument. **Note:** The first gas in the list is always isobutylene (it cannot be removed from the list).
- Last Ten is a list of the last ten gases used by your instrument. The list is built automatically and is only updated if the gas selected from Custom Gases or Library is not already in the Last Ten. This ensures that there is no repetition.
- Gas Library is a library that consists of many of the gases found in RAE Systems' Technical Note TN-106 (available online at www.raesystems.com).
- Custom Gases are gases with user-modified parameters. Using ProRAE Studio, all parameters defining a gas can be modified, including the name, span value(s), correction factor, and default alarm limits.

1. Scroll through each list by pressing [N/-].
2. Press [Y/+] to select one (My List, Last Ten, Gas Library, or Custom Gases).

3. Once you are in one of the categories, press [N/-] to scroll through its list of options and [Y/+] to select one. (If you press [MODE], you exit to the next submenu.)
4. Press [Y/+] to save your choice or [N/-] to undo your selection.

Leave the sub-menu and return to the Programming Mode menus by pressing [MODE].

22.4.2 Meas. Unit

Standard available measurement units include:

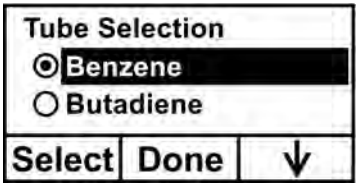
Abbreviation	Unit	UltraRAE 3000
ppm	parts per million	Yes
ppb	parts per billion	
mg/m3	milligrams per cubic meter	Yes
ug/m3	micrograms per cubic meter	

- Scroll through the list by pressing [N/-].
- Select by pressing [Y/+].
- Save your selection by pressing [Y/+] or undo your selection by pressing [N/-].

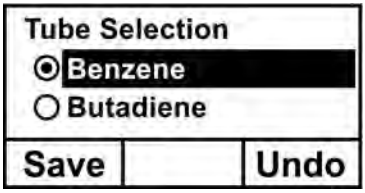
Leave the sub-menu and return to the Programming Mode menus by pressing [MODE].

22.4.3 Tube Selection

When operating the UltraRAE 3000 in Compound Specific mode, the internal computer works most effectively when it is told which type of separation tube is being used.



1. Scroll through the menu by pressing [N/-].
2. Press [Y/+] to make a selection.
3. Press [MODE] when you are done.
4. Press [Y/+] to save your choice or [N/-] to undo your selection.

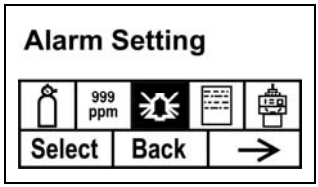


22.5 Alarm Setting

During each measurement period, the gas concentration is compared with the programmed alarm limits (gas concentration alarm limit settings: Low, High, TWA and STEL). If the concentration exceeds any of the preset limits, the loud buzzer and red flashing LED are activated immediately to warn of the alarm condition.

An alarm signal summary is shown on page 42.

In this menu, you can change the High and Low alarm limits, the STEL limit, and the TWA. Press [Y/+] to to enter the Alarm Setting menu. **Note:** All settings are shown in ppb (parts per billion), or µg/m^3 (micrograms per cubic meter), depending on your setting.



1. Scroll through the Alarm Limit sub-menu using the [N/-] key until the display shows the desired limit to be changed (High Alarm, Low Alarm, STEL Alarm, and TWA Alarm)
2. Press [Y/+] to select one of the alarm types. The display shows a flashing cursor on the left-most digit of the previously stored alarm limit.
3. Press [Y/+] to increase each digit's value.
4. Press [N/-] to advance to the next digit.
5. Again, use [Y/+] to increase the number.

Repeat this process until all numbers are entered.

Press [MODE] when you are done.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

When all alarm types have been changed or bypassed, press [MODE] to exit to the Programming Menu.

22.5.1 High Alarm

You can change the High Alarm limit value. The value is typically set by the instrument to match the value for the current calibration gas. It is expressed in parts per billion (ppb). **Note:** The default value depends on the measurement gas.

To change the High Alarm value:

1. Press [Y/+] to increase each digit's value.
2. Press [N/-] to advance to the next digit.
3. Again, use [Y/+] to increase the number.

Repeat this process until all numbers are entered.
When you have completed your selections, press [MODE]. You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

Press [Y/+] to save the changes.
Press [N/-] to undo the changes and revert to the previous settings.

22.5.2 Low Alarm

You can change the Low Alarm limit value. The value is typically set by the instrument to match the value for the current calibration gas. It is expressed in parts per billion (ppb). **Note:** The default value depends on the measurement gas.

To change the Low Alarm value:

1. Press [Y/+] to increase each digit's value.
2. Press [N/-] to advance to the next digit.
3. Again, use [Y/+] to increase the number.

Repeat this process until all numbers are entered.

When you have completed your selections, press [MODE]. You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

22.5.3 STEL Alarm

You can change the STEL Alarm limit value. The value is typically set by the instrument to match the value for the calibration gas. It is expressed in parts per billion (ppb). **Note:** The default value depends on the measurement gas.

To change the STEL Alarm value:

1. Press [Y/+] to increase each digit's value.
2. Press [N/-] to advance to the next digit.
3. Again, use [Y/+] to increase the number.

Repeat this process until all numbers are entered.

When you have completed your selections, press [MODE]. You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

22.5.4 TWA Alarm

You can change the TWA (time-weighted average) Alarm limit value. The value is typically set by the instrument to match the value for the calibration gas. It is expressed in parts per billion (ppb). **Note:** The default value depends on the measurement gas.

To change the TWA Alarm value:

1. Press [Y/+] to increase each digit's value.
2. Press [N/-] to advance to the next digit.
3. Again, use [Y/+] to increase the number.

Repeat this process until all numbers are entered.

When you have completed your selections, press [MODE]. You will see two choices:

- Save
- Undo

You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

22.5.5 Alarm Mode

There are two selectable alarm modes:

Latched	When the alarm is triggered, you can manually stop the alarm. The latched setting only controls alarms for High Alarm, Low Alarm, STEL Alarm, and TWA alarm. **Note:** To clear an alarm when the instrument is set to "Latched," press [Y/+] when the main (Reading) display is shown.
Automatic Reset	When the alarm condition is no longer present, the alarm stops and resets itself.

1. Press **[N/-]** to step from one alarm mode to the other.
2. Press **[Y/+]** to select an alarm mode.

When you have completed your selections, press [MODE].

You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

22.5.6 Buzzer & Light

The buzzer and light alarms can be programmed to be on or off individually or in combination. Your choices are:

- Both on
- Light only
- Buzzer only
- Both off

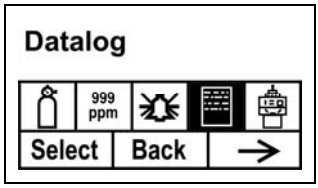
1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates your selection).
3. When you have completed your selections, press [MODE].

   You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

   - Press [Y/+] to save the changes.
   - Press [N/-] to undo the changes and revert to the previous settings.

22.6 Datalog

The instrument calculates and stores the concentration and ID of each sample taken. In the datalog sub-menu, a user can perform the tasks and functions shown below.



1. Scroll through the Datalog sub-menu using the [N/-] key until the display shows the desired parameter to be changed:

   Clear Datalog
   Interval
   Data Selection
   Datalog Type

2. Press [Y/+] to make your selection. Exit by pressing [MODE] for Back.

22.6.1 Clear Datalog

This erases all the data stored in the datalog.

Note: Once the datalog is cleared, the data cannot be recovered.

Press [Y/+] to clear the datalog. The display asks, "Are you sure?"

- Press [Y/+] if you want to clear the datalog. When it has been cleared, the display shows "Datalog Cleared!"
- Press [N/-] if you do not want to clear the datalog.

The display changes, and you are taken to the next sub-menu, Interval.

22.6.2 Interval

Intervals are shown in seconds. The default value is 60 seconds. The maximum interval is 3600 seconds.

1. Press [Y/+] to increase each digit's value.
2. Press [N/-] to advance to the next digit.
3. Again, use [Y/+] to increase the number.

Repeat this process until all numbers are entered.

When you have completed your selections, press [MODE].

You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

22.6.3 Data Selection

Data Selection allows you to select which types of data are stored and made available when you offload your datalog to a computer via ProRAE Studio software.

You can choose any or all of three types of data (you must choose at least one):

- Average
- Maximum
- Minimum

1. Press [N/-] to step from one option to the next. The highlighter indicates your choice.
2. Press [Y/+] to toggle your selection on or off (the check box indicates "on" with an "X").
3. When you have completed your selections, press [MODE].

You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.
- Press [N/-] to undo the changes and revert to the previous settings.

22.6.4 Datalog Type

The instrument has three datalog types:

Auto	Default mode. Collects datalog information when the instrument is sampling.
Manual	Datalogging occurs only when the instrument's datalogging is manually started (see below for details).
Snapshot	Datalogs only during single-event capture sampling.

Note: You can only choose one datalog type to be active at a time.

1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates "on").
3. When you have completed your selection, press [MODE].

You will see two choices: Save and Undo. You have the opportunity to register the new settings or to change your mind and revert to your previous settings.

- Press [Y/+] to save the changes.

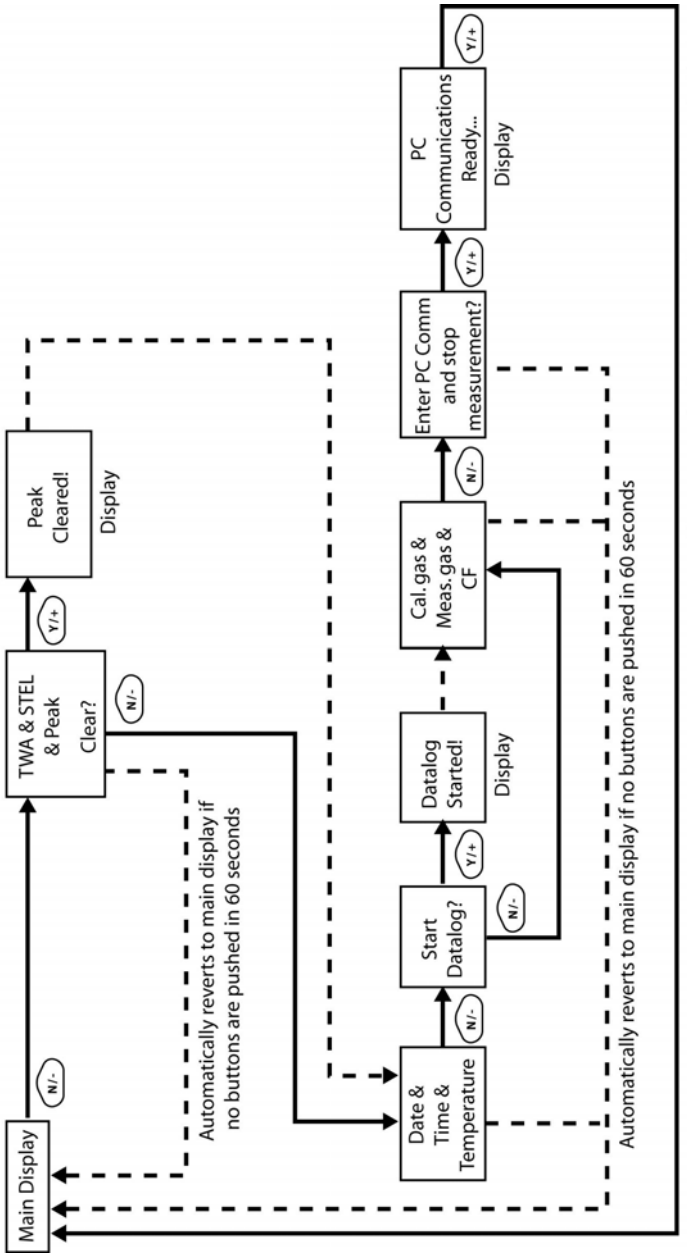
Press [N/-] to undo the changes and revert to the previous settings.

22.6.5 Manual Datalog

When the instrument is set to Manual Datalog, you turn datalogging on and off by stepping through the displays from the Main Display, and then pressing the keys to select datalog on/off functions.

- When you reach the screen that says "Start Datalog?" press [Y/+] to start it. You see "Datalog Started," confirming that datalogging is now on.

When you reach the screen that says "Stop Datalog?" press [Y/+] to stop it. You see "Datalog Stopped," confirming that datalogging is now off.



Note: Dashed line indicates automatic progression.

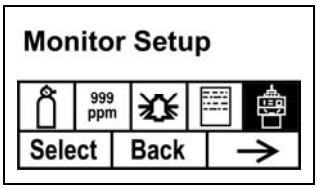
22.6.6 Snapshot Datalog

When the instrument is in Snapshot datalogging mode, it captures a single "snapshot" of the data at the moment of your choosing. Whenever the instrument is on and it is set to Snapshot, all you have to do is press [MODE] each time you want to capture a snapshot of the data at that instant.

When you send the data to a computer using ProRAE Studio, the data snapshots are uniquely identified by time and other parameters.

22.7 Monitor Setup

Many settings can be accessed in this menu, including setting the date and time and adjusting the pump's on/off duty cycle.



22.7.1 Radio Power

The radio connection can be turned on or off. (The default value is off.)

1. Press [N/-] to step from one option to the next (on or off).
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates that the option is selected).
3. When you have completed your selection, press [MODE].

    - Press [Y/+] to accept the new radio setting (on or off).
    - Press [N/-] to discard the change and move to the next sub-menu.

22.7.2 Op Mode

Under Monitor Setup is "Op Mode."

Press [Y/+] to select.

You see two options (one is highlighted):

Hygiene
Search

The current mode is indicated by a dark circle within the circle in front of either Hygiene or Search.

1. Select Hygiene or Search by pressing [N/-]. The highlighting changes from one to the other each time you press [N/-].
2. Press [Y/+] to select that mode for the instrument.
3. Press [MODE] when you want to register your selection to place the instrument in the selected mode.
4. Press [Y/+] to commit the change and exit to the Monitor Setup screen, or press [N/-] to Undo (exit to the Monitor Setup screen without changing the Mode).

22.7.3 Site ID

Enter an 8-digit alphanumeric/character Site ID in the programming mode. This Site ID is included in the datalog report.

1. Press [Y/+] and the display shows the current site ID. Example: "RAE00001." Note that the left-most digit flashes to indicate it is the selected one.
2. Press [Y/+] to step through all 26 letters (A to Z) and 10 numerals (0 to 9).
   Note: The last four digits must be numerals.
3. Press [N/-] to advance to the next digit. The next digit to the right flashes.

Repeat this process until all eight digits of the new site ID are entered.

Press [MODE] to exit.

If there is any change to the existing site ID, the display shows "Save?" Press [Y/+] to accept the new site ID. Press [N/-] to discard the change and move to the next sub-menu.

22.7.4 User ID

Enter an 8-digit alphanumeric User ID in the programming mode. This User ID is included in the datalog report.

1. Press [Y/+] and the display shows the current User ID. Example: "RAE00001." Note that the left-most digit flashes to indicate it is the selected one.
2. Press [Y/+] to step through all 26 letters (A to Z) and 10 numerals (0 to 9).
3. Press [N/-] to advance to the next digit. The next digit to the right flashes.

   Repeat this process until all eight digits of the new User ID are entered.

Press [MODE] to exit.

If there is any change to the existing User ID, the display shows "Save" Press [Y/+] to accept the new site ID. Press [N/-] to discard (undo) the change and move to the next sub-menu.

22.7.5 User Mode

The instrument has two user modes:

Basic	Basic users can only see and use a basic set of functions.
Advanced	Advanced users can see all screens and perform all available functions.

Note: The default value for User Mode is Basic.

To change the User Mode:

1. Press [N/-] to step from one option to the next. The highlighting changes each time you press [N/-].
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates "on").
3. When you have completed your selection, press [MODE].
4. Press [Y/+] to accept the new User Mode. Press [N/-] to discard the change and move to the next sub-menu.

22.7.6 Date

The Date is expressed as Month/Day/Year, with two digits for each.

1. Press [Y/+] and the display shows the current date. Note that the left-most digit flashes to indicate it is selected.
2. Press [Y/+] to step through all 10 numerals (0 to 9).
3. Press [N/-] to advance to the next digit. The next digit to the right flashes.

   Repeat this process until all six digits of the new date are entered.

Press [MODE] to exit.

- Press [Y/+] to save the new date.
- Press [N/-] to undo the change and move to the next sub-menu.

22.7.7 Time

The Time is expressed as Hours/Minutes/Seconds, with two digits for each. The time is in 24-hour (military) format.

1. Press [Y/+] and the display shows the current time. Note that the left-most digit flashes to indicate it is selected.
2. Press [Y/+] to step through all 10 numerals (0 to 9).
3. Press [N/-] to advance to the next digit. The next digit to the right flashes.

   Repeat this process until all six digits of the new time are entered.

Press [MODE] to exit.

- Press [Y/+] to save the new date.
- Press [N/-] to undo the change and move to the next sub-menu.

22.7.8 Duty Cycle

The pump's duty cycle is the ratio of its on time to off time. The duty cycle ranges from 50% to 100% (always on; this is the default value), and the period is 10 seconds. Therefore, a duty cycle of 60% means that the pump is on for 6 seconds and off for four seconds. Duty cycling is employed by the instrument to clean the PID. A lower duty cycle has a greater effect on keeping the PID clean than a higher duty cycle.

Important! Pump duty cycling is interrupted when the instrument senses a gas. The pump's duty cycle is disabled when the measurement is greater than the 2ppm threshold and is re-enabled when the reading falls below 90% of the threshold (1.8 ppm).

1. Press [Y/+] to increase the value.
2. When you have completed your selection, press [MODE].
   - Press [Y/+] to save the new duty cycle value.
   - Press [N/-] to undo the change and move to the next sub-menu.

22.7.9 Temperature Unit

The temperature display can be switched between Fahrenheit and Celsius units.

1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates "on").
3. When you have completed your selection, press [MODE].
   - Press [Y/+] to save the new temperature unit.
   - Press [N/-] to undo the change and move to the next sub-menu.

22.7.10 Pump Speed

The pump can operate at two speeds, high and low. Running at low speed is quieter and conserves a small amount of power. There is almost no difference in sampling accuracy.

1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates "on").
3. When you have completed your selection, press [MODE].
   - Press [Y/+] to save the new temperature unit.
   - Press [N/-] to undo the change and move to the next sub-menu.

22.7.11 Language

English is the default language, but other languages can be selected for the instrument.

1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates "on").
3. When you have completed your selection, press [MODE].
   - Press [Y/+] to save your new language choice.
   - Press [N/-] to undo it and return to the previous language selection.

22.7.12 Real Time Protocol

Real Time Protocol is the setting for data transmission.

The choices are:

P2M (cable)	Point to multipoint. Data is transferred from the instrument to multiple locations using a wired connection. Default data rate: 19200 bps.
P2P (cable)	Point to point (default). Data is transferred only between the instrument and one other location, such as a computer. Default data rate: 9600 bps.
P2M (wireless)	Point to multipoint, wireless. Data is transferred wirelessly and can be received by multiple receivers. Use this setting with a RAELink3.

1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates "on").
3. When you have completed your selection, press [MODE].
   - Press [Y/+] to save the new real-time communications protocol.
   - Press [N/-] to undo the change and move to the next sub-menu.

22.7.13 Power On Zero

When Power On Zero is on, the instrument is ready to perform a zero calibration when it is turned on.

1. Press [N/-] to step from one option to the next.
2. Press [Y/+] to make your selection (the dark circle in the "radio button" indicates your selection).
3. When you have completed your selection, press [MODE].
   - Press [Y/+] to save the change.
   - Press [N/-] to discard the change and move to the next sub-menu.

22.7.14 Unit ID

This three-digit number keeps data separated by instrument when more than one instrument is used in a network. If multiple sensing units are attempting to communicate with the same Host, then the units must all have a different Unit ID.

1. Press [Y/+] to step through all 10 numerals (0 to 9). If you pass the numeral you want, keep pressing [Y/+]. After it counts up to 9, it starts counting up from 0 again.
2. Press [N/-] to advance to the next digit. The next digit to the right flashes.

Repeat this process until all three digits of the Unit ID are entered.

3. Press [MODE] when you are done.
   - Press [Y/+] to save the change.
   - Press [N/-] to discard the change and move to the next sub-menu.

Note: If you are using an UltraRAE 3000 with a RAELink3, this unit ID is displayed by the RAELink3.

22.7.15 LCD Contrast

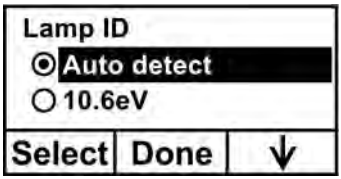
The display's contrast can be increased or decreased from its default setting. You may not need to ever change the default setting, but sometimes you can optimize the display to suit extreme temperature and ambient brightness/darkness conditions.

- The minimum value is 20.
- The maximum value is 60.

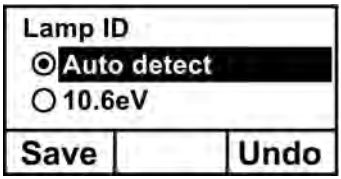
1. Press [Y/+] to increase the value or [N/-] to decrease the value.
2. Press [MODE] to save your selection.
   - Press [Y/+] to save your new contrast value.
   - Press [N/-] to undo it and return to the previous value.

22.7.16 Lamp ID

The UltraRAE can automatically identify the type of lamp, or you can select a lamp type manually.



1. Scroll through the menu by pressing [N/-].
2. Press [Y/+] to make a selection.
3. Press [MODE] when you are done.
4. Press [Y/+] to save your choice or [N/-] to undo your selection.



23 Humidity Compensation

The UltraRAE 3000 has a humidity sensor and humidity compensation circuitry. By default it is on, but it can be turned off or on by using ProRAE Studio software. RAE Systems recommends testing the humidity sensor once a year. See page 99 for the simple procedure.

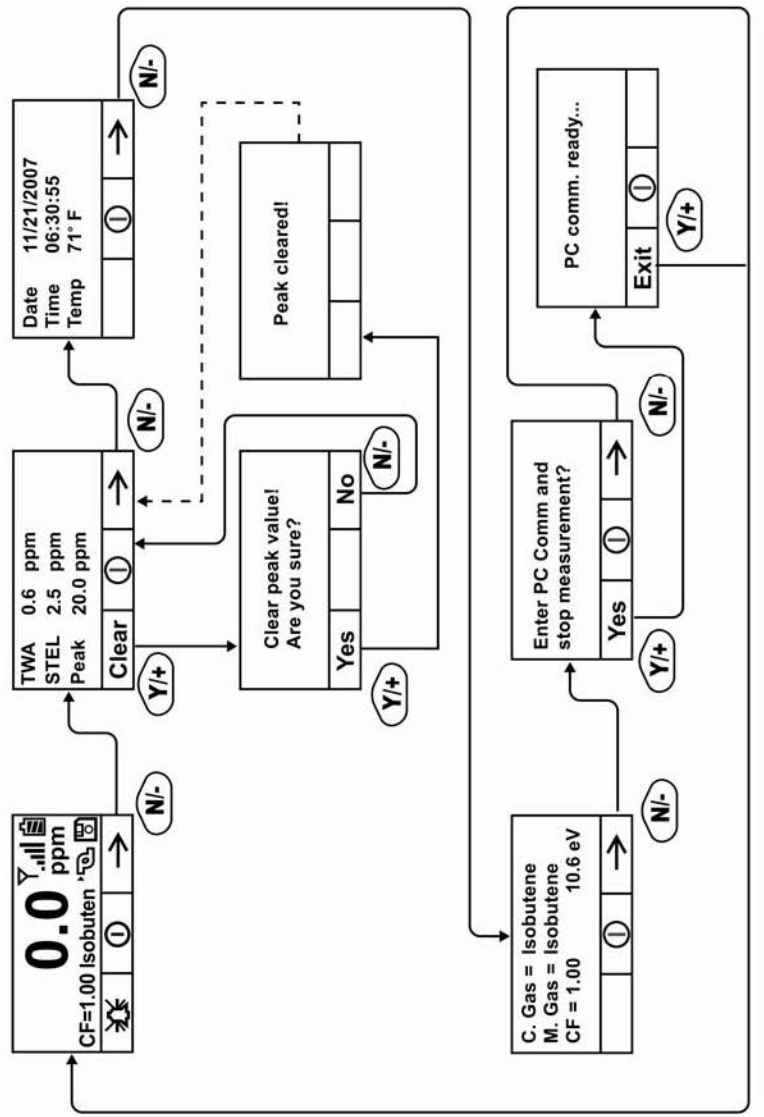
24 Hygiene Mode

The instrument usually operates in Hygiene Mode, which provides basic functionality. However, it is possible to operate it in a second mode called Search Mode. Here are the primary differences:

Hygiene Mode:	Automatic measurements, continuously running and datalogging, and calculates additional exposure values.
Search Mode:	Manual start/stop of measurements and display of certain exposure values.

24.1 Basic User Level & Hygiene Mode

The default setting is navigated in the following way:



Note: Dashed line indicates automatic progression.

Pressing [N/-] steps you from screen to screen. Options include clearing the Peak value and turning on the instrument's PC Communications for data transfer to a PC.

24.2 Entering Search Mode From Hygiene Mode

In order to change the instrument's operational mode from Hygiene Mode to Search Mode, you must enter the password-protected Programming Mode:

1. Hold [MODE] and [N/-] until you see the password screen.
2. Use [Y/+] to increment to the number you want for the first digit. (If you pass by the desired number, press [Y/+] until it cycles through to 0 again. Then press [Y/+] until you reach the desired number.)
3. Press [N/-] to advance to the next digit.
4. Again press [Y/+] to increment the number.
5. Press [N/-] to advance to the next digit.

Continue the process until all four numbers of the password have been input. Then press [MODE] to proceed.

The screen changes to icons with the label "Calibration."

1. Press [N/-] to advance to "Monitor Setup."
2. Press [Y/+] to select Monitor Setup.

Under Monitor Setup, you will see "Op Mode."

Press [Y/+] to select.

You will see:

Hygiene
Search

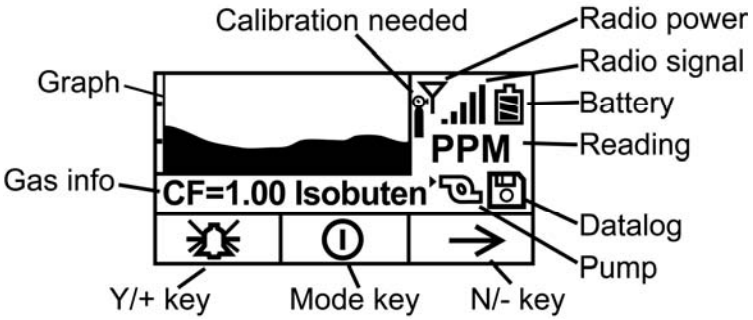
The current mode is indicated by a dark circle within the circle in front of either Hygiene or Search.

1. Select Hygiene or Search by pressing [N/-].
2. Press [Y/+] to place the instrument into the selected mode.

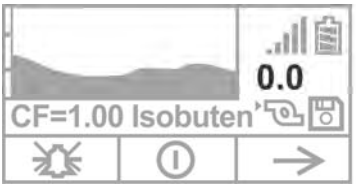
3. Press [MODE] when you want to register your selection to place the instrument in the selected mode.
4. Press [Y/+] to commit the change and exit to the Monitor Setup screen, or press [N/-] to Undo (exit to the Monitor Setup screen without changing the Mode).

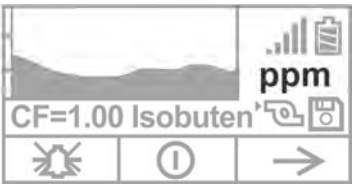
24.3 Optional Graphic Screen In Search Mode

Using ProRAE Studio, you can set your instrument to show a graphic display instead of a numeric display of ongoing data. Consult your ProRAE Studio disc for information.



During sampling, the display's readings are shown numerically, plus the graph tracks the highest readings over time. The numeric reading alternates between the value and the measurement units, as well:





25 Advanced User Level (Hygiene Mode Or Search Mode)

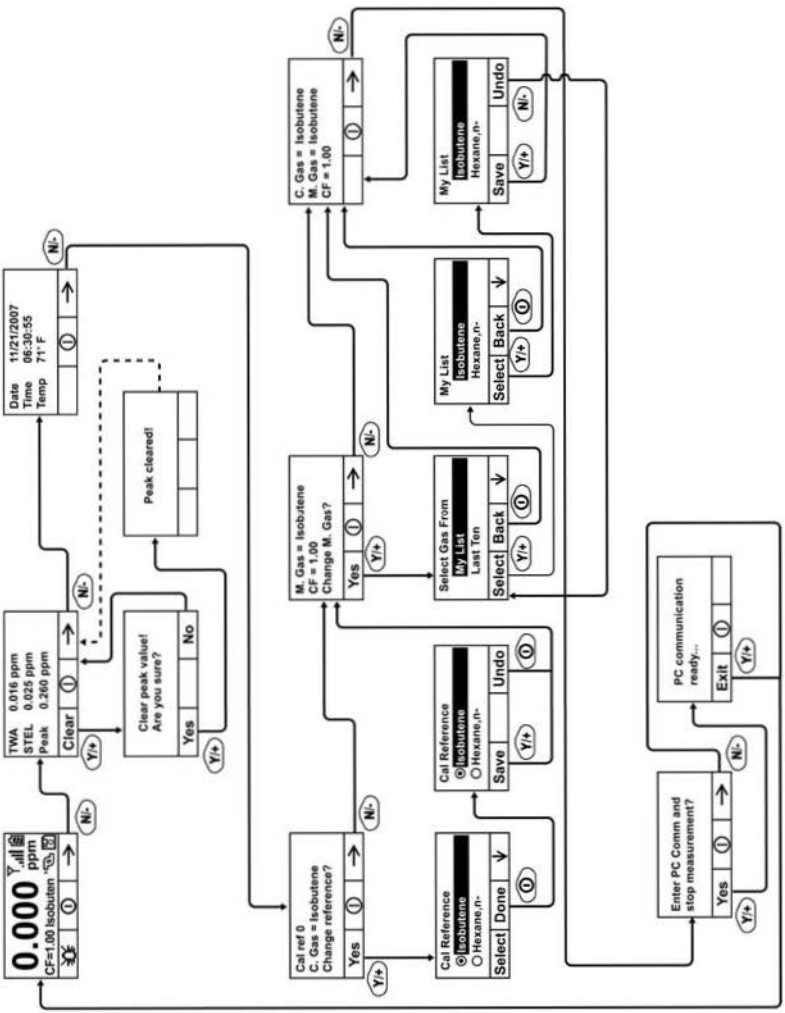
The User Mode called Advanced User Level allows a greater number of parameters to be changed than Basic User Level. It can be used with either of the Operation Modes, Hygiene Mode or Search Mode.

25.1 Advanced User Level & Hygiene Mode

With the instrument in Operation Mode: Hygiene Mode, enter User Mode: Advanced User Level (refer to the section called Monitor Mode for instructions).

Once you are in Advanced User Level and Hygiene Mode together, you can change the calibration reference and measurement gas, in addition to performing normal monitoring functions.

Pressing [N/-] progresses through the screens, while pressing [Y/+] selects options. Pressing [MODE] makes menu choices when it is shown for "Done" or "Back." Pressing and holding [Mode] whenever the circle with a vertical line in the middle is shown activates the countdown to shutoff.

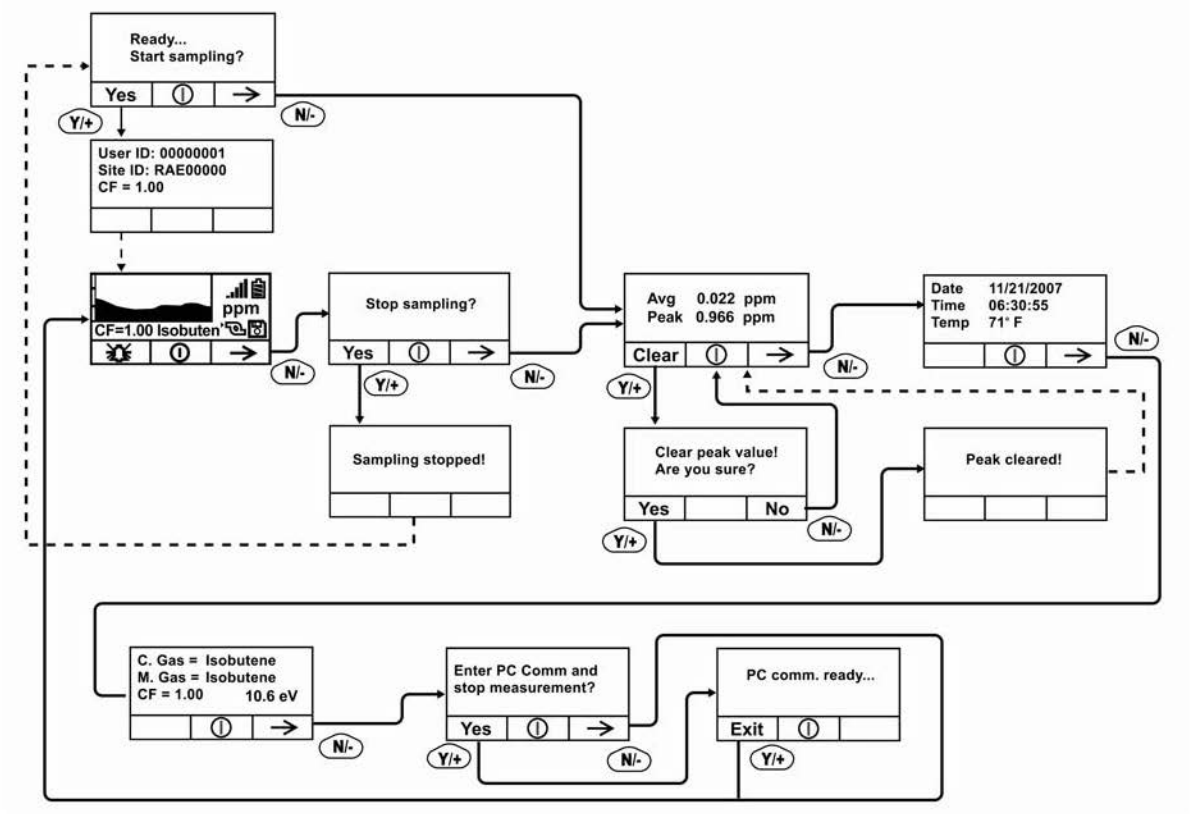


Note: Dashed line indicates automatic progression.

25.2 Basic User Level & Search Mode

With the instrument in Operation Mode: Search Mode, enter User Mode and select Basic User Level (refer to the section called User Mode for instructions).

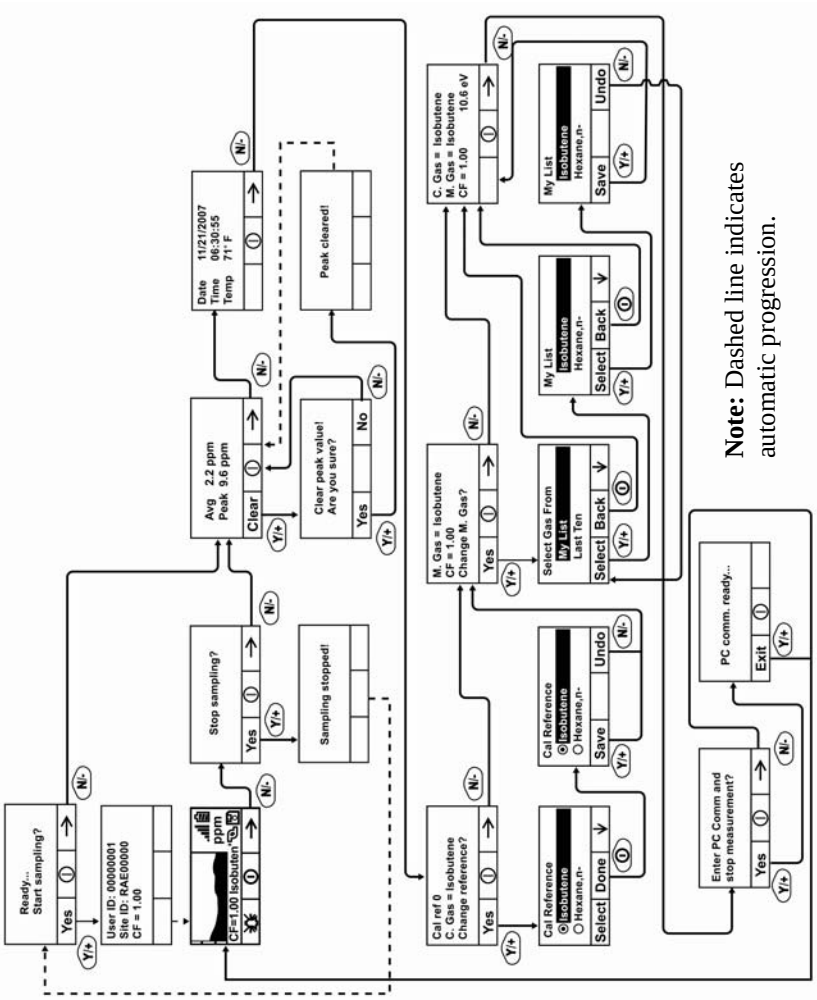
When the instrument is in Search Mode, it only samples when you activate sampling. When you see the display that says, "Ready…Start sampling?" press [Y/+] to start. The pump turns on and the instrument begins collecting data. To stop sampling, press [N/-] while the main display is showing. You will see a new screen that says, "Stop sampling?" Press [Y/+] to stop sampling. Press [N/-] if you want sampling to continue.



Note: Dashed line indicates automatic progression.

25.3 Advanced User Level & Search Mode

With the instrument in Operation Mode: Search Mode, enter User Mode and select Advanced User Level (refer to the section called Monitor Mode for instructions). Operation is similar to Basic User Level & Sampling Mode, but now allows you to change calibration and measurement reference gases. Refer to the section on measurement gases on page 65 for more details.



25.4 Diagnostic Mode

IMPORTANT! Diagnostic Mode is designed for servicing and manufacturing, and therefore is not intended for everyday use, even by advanced users. It provides raw data from sensors and about settings, but only allows adjustment of pump stall parameters, which should only be changed by qualified personnel.

Note: If the instrument is turned on in Diagnostic Mode and you switch to User Mode, datalog data remains in raw count form. To change to standard readings, you must restart the instrument.

25.4.1 Entering Diagnostic Mode

Note: To enter Diagnostic Mode, you must begin with the instrument turned off.

Press and hold [Y/+] and [MODE] until the instrument starts.

The instrument goes through a brief startup, and then displays raw data for the PID sensor. These numbers are raw sensor readings without calibration. The instrument is now in Diagnostic Mode.

Note: In Diagnostic Mode, the pump and lamp are normally on.

You can enter Programming Mode and calibrate the instrument as usual by pressing both [MODE] and [N/-] for three seconds.

You can enter Monitoring Mode by pressing [MODE] and [Y/+] together for three seconds.

Once the instrument is started up in Diagnostic Mode, you can switch between Diagnostic Mode and Monitoring Mode by pressing and holding [MODE] and [Y/+] simultaneously for two seconds.

In Diagnostic mode, you can step through parameter screens by pressing [MODE].

25.4.2 Adjusting The Pump Stall Threshold

If the gas inlet is blocked but the pump does not shut down, or the pump shuts down too easily with a slight blockage, the pump stall threshold value may be set too high or too low.

Use the following steps to adjust the pump stall threshold:

25.4.3 Pump High

In Diagnostic Mode, press the [MODE] key until "Pump High" is displayed. The display shows the maximum, minimum, and stall values for the pump at its high speed. Write down the "Max" reading.

Block the gas inlet and watch the pump current reading (labeled "I") increase. Write down its blocked reading. **Note:** If the pump current reading does not increase significantly (less than 10 counts), then there may be a leak in the gas inlet or the pump is weak or defective.

Add the two readings you wrote down. This is the average of the maximum block count and the maximum idle count. Divide that number by 2. Use the [Y/+] or [N/-] key to increase or decrease the stall value to equal that number.

Press the [MODE] key to exit this display.

25.4.4 Pump Low

In Diagnostic Mode, press the [MODE] key until "Pump Low" is displayed. The display shows the maximum, minimum, and stall values for the pump at its low speed. Write down the "Max" reading.

Block the gas inlet and watch the pump current reading (labeled "I") increase. Write down its blocked reading. **Note:** If the pump current reading does not increase significantly (less than 10 counts), then there may be a leak in the gas inlet or the pump is weak or defective.

Add the two readings you wrote down. This is the average of the maximum block count and the maximum idle count. Divide that

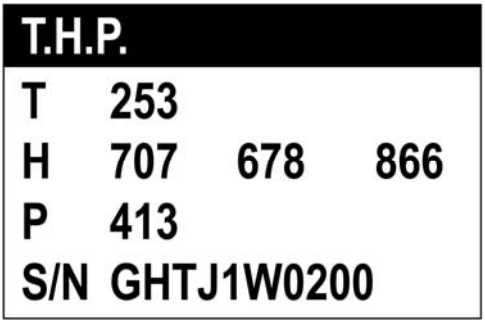
number by 2. Use the [Y/+] or [N/-] key to increase or decrease the stall value to equal that number.

Press the [MODE] key to exit this display.

25.4.5 Testing The Humidity Sensor

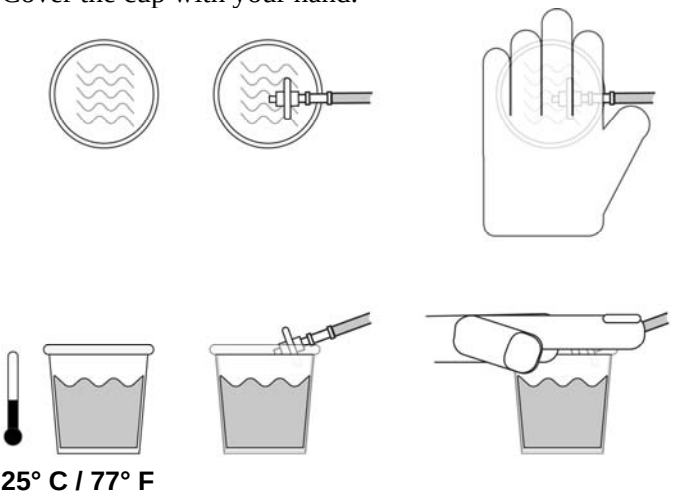
1. Press [MODE] to step through the diagnostic screens until you reach a screen that says "T.H.P" (for "temperature, humidity, pressure") at the top.

   There are three numbers for the humidity reading ("H"). The first number is the current humidity reading from the sensor. The second is the reference number for 0% humidity, and the third number is the reference for 100% humidity.



2. Fill a cup with warm water (>25° C/77° F).
3. Put a filter on the UltraRAE 3000's inlet probe.
4. Place the inlet probe over the warm water.

5. Cover the cup with your hand.



6. Wait a few seconds and check the high-humidity reading.
7. The humidity reading should be within ±10% of the 100% humidity reading. If it is not, then the THP Sensor (part number 023-3011-000-FRU) should be replaced.
8. Check the low-humidity reading by connecting the inlet probe to a tank of zero gas (air at 0% humidity).
9. Turn on the zero gas and wait a few seconds for the sensor reading to stabilize. It should read within 10% of the low-reference number. If it does not, replace the T.H.P. sensor.
10. Once you have finished testing the humidity sensor, exit Diagnostic Mode by shutting down the UltraRAE 3000 (hold [MODE] through the countdown, and then release when it is off).

25.4.6 Exiting Diagnostic Mode

You can exit Diagnostic Mode and go directly to Programming Mode or Monitor Mode as outlined above, or you can exit Diagnostic Mode completely.

To exit Diagnostic Mode so that it cannot be re-entered without a restart:

Shut down the instrument. When it is off, restart it by holding the [MODE] key. Diagnostic Mode cannot be entered until the instrument is restarted as outlined in "Entering Diagnostic Mode."

26 Transferring Data To & From Computer

Once you have connected your instrument cradle to the PC, you can can transfer data, including a download of the datalog to the computer and updates of firmware to the instrument (should this ever be necessary).

26.1 Downloading The Datalog To A PC

1. Connect the data cable to the PC and the cradle.
2. Place the instrument into its cradle. The charging LED should be illuminated.
3. Start ProRAE Studio on your PC.
4. From ProRAE Studio, select "Operation" and select Setup Connection.
5. Select the COM port to establish a communication link between the PC and the instrument.
6. To receive the datalog in the PC, select "Downlog Datalog."
7. When you see "Unit Information," click OK.

During the data transfer, the display shows a progress bar.

When the transfer is done, you will see a screen with the datalog information. You can now export this datalog for other use or printing.

26.2 Uploading Firmware To The instrument From A PC

Uploading new firmware to your instrument requires connecting the instrument and PC. Follow these steps to make the connection:

1. Connect the data cable to the PC and the cradle.
2. Place the instrument into its cradle. The charging LED should be illuminated.
3. Start RAEProgrammer 7000 on your PC.
4. From RAEProgrammer 7000, select "Operation" and select Setup Connection.
5. Select the COM port to establish a communication link between the PC and the instrument.
6. Select Operation → Download Firmware.

Once communication is established, follow the instructions that accompany RAEProgrammer 7000 and the firmware to upload the new firmware to your instrument.

Note: Check for the latest updates to ProRAEProgrammer 7000 at www.raesystems.com.

27 Maintenance

The major maintenance items of the instrument are:

- Battery pack
- Sensor module
- PID lamp
- Sampling pump
- Inlet connectors and filters

In addition, you can test the humidity sensor (this should be done annually, in order to ensure the most accurate operation).

Note: Maintenance should be performed by qualified personnel only.

NOTE: The printed circuit board of the instrument is connected to the battery pack even if the power is turned off. **Therefore, it is very important to disconnect the battery pack before servicing or replacing any components inside the instrument**. **Severe damage to the printed circuit board or battery may occur if the battery pack is not disconnected before servicing the unit.**

27.1 Battery Charging & Replacement

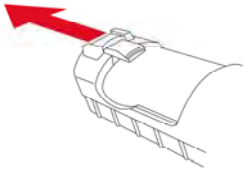
When the display shows a flashing empty battery icon, the battery requires recharging. It is recommended to recharge the instrument upon returning from fieldwork. A fully charged battery runs a instrument for 16 hours continuously. The charging time is less than 8 hours for a fully discharged battery. The battery may be replaced in the field (in areas known to be non-hazardous), if required.

WARNING!

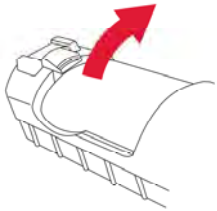
To reduce the risk of ignition of hazardous atmospheres, recharge battery only in area known to be non-hazardous. **Remove and replace battery only in areas known to be non-hazardous.**

27.1.1 Replacing The Li-ion Battery

1. Turn off the instrument.
2. Located on the rear of the instrument is a battery tab. Slide it down to unlock the battery.



3. Remove the battery pack from the battery compartment by tilting it out.



4. Replace a fully charged spare battery pack inside the battery compartment. Make sure the battery pack is oriented properly inside the compartment.
5. Slide the capture tab back up to its locked position.

27.1.2 Replacing The Alkaline Battery Adapter

An alkaline battery adapter is supplied with each instrument. The adapter (part number 059-3052-000) accepts four AA alkaline batteries (use only Duracell MN1500 or Energizer E91) and provides approximately 12 hours of operation. The adapter is intended to be used in emergency situations when there is no time to charge the Li-ion battery pack.

To insert batteries into the adapter:

1. Remove the three hex-socket screws to open the compartment.
2. Insert four fresh AA batteries as indicated by the polarity (+/-) markings.

3. Replace the cover. Replace the three screws.

To install the adapter in the instrument:

1. Remove the Li-ion battery pack from the battery compartment by sliding the tab and tilting out the battery.
2. Replace it with the alkaline battery adapter
3. Slide the tab back into place to secure the battery adapter.

IMPORTANT!

Alkaline batteries cannot be recharged. The instrument's internal circuit detects alkaline batteries and will not allow recharging. If you place the instrument in its cradle, the alkaline battery will not be recharged. The internal charging circuit is designed to prevent damage to alkaline batteries and the charging circuit when alkaline batteries are installed inside the instrument.

Note: When replacing alkaline batteries, dispose of old ones properly.

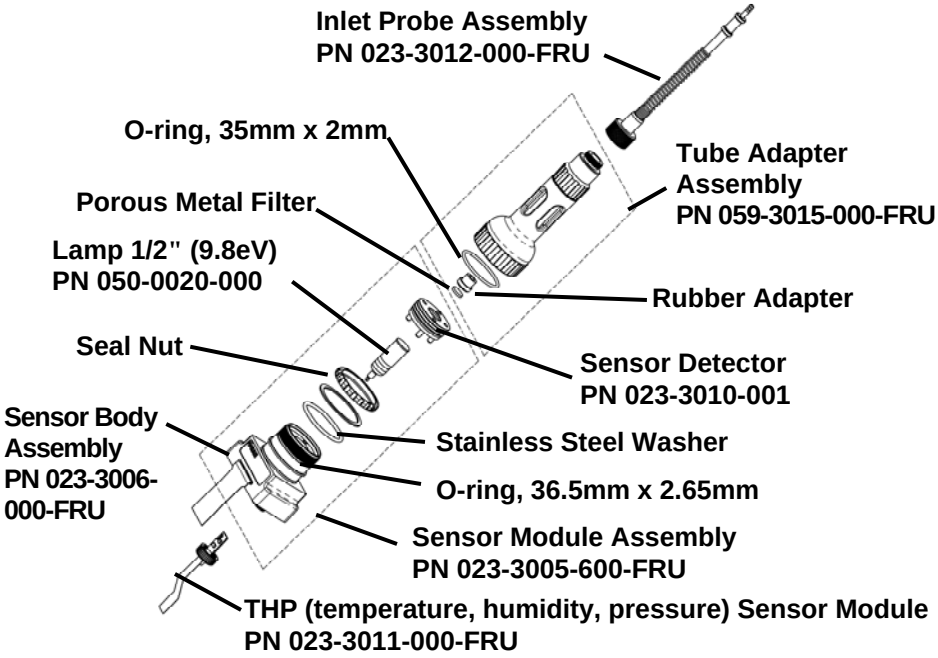
WARNING!

To reduce the risk of ignition of hazardous atmospheres, recharge the battery only in areas known to be non-hazardous. Remove and replace the battery only in areas known to be non-hazardous.

Note: The internal charging circuit is designed to prevent charging to alkaline batteries.

27.2 PID Sensor & Lamp Cleaning/Replacement

The sensor module is made of several components and is attached to the lamp-housing unit as shown below.



Sensor Components

Note: The cleaning procedure is not normally needed. Clean the PID sensor module, the lamp and the lamp housing only if:

1. The reading is inaccurate even after calibration.
2. The reading is very sensitive to air moisture.
3. A liquid has been sucked into the unit and damaged the unit.

Use of the external filter helps to prevent contamination of the sensor.

To access the sensor components and lamp, gently unscrew the lamp-housing cap, remove the sensor adapter with the gas inlet probe and the metal filter all together. Then hold the PID sensor and pull it straight out. A slight, gentle rocking motion helps release the sensor.

Note: The 10.6eV lamp requires a Teflon O-ring. The 9.8eV and 11.7eV lamps do not require the O-ring.

27.3 Cleaning The PID Sensor

Place the entire PID sensor module into GC grade methanol. It is highly recommended that an ultrasound bath to be used to clean the sensor for at least 15 minutes. Then dry the sensor thoroughly. Never touch the electrodes of the sensor by hand.
Also use a methanol-soaked cotton swab to wipe off the lamp housing where it contacts the sensor when the sensor is installed.

Turn over the sensor so that the pins point up and the sensor cavity is visible. Examine the sensor electrodes for any corrosion, damage, or bending out of alignment. The metal sensor electrode "fingers" should be flat and straight. If necessary, carefully bend the sensor fingers to ensure that they do not touch the Teflon portions and that they are parallel to each other. Make sure that the nuts on the sensor pins are snug but not overtight. If the sensor is corroded or otherwise damaged, it should be replaced.

27.3.1 Cleaning The Lamp Housing Or Changing The Lamp

If the lamp does not turn on, the instrument will display an error message to indicate replacement of the lamp may be required.

1. If the lamp is operational, clean the lamp window surface and the lamp housing by wiping it with GC grade methanol using a cotton swab using moderate pressure. After cleaning, hold the lamp up to the light at an angle to detect any remaining film. Repeat the process until the lamp window is clean. Never use water solutions to clean the lamp. Dry the lamp and the lamp housing thoroughly after cleaning.

   CAUTION: Never touch the window surface with the fingers or anything else that may leave a film. Never use acetone or aqueous solutions.

2. If the lamp does not turn on, remove the lamp from the lamp housing. Place the lamp O-ring onto the new lamp. Insert the new lamp, avoiding contact with the flat window surface.
3. Reinstall the PID sensor module.
4. Tighten the Lamp Housing Cap.

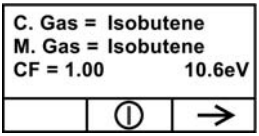
27.3.2 Determining The Lamp Type

The monitor can accommodate three lamp values: 10.6eV (standard), 9.8eV, and 11.7eV. The monitor automatically reads a marking on the side of the lamp to set the proper Correction Factor. There are two ways to determine the lamp type:

Remove the lamp and look for markings (bars) on the side:

- No bars: 10.6eV
- 1 bar: 11.7eV
- 2 bars: 9.8eV

Also, when the monitor is running, the lamp type is shown along with the calibration and measurement gas and Correction Factor:



Note: This screen can be accessed from the reading screen by pressing [N/-] four times.

27.3.3 Sampling Pump

When approaching the end of the specified lifetime of the pump, it will consume higher amount of energy and reduce its sample draw capability significantly. When this occurs, it is necessary to replace or rebuild the pump. When checking the pump flow, make sure that the inlet connector is tight and the inlet tubing is in good condition. Connect a flow meter to the gas inlet probe. The flow rate should be above 450 cc/min when there is no air leakage.

If the pump is not working properly, refer the instrument to qualified service personnel for further testing and, if necessary, pump repair or replacement.

27.3.4 Testing The T.H.P. Sensor

It is recommended that you periodically test the humidity sensitivity of the T.H.P. (temperature/humidity/pressure) sensor. See page 99 for a simple procedure.

27.3.5 Cleaning The Instrument

Occasional cleaning with a soft cloth is recommended. Do not use detergents or chemicals.

Visually inspect the contacts at the base of the instrument, on the battery, and on the charging cradle to make sure they are clean. If they are not, wipe them with a soft, dry cloth. Never use solvents or cleaners.

27.3.6 Ordering Replacement Parts

If you need replacement parts, contact your local RAE Systems distributor. A list is available online:

http://www.raesystems.com

In the U.S., you can order sensors, replacement batteries, and other accessories online at:

http://istore.raesystems.com/

27.4 Special Servicing Note

If the instrument needs to be serviced, contact either:

1. The RAE Systems distributor from whom the instrument was purchased; they will return the instrument on your behalf.

   or

2. The RAE Systems Technical Service Department. Before returning the instrument for service or repair, obtain a Returned Material Authorization (RMA) number for proper tracking of your equipment. This number needs to be on all documentation and posted on the outside of the box in which the instrument is returned for service or upgrade. Packages without RMA Numbers will be refused at the factory.

28 Troubleshooting

Problem	Possible Reasons & Solutions	
Cannot turn on power after charging the battery	**Reasons:**	Discharged battery. Defective battery.
	Solutions:	Charge or replace battery.
Lost password	**Solutions:**	Call Technical Support at +1 408-752-0723 or toll-free at +1 888-723-4800
Reading abnormally High	**Reasons:**	Dirty filter. Dirty sensor module. Excessive moisture and water condensation. Incorrect calibration.
	Solutions:	Replace filter. Blow-dry the sensor module. Calibrate the unit.
Reading abnormally Low	**Reasons:**	Dirty filter. Dirty sensor module. Weak or dirty lamp. Incorrect calibration.
	Solutions:	Replace filter. Remove Calibration Adapter. Calibrate the unit. Check for air leakage.
Buzzer Inoperative	**Reasons:**	Bad buzzer.
	Solutions:	Check that buzzer is not turned off. Call authorized service center.

Inlet flow too low	**Reasons:**	Pump diaphragm damaged or has debris. Flow path leaks.
	Solutions:	Check flow path for leaks; sensor module O-ring, tube connectors, Teflon tube compression fitting. Call Technical Support at +1 408-752-0723 or toll-free at +1 888-723-4800
"Lamp" message during operation	**Reasons:**	Lamp drive circuit. Weak or defective PID lamp, defective.
	Solutions:	Turn the unit off and back on. Replace UV lamp

29 Technical Support

To contact RAE Systems Technical Support Team:

Monday through Friday, 7:00AM to 5:00PM Pacific (US) Time
Phone (toll-free): +1 888-723-4800
Phone: +1 408-952-8461
Email: tech@raesystems.com

Life-critical after-hours support is available:

+1 408-952-8200 select option 8

30 RAE Systems Contacts

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Fax: +1 408.952.8480

E-mail: customerserv@raesystems.com
Web Site: www.raesystems.com

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Life-critical after-hours support is available:
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Email: krsales@raesystems.com

31 Regulatory Information

Intrinsic Safety:	US and Canada: Class I, Division 1, Group A, B, C, D
	Europe: ATEX (II 2G EEx ia IIC T4)
Temperature:	-20º C to 50º C (-4º to 122º F)
Humidity:	0% to 95% relative humidity (non-condensing)

32 Basic Operation

32.1 Turning The Instrument On

1. With the instrument turned off, press and hold [MODE].
2. When the display turns on, release the [MODE] key.

The instrument is now operating and performs self tests. Once the self tests are complete, the display shows a graph or numerical gas reading. This indicates that the instrument is fully functional and ready to use.

32.2 Turning The Instrument Off

1. Press and hold the Mode key for 3 seconds. A 5-second countdown to shutoff begins.
2. When you see "Unit off..." release your finger from the [MODE] key. The instrument is now off.

Note: You must hold your finger on the key for the entire shutoff process. If you remove your finger from the key during the

countdown, the shutoff operation is canceled and the instrument continues normal operation.

33 Alarm Signals

During each measurement period, the gas concentration is compared with the programmed alarm limits (gas concentration alarm limit settings). If the concentration exceeds any of the preset limits, the loud buzzer and red flashing LED are activated immediately to warn you of the alarm condition.

In addition, the instrument alarms if one of the following conditions occurs: battery voltage falls below a preset voltage level, failure of the UV lamp, pump stall, or when the datalog memory is full.

33.1 Alarm Signal Summary

Message	Condition	Alarm Signal
HIGH	Gas exceeds "High Alarm" limit	3 beeps/flashes per second*
OVR	Gas exceeds measurement range	3 beeps/flashes per second*
MAX	Gas exceeds electronics' maximum range	3 beeps/flashes per second*
LOW	Gas exceeds "Low Alarm" limit	2 beeps/flashes per second*
TWA	Gas exceeds "TWA" limit	1 Beep/flash per second*
STEL	Gas exceeds "STEL" limit	1 Beep/flash per second*
Pump icon flashes	Pump failure	3 beeps/flashes per second

Lamp	PID lamp failure	3 beeps/flashes per second plus "Lamp" message on display
Battery icon flashes	Low battery	1 flash, 1 beep per minute plus battery icon flashes on display
CAL	Calibration failed, or needs calibration	1 beep/flash per second
NEG	Gas reading measures less than number stored in calibration	1 beep/flash per second

34 Preset Alarm Limits & Calibration

The instrument is factory calibrated with standard calibration gas, and is programmed with default alarm limits.

Cal Gas (Isobutylene)	**Cal Span**	**unit**	**Low**	**High**	**TWA**	**STEL**
ppbRAE 3000	10	ppm	10	25	10	25
MiniRAE 3000	100	ppm	50	100	10	25
MiniRAE Lite	100	ppm	50	100	10	25
UltraRAE 3000	100	ppm	50	100	10	25

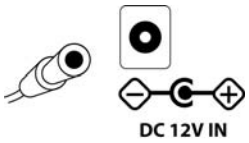
35 Charging The Battery

Always fully charge the battery before using the instrument. The instrument's Li-ion battery is charged by placing the instrument in its cradle. Contacts on the bottom of the instrument meet the cradle's contacts, transferring power without other connections.

Note: Before setting the instrument into its charging cradle, visually inspect the contacts to make sure they are clean. If they are not, wipe them with a soft cloth. Do not use solvents or cleaners.

Follow this procedure to charge the instrument:

1. Plug the AC/DC adapter's barrel connector into the instrument's cradle.



2. Plug the AC/DC adapter into the wall outlet.
3. Place the instrument into the cradle, press down, and lean it back. It locks in place and the LED in the cradle glows.

Note: To release the instrument, press down and tilt the top out of the cradle and lift up.

The instrument begins charging automatically. The LED on the front of the cradle marked "Primary" blinks during charging. During charging, the diagonal lines in the battery icon on the instrument's display are animated and you see the message "Charging..."

When the instrument's battery is fully charged, the battery icon is no longer animated and shows a full battery. The message "Fully charged!" is shown and the Primary LED on the cradle glows continuously green.

Note: A spare Li-ion battery (part number 059-3051-000) can be charged by placing it directly in the charging port on the back of the cradle. It can be charged at the same time as the instrument. Press the battery in place, sliding it slightly toward the front of the cradle. This locks it in the cradle. To release the battery, slide it forward again and tilt it up.

Note: An Alkaline Battery Adapter (part number 059-3052-000), which uses four AA alkaline batteries (Duracell MN1500 or Energizer E91), may be substituted for the Li-Ion battery.

WARNING!

To reduce the risk of ignition of hazardous atmospheres, recharge and replace batteries only in areas known to be non-hazardous. Remove and replace batteries only in areas known to be non-hazardous.

ATEX WARNING!

To reduce the risk of electrostatic ignition, do not use the instrument without the rubber boot in place.

35.1 Low Voltage Warning

When the battery's charge falls below a preset voltage, the instrument warns you by beeping once and flashing once every minute, and the battery icon blinks once per second. You should turn off the instrument within 10 minutes and either recharge the battery by placing the instrument in its cradle, or replace the battery with a fresh one with a full charge.

35.2 Clock Battery

An internal clock battery is mounted on one of the instrument's printed circuit boards. This long-life battery keeps settings in memory from being lost whenever the Li-ion battery or alkaline batteries are removed. This backup battery should last approximately five years, and must be replaced by an authorized RAE Systems service technician. It is not user-replaceable.

WARNING

To reduce the risk of ignition of hazardous atmospheres, recharge battery only in area known to be non-hazardous. Remove and replace battery only in an area known to be non-hazardous.

35.3 Replacing The Rechargeable Li-Ion Battery

Caution: Turn off the instrument before removing or replacing the battery.

35.4 Alkaline Battery Adapter

An alkaline battery adapter is supplied with each instrument. The adapter (part number 059-3052-000) accepts four AA alkaline batteries (use only Duracell MN1500 or Energizer E91).

Do not mix old and new batteries or batteries from different manufacturers.

36 Troubleshooting

Problem	Possible Reasons & Solutions	
Cannot turn on power after charging the battery	**Reasons:**	Discharged battery. Defective battery.
	Solutions:	Charge or replace battery.
Lost password	**Solutions:**	Call Technical Support at +1 408-752-0723 or toll-free at +1 888-723-4800
Reading abnormally High	**Reasons:**	Dirty filter. Dirty sensor module. Excessive moisture and water condensation. Incorrect calibration.
	Solutions:	Replace filter. Blow-dry the sensor module. Calibrate the unit.
Reading abnormally Low	**Reasons:**	Dirty filter. Dirty sensor module. Weak or dirty lamp. Incorrect calibration.
	Solutions:	Replace filter. Remove Calibration Adapter. Calibrate the unit. Check for air leakage.
Buzzer Inoperative	**Reasons:**	Bad buzzer.
	Solutions:	Check that buzzer is not turned off. Call authorized service center.

Inlet flow too low	**Reasons:**	Pump diaphragm damaged or has debris. Flow path leaks.
	Solutions:	Check flow path for leaks; sensor module O-ring, tube connectors, Teflon tube compression fitting. Call Technical Support at +1 408-752-0723 or toll-free at +1 888-723-4800
"Lamp" message during operation	**Reasons:**	Lamp drive circuit. Weak or defective PID lamp, defective.
	Solutions:	Turn the unit off and back on. Replace UV lamp

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Rev. A
May 2008
P/N 059-4023-000

To run SAFER v. 9.0:

Steps 1-2 – only if you are using a removable drive to store your data, but not to run the program

1. Connect the removable drive to PC.
2. Copy the appropriate state folder (they can be identified by their two-letter USPS abbreviation) from the removable drive into C:/GISData/World/USA/. If you wish, you may copy only the counties that you're interested in. The process is a *little* more involved, but possible with practice.

Steps 3-end – everyone.

3. Open the STAR Site Manager.

4. Create a new site by selecting the icon.
5. Name the site and proceed by clicking the icon.
6. To locate the site, left-click on the map (the icon should already be selected) near where the incident is located. The coordinates at the location where you click will appear at the bottom left of the screen. It is NOT critical at this stage to locate the site exactly. For best results, shoot for +/- 15 miles.
7. Copy the coordinates obtained in step 3 into the boxes at the top left of the screen. Select the coordinates, then right-click, select 'copy;' right-click and select 'paste' to paste the coordinates. (If an exact address is known, this may also be entered).
8. Once the coordinates have been selected, click the icon. This will bring up more detailed GIS data around the incident site.
9. Determine the exact location of the incident site by zooming (and icons) and panning (icon). Use the icon to determine names of places. After selecting the icon, simply mouse over the place of interest and hold the left-mouse button
10. After finding the exact incident site location, choose the icon, and select that location as the center of the map.
11. Click the icon.
12. Locate the weather station (the icon should already be selected) by clicking on the map.

13. Click the icon.
14. Select the surface roughness that you wish to use. Try to match the qualitative surface characteristics of the site. This parameter is most critical in an urban or dense forest environment.
15. Select the icon.
16. When back to the main screen, select the icon again. When prompted if you want to collect met/sen data, select "Yes."
17. This will bring you to the Launch Pad. Data Acquisition should start automatically. Start the Emergency Response program and click on the Stoplight icon, and model away!

Manual Met Notes:

a. Maximum solar radiation = 1000 W/. Take a fraction of this based on cloud cover.
b. Stability class can be estimated from wind speed, solar radiation (qualitative), and ceiling height.

FROM EPA's
"Meteorological Monitoring Guidance for Regulatory Modeling Applications"
(EPA-454/R-99-005, February, 2000)

Step 1.
Determine the "Net Radiation Index"

1. If the total cover is 10/10 and the ceiling is less than 7,000 feet, use net radiation index equal to 0 (whether day or night)
2. For **Nighttime**: (from one hour before sunset to one hour after sunrise):
   a. If total cloud cover $\leq$ 4/10, use net radiation index equal to -2.
   b. If total cloud cover > 4/10, use net radiation index equal to -1.
3. For **Daytime**
   a. Determine the insolation class number as a function of solar altitude from Table 1, below
   b. If total cloud cover $\leq$ 5/10, use the net radiation index in Table 2 corresponding to the insolation class number.
   c. If cloud cover > 5/10, modify the insolation class number using the following six steps.
      1.) Ceiling < 7,000 ft, subtract 2
      2.) Ceiling $\geq$ 7,000 ft, but < 160,000 ft, subtract 1
      3.) Total cloud cover equal to 10/10, subtract 1. (This will only apply to ceiling $\geq$ 7,000 ft since cases with 10/10 coverage below 7,000 ft are considered in item 1

above.)

4.) If insolation class number has not been modified by steps 1.), 2.) or 3.) above, assume modified class number equal to insolation class number.

5.) If modified insolation class number is less than 1, let it equal 1.

6.) Use the net radiation index in Table 6-4 corresponding to the modified insolation class number.

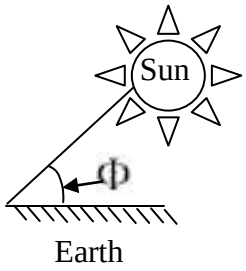

Table 1
Insolation Class as a Function of Solar Altitude

Solar Altitude Φ (degrees)	Insolation	Insolation Class Number
$60 < \Phi$	strong	4
$35 < \Phi \leq 60$	moderate	3
$15 < \Phi \leq 35$	slight	2
$\Phi \leq 15$	weak	1

Table 2.
Turner's Key to the P-G Stability Categories

Wind Speed		Net Radiation Index						
(knots)	*(m/s)*	*4*	*3*	*2*	*1*	*0*	*- 1*	*- 2*
0,1	0 - 0.7	1	1	2	3	4	6	7
2,3	0.8 - 1.8	1	2	2	3	4	6	7
4,5	1.9 - 2.8	1	2	3	4	4	5	6
6	2.9 - 3.3	2	2	3	4	4	5	6
7	3.4 - 3.8	2	2	3	4	4	4	5
8,9	3.9 - 4.8	2	3	3	4	4	4	5
10	4.9 - 5.4	3	3	4	4	4	4	5
11	5.5 - 5.9	3	3	4	4	4	4	4
≥ 12	≥ 6.0	3	4	4	4	4	4	4

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

Toxicology Emergency Response Program (DATE)
STANDARD OPERATING PROCEDURE NO. ( )

SUBJECT: Data Collection and Management

Description of the SOP. This SOP describes record-keeping processes.

Key Personnel with Responsibility to Manage this Equipment.

Amanda Fincher

Calibration Instructions

1. All instrument calibrations are documented on CTEH Calibration Logs with the following information: date, time instrument identification, calibration gas/filter identification, user initials.

2. Calibration logs are stored together in project file.

Sampling Data Collection and Management Instructions

1. Laboratory Samples

a) Sample collection information is documented on CTEH field forms. Sampling information includes the following: date, time, location, sampler identification, and sample collection device information (if applicable).
    1) Sample collection forms are stored together in project file.
    2) Sample collection information is databased using Microsoft Access and/or summarized on sample collection maps made with ArcGIS.

b) Analysis requests are made on CTEH-prepared chains of custody (COCs). Copies of original COCs sent to the laboratory are stored together in the project file. The original COCs are also stored together in the project file, upon receipt from the laboratory.

c) Laboratory results are received in EDD format, in PDF format, and in hard copy data packets.
    1) EDDs and PDFs are stored in an electronic project folder. Hard copies are stored together in the project file.
    2) Laboratory results are compiled and databased using Microsoft Access and/or summarized on sample collection maps made with ArcGIS. Within the database and/or map summary, laboratory results are associated with sample collection information.

2. Instantaneous "Real-Time" Measurements

a) Manually-logged data
    1) Instantaneous measurements are documented on CTEH field forms or in bound notebooks. Information documented includes: date, time, location, instrument information, sample result, sampler observations, and sampler identification.

2) Copies of measurements from notebooks are stored with field forms in the "real-time" section of the project file. Notebooks are stored together in the project file.
3) Information from real-time forms and notebooks are databased using Microsoft Access.

b) Instrument-logged data
1) Instrument information, location information, and general observations associated with instrument-logged data are documented either on CTEH real-time field forms or in bound notebooks. This information is filed in the same manner as manually-logged data.
2) Instrument-logged data are downloaded from the instrument using the appropriate software. These data are then databased using Microsoft Access. Within the database, instrument-logged data are associated with sample collection information.
3) Sample collection information is mapped using ArcGIS, and associated data are configured into graphs using SigmaPlot.

c) Radio-telemeted data
1) Instrument information, location information, and observations are documented on CTEH field forms or in bound notebooks. This information is filed in the same manner as manually-logged data.
2) Telemeted data are recorded using software associated with the transmitters. Stored data are backed up on a daily basis. These data are then databased using Microsoft Access. Within the database, instrument-logged data are associated with sample collection information.
3) Sample collection information is mapped using ArcGIS, and associated data are configured into graphs using SigmaPlot.

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

Toxicology Emergency Response Program (June 15, 2011)
STANDARD OPERATING PROCEDURE NO. (1.0)

SUBJECT: MultiRAE Worker Exposure Monitoring

Description of the SOP. This SOP describes the use of the MultiRAE plus PID as a personal monitoring device for the collection of real-time worker exposure data.

Key Personnel with Responsibility to Manage this Operation.

Any environmental scientist or IH technician responsible for the collection of real-time worker exposure data using the MultiRAE plus PID.

MultiRAE Worker Exposure Preparation Instructions

1. Calibration

a) Please follow the CTEH MultiRAE plus PID Standard Operating Procedures Version 1.1, latest version.

2. Equipment Preparation

a) Connect a 3-4 ft piece of Teflon® tubing using RAE approved connectors to the MultiRAE inlet. Connect the Teflon® tubing directly to the MultiRAE, do not connect to the water-trap.
b) Install a water-trap to the inlet end of the Teflon® tubing. Ensure that the inlet of the Teflon® tubing is equipped with a connection device that can be clipped to the worker's lapel or clothing in the breathing zone.

3. Instrument Set-Up

*a) Ensure that the MultiRAE is **NOT** in Diagnostics Mode.*
*b) Set up the MultiRAE to data-log at the appropriate data-log interval. If no specific data-log interval is desired, use the **5-minute interval**.*
*c) Ensure that the MultiRAE reflects the correct **DATE and Time (time zone where sample will be collected).***
d) Ensure that the appropriate sensors are enabled for data-log. Additionally, ensure that irrelevant sensors are disabled.

4. Instrument Installation on Worker

a) Clip the calibrated MultiRAE onto the belt of the worker. If no belt is available or the worker is wearing chemical or flame-resistant protective clothing, use an auxiliary belt on the outside of the chemical or flame-resistant protective clothing.
b) Going across the worker's back, locate the Teflon® tubing inlet in the worker's breathing zone, clipping the inlet to the worker's lapel or clothing.
c) Ensure that the inlet is located on the outside of any clothing, vest, or other material that may block the inlet from drawing air from the worker's breathing zone.

Sampling Data Sheet Instructions

1. Use an appropriate field data sheet prior to deploying the MultiRAE to collect worker exposure data. The data sheet should capture the following information:

a) CTEH Project Number
b) MultiRAE Instrument Serial Number
c) Calibration Information (specifically the: calibration date, calibration gas type, calibration gas lot number, calibration gas expiration date.)
d) Worker's Full Name, Contact Information, and Company Information,
e) Worker's Job Task,
f) Worker's Work Site Location Information,
g) Sample Information for Co-located samples (i.e. 3M 3500 badge information, sample ID, etc…),
h) Start Date and Time,
i) Stop Date and Time,
j) Worker's Smoking Habit,
k) Other Potential Cross-Contamination Sources (i.e. bug spray, cologne, hand sanitizer etc…)
l) Sampler's Name and Contact Information

Post-Sampling Event Collection of MultiRAE and Data Processing

1.At the end of the worker's job task or work shift, collect the MultiRAE from the worker:

2.Conduct an end of shift interview with the employee to gather information related to work shift activities

3. Immediately download the MultiRAEs data-logged data using ProRAE suite. Save the data file in the appropriate project folder location.

4. Replace the MultiRAEs batteries and prepare the instrument for subsequent use of the device.

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- Equipment Room Manager 801.501.8580

RED TAG inoperable equipment properly, example following SOP

References and Further Assistance

Review Date for this SOP

Nathan Williams 4/12/2011

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 (June 15, 2011)
STANDARD OPERATING PROCEDURE NO. (1.0)

SUBJECT: MultiRAE Worker Exposure Monitoring

Description of the SOP. This SOP describes the use of the MultiRAE plus PID as a personal monitoring device for the collection of real-time worker exposure data.

Key Personnel with Responsibility to Manage this Operation.

Any environmental scientist or IH technician responsible for the collection of real-time worker exposure data using the MultiRAE plus PID.

MultiRAE Worker Exposure Preparation Instructions

1. Calibration

a) Please follow the CTEH MultiRAE plus PID Standard Operating Procedures Version 1.1, latest version.

2. Equipment Preparation

a) Connect a 3-4 ft piece of Teflon® tubing using RAE approved connectors to the MultiRAE inlet. Connect the Teflon® tubing directly to the MultiRAE, do not connect to the water-trap.
b) Install a water-trap to the inlet end of the Teflon® tubing. Ensure that the inlet of the Teflon® tubing is equipped with a connection device that can be clipped to the worker's lapel or clothing in the breathing zone.

3. Instrument Set-Up

*a) Ensure that the MultiRAE is **NOT** in Diagnostics Mode.*
*b) Set up the MultiRAE to data-log at the appropriate data-log interval. If no specific data-log interval is desired, use the **5-minute interval**.*
*c) Ensure that the MultiRAE reflects the correct **DATE and Time (time zone where sample will be collected).***
d) Ensure that the appropriate sensors are enabled for data-log. Additionally, ensure that irrelevant sensors are disabled.

4. Instrument Installation on Worker

a) Clip the calibrated MultiRAE onto the belt of the worker. If no belt is available or the worker is wearing chemical or flame-resistant protective clothing, use an auxiliary belt on the outside of the chemical or flame-resistant protective clothing.
b) Going across the worker's back, locate the Teflon® tubing inlet in the worker's breathing zone, clipping the inlet to the worker's lapel or clothing.
c) Ensure that the inlet is located on the outside of any clothing, vest, or other material that may block the inlet from drawing air from the worker's breathing zone.

Sampling Data Sheet Instructions

1. Use an appropriate field data sheet prior to deploying the MultiRAE to collect worker exposure data. The data sheet should capture the following information:

a) CTEH Project Number
b) MultiRAE Instrument Serial Number
c) Calibration Information (specifically the: calibration date, calibration gas type, calibration gas lot number, calibration gas expiration date.)
d) Worker's Full Name, Contact Information, and Company Information,
e) Worker's Job Task,
f) Worker's Work Site Location Information,
g) Sample Information for Co-located samples (i.e. 3M 3500 badge information, sample ID, etc…),
h) Start Date and Time,
i) Stop Date and Time,
j) Worker's Smoking Habit,
k) Other Potential Cross-Contamination Sources (i.e. bug spray, cologne, hand sanitizer etc…)
l) Sampler's Name and Contact Information

Post-Sampling Event Collection of MultiRAE and Data Processing

1.At the end of the worker's job task or work shift, collect the MultiRAE from the worker:

2.Conduct an end of shift interview with the employee to gather information related to work shift activities

3. Immediately download the MultiRAEs data-logged data using ProRAE suite. Save the data file in the appropriate project folder location.

4. Replace the MultiRAEs batteries and prepare the instrument for subsequent use of the device.

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- Equipment Room Manager 801.501.8580

RED TAG inoperable equipment properly, example following SOP

References and Further Assistance

Review Date for this SOP

Nathan Williams 4/12/2011

Attachments

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

Attachment E

Galson Laboratories SOP for VOCs by OSHA PV-2120 & EPA TO-15

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

Toxicology Emergency Response Program (June 15, 2011)
STANDARD OPERATING PROCEDURE NO. (1.0)

SUBJECT: 3M 3500_3520 OVM Badge SOP

Description of the SOP. This SOP describes the use of the 3M 3500/3520 Organic Vapor Monitor (OVM) badge as a passive dosimeter for the collection of analytical worker exposure data.

Key Personnel with Responsibility to Manage this Operation.

Any environmental scientist or IH technician responsible for the collection of real-time worker exposure data using the 3M 3500/3520 OVM badge.

3M 3500/3520 OVM Badge Preparation Instructions

1. Calibration

a) Neither calibration, nor flow calibration is required.

2. OVM Badge Preparation

NOTE: While handling un-exposed and/or exposed OVM badges, please consider using proper media handling techniques. Sample handling should take place in a location, removed from any areas of contamination or potential sources of cross-contamination. The researcher should use clean/covered hands, surfaces, and tools when working with OVM badges.

a) Inspect the badge container to identify potential tampering or un-intentional disturbances to the OVM badge prior to use. An un-used OVM badge should be housed in a sealed aluminum canister as sent from the manufacturer or laboratory.
b) Remove the badge from the canister only at the time of sample deployment.

3. OVM Badge Deployment

a) Place the OVM badge on the worker's lapel or clothing within the breathing zone (i.e. within 10 inches from the nose or mouth as per NIOSH recommendations).
b) Ensure that the OVM badge is located on the outside of any clothing, vest, or other material that may block the inlet from drawing air from the worker's breathing zone.
c) Instruct the worker to avoid covering the OVM badge with clothing, vests, PPE, etc…
d) Instruct the worker to avoid introducing cross-contamination across the surface of the OVM badge (i.e. bug spray, cologne, hand sanitizer, etc…)

Sampling Data Sheet Instructions

1. Use an appropriate field data sheet prior to deploying the OVM badge. The data sheet should capture the following information:

a) CTEH Project Number
b) Sample Identification Number

c) Worker's Full Name, Contact Information, and Company Information,
d) Worker's Job Task,
e) Worker's Work Site Location Information,
f) Sample Information for Co-located samples (i.e. 3M 3500 badge information, sample ID, etc…),
g) Start Date and Time,
h) Stop Date and Time,
i) Worker's Smoking Habit,
j) Other Potential Cross-Contamination Sources (i.e. bug spray, cologne, hand sanitizer etc…)
k) Sampler's Name and Contact Information

Post-Sampling OVM Badge Collection and Data Processing

1. At the end of the worker's job task or work shift:

a) collect the exposed OVM badge from the worker,
b) remove the OVM badge's outer ring and permeation membrane,
c) and, place the clear plastic lid over the OVM badge. Ensure that the clear plastic lid closely firmly.

2. Place the exposed, sealed OVM badge back into the original canister and complete the canister's label with the appropriate sample information.

3. Conduct the post-sample interview with the sampled worker to identify problems and/or potential cross contamination to the sample. This information should be entered onto the Sampling Data Sheet.

4. Document the stop time and date of the sampling event.

5. Place the canister and corresponding OVM badge with the appropriate sample lot and prepare COC for shipment to the laboratory.

GALSON LABORATORIES STANDARD OPERATING PROCEDURE

SUBJECT: WHOLE AIR AND SUMMA CAN REGULATOR CALIBRATION AND CLEANING

SOP ID:	AUTHOR: Anthony Marchetti
IN-AIRREG	SECTION SUPERVISOR: ***Gale S. Peterson***
	QA OFFICER: Wendy Ferro
COPYRIGHT	LABORATORY DIRECTOR: Mary Unangst

1.0 PURPOSE

This SOP describes the calibration and cleaning procedure for flow controllers and the regulators used to collect samples in 400cc, *450cc,* ***1000cc MiniCans or Summa Cans.***

2.0 RESPONSIBILITIES

2.1 All technicians performing this procedure are required to read and understand the SOP as written.

2.2 The Section Supervisor is required to read and understand the SOP as written in addition to assuming responsibility for the training and continued education of technicians performing this procedure.

3.0 DEFINITIONS

3.1 SOP – Standard Operation Procedure

3.2 PSI: pounds/sq. inch

3.3 QC: Quality Control

3.4 "Hg: inches of Mercury

3.5 UHP: Ultra High Purity (Nitrogen Grade 4.8 or higher)

3.6 Psig: pounds/sq. inch gauge

3.7 Mini Can: metal canister with valve

3.8 Summa Can: Round Metal Canister with Valve

3.9 Flow controller or regulator: mechanism used to fill Mini can

3.10 LP: Low Pressure

4.0 METHOD SUMMARY

4.1 The Mini Can regulator is a high purity flow regulation system used to fill canisters

(Mini Cans or ***Summa Cans***) at a constant rate from vacuum to within 1 psi of atmospheric pressure, without requiring power.

4.2 The regulator consists of two main parts; the vacuum controller body and an interchangeable sapphire restrictor. The vacuum controller maintains a –0.3 to –1 psi atmospheric pressure regardless of what the vacuum is on the outlet. By changing the value of the restrictor on the inlet, different flow rates (corresponding to canister fill times) can be achieved. For any given restrictor, the flow rate can only be changed by a factor of 2-3x. This is done by adjusting the hex head set screw on the center of the vacuum controller body. Refer to MS-FORM-1 for restrictor settings for various applications.

4.3 In the laboratory, regulators are cleaned between each use and set to the flow rate requested by the client.

4.4 Canisters are leak-checked in the following manner: when can-cleaning has been completed, each canister is put under full vacuum and the vacuum reading (usually 30" of Mercury) is recorded in the Can-Cleaning Logbook along with the date/time and analyst's initials. The prep group will check and record the vacuum reading for each canister before shipping to a client and place a full vacuum sticker along with a date/sample label. Acceptance criteria are +/- 2" of Hg variance for a >= 24 hour leak check.

5.0 INTERFERENCES

Not Applicable

6.0 SAFETY

6.1 Safety glasses with side shields are required when working in the laboratory.

7.0 MATERIALS AND APPARATUS

7.1 UHP nitrogen for the cleaning gas.

7.2 Regulators, with a selection of #2 through #5 restrictors. Restek requlators have a #8 restrictor which are comparable to a #5 restrictor.

7.3 Alicat Scientific flow meters: Model #01-39-20035.01 and Model #01-03-200020.

7.4 1/2" and 9/16" open end wrenches and a 1/8" hex key.

8.0 REAGENTS AND STANDARDS

8.1 Nitrogen @ 99.9999% purity (UHP N2)

9.0 PROCEDURE

9.1 For Flow Settings

9.1.1 Select a flow controller with the correct restrictor code. See MS-FORM-1 for guidelines.

9.1.2 Ensure all possible leak points are tightened prior to calibration.

9.1.3 The Regulator Calibration Data Sheet located in P:\Prep Group\Pump Loan\Approved Forms\ Regulator Cal Sheet and update to reflect calibration results.

9.1.4 Connect the appropriate Alicat Scientific flow calibrator to the inlet of the regulator. Alicat Model #01-39-20035.01 is used with restrictors coded 2 and 3, Model #01-03-20020 is used with restrictors coded 4 and 5. Verify the gauge is functioning.

9.1.5 Connect an evacuated calibration canister that is between 10 & 30 inches of Hg (gauge) to the outlet of the flow controller body to start flow.

9.1.6 Allow about 1 minute for the flow to equilibrate, then note the inches of Hg regulator is reading. Visually observe regulator dial for 30 seconds to verify the regulator is not leaking (i.e. the inches of Hg is dropping very quickly). Recheck what regulator is reading when the regulator is calibrated, prior to removing from Alicat, to ensure it has not leaked. If there is a drastic drop in pressure, place regulator in repair bin.

9.1.7 Verify that the Alicat is reading 0 when the regulator is removed. If it is not reading 0, press the reset button and repeat 9.1.3 - 9.1.5. Change the battery if abnormal fluctuation is noticed on the display of the Alicat during calibration. ***The battery of the Alicat should be changed every six months. Attach a label with the date of battery change and check that it is not past six months before each use. Replace the label with the correct date anytime the battery is changed.***

9.1.8 Remove the hex screw cover located in the center of the regulator body using a 1/8" hex key.

9.1.9 Adjust the set screw using the hex wrench so that the flows agree with MS-FORM-1 ***(Figure 1)***, enter this data into the cells that correspond to the regulator you are calibrating. Turning the screw clockwise will result in a lower flow rate; turning the screw counterclockwise raises the flow rate. The adjustment must be done slowly (1/4 of full turn intervals), allowing the regulator body adequate time to "equalize" with any adjustments made. Add a label with the appropriate hours on it for what the regulator was calibrated to. Print out "Regulator Calibration Data Sheet"and include in paperwork that goes to client.

9.1.10 CAUTION: If 1-2 turns do not result in a change of flow rate, STOP and check the flow calibrator for proper operation or blockages in the inlet plenum. The internal diaphragm of the regulator may be damaged by over tightening. If flow readings are unsteady or erratic, select another regulator.

9.2 PROCEDURE FOR CLEANING

9.2.1 Remove all tape or labels added to the regulators. Be sure not to remove the barcode label or the label containing the serial number.

9.2.2 Remove back flush port screw from the body of the regulator. This is located to the right center of the diaphragm housing, it is a 1/8" hex screw.

9.2.3 Remove the restrictor and particulate filter located on the inlet side of the regulator.

9.2.4 The regulator can be cleaned, by connecting LP UHP N2 hose at 5-10 psi at the flush port and back flush for about 20 seconds.

9.2.5 The restrictors can be cleaned by using UHP N2 at 30-40 psig to remove any solid particulate caught in the sapphire orifice (use the dilution manifold). Be sure to connect the restrictors with the flat side (inlet side) facing out so any blockages will be blown out.

9.2.6 Clean the particulate filter with UHP N2 by same method as above. Ensuring positive air flow through the filter.

9.2.7 Reassemble the unit taking great care not to over tighten any screws. Check the gap between the restrictor and the ferrule nut using the nogo gap gauge at the 1/4"/ 6mm setting.

9.2.8 Grab regulators must also be flushed briefly with UHP N2 to ensure cleanliness using the dilution manifold.

10.0 DOCUMENTATION
Not Applicable

11.0 CALCULATIONS
Not Applicable

12.0 QUALITY CONTROL CHECKS AND CRITERIA
Not Applicable

13.0 CORRECTIVE ACTION PLAN
Not Applicable

14.0 WASTE DISPOSAL
Not Applicable

15.0 REFERENCES
15.1 MS-FORM-1

16.0 METHOD MODIFICATIONS
Not Applicable

Minican Regulator	Setting Guidelines							
	400 cc Minican							
2	Time (minutes)	5	10	15	30			
	Flow (cc/minute)	***72***	***36***	***24***	***12***			
3	Time (minutes)	15	30	45	60	90	120	
	Flow (cc/minute)	***24***	***12***	***8***	***6***	***4***	***3***	
4	Time (hours)	1	1.5	2	3	4**		
	Flow (cc/minute)	***6***	***4***	***3***	***2***	***1.5***		
5	Time (hours)	4**	6	8	10	12	14	16
	Flow (cc/minute)	***1.5***	***1***	***0.75***	***0.6***	***0.5***	***0.43***	***0.37***

	450 cc Minican							
2	Time (minutes)	5	10	15	30			
	Flow (cc/minute)	***81***	***40.5***	***27***	***13.5***			
3	Time (minutes)	15	30	45	60	90	120	
	Flow (cc/minute)	***27***	***13.5***	***9***	***6.8***	***4.5***	***3.4***	
4	Time (hours)	1	1.5	2	3	4**		
	Flow (cc/minute)	***6.75***	***4.5***	***3.38***	***2.25***	***1.69***		
5	Time (hours)	4**	6	8	10	12	14	16
	Flow (cc/minute)	***1.69***	***1.13***	***0.84***	***0.68***	***0.56***	***0.48***	***0.42***

	1 Liter Minican							
4	Time (hours)	1	2	3	4	5	6	
	Flow (cc/minute)	***15***	***7.5***	***5***	***3.75***	***3***	***2.5***	
5	Time (hours)	8	12	16	18	24		
	Flow (cc/minute)	***1.87***	***1.25***	***0.94***	***0.83***	***0.62***		

Minican Regulator	Setting Guidelines	
	6 Liter Canister	
3	Time (hours)	24
	Flow (cc/minute)	***3.8***
4	Time (hours)	24
	Flow (cc/minute)	***3.75***
5	Time (days)	7
	Flow (cc/minute)	***0.54***

Note: Minimum vacuum allowable for acceptable minican/canister is ***-28" Hg***

Note: Flow rate as read from the Alicat Scientific flow calibrator

Note: Regulator setting determined by using this formula

$$\frac{\text{Target Volume (cc)}}{\text{Total Time (minutes)}} \times .9$$

Note: When using a 1 Liter can for under 8 hours you need to use a #4 restrictor.

**Preferable to use #4 restrictor for 4 hour setting

(Figure 1)

SUBJECT: **VOLATILE ORGANIC COMPOUNDS BY OSHA PV2120 & EPA TO-15**

SOP ID: IN-VOCS
AUTHOR: Justin Palmer/ Rob Wilson
SECTION SUPERVISOR: Justin Palmer
QA OFFICER: Wendy Ferro
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LABORATORY DIRECTOR: Mary Unangst

1.0 PURPOSE

1.1 This SOP describes the procedure for determining contaminants in whole air samples collected in a fused silica-lined stainless steel canister (following OSHA method PV2120 and Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method TO-15). This method utilizes GC/MS for the determination of a wide range of volatile and semi-volatile organic compounds (as listed in Table 1).

2.0 RESPONSIBILITIES

2.1 All GC/MS analysts performing this method are required to read and understand the method as written in OSHA PV2120, and are required to meet all QC requirements (as described in EPA TO-15) before attempting analysis of samples.

2.2 The section supervisor is required to read and understand the method as written, but is also responsible for the training and continued education of technicians performing this method.

2.3 The section supervisor is required to review reports and packages to ensure that all data are valid prior to client receipt.

3.0 DEFINITIONS

3.1 GC/MS: Gas Chromatography/Mass Spectrometry

3.2 Capillary: Analytical column with an internal diameter less than or equal to 0.32 mm

3.3 EICP: Extracted ion current profile: Plot of ion abundance vs. GC retention time for a single characteristic mass (amu)/charge ratio.

3.4 AMU: Atomic Mass Unit

3.5 ppbv: part per billion by volume for component concentration in the gas phase.

3.6 Mini Can: Canisters ranging from 400mL to 1000mL in volume; these are associated with an injection volume of 100mL.

3.7 Summa Canisters: Canisters with a 6L volume; these are associated with an injection volumes of ***500 to 1000-cc.***

3.8 SCAN: Normal MS acquisition mode where mass ranges from 35 to 300 amu are scanned to produce a Total Ion Chromatogram.

3.9 SIM: Selective Ion Mode; only scans certain ions per sample to increase sensitivity. Used for only certain projects that require low level analysis.

4.0 METHOD SUMMARY

4.1 The sample is prepared for analysis by pre-concentration, which removes potential interference and dries the sample. After the pre-concentration and drying steps are completed, the analytes are cryo-focused onto the head of the GC column via reduced temperature trapping, followed by rapid thermal desorption.

4.2 Separation of the analytes is achieved by temperature programming of the GC oven.

4.3 The eluent from the capillary column is introduced directly to the mass spectrometer, which is operated in the electron impact mode. Identification of target analytes is accomplished by comparing sample mass spectra with reference spectra generated from purchased standards on the GC/MS system used to analyze the samples. Quantitation is achieved using the internal standard technique. The response of a selected quantitation ion for each analyte relative to the quantitation ion of the designated internal standard (relative response factor, or RRF) is determined over a minimum five-point calibration range.

5.0 INTERFERENCES

5.1 Raw GC/MS data from all samples and blanks must be evaluated for interference. Determine if the source of interference is in the sample introduction system. If so, take corrective action to eliminate the problem.

5.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Each auto-sampler port is flushed with nitrogen after use (prior to set-up of the next batch of samples).

5.3 Interferences are minimal by GC/MS as this type of detector allows the determination if compounds are co-eluting in the chromatographic system. Quantification can be done on alternate ions so interferences are eliminated in most cases. In other instances, a dilution may be performed to allow better separation or results may be considered estimated if the interference cannot be removed.

6.0 SAFETY

6.1 Most volatile compounds are considered hazardous. Always wear gloves and a lab coat when handling stock standards.

6.2 Safety glasses with side-shields are required whenever working in the laboratory.

6.3 It is very important that special precaution be used when working with liquid nitrogen, as it can cause serious burns.

6.4 Be sure that only radiation worker trained personnel handle Mini Cans that have been screened for radiation. These cans will have an orange dot on them.

7.0 MATERIALS AND APPARATUS

7.1 Agilent (previously Hewlett Packard (HP)- may be used interchangeably) 5890, 6890, or 7890 Series GC, in conjunction with an HP model 5972, 5973, or 5975 mass spectrometer (capable of scanning from 35 to 300 amu every 1-second or less using 70 volts (nominal) electron energy in the electron impact ionization mode).

7.2 Entech 7032, 7032L, 7032A, or 7016CA autosampler models with the Entech 7100 or 7100A three stage Preconcentrator.

7.2.1 Microscale Purge and Trap (MPT) analysis is performed by utilizing a glass bead trap in module 1 and a Tenax sorbent trap in module 2. Module 3 contains an empty trap.

7.2.2 Cold Trap Dehydration analysis (CTD) employs an empty trap in module 1 and a Tenax trap in module 2. Module 3 contains an empty trap.

7.3 Analytical Chromatography column: 0.32mm ID x 60m length silicone-coated capillary column with a 1 um film thickness – Restek RTX-1 or equivalent.

7.4 GC/MS Interface - The GC column is directly coupled to the mass spectrometer ion source. Acceptable tuning and calibration performance must be demonstrated on a daily basis.

7.5 Data System – The data system used is the HP Chemstation G1701BA with (at minimum) Revision B.01.00 software package for the HP5972, 5973, or 5975 MS. This system allows continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software allows for searching any GC/MS data file for ions of a specific mass, and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile. The software allows integration of the abundance in any EICP between specified time or scan number limits. The NIST 129K version mass spectral library is being used for a reference library.

8.0 REAGENTS AND STANDARDS

8.1 Helium @ 99.9999% purity

8.2 Liquid nitrogen

8.3 Stock standards

8.3.1 Stock standard solutions are purchased as certified solutions.

8.3.1.1 TO-15 Subset standard is purchased from Spectra gases

8.3.1.1.1 (Catalogue # ENT15-25S-6A-1M*)* or Scott gases (item# 0104AZ00025).

8.3.1.2 TO-14 standard is purchased from Spectra gases

8.3.1.2.1 (Catalogue # ENT14/39S/6A1M) or Scott gases (item# 01049Z90001).

8.3.1.3 Ethylene oxide standard is purchased from Spectra gases

8.3.1.3.1 (ETOX/CGA3501M) or Scott gases (item# 08020001310PAL).

8.3.1.4 4-Phenylcyclohexene standard is purchased from Scott gases (item# 0104P200046).

8.3.1.5 TO-15 100-ppbv 75 compound standard

8.3.1.6 TO-15 10-ppbv project specific compound list

8.3.1.6.1 Used for ultra low level SIM analysis.

8.3.2 Stock standard solutions must be stored at room temperature, or as recommended by the manufacturer.

8.3.3 Stock standard solutions must be replaced after 1 year, or sooner depending on manufacturer's expiration date.

8.4 Internal Standard and Surrogate

8.4.1 The internal standards are Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5.

8.4.2 The surrogate is Bromofluorobenzene.

8.4.3 Each sample undergoing analysis, as well as all calibration standards must be spiked with 50-ppbv of each internal standard and surrogate.

8.4.4 A certified stock internal and surrogate standard mixture must be purchased every 12 months (or sooner, if degradation is observed). (Spectra Gases, TO-14 IS/Surr. mix, catalogue # ENT14ITS-6A-1M) or (Scott Gases, TO-14 IS/Surr. Mix, P/N 24087828)

8.4.5 Store the internal/surrogate standard at room temperature.

8.5 GC/MS Tuning standard

8.5.1 In a 6L Summa canister, prepare a 100-ppbv standard of Bromofluorobenzene (BFB). This standard contains the internal standard compounds as well.

8.5.2 The tuning standard is stored at room temperature when not in use. When using

premixed certified gases, store according to the manufacturer's documented holding time and storage temperature recommendations.

8.6 Intermediate (working) standards

8.6.1 A working standard of the target compounds is prepared at 5-ppbv, 25-ppbv, and 100-ppbv for both 100cc and 500cc injection methods. This is used to generate the instrument calibration curve. The working standard must contain all of the analytes of interest. Target compound working standards expire one month after preparation.

8.6.2 The internal / surrogate working standard is prepared at 100 ppbv. This is also used as the tuning standard. Working internal standards expire two months from preparation date.

8.7 Calibration standards

8.7.1 Calibration standards must be analyzed at a minimum of five different concentrations. One of the calibration standards must correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards must correspond to the range of concentrations expected to be found in the actual samples. The typical calibration curve range for TO15 (Minican) list is 5-ppbv to 150-ppbv for most analytes. TO-15 (6L Summa can) list is from 1-ppbv to 30-ppbv. ***TO-15 low level list is from 0.2-ppbv to 30-ppbv. TO-15 SIM is dependent on project specific reporting limits.*** Ethylene Oxide ranges from 20-400-ppbv and 4-Phenylcyclohexene ranges from 1-20-ppbv.

8.7.2 Internal standards and surrogate are added to all calibration standards during analysis.

9.0 PROCEDURES

9.1 Sample collection, preservation and handling

9.1.1 Whole air samples are collected in 400cc or 1000cc fused silica lined stainless steel canisters (Mini Cans) or 6-liter Summa canisters that are stored at room temperature until analysis. Sample stability is unknown, therefore samples should be analyzed as soon as possible.

9.2 Sample Preparation

9.2.1 Once the GCMS group has received the samples, the vacuum in the can is measured to verify the amount of sample collected. If the vacuum reading is > 5 inches of Hg, the project manager must notify the customer. This can be caused by either improper sample collection or a malfunction of the regulator. A full canister will read < 5 inches of Mercury. ***There should be a partial vacuum remaining (@ 1 to < 5 inches of Mercury) to evidence that a full sampling event took place. No measurable vacuum may be an indication that the canister was not collecting the sample over the full duration of the sampling***

period or that the canister was leaking during sampling. The customer must be notified if there is no measurable vacuum. Pump group will set regulators to leave a partial vacuum for the specified sampling time (8 hrs, 24 hrs, or week). A volume of Nitrogen can be added to bring the volume above 5" Mercury with the use of the Entech 7100 sample diluter. The initial and final pressure readings must be recorded in the can dilution logbook. The dilution factor is calculate according to the equation:

$$DF = \frac{PSIA_f}{PSIAi}$$ Where $PSIA_f$ = final pressure reading
$PSIA_I$ = initial pressure reading

Detection limits will be raised proportionately.

9.3 Analytical Procedure

9.3.1 Instrument Maintenance

9.3.1.1 Appropriate instrument maintenance must be performed as necessary prior to initial calibration. Indications of the need for maintenance include poor peak shape, inadequate sensitivity, and inability to pass BFB tune. Steps that may be required to address these problems include replacing one or both traps in the Entech 7100, baking the transfer line and GC column, trimming or replacing the column, and/or cleaning the ion source.

9.3.2 Instrument conditions for TO-15 regular list and Hydrocarbon analysis:

The following GC/MS instrument conditions are used:

Mass range:	35-300 amu
Scan time:	2.82 scan/sec
Initial temperature:	34 ^{0}C, hold for 5.5 minutes
Temperature program	increase at 5 ^{0}C /minute to 70^{0}C, then increase at 15^{0}C /minute to 170^{0}C, then increase at 25^{0}C/ minute to 240^{0}C, holding there for 1-10 minutes.
Final temperature:	240 ^{0}C, hold 1-10 minutes after Hexachloro-1,3-Butadiene elutes.
Injector temperature:	150 ^{0}C
Injection volume:	100cc
Carrier gas:	Helium at 20 cm/sec

9.3.3 Instrument conditions for Ethylene Oxide analysis:

Mass range:	28-250 for Ethylene oxide then at 6.9 min. 29-250 amu
Initial temperature:	34 ^{0}C, hold for 5.5 minutes,
Temperature program	increase at 15 ^{0}C /minute to
Final temperature:	240 ^{0}C, hold 1-10 minutes
Injector temperature:	150 ^{0}C
Injection volume:	100cc

Carrier gas:	Helium at 20 cm/sec

9.3.4 Instrument conditions for 4-Phenylcyclohexene analysis:

Mass range:	SIM Mode (4PCH 74, 108, 158 amu)
Initial temperature:	50 ^{0}C
Temperature program	increase at 10 ^{0}C /minute to 200^{0}C, then increase at 25 ^{0}C /minute.
Final temperature:	250 ^{0}C, hold 1-10 minutes.
Injector temperature:	150 ^{0}C
Injection volume:	100cc
Carrier gas:	Helium at 20 cm/sec

9.4 Instrument Calibration

9.4.1 Instrument Performance Check: At the beginning of a 24-hour analysis sequence it is necessary to show that the GC/MS system meets the instrument performance criteria. This is accomplished by the analysis of a 50-ppbv injection of BFB to demonstrate correct mass calibration, mass resolution, and mass transmission. Any injection containing 50-ppbv of BFB can be used for this purpose.

9.4.1.1 BFB must meet the criteria listed in 9.4.1.2 before standards and samples are analyzed. An acceptable BFB tune is demonstrated once at the beginning of each 24-hour period during which samples or standards are analyzed. The 24-hour period begins with the injection time of the BFB and ends after 24 hours according to the system clock. The following abundance criteria are required to establish instrument tune compliance:

9.4.1.2 Tune acceptance criteria:

Mass	Ion Abundance Criteria
50	8.0-40.0 percent of mass 95
75	30.0-66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95
173	Less than 2.0 percent of mass 174
174	50.0 - 120 percent of mass 95
175	4.0-9.0 percent of mass 174
176	Greater than 93.0 percent but less than 101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

9.4.1.3 For demonstrating an acceptable tune, the mass spectrum of BFB must be obtained. This is can be performed by the HP/Agilent Chemstation Software using the Auto-find BFB function. This function works as follows: three scans are taken (the peak apex scan, and the scans immediately preceding and following the apex) and then averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction is designed to eliminate column bleed and instrument background ions. Alternately, the BFB spectrum can be obtained/performed

manually.

9.4.2 Calibration standards are analyzed concurrently or once BFB meets acceptance criteria.

9.4.3 Initial Calibration

9.4.3.1 For use with 100cc-sample injection volume TO15 analysis (i.e. 400-1000cc canisters): A minimum 5-point calibration curve must be analyzed prior to sample analysis. The internal standards must be added at 50-ppbv to each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from the 25 and/or 50-ppbv working standard canister to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. A 5-ppbv standard is utilized (100-cc injection volume) for the 5-ppbv level on some instruments. A blank should be run in-between the three highest standards (for example, between the 100 and 150-ppbv standards).

Standard Level	25-ppbv working standard	50-ppbv working standard
5-ppbv standard	Use 20cc	Use 10cc
20-ppbv standard	Use 80cc	Use 40cc
50-ppbv standard	Use 200cc	Use 100cc
100-ppbv standard	Use 400cc	Use 200cc
150-ppbv standard	Use 600cc	Use 300cc
200-ppbv standard	N/A	Use 400cc

9.4.3.2 For use with 500cc-sample injection volume analysis (i.e. 6-liter canisters): A minimum 5-point calibration curve must be analyzed prior to sample analysis. The internal standards must be added at 10-ppbv for each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from the 25-ppbv working standard canister to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. Blanks should be run in-between the three highest standards (for example, between the 20 & 30-ppbv standards).

Standard Level	1-ppbv working standard	5-ppbv working standard	25-ppbv working standard
0.2-ppbv standard	Use 100cc	Use 500cc	N/A
1-ppbv standard	N/A	Use 100cc	Use 20cc
5-ppbv standard	N/A	N/A	Use 100cc
10-ppbv standard	N/A	N/A	Use 200cc
20-ppbv standard	N/A	N/A	Use 400cc
30-ppbv standard	N/A	N/A	Use 600cc

9.4.3.3 For use with 1000cc-sample injection volume analysis (6 liter SIM): A minimum 5-point calibration curve must be analyzed prior to sample

analysis. The internal standards must be added at midpoint for each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from either 0.05-ppbv working standard canister or 1-ppbv working standard canister to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. Blanks should be run in-between the highest standards (for example, between the 0.4 & 0.6-ppbv standards) and blanks should be run after the calibration to clean out the system.

Standard Level	0.05-ppbv working standard	1-ppbv working standard
0.005-ppbv standard	Use 100cc	N/A
0.025-ppbv standard	Use 500cc	N/A
0.1-ppbv standard	N/A	Use 100cc
0.2-ppbv standard	N/A	Use 200cc
0.4-ppbv standard	N/A	Use 400cc
0.6-ppbv standard	N/A	Use 600cc

9.4.3.4 Calculate the relative response factor for each compound using the following equation:

$$RRF = \frac{A_x}{A_{is}} * \frac{C_{is}}{C_x}$$

Where:

A_x = Area of the characteristic quant ion for the compound to be measured (see *Table 1 and 2*).

A_{is} = Area of the characteristic quant ion for the designated internal standard (see *Table 1*).

C_{is} = Concentration of the internal standard (ppbv).
C_x = Concentration of the compound to be measured (ppbv).

9.4.3.5 Calculate the average RRF for each analyte in the curve.

9.4.3.6 Calculate the % Relative Standard Deviation (%RSD) of RRF values for the initial calibration curve using the following equation:

$$\%RSD = \frac{\text{Standard Deviation (n-1)}}{\text{Average RRF}} * 100$$

9.4.3.7 Calculate the average RT for each internal standard over the initial calibration range.

9.4.4 Calibration acceptance criteria

9.4.4.1 The BFB must meet the specified criteria

9.4.4.2 The %RSD is calculated and must be less than or equal to 30% for all compounds. This criterion must be met for the initial calibration to be

valid. However, an exception can be made for up to 2 compounds that may exceed 30% RSD, but the RSD for these compounds must be <40.0%. Refer to QC-SOP-12 (current revision) for calibration level rejection criteria.

9.4.4.3 Evaluation of IS retention time: The retention time shift for each of the internal standards at each calibration level must be within 20s of the mean retention time over the initial calibration range.

9.4.4.4 Evaluation of target compound retention time: The relative retention time (RRT) of each target analyte in each calibration level must be within 0.06 RRT units of the mean RRT for that compound

9.5 Calibration verification

9.5.1 Instrument Performance Check: Prior to sample analysis, a 10/50-ppbv injection of BFB must meet the criteria listed in 9.4.1.2.

9.5.2 Calibration verification standard: The initial calibration must be verified on a daily basis prior to the analysis of any samples. Analyze a mid-level (10/50-ppbv)-calibration standard at the beginning and end of each 24-hour working period after meeting BFB tune criteria.

9.5.2.1 Calculate the % Difference between the average response factor from the calibration curve and the response factor from the daily standard using the equation below:

$$\% \text{ Difference} = \frac{\overline{|RRF_i - RRF_c|}}{RRF_i} * 100$$

Where:

RRF_i = Average relative response factor from initial calibration.

RRF_c = Relative response factor from the current calibration check standard.

The %D in the daily standard must be +/-30% for all compounds.

The %D report is monitored daily to evaluate instrument performance and watch for trends that might indicate the need for corrective action.

9.6 Method Blank

9.6.1 A Method blank is a volume of a clean reference matrix (Nitrogen @ 99.9999% purity) carried through the entire analytical procedure. The volume of the method blank must be approximately equal to the volume of the associated samples.

9.7 Laboratory Control Sample and Duplicate (LCS/LCSD)

9.7.1 A laboratory control sample and duplicate (consisting of a representative list of target analytes prepared near the mid-level of the calibration curve) are analyzed daily. The LCS/LCSD are spiked into Mini Cans or 6 liter canisters and are analyzed in the same manner as client samples. The LCS/LCSD standard must be from a separate source than that of the calibration standards. Sub-sampling for an LCS or LCSD from a 6 liter standard stock canister requires the 6 liter canister to be > or = 10 psig to minimize any sub-sampling biases for the wide variety of volatile compounds analyzed by this method.

9.8 Detection Limit Standard (DLS)

9.8.1 The lower limit of quantitation is verified daily by the analysis of a standard at the detection limit (5-ppbv for most compounds in Minican, 0.2-ppbv or 1-ppbv for 6 liter) in the TO15 list analysis. ***The lower limit of quantitation for SIM analysis will depend on client specifications and targets.*** Recovery of all compounds with the DLS should be within the range of 60-140%. The Ethylene Oxide DLS is analyzed at 20-ppbv and the 4-Phenylcyclohexene DLS is at 1-ppbv (limits are also 60-140%).

9.9 Sample analysis

9.9.1 Once the instrument check and calibration verification standards have passed the acceptance criteria, samples may be analyzed.

9.9.2 Add 50cc of the 100-ppbv internal standard/surrogate mixture (for a level of 50-ppbv for a 100cc-sample injection and 10-ppbv for a 500cc-sample injection) to the sample extract obtained from the sample mini-canister.

9.9.3 Analyze the sample on the GC/MS system using the same operating conditions that were used for the calibration.

9.9.4 If the concentration of any target analyte in the sample exceeds the initial calibration range of the GC/MS system, the sample must be diluted and reanalyzed.

9.9.4.1 Dilutions can be automated by using the Entech 7100 system. However, the smallest sample size that can be analyzed reliably is 10cc. If greater than a 10X dilution is needed on the can, the analyst must pressurize the canister with nitrogen to further dilute the sample. The pressurization factor is multiplied by the instrument dilution to obtain the total dilution factor:

$$\text{Total Df} = \frac{P_{sia}\ \text{final} \times 100\text{cc}}{P_{sia}\ \text{initial}\quad \text{inj vol}} \times \text{(split factor for loop injector, if used)}$$

Once the canister is pressurized above atmospheric pressure, or 14.7 P_{sia}, the Entech 7032 loop injector may be used to withdraw a 1-cc injection volume. Automated splitting of the sample stream can further dilute this volume up to a factor of 10x. If the sample is to be reanalyzed via normal injection, it must be vented to ambient pressure by depressing the quick-connect pin on the Mini Can.

9.10 Qualitative analysis

9.10.1 Identification of Target Compounds

The qualitative identification of compounds is based on retention time and comparison of the sample spectrum with characteristic ions in a reference mass spectrum. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The list of characteristic ions for each analyte is presented in *Table 1*. Target compounds are positively identified when the following criteria are met:

9.10.1.1 The EICPs of the characteristic ions of an analyte must maximize within one scan of each other.

9.10.1.2 The RRT of the sample component is within +/- 0.06 RRT units of the RRT of the standard component.

9.10.1.3 The relative intensities of the characteristic ions in the sample analyte must agree within 30 percent of the relative intensities of these ions in the reference spectrum from the most recent calibration verification standard. The analyst must account for deviations from this criterion such as in the case of interference/co-elution.

9.10.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 percent of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs (for example, m- & p-xylene).

9.10.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important. When analytes coelute the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

9.10.2 Identification of Non-Target Compounds

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. Up to 20 organic compounds with greatest concentration excluding surrogate and internal standards will be identified and reported. ***Non-Target compounds identification is not possible in SIM analysis.***

9.10.2.1 Major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

9.10.2.2 The relative intensities of the major ions should agree within +/-20 percent. For example: an ion with an absolute abundance of 50 percent in the standard spectrum must be between 30 and 70 percent in the corresponding sample spectrum.

9.10.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

9.11 Quantitative identification

9.11.1 Once a target compound has been identified, the quantitation of that compound is based on the total abundance, or EICP integration area, of the primary characteristic ion.

9.11.2 The concentration of a compound in the sample is determined using the mean relative response factor determined from the initial calibration.

9.11.3 Concentration is calculated from the equation:

$$ppbv = \frac{(Ax)(Is)(Df)}{(Ais)(RRF_i)}$$

Where: Ax = Area of the compound characteristic ion in the sample.
Ais = Area of the characteristic ion for the corresponding internal standard.
Is = Concentration of internal standard in ppbv
RRF_i = Mean relative response factor (from initial calibration) for the compound being measured.
Df = Dilution factor

9.11.4. In all instances where the quantitation report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify edits or manual procedures by initialing and dating the changes made to the report. The data system flags a manual integration on the quantitation report by placing the symbol "m" next to the area. The analyst who performed the integration should initial and date this flag.

9.11.5 Samples that contain target analytes above the linear range of the curve must be diluted to bring the analytes within the curve range. If a dilution was initially performed and no target analytes are detected above the LOQ, the sample must be reanalyzed at a more concentrated level.

9.12 Technical Acceptance Criteria for Sample analysis

9.12.1 The samples must be analyzed on a system meeting BFB, initial calibration and calibration verification criteria.

9.12.2 The sample must have an associated method blank meeting acceptance criteria (see section 11.2).

9.12.3 Surrogate recovery must fall within default limits of 80-120% for all samples and blanks.

9.12.4 The retention time of each internal standard must be within ±20s of the retention time in the most recent calibration verification standard.

9.12.5 The instrumental response (EICP area) for each of the internal standards must be within ± 40% of the area response in the most recent calibration verification standard. If analyzed within the same sequence a calibration curve, then the average of the area responses for all calibration standards can be used for this criteria comparison.

9.12.6 Concentration of all analytes must be within the calibration range determined from the initial calibration.

9.12.7 Control Sample/Duplicate must be evaluated to determine if recoveries (and RPDs) are within control limits.

9.13 Hydrocarbon Analysis

9.13.1 Initial Calibration

9.13.1.1 A copy of the day's data folder is made and renamed "InstID+date+HC." For example, if the date is 02/25/2011 on instrument J, the new folder will be named J022511HC. Load the previous hydrocarbon calibration curve, rename with the current date and save the method.

9.13.1.2 With the global detection limit set to zero, re-quantitate the same data files used for the TO-15 calibration curve. Q-Edit the files to ensure that all of the hydrocarbon peaks are correct, using the following table.

Name	Major Peak
Bromochloromethane	130
1,4-Difluorobenzene	114
Chlorobenzene-d5	117
Bromofluorobenzene	174
Total VOC's as n-Heptane	43,57,71,100
Trimethyl Siloxanol	75
Hexmethyl Cyclotrisiloxane	207
Octomethyl Cyclotetrasiloxane	281
Siloxane	267

Note: In standards and blanks, the Trimethyl Siloxanol and Siloxane may not be present. Highlight the peak around the retention time of where it should be, with the lowest level present. This is usually the beginning of the peak found.

9.13.1.3 Once the peaks have been selected correctly, clear the calibration responses in the curve. Update all the levels of the calibration using the same data files that were used for the TO-15 curve. Ensure that you select "Quantitate Using Initial Cal RF's" under the "Quant" menu

before saving the method.

9.13.1.4 Repeat steps 9.4.3.2 – 9.4.3.5 for n-Heptane only. An additional conversion may be necessary, depending on client, to convert n-Heptane to Gasoline (M.W. Gasoline divided by M.W. of n-Heptane). Siloxanes are not calibrated compounds. RSD for siloxanes should be crossed out and marked "Not calibrated for these compounds." Update the Custom Report Response factor using the Average of the Total VOC's as n-Heptane.

9.14 SIM Analysis

9.14.1 SIM analysis is a technique used to increase sensitivity with GCMS for for target compounds using only specific ions. The only ions scanned for are those that are characteristic of target compounds only. As a result non target compounds are not able to be detected using SIM analysis.

9.14.2 SIM analysis can be done upon client request for compounds that require lower detection limits than the low level 0.2-ppbv standard.

9.14.3 Target compounds will depend on client target list and will be ordered at a lower level primary standard if needed (example: Order a 10-ppbv standard if client requests detection limit of 0.005-ppbv)

9.14.4 If the detection limits can be meet with a standard SCAN TO-15 method but client requests SIM analysis, the same stock and working standards used for SCAN analysis can be used.

9.14.5 Target compounds will be quantitated from the primary ion for each respective compound with at least 1 secondary ion for qualitative identification. Retention time will be the primary method of identification per 9.10.1.

9.14.6 SIM analysis will be set up using a separate chemstation method using only the ions for compounds that require SIM analysis. This will keep from scanning non target compound ions which will increase sensitivity. Target ions will depend on client request and the ions used should be seen in regular TO-15 SCAN ECIP.

9.14.7 SIM methods will be made per client project to maximize sensitivity by minimizing dwell time by the mass spectrometer. See section supervisor or alternate for any questions.

9.14.8 Blank should be run after any QC until system is fully cleaned out before running any client samples. This will ensure that client samples are free from any possible carry over effects from working standards used for QC. Blanks should be run at the end of client sample batch to ensure that there is no carry over. Blanks should be run in between any client samples with a hit at or greater than the mid point calibration level, to ensure that subsequent client samples are not contaminated with carry over.

9.15 Corrective Action

9.15.1 Corrective Action for sample analysis: the sample technical acceptance criteria must be met. If any samples do not meet acceptance criteria, consult with the section supervisor to determine whether reanalysis is required.

9.15.2 Corrective Action for surrogate recovery failure: check calculations and examine the chromatogram for interference. If no interference is noted, reanalyze any sample that exceeds criteria. If the sample meets criteria upon reanalysis, report the reanalysis only. If the sample produced similar results upon reanalysis, the problem may be matrix-related. Contact the project manager so the client may be notified.

9.15.3 Corrective Action for Internal Standard Response failures: if any internal standard exceeds acceptance criteria, check calculations. Verify that the standard concentration is accurate, and that the instrument did not malfunction. Reanalyze the sample to see if the problem was matrix related. If the reanalysis meets criteria, report the reanalysis only. If the reanalysis produced similar results, consult with the section supervisor and project manager to determine the best course of action.

9.15.4 Corrective Action for Internal Standard Retention Time: if any internal standard exceeded retention time criteria, follow the same guidelines used in Section 9.14.3.

9.15.5 Corrective Action for Instrument Contamination: if an instrument has come into contact with a PPM level of analytes, the instrument might need extra cleaning to ensure that there is no carry-over to other client samples. Block access to the ports affected on the Entech autosampler until they go through at least 5 flush and bake cycles. Test the ports, as room air blanks, to see if there is carry-over. If there no carry-over, go ahead and use the ports during the next run. If there is carry-over, see section supervisor for other possible actions, which may include cleaning the source.

10.0 DOCUMENTATION

10.1 The raw data is archived to CD-ROM and is stored in a secured area. Hard copies of raw data are kept for a period of ~1 year in the laboratory and then stored for a total time of 5 years before disposal.

10.2 Chain of custody forms, instrument maintenance logs, standards preparation logs, analytical run logs, and corrective action logs must be filled out in a timely manner**.** These records are maintained in the laboratory for five years.

11.0 CALCULATIONS

All calculations are covered in Section 9.

12.0 QUALITY CONTROL CHECKS & CRITERIA

12.1 Instrument performance must be monitored to ensure that all of the tuning, initial calibration and calibration verification criteria requirements are met.

12.2 Method blanks

12.2.1 A method blank is a volume of a clean reference matrix (nitrogen @ 99.9999% purity) carried through the entire analytical procedure. The volume of the method blank must be approximately equal to the volume of the associated samples. The purpose of the method blank is to determine the level of contamination associated with the preparation and analysis of samples.

12.2.2 Method blanks must be analyzed with each batch of samples, or at a minimum frequency of 1 for every 20 samples.

12.2.3 A method blank is analyzed following the calibration verification standard under the same conditions as the standards and samples before any samples may be analyzed.

12.2.4 The method blank must contain no targets above the LOQ of 5-ppbv (100cc injection for Minican) and 0.2-ppbv (500cc injection for 6-L Summa canisters) for the TO15 list. ***They should contain no targets above client specific detection limits for SIM analysis.*** The LOQ for Ethylene Oxide is 20-ppbv and the 4-Phenylcyclohexene LOQ is 1-ppbv.

12.2.5 If the method blank does not meet this criterion, repeat the analysis until an acceptable blank is obtained. Sample analysis may not begin until a method blank meeting criteria has been successfully analyzed.

12.2.6 If the surrogate recovery in the method blank does not meet control limits, reanalyze the method blank. If the surrogate recovery is still outside control limits, it may be necessary to re-prepare the internal standard/surrogate mixture or recalibrate the instrument.

12.3 Laboratory Control Sample/ Laboratory Control Sample Duplicate

12.3.1 A laboratory control sample & duplicate (LCS/LCSD) consist of an aliquot of a clean reference matrix (UHP nitrogen), spiked with a representative list of the target analytes at the mid-level of the calibration curve. The spiking standard must be from a source different from that of the calibration standards.

12.3.2 The LCS & LCSD must be analyzed with each analytical run. The recoveries should fall within the range of 70-130%. For compounds 1,2,4-Trichlorobenzene and Hexachloro-1, 3-Butadiene, separate limits have been established based on historical laboratory data (these compounds are no longer in the TO-15 regular list). RPD method default limits of 25% are used to assess analytical precision. If recovery and/or RPD are not within this range, the possible effect(s) on the sample data must be determined. The data may be qualified or the LCS/LCSD sample may be reanalyzed.

12.4 Surrogate Recoveries

12.4.1 All samples, including quality control samples, are spiked with 50ppbv Bromofluorobenzene as a surrogate.

12.4.2 The surrogate (BFB) recovery control limits are 80-120%. All samples should meet the surrogate recovery criterion. If BFB recovery falls outside control limits for any sample, the sample must be reanalyzed. If the reanalysis produces similar results, contact the project manager.

12.5 Duplicate analysis.

12.5.1 A sample is analyzed in duplicate to assess precision. Duplicates must be analyzed with each batch of samples, or at a minimum frequency of 1 for every 24-hour analytical sequence. The relative percent difference (RPD) between measurements should be 25% or less.

12.6 Initial Demonstration of Proficiency (IDP)

12.6.1 Demonstration of proficiency is established by generating data of acceptable accuracy and precision for target analytes for each preparative method and matrix by analyzing reference samples. On-going demonstration is performed on a semiannual basis.

12.6.2 Four reference samples are prepared so that each analyst tests 4 samples of unknown concentration containing all analytes of interest. Analyst One prepares two different stock standards independently and fills two sample canisters from each. The preparing analyst labels the canisters with the injection volume to use and gives them a sample ID. This results in 4 different concentrations for each analyst. A second analyst repeats the process for any other analysts. The standards must be made from stock standards prepared independently from those used for calibration. The concentration of targets in the four reference samples may be anywhere within the current calibration range of the instrument.

12.6.3 Analyze the four reference samples by the same procedure used for analyzing actual samples. Calculate both the average recoveries in ppbv and the relative standard deviations of the recovery for each analyte of interest. The average recovery should fall within the in-house generated control limits for each analyte.

12.6.4 IDP procedures must be repeated whenever new staff is trained or significant changes in preparative or analytical methods are made.

12.7 Verification of Method Detection Limit

12.7.1 Instrument reporting limits are verified (at least) annually by analyzing 7 replicates at the reporting limit. All compounds must be within 60-140% recovery for the detection limit standard (DLS) when using a nominal sample injection volume of 100-cc for MiniCan, 500-cc for Summa Canisters ***or 1000-***

cc for SIM analysis.

12.7.2 Alternatively, an MDL study can be performed if needed. MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined by the analysis of seven replicate injections of each compound of interest at a level near the expected detection limit. The standard deviation of the seven measurements multiplied by 3.14 (Student's *t* value for 99% confidence for seven values) defines the MDL for each analyte.

12.7.3 MDLs are determined only if needed for each instrument, as the detection limit studies (described in 12.7.1) are used to verify instrument-reporting limits.

12.7.4 ***For SIM analysis, detection limits should meet or exceed client specifications.***

12.8 Additional Control Procedures

12.8.1 Logbook Review Procedure:
The supervisor or designee will review GCMS run logs and maintenance logs weekly. The logbooks will be reviewed for content and for the absence of cross outs. All forms will be verified to be the most recent approved version. Logbooks will be initialed and dated as to the date of review. MS-Form-6 will be used to document that all logbooks are reviewed as per their set schedule. The preventative maintenance log will be reviewed as the maintenance is done (some is weekly, some monthly and also some at 6-12 month intervals). The standards logbooks are reviewed each time a standard is made. Can cleaning logbooks and canister dilution logbooks will be reviewed weekly.

12.8.2 Forms Control Procedure:
In addition to forms being reviewed on a weekly basis new forms once approved (notification through email) will be printed and a new logbook made by the end of the next business day. Previous logbooks will be closed out and archived.

12.8.3 Preventative Action Plan Initiation/Review Policy:
A PAP should be initiated whenever an action can be initiated to prevent a future problem. Consultation with the QC group will be used to determine if a PAP is required. PAPs will be reviewed at least weekly until completed.

12.8.4 Entech auto-sampler ports are flushed before use and this is indicated on system injection log.

12.8.5 All working standard numbers (IH numbers) will be verified on hard copy reports and in LIMS to ensure accuracy and traceability for standard documentation.

12.8.6 Sample Canister Cleaning Approval Procedure.
This procedure is used to ensure sample analysis is complete before sample canisters are cleaned. After a sample analysis sequence is complete, canisters are placed in project holding bin (red or purple) waiting for approval of all Quality control and sample results. If any re-analysis is required, those samples are kept

in this bin until re-analysis is performed. When approval is given by supervisor and/or designee to clean sample canisters, canisters are then transferred to the "approved for cleaning bin" (black or blue) by verifying sample identification using Galson Login number and individual sample number. This bin is then taken to the sample cleaning area.

13.0 CORRECTIVE ACTION

13.1 See section 9.14 for corrective actions.

14.0 WASTE DISPOSAL

14.1 Refer to Galson Laboratories SOP LF-DISPO (current revision).

15.0 REFERENCES

15.1 Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) In Air Collected I Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Second Edition, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711, EPA/626/R-96/010b, January 1999.

15.2 PV2120: Volatile Organic Compounds in Air, U. S. Department of Labor – Occupational Safety & Health Administration, Control Number T-PV2120-01-0305-ACT, May 2003

16.0 METHOD MODIFICATIONS

Method PV2120:

The samples arrive in the lab at ~ 15 psia (atmospheric pressure, 0 psig) and this is adequate to sample without pressurizing (diluting) the sample up to 30 psig (45 psia).

Method TO-15: (parentheses denote method-referenced sections)

(10.7.5)
Daily blank limit is set at 5-ppbv for TO15 list (the normal reporting limit for most compounds), not 3x the MDL.

(8.4.1.2)
Can leak-checks are done by evacuating cans to ~ 30" of Mercury (vacuum reading), and then checking them before sample shipment. If vacuum falls to <28" of Mercury within 24 hours, a can is considered to be leaking (TO-15 leak-checks by pressurizing cans to 30 psig and has pass/fail criteria of <+/- 2 psig) in 24 hours.

(8.4.1.6)
Cans containing less than 2-ppm of individual contaminants are cleaned in batches where a representative can is tested to demonstrate cleanliness of the batch. For cans containing analytes greater than 2-ppm, these cans are tested individually to verify cleanliness. Can cleaning limits are higher (refer to section 9.2.2.2). For MiniCans: the

representative can cleaning blank limit (or individual can) for TO-15 list is set at 5-ppbv, the normal reporting limit. The warning limit is 2.5-ppbv. Quantitation in general is not reliable below 5-ppbv. Cans are generally re-cleaned if above 2.5-ppbv for any analyte. For 6-L Summa Canisters: the cleaning blank limit is 0.2-ppbv (IDL for most compounds), anything less than 0.2-ppbv is considered clean. Correspondingly, for Ethylene Oxide the limit is 20-ppbv and for 4-Phenylcyclohexene the limit is 1 ppbv.

(10.8.1)
For Minican analysis: 100mL-sample injection volume is used when sampling is done with 400mL and 1-liter canisters rather than 6-liter summa canisters. Therefore, MDL limits, etc. are ~ 5x higher because the sample injection volume is 5x less.

(9.2.2.3)
For Minican analysis: Internal standard/surrogate levels are spiked at 50-ppbv rather than 10-ppbv to be consistent with calibration levels for TO15 list analyses.

(10.7.2)
A blank is not always analyzed after a high level sample. If the compound that was high is detected in samples injected after the high level sample, those samples would be reanalyzed after the system was shown to be clean.

(10.7.5)
Internal standard area limit of +/- 40% is calculated versus the daily standard for all injections that day (24 hour window) not versus the most recent calibration curve average areas.

Table 1
Characteristic Ions, PQLs

COMPOUND	EI PRIMARY	EI SECONDARY	EI TERTIARY	PQL ppb	
				Summa	Minican
Propylene	41	39		0.2	5
Freon-12	85	87		0.2	5
Chloromethane	50	52		0.2	5
Freon-114	85	135	87	0.2	5
Vinyl Chloride	62	64		0.2	5
1,3-Butadiene	39	54		0.2	5
Bromomethane	94	96		0.2	5
Chloroethane	64	66		0.2	5
Vinyl Bromide	106	108		0.2	5
Freon-11	101	103	105	0.2	5
Isopropyl Alcohol	45	43		0.2	5
Acetone	43	58		0.2	5
1,1-Dichloroethene	96	61	98	0.2	5
Methylene Chloride	84	86	49	0.2	5
Freon-113	101	101	151	0.2	5
Allyl chloride	76	41	39	0.2	5
Carbon Disulfide	76	78		0.2	5
Trans-1,2-Dichloroethene	61	96	98	0.2	5
Methyl Tert-Butyl Ether	73	41	57	0.2	5
1,1-Dichloroethane	63	65		0.2	5
Vinyl Acetate	43	86		0.2	5
Methyl Ethyl Ketone	43	57	72	0.2	5
cis-1,2-Dichloroethylene	61	96	98	0.2	5
Hexane	57	41	43	0.2	5
Ethyl Acetate	43	45	61	0.2	5
Chloroform	83	85	47	0.2	5
Tetrahydrofuran	42	71	72	0.2	5
COMPOUND	**EI PRIMARY**	**EI SECONDARY**	**EI TERTIARY**	**PQL ppb**	
				Summa	**Minican**

1,2-Dichloroethane	62	64		0.2	5
1,1,1-Trichloroethane	97	99	61	0.2	5
Cyclohexane	56	41	84	0.2	5
Carbon Tetrachloride	117	119		0.2	5
Benzene	78	77	50	0.2	5
1,4-Dioxane	88	58		0.8	20
2,2,4-Trimethylpentane	57	41	56	0.2	5
Heptane	43	57	71	0.2	5
1,2-Dichloropropane	63	41	62	0.2	5
Trichloroethylene	130	132	95	0.2	5
Bromodichloromethane	83	85		0.2	5
cis-1,3-Dichloropropene	75	39	77	0.2	5
Trans-1,3-Dichloropropene	75	39	77	0.2	5
1,1,2-Trichloroethane	97	83	61	0.2	5
Toluene	92	91	92	0.2	5
Dibromochloromethane	129	127		0.2	5
Methyl Isobutyl Ketone	43	57	58	0.8	20
Methyl Butyl Ketone	43	57	58	0.8	20
1,2-Dibromomethane	107	109		0.2	5
Tetrachloroethylene	164	166	131	0.2	5
Chlorobenzene	112	77	114	0.2	5
Ethylbenzene	91	106		0.2	5
Bromoform	173	175		0.2	5
Styrene	104	78	103	0.2	5
o-xylene	91	106		0.2	5
m- & p-xylene (co-elute)	91	106		0.4	10
1,1,2,2-Tetrachloroethane	83	85		0.2	5
4-Ethyltoluene	105	120		0.2	5
1,3,5-Trimethylbenzene	105	120		0.2	5
COMPOUND	**EI PRIMARY**	**EI SECONDARY**	**EI TERTIARY**	**PQL ppb**	
				Summa	**Minican**
1,2,4-Trimethylbenzene	105	120		0.2	5
1,3-Dichlorobenzene	146	148	111	0.2	5

Benzyl Chloride	91	126		0.2	5
1,4-Dichlorobenzene	146	148	111	0.2	5
1,2-Dichlorobenzene	146	148	111	0.2	5
1,2,4-Trichlorobenzene	180	182	184	0.2	5
Hexachloro-1,3-Butadiene	225	227	223	0.2	5
Ethylene Oxide	44	29	NA		20
4-Phenylcyclohexene	104	158	78		1
Bromofluorobenzene (surrogate)	95			-	
*Bromochloromethane	128			-	
*1,4-Difluorobenzene	114			-	
*Chlorobenzene-d5	117			-	

*Indicates internal standard

Table 2

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

*Bromochloromethane	*1,4-Difluorobenzene	*Chlorobenzene-d5
Propylene	1,1,1-Trichloroethane	Toluene
Freon-12	Cyclohexane	Dibromochloromethane
Chloromethane	Carbon Tetrachloride	Methyl Isobutyl ketone
Freon-114	Benzene	Methyl Butyl ketone
Vinyl Chloride	1,4-Dioxane	1,2-Dibromoethane
1,3-Butadiene	2,2,4-Trimethylpentane	Tetrachloroethylene
Bromomethane	Heptane	Chlorobenzene
Chloroethane	1,2-Dichloropropane	Ethylbenzene
Vinyl bromide	Trichloroethylene	m- & p-xylene (co-elute)
Freon-11	Bromodichloromethane	Styrene
Isopropyl alcohol	cis-1,3-Dichloropropene	o-xylene
Acetone	trans-1,3-Dichloropropene	Bromoform
1,1-Dichloroethene	1,1,2-Trichloroethane	1,1,2,2-Tetrachloroethane
Methylene Chloride		4-Ethyltoluene
Freon-113		1,3,5-Trimethylbenzene
Allyl chloride		1,2,4-Trimethylbenzene
Carbon disulfide		Benzyl chloride
Trans-1,2-Dichloroethene		1,3-Dichlorobenzene
Methyl tert-butyl ether		1,4-Dichlorobenzene
1,1-Dichloroethane		1,2-Dichlorobenzene
Vinyl acetate		1,2,4-Trichlorobenzene
Methyl ethyl ketone (2-butanone)		Hexachloro-1,3-Butadiene
Cis-1,2-Dichloroethylene		Bromofluorobenzene (surrogate)
Hexane		4-Phenylcyclohexene
Ethyl acetate		
Chloroform		
Tetrahydrofuran		
1,2-Dichloroethane		
Ethylene Oxide		

Enbridge Energy, Limited Partnership
1601 Pratt Avenue
Marshall, Michigan 49068

September 9, 2011

Mr. Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. Environmental Protection Agency
801 Garfield Avenue, #229
Traverse City, MI 49686

Re: In the Matter of Enbridge Energy Partners, L.P., *et al*,
Docket No. CWA 1321-5-10-001

Dear Mr. Dollhopf:

Enbridge Energy, Limited Partnership (Enbridge) is requesting that the United States Environmental Protection Agency (U.S. EPA) consider the following modification to the 2011 Air Monitoring and Sampling Addendum dated June 21, 2011. The proposed modifications are being requested for immediate implementation.

The specific request includes modification of Community Air Sampling laboratory analysis turn-around time. This request excludes Odor Response sampling activities which will continue with expedited shipping and 24-hour analytical turnaround times for samples collected. In accordance with the approved Plan, based on community monitoring and sampling analytical results obtained throughout the 2011 work activities, we are requesting the Community Air Sampling laboratory analysis turn-around time be changed from a 24-hour analytical period to a 5 day analytical turn-around time period.

This request for modification is supported by 411 work area perimeter samples and 815 Community Air samples over 67 days with only 10 individual detections of four Target Analytesabove the Human Health Screening Levels. Detections above screening levels for Target Analytes include 1,2,4 Trimethylbenzene (1 sample), benzene (1 sample), toluene (4 samples), and xylene (4 samples). In addition, we have collected over 12,000 real-time community monitoring readings for VOCs, H2S, SO2, and benzene (all non-detect) throughout the monitoring period.

Assessment of community air sampling and monitoring results lead us to conclude:

- That our analytical data set is established,
- Concentrations of Target Analytes in community air are stable,
- Work activities do not influence air sampling results, and
- The necessity for expedited analytical turn-around times reduced.

Enbridge welcomes the opportunity to present additional information regarding our sampling and monitoring strategy, a review of data collected, and a detailed assessment of results. If you have any questions regarding this request, please do not hesitate to contact me.

Sincerely,

ENBRIDGE ENERGY, LIMITED PARTNERSHIP
By Enbridge Pipelines (Lakehead) L.L.C.
Its General Partner

Richard Adams
Vice President, U.S. Operations

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Enbridge Energy, Limited Partnership
1601 Pratt Avenue
Marshall, Michigan49068

October 13, 2011

Mr. Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. Environmental Protection Agency
801 Garfield Avenue, #229
Traverse City, MI49686

Re: In the Matter of Enbridge Energy Partners, L.P., *et al*,
Docket No. CWA 1321-5-10-001

Dear Mr. Dollhopf:

Enbridge Energy, Limited Partnership (Enbridge) is requesting the United States Environmental Protection Agency (U.S. EPA) approve the following modification to the *2011 Air Monitoring and Sampling Addendum* (dated June 21, 2011) of the *Sampling and Analysis Plan* (SAP) (dated August 2010). The proposed modifications are being requested for immediate implementation.

Enbridge is requesting an indefinite suspension of all Community Air Sampling and Monitoring activities, Work Area Monitoring, and elimination of River Opening Sampling effective immediately. The air sampling and monitoring program was designed to protect worker safety and public health during assessment and recovery operations. Work activities during these air sampling and monitoring periods included overbank surface soil oil recovery, overbank excavation oil recovery, and submerged oil recovery during a wide range of atmospheric conditions over the 2011 work periods. This request excludes Odor Response sampling activities which will continue with expedited shipping and 24-hour analytical turnaround times for samples collected.

This request for modification is supported by 2,059 Work Area and Community Air samples collected during 2010 and 1,266 Work Area and Community Air samples collected in 2011, as of September 16, 2011. In addition to the lab analyzed samples, we have collected 66,922 real-time community readings in 2010 and 18,662 in 2011, as of September 16, 2011for VOCs, H2S, SO2, and benzene (all non-detect above screening limits).

Between June 3, 2011 and September 16, 2011, a total of 10 Target Analytes have been detected above Human Health Air Screening Levels (HHASLs) in 2011 along with 22 detections of Non-Target Analytes above HHASLs, which are not related to crude oil released from Line 6B MP 608. Detections of both Target and Non-Target Analytes have been inconsistent and do not alter our conclusions regarding air sampling and monitoring results. In addition, efforts have been taken to evaluate potential lab related issues for select contaminants including isopropyl alcohol and acetone, which revealed these contaminants along with carbonyl sulfide in the laboratory carrier gas. It is important to note that these are 8-, 12-, and 24-hour samples (acute exposure) being compared to chronic exposure based screening levels (greater than one year). Therefore we also compared measures of central tendency (including median and mean values) of contaminant levels over the sampling duration in 2011, which indicated values well below the applicable HHASLs.

The attached tables and figures provide details regarding chemicals detected and comparisons with applicable HHASLs. Please refer to the attached **Table 1:** Cumulative Air Sample Summary – Target Analytes and **Table 2:** Cumulative Air Sample Summary – Non-Target

Analytes for a summary of analytical results from June 3, 2011 to September 16, 2011 for Target Analytes and Non-Target Analytes, respectively. In addition, see attached figures for visual depictions of sampling results compared against applicable HHASLs for each of the detected Target Analytes and specific Non-Target Analytes of interest.

Enbridge is also requesting the elimination of River Opening Sampling and Monitoring, as included in *Memorandum -RE: Modification of the 2011 Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan*, dated July 6, 2011, due to the lack of applicability based on the extensive Work Area and Community Air Sampling and Monitoring conducted in 2010 and 2011 with minimal detections of Target Analytes as outlined in the above text and associated tables and figures.

Assessment of Community Air Sampling and Monitoring results lead us to conclude that our analytical data set is well established, concentrations of Target Analytes in ambient air throughout the community are stable and below levels of concern, and that work activities do not negatively influence ambient air concentrations. Additionally, as ambient air temperatures continue to decrease for the remainder of 2011, weather conditions substantiate a lesser potential for volatilization of chemicals in comparison to the higher ambient air temperatures observed during the sample collection conducted in 2011 to date. Therefore, Enbridge believes it has been demonstrated that continued air sampling and monitoring is unnecessary.

Enbridge welcomes the opportunity to present additional information regarding our sampling and monitoring strategy, a review of data collected, and a detailed assessment of results. If you have any questions regarding this request, please do not hesitate to contact me.

Sincerely,

ENBRIDGE ENERGY, LIMITED PARTNERSHIP
By Enbridge Pipelines (Lakehead) L.L.C.
Its General Partner

Richard Adams
Vice President, U.S.Operations

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Mike Alexander, MDEQ

Table 1. Cumulative Air Sample Summary - Target Analytes
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release
Enbridge Energy, Limited Partnership

Target Analytes - Predominant Crude Oil VOCs Detected by TO-15 Analysis (including TICs)	CAS NO	Human Health Air Screening Level (ppbv)	Source	All Sample Durations†				8-hour Target Period				12-hour Target Period				24-hour Target Period			
				N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)
1,2,4-Trimethylbenzene	95-63-6	1.5	EPA RfC(1)	1266	1	1.0	3.0	364	0	ND	ND	117	0	ND	ND	785	1	1.0	3.0
Benzene	71-43-2	3	ATSDR Chr. MRL(1)	1266	4	1.0	4.0	364	0	ND	ND	117	0	ND	ND	785	4	1.0	4.0
2-Methylbutane*	78-78-4	6000	MDEQ(1)	1266	43	10.4	83.0	364	0	ND	ND	117	0	ND	ND	785	43	10.4	83.0
Cyclohexane	110-82-7	2000	EPA RfC(1)	1266	25	1.0	63.0	364	1	5.0	63.0	117	0	ND	ND	785	24	1.0	20.0
1,3-Dimethylcyclohexane*	591-21-9	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Methylcyclopentane*	96-37-7	200	MDEQ(1)	1266	2	2.6	3.7	364	0	ND	ND	117	0	ND	ND	785	2	2.6	3.7
cis-1,3-Dimethylcyclohexane*	638-04-0	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Butylcyclohexane*	1678-93-9	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Ethylcyclohexane*	1678-91-7	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Methylcyclohexane*	108-87-2	4000	MDEQ(1)	1266	2	3.9	4.6	364	0	ND	ND	117	0	ND	ND	785	2	3.9	4.6
Propylcyclohexane*	1678-92-8	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1-Dimethylcyclopentane*	1638-26-2	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
trans-1,3-Dimethylcyclopentane*	1759-58-6	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
trans-1,2-Dimethylcyclopentane*	822-50-4	0.025	MDEQ(1)	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
3-Methylheptane*	589-81-1	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
2,6-Dimethyl-2-Octene*	4057-42-5	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Decane*	124-18-5	NA	NA	1266	3	4.7	8.9	364	0	ND	ND	117	0	ND	ND	785	3	4.7	8.9
Dodecane*	112-40-3	NA	NA	1266	4	2.5	5.6	364	0	ND	ND	117	0	ND	ND	785	4	2.5	5.6
Ethylbenzene	100-41-4	60	ATSDR Chr. MRL(1)	1266	3	1.0	3.0	364	0	ND	ND	117	0	ND	ND	785	3	1.0	3.0
4-Ethyltoluene	622-96-8	70	MDEQ(1)	1266	1	1.0	1.0	364	0	ND	ND	117	0	ND	ND	785	1	1.0	1.0
n-Heptane	142-82-5	850	MDEQ(1)	1266	13	1.0	14.0	364	0	ND	ND	117	0	ND	ND	785	13	1.0	14.0
n-Hexane	110-54-3	200	EPA RfC(1)	1266	18	1.0	3.0	364	0	ND	ND	117	0	ND	ND	785	18	1.0	3.0
Naphthalene*	91-20-3	1	ATSDR Chr. MRL(1)	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Nonane*	111-84-2	40	EPA RfC(1)	1266	1	18.0	18.0	364	0	ND	ND	117	0	ND	ND	785	1	18.0	18.0
2-Methylhexane*	591-76-4	850	MDEQ(1)	1266	4	18.3	35.0	364	1	35.0	35.0	117	0	ND	ND	785	3	12.7	29.0
Octane*	111-65-9	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
3-Methyloctane*	2216-33-3	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
2-Methylpentane*	107-83-5	5000	MDEQ(1)	1266	1	1.7	1.7	364	0	ND	ND	117	0	ND	ND	785	1	1.7	1.7
Toluene	108-88-3	80	ATSDR Chr. MRL(1)	1266	256	4.5	270.0	364	3	5.0	54.0	117	1	5.0	17.0	785	252	3.9	270.0
3-Methylhexane*	589-34-4	850	MDEQ(1)	1266	4	16.5	48.0	364	0	ND	ND	117	0	ND	ND	785	4	16.5	48.0
2-Methylheptane*	592-27-8	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1,3- Trimethylcyclohexane*	3073-66-3	NA	NA	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,3,5-Trimethylbenzene	108-67-8	45	MDEQ(1)	1266	0	ND	ND	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Undecane*	1120-21-4	NA	NA	1266	1	1.5	1.5	364	0	ND	ND	117	0	ND	ND	785	1	1.5	1.5
m&p-Xylene	179601-23-1	50	EPA RfC(1)	1266	6	2.0	10.0	364	0	ND	ND	117	0	ND	ND	785	6	2.0	10.0
o-Xylene	95-47-6	50	EPA RfC(1)	1266	3	1.0	3.0	364	0	ND	ND	117	0	ND	ND	785	3	1.0	3.0

PPBV - Parts Per Billion Volume

*** -** TIC (tentatively identified compound)

** - Average Levels for compounds that were detected in <5% of samples are the median value using the detection limit for non-detects. Average Levels for compounds that were detected in >5% of samples are the mean using the detection limit for non-detects. Average Levels for tentatively identified compounds are the mean of detects.

†Samples reported do not include instantaneous 'grab' samples. Samples with 8-24 hour target sample periods are included.

NA - Not Available/**ND** - Not Detected

N - Number of samples analyzed/**NDET** - Number of detections

(1) - Unless otherwise noted, the screening level was obtained from Enbridge Oil Spill Human Health Air Screening Levels, August 31, 2011.

ATSDR Chr. MRL - Agency for Toxic Substances and Disease Registry - Chronic Minimal Risk Level for Inhalation

EPA RfC - If no Chronic MRL is available, the screening level is the EPA Chronic Reference Concentration (RfC).

EPA RSL - If none of the above are available, the EPA Regional Screening Level (RSL) is used.

MDEQ - If none of the above are available, the Michigan DEQ Air Quality Division, Air Toxics Screening Level is the screening level.

Table 2. Cumulative Air Sample Summary - Non-Target Analytes
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release
Enbridge Energy, Limited Partnership

Non-Target Analytes (including TICs)	CAS NO	Human Health Air Screening Level (ppbv)	Source	All Sample Durations†				8-hour Target Period				12-hour Target Period				24-hour Target Period			
				N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)
1,1,1-trichloroethane	71-55-6	1000	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1,2,2-Tetrachloroethane	79-34-5	0.006	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4000	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1,2-Trichloroethane	79-00-5	0.04	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1-Dichloroethane	75-34-3	0.4	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,1-Dichloroethene	75-35-4	50	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,2,4-Trichlorobenzene	120-82-1	0.3	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,2-Dibromoethane	106-93-4	1	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9900	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,2-Dichlorobenzene	95-50-1	30	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,2-Dichloroethane	107-06-2	600	ATSDR Chr. MRL(1)	1266	2	1	3.0	364	0	ND	ND	117	0	ND	ND	785	2	1.0	3.0
1,2-Dichloropropane	78-87-5	1	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,2-PENTADIENE*	591-95-7	NA	NA	1266	1	1.6	1.6	364	0	ND	ND	117	0	ND	ND	785	1	1.6	1.6
1,3-Butadiene	106-99-0	1	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,3-BUTADIENE, 2-METHYL-*	78-79-5	NA	NA	1266	4	2.7	6.4	364	1	6.4	6.4	117	0	ND	ND	785	3	1.5	1.6
1,3-Dichlorobenzene	541-73-1	0.5	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,3-PENTADIENE*	504-60-9	NA	NA	1266	2	8.4	8.9	364	0	ND	ND	117	0	ND	ND	785	2	8.4	8.9
1,3-PENTADIENE, (E)-*	2004-70-8	NA	NA	1266	2	1.8	1.9	364	0	ND	ND	117	0	ND	ND	785	2	1.8	1.9
1,4-Dichlorobenzene	106-46-7	10	ATSDR Chr. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1,4-Dioxane	123-91-1	1000	ATSDR Chr. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1-DECENE*	872-05-9	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
1-HEPTANAL, 3,5,5-TRIETHYL-*	1000160-77-0	NA	NA	1266	4	14.6	29.0	364	0	ND	ND	117	0	ND	ND	785	4	14.6	29.0
1-HEPTANOL, 2-PROPYL-*	10042-59-8	NA	NA	1266	1	1.5	1.5	364	0	ND	ND	117	0	ND	ND	785	1	1.5	1.5
1-HEXENE, 4-METHYL-*	3769-23-1	NA	NA	1266	1	5.6	5.6	364	0	ND	ND	117	0	ND	ND	785	1	5.6	5.6
1-METHYL-2-METHYLENECYCLOHEXANE*	2808-75-5	NA	NA	1266	1	1.2	1.2	364	0	ND	ND	117	0	ND	ND	785	1	1.2	1.2
1-METHYLDECAHYDRONAPHTHALENE*	2958-75-0	NA	NA	1266	7	10.9	26.0	364	0	ND	ND	117	0	ND	ND	785	7	10.9	26.0
1-TRIDECENE*	2437-56-1	NA	NA	1266	1	1.3	1.3	364	0	ND	ND	117	0	ND	ND	785	1	1.3	1.3
2(1H)-NAPHTHALENONE, OCTAHYDRO-4…*	938-06-7	NA	NA	1266	1	29	29.0	364	0	ND	ND	117	0	ND	ND	785	1	29.0	29.0
2,2,4-Trimethylpentane	540-84-1	750	MDEQ(1)	1266	1	1	1.0	364	0	ND	ND	117	0	ND	ND	785	1	1.0	1.0
2,2,7,7-TETRAMETHYLOCTANE*	1071-31-4	NA	NA	1266	1	1.2	1.2	364	0	ND	ND	117	0	ND	ND	785	1	1.2	1.2
2,3,4,5-TETRAHYDROPYRIDAZINE*	694-06-4	NA	NA	1266	1	2.2	2.2	364	0	ND	ND	117	0	ND	ND	785	1	2.2	2.2
2-BUTENAL*	4170-30-3	3	MDEQ(1)	1266	1	1.7	1.7	364	0	ND	ND	117	0	ND	ND	785	1	1.7	1.7
2-BUTENAL, (E)-*	123-73-9	NA	NA	1266	4	1.9	2.7	364	0	ND	ND	117	0	ND	ND	785	4	1.9	2.7
2-BUTENOIC ACID, METHYL ESTER, (Z)-*	4358-59-2	NA	NA	1266	1	8	8.0	364	0	ND	ND	117	0	ND	ND	785	1	8.0	8.0
2-Chloro-1,3-butadiene	126-99-8	6	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
2-DECENAL, (E)-*	3913-81-3	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
2-HEPTANONE*	110-43-0	500	MDEQ(1)	1266	1	11	11.0	364	0	ND	ND	117	0	ND	ND	785	1	11.0	11.0
2-PENTANONE*	107-87-9	1500	MDEQ(1)	1266	2	23.5	29.0	364	0	ND	ND	117	0	ND	ND	785	2	23.5	29.0
2-PROPANOL, 2-METHYL-*	75-65-0	600	MDEQ(1)	1266	6	47.6	120.0	364	0	ND	ND	117	2	120.0	120.0	785	4	11.4	18.0
3,5-DECADIENE, 2,2-DIMETHYL-, (Z…*	55638-50-1	NA	NA	1266	1	6.4	6.4	364	0	ND	ND	117	0	ND	ND	785	1	6.4	6.4
3,5-OCTADIENE, 4,5-DIETHYL-*	67652-84-0	NA	NA	1266	1	10	10.0	364	0	ND	ND	117	0	ND	ND	785	1	10.0	10.0
3-Chloropropene	107-05-1	32	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
3-HEPTANONE*	106-35-4	NA	NA	1266	1	2.4	2.4	364	0	ND	ND	117	0	ND	ND	785	1	2.4	2.4
4-DECENE, 2,2-DIMETHYL-, (E)-*	55534-69-5	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
4-NONENE, 5-BUTYL-*	7367-38-6	NA	NA	1266	1	3.9	3.9	364	0	ND	ND	117	0	ND	ND	785	1	3.9	3.9
4-TRIFLUOROACETOXYTRIDECANE*	1000245-47-3	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
5-OCTEN-2-YN-4-OL*	1000196-87-1	NA	NA	1266	1	11	11.0	364	0	ND	ND	117	0	ND	ND	785	1	11.0	11.0

Non-Target Analytes (including TICs)	CAS NO	Human Health Air Screening Level (ppbv)	Source	All Sample Durations†				8-hour Target Period				12-hour Target Period				24-hour Target Period			
				N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)
7-METHYLBICYCLO[4.2.0]OCTANE*	1000210-90-2	NA	NA	1266	1	4.5	4.5	364	0	ND	ND	117	0	ND	ND	785	1	4.5	4.5
7-NORBORNYL T-BUTYL ETHER*	3391-07-9	NA	NA	1266	1	14	14.0	364	0	ND	ND	117	0	ND	ND	785	1	14.0	14.0
ACETALDEHYDE*	75-07-0	5	EPA RfC(1)	1266	26	6.9	15.0	364	5	7.7	10.0	117	3	8.2	11.0	785	18	6.5	15.0
ACETIC ACID, 1,1-DIMETHYLETHYL ESTER*	540-88-5	2000	MDEQ(1)	1266	1	2.2	2.2	364	0	ND	ND	117	0	ND	ND	785	1	2.2	2.2
ACETIC ACID, 2-ETHYLHEXYL ESTER*	103-09-3	2	MDEQ(1)	1266	1	6.2	6.2	364	0	ND	ND	117	1	6.2	6.2	785	0	ND	ND
ACETOACETIC ACID, 1-THIO-, S-ALLYL*	15780-65-1	NA	NA	1266	3	1.6	1.8	364	0	ND	ND	117	0	ND	ND	785	3	1.6	1.8
Acetone	67-64-1	13000	EPA RSL(1)	1266	1096	8.1	300.0	364	339	9.9	120.0	117	116	17.3	300.0	785	641	5.9	89.0
ACETONITRILE*	75-05-8	36	EPA RfC(1)	1266	62	7.7	47.0	364	5	8.3	12.0	117	2	5.9	6.4	785	55	7.7	47.0
Acrylonitrile	107-13-1	1	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
ALPHA-PINENE*	80-56-8	200	MDEQ(1)	1266	2	7.1	13.0	364	0	ND	ND	117	0	ND	ND	785	2	7.1	13.0
BENZENE, 1,3,5-TRICHLORO-*	108-70-3	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
BENZENE, 1,3-DIETHYL-*	141-93-5	NA	NA	1266	1	1.9	1.9	364	0	ND	ND	117	0	ND	ND	785	1	1.9	1.9
BENZENE, 1-METHYL-4-(1-METHYLETHYL)*	99-87-6	1.8	MDEQ(1)	1266	1	2.7	2.7	364	0	ND	ND	117	0	ND	ND	785	1	2.7	2.7
Benzyl chloride	100-44-7	0.2	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
BETA-PINENE*	127-91-3	200	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Bromodichloromethane	75-27-4	0.01	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Bromoform	75-25-2	0.2	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
BROMOMETHANE	74-83-9	5	ATSDR Chr. MRL(1)	1266	10	1	23.0	364	1	5.0	15.0	117	3	5.0	23.0	785	6	1.0	7.1
BUTANAMIDE, 3,3-DIMETHYL-*	926-04-5	NA	NA	1266	1	5.6	5.6	364	0	ND	ND	117	0	ND	ND	785	1	5.6	5.6
BUTANE*	106-97-8	10000	MDEQ(1)	1266	7	4.8	10.0	364	0	ND	ND	117	0	ND	ND	785	7	4.8	10.0
BUTANOIC ACID, 2-METHYLPROPYL ESTER*	539-90-2	NA	NA	1266	1	1.9	1.9	364	0	ND	ND	117	0	ND	ND	785	1	1.9	1.9
BUTANOIC ACID, BUTYL ESTER*	109-21-7	NA	NA	1266	1	14	14.0	364	0	ND	ND	117	0	ND	ND	785	1	14.0	14.0
BUTANOIC ACID, ETHYL ESTER*	105-54-4	NA	NA	1266	1	17	17.0	364	0	ND	ND	117	0	ND	ND	785	1	17.0	17.0
BUTANOIC ACID, METHYL ESTER*	623-42-7	NA	NA	1266	1	4.8	4.8	364	0	ND	ND	117	0	ND	ND	785	1	4.8	4.8
BUTANOIC ACID, PROPYL ESTER*	105-66-8	NA	NA	1266	1	16	16.0	364	0	ND	ND	117	0	ND	ND	785	1	16.0	16.0
CARBON DISULFIDE	75-15-0	200	EPA RfC(1)	1266	60	2	120.0	364	0	ND	ND	117	0	ND	ND	785	60	3.1	120.0
Carbon tetrachloride	56-23-5	30	ATSDR Chr. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
CARBONYL SULFIDE*	463-58-1	4	MDEQ(1)	1266	5	2.3	5.2	364	0	ND	ND	117	0	ND	ND	785	5	2.3	5.2
Chlorobenzene	108-90-7	10	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Chloroethane	75-00-3	4000	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Chloroform	67-66-3	20	ATSDR Chr. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Chloromethane	74-87-3	50	ATSDR Chr. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
cis-1,2-dichloroethene	156-59-2	9	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
cis-1,3-Dichloropropene	10061-02-6	4	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Cumene	98-82-8	80	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
CYCLODECENE, 1-METHYL-*	66633-38-3	NA	NA	1266	2	4.7	5.2	364	0	ND	ND	117	0	ND	ND	785	2	4.7	5.2
CYCLODODECANE*	294-62-2	NA	NA	1266	1	1.7	1.7	364	0	ND	ND	117	0	ND	ND	785	1	1.7	1.7
CYCLODODECENE*	1501-82-2	NA	NA	1266	1	8.6	8.6	364	0	ND	ND	117	0	ND	ND	785	1	8.6	8.6
CYCLODODECENE, (E)-*	1486-75-5	NA	NA	1266	1	7.7	7.7	364	0	ND	ND	117	0	ND	ND	785	1	7.7	7.7
CYCLOHEXANE, 1,2,3-TRIMETHYL-*	7667-55-2	NA	NA	1266	1	3.8	3.8	364	0	ND	ND	117	0	ND	ND	785	1	3.8	3.8
CYCLOHEXANE, 2-BUTYL-1,1,3-TRIMETHYL-*	54676-39-0	NA	NA	1266	4	22.8	48.0	364	0	ND	ND	117	0	ND	ND	785	4	22.8	48.0
CYCLOHEXANOL, 3-(3,3-DIMETHYLBUTYL)-*	40564-98-5	NA	NA	1266	3	10.2	15.0	364	0	ND	ND	117	0	ND	ND	785	3	10.2	15.0
CYCLOHEXANONE, 2,3-DIMETHYL-*	13395-76-1	NA	NA	1266	1	26	26.0	364	0	ND	ND	117	0	ND	ND	785	1	26.0	26.0
CYCLOPENTANE*	287-92-3	6000	MDEQ(1)	1266	2	3.4	5.1	364	0	ND	ND	117	0	ND	ND	785	2	3.4	5.1
CYCLOPENTANE, 1,1'-ETHYLIDENEBIS-*	4413-21-2	NA	NA	1266	1	9.7	9.7	364	0	ND	ND	117	0	ND	ND	785	1	9.7	9.7
CYCLOPENTANE, 1-HYDROXYMETHYL-*	1000156-73-8	NA	NA	1266	1	6.1	6.1	364	0	ND	ND	117	0	ND	ND	785	1	6.1	6.1
CYCLOPENTANE, 1-PENTYL-2-PROPYL-*	62199-51-3	NA	NA	1266	1	1.1	1.1	364	0	ND	ND	117	0	ND	ND	785	1	1.1	1.1

Non-Target Analytes (including TICs)	CAS NO	Human Health Air Screening Level (ppbv)	Source	All Sample Durations†				8-hour Target Period				12-hour Target Period				24-hour Target Period			
				N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)
CYCLOPENTANE, PROPYL-*	2040-96-2	NA	NA	1266	1	6.1	6.1	364	0	ND	ND	117	0	ND	ND	785	1	6.1	6.1
DECANAL*	112-31-2	NA	NA	1266	2	7.9	8.7	364	0	ND	ND	117	0	ND	ND	785	2	7.9	8.7
DECANE, 2,2,4-TRIMETHYL-*	62237-98-3	NA	NA	1266	1	1.1	1.1	364	0	ND	ND	117	0	ND	ND	785	1	1.1	1.1
DECANE, 2,2,6-TRIMETHYL-*	62237-97-2	NA	NA	1266	1	4.3	4.3	364	0	ND	ND	117	0	ND	ND	785	1	4.3	4.3
DECANE, 2,2,8-TRIMETHYL-*	62238-01-1	NA	NA	1266	1	14	14.0	364	0	ND	ND	117	0	ND	ND	785	1	14.0	14.0
DECANE, 2,2-DIMETHYL-*	17302-37-3	NA	NA	1266	1	1.3	1.3	364	0	ND	ND	117	0	ND	ND	785	1	1.3	1.3
DECANE, 2,3,4-TRIMETHYL-*	62238-15-7	NA	NA	1266	1	1.5	1.5	364	0	ND	ND	117	0	ND	ND	785	1	1.5	1.5
DECANE, 2,3,5-TRIMETHYL-*	62238-11-3	NA	NA	1266	1	6.1	6.1	364	0	ND	ND	117	0	ND	ND	785	1	6.1	6.1
DECANE, 2,6,7-TRIMETHYL-*	62108-25-2	NA	NA	1266	1	6.6	6.6	364	0	ND	ND	117	0	ND	ND	785	1	6.6	6.6
DIACETYL*	431-03-8	NA	NA	1266	1	1.8	1.8	364	0	ND	ND	117	0	ND	ND	785	1	1.8	1.8
Dibromochloromethane	124-48-1	0.01	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
DICHLOROACETIC ACID, 4-TRIDECYL ESTER*	1000280-64-3	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Dichlorodifluoromethane	75-71-8	20	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
DIMETHYL ETHER*	115-10-6	35	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
DISULFIDE, DIMETHYL*	624-92-0	7.3	MDEQ(1)	1266	1	2.4	2.4	364	0	ND	ND	117	0	ND	ND	785	1	2.4	2.4
DISULFIDE, FLUOROMETHYL METHYL*	60307-49-5	NA	NA	1266	1	2	2.0	364	0	ND	ND	117	0	ND	ND	785	1	2.0	2.0
DODECANE, 2,2,11,11-TETRAMETHYL-*	127204-12-0	NA	NA	1266	1	6.6	6.6	364	0	ND	ND	117	0	ND	ND	785	1	6.6	6.6
DODECANE, 2,6,11-TRIMETHYL-*	31295-56-4	NA	NA	1266	1	1.6	1.6	364	0	ND	ND	117	0	ND	ND	785	1	1.6	1.6
DODECANE, 6-METHYL-*	6044-71-9	NA	NA	1266	1	1.7	1.7	364	0	ND	ND	117	0	ND	ND	785	1	1.7	1.7
ETHANE, 1,1-DIFLUORO-*	75-37-6	14800	EPA RfC(1)	1266	9	6	12.0	364	0	ND	ND	117	0	ND	ND	785	9	6.0	12.0
ETHYL ACETATE	141-78-6	890	MDEQ(1)	1266	67	3	76.0	364	2	5.0	76.0	117	0	ND	ND	785	65	1.6	33.0
ETHYL ALCOHOL*	64-17-5	10000	MDEQ(1)	1266	29	68.9	220.0	364	1	7.3	7.3	117	1	15.0	15.0	785	27	73.2	220.0
EUCALYPTOL*	470-82-6	NA	NA	1266	1	6.9	6.9	364	0	ND	ND	117	1	6.9	6.9	785	0	ND	ND
FURAN, 2,3-DIHYDRO-3-METHYL-*	1708-27-6	NA	NA	1266	1	1.5	1.5	364	0	ND	ND	117	0	ND	ND	785	1	1.5	1.5
HENEICOSANE*	629-94-7	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
HEPTADECANE, 7-METHYL-*	20959-33-5	NA	NA	1266	1	1.4	1.4	364	0	ND	ND	117	0	ND	ND	785	1	1.4	1.4
HEPTANE, 2,2,3,4,6,6-HEXAMETHYL-*	62108-32-1	NA	NA	1266	2	3.9	6.5	364	0	ND	ND	117	0	ND	ND	785	2	3.9	6.5
HEPTANE, 2,2,4,6,6-PENTAMETHYL-*	13475-82-6	NA	NA	1266	2	3.1	3.9	364	0	ND	ND	117	0	ND	ND	785	2	3.1	3.9
HEPTANE, 2,2,4-TRIMETHYL-*	14720-74-2	NA	NA	1266	1	13	13.0	364	0	ND	ND	117	0	ND	ND	785	1	13.0	13.0
HEPTANE, 2,2-DIMETHYL-*	1071-26-7	NA	NA	1266	1	57	57.0	364	0	ND	ND	117	0	ND	ND	785	1	57.0	57.0
HEPTANE, 4-ETHYL-2,2,6,6-TETRAMER*	62108-31-0	NA	NA	1266	1	6.4	6.4	364	0	ND	ND	117	0	ND	ND	785	1	6.4	6.4
Hexachlorobutadiene	87-68-3	0.01	EPA RSL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
HEXADECANE*	544-76-3	NA	NA	1266	1	1.5	1.5	364	0	ND	ND	117	0	ND	ND	785	1	1.5	1.5
HEXADECANE, 2,6,10,14-TETRAMETHYL-*	638-36-8	NA	NA	1266	1	29	29.0	364	0	ND	ND	117	0	ND	ND	785	1	29.0	29.0
HEXANAL*	66-25-1	0.49	MDEQ(1)	1266	7	3.9	9.2	364	1	6.0	6.0	117	0	ND	ND	785	6	3.6	9.2
HEXANE, 2,2,5,5-TETRAMETHYL-*	1071-81-4	NA	NA	1266	1	1.2	1.2	364	0	ND	ND	117	0	ND	ND	785	1	1.2	1.2
HEXANE, 2,2,5-TRIMETHYL-*	3522-94-9	NA	NA	1266	2	3.5	5.2	364	0	ND	ND	117	0	ND	ND	785	2	3.5	5.2
HEXANE, 2,3,4-TRIMETHYL-*	921-47-1	NA	NA	1266	1	15	15.0	364	0	ND	ND	117	0	ND	ND	785	1	15.0	15.0
HEXANE, 2,4-DIMETHYL-*	589-43-5	NA	NA	1266	3	5	8.8	364	0	ND	ND	117	0	ND	ND	785	3	5.0	8.8
HEXANOIC ACID, METHYL ESTER*	106-70-7	NA	NA	1266	1	2.4	2.4	364	0	ND	ND	117	0	ND	ND	785	1	2.4	2.4
HEXATRIACONTANE*	630-06-8	NA	NA	1266	1	5.2	5.2	364	0	ND	ND	117	0	ND	ND	785	1	5.2	5.2
HEXYL N-VALERATE*	1117-59-5	NA	NA	1266	1	2.2	2.2	364	0	ND	ND	117	0	ND	ND	785	1	2.2	2.2
ISOBUTANE*	75-28-5	10000	MDEQ(1)	1266	37	11.7	38.0	364	10	13.2	38.0	117	0	ND	ND	785	27	11.1	38.0
Isopropyl Alcohol	67-63-0	3000	EPA RfC(1)	1266	1098	11.8	530.0	364	274	11.9	150.0	117	113	22.8	130.0	785	711	10.1	530.0
LIMONENE*	138-86-3	NA	NA	1266	6	7.9	21.0	364	1	21.0	21.0	117	0	ND	ND	785	5	5.3	8.1
METHYL 3-BUTENOATE*	3724-55-8	NA	NA	1266	2	5.1	8.8	364	0	ND	ND	117	0	ND	ND	785	2	5.1	8.8
Methyl butyl ketone	591-78-6	10	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND

Non-Target Analytes (including TICs)	CAS NO	Human Health Air Screening Level (ppbv)	Source	All Sample Durations†				8-hour Target Period				12-hour Target Period				24-hour Target Period			
				N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)
METHYL ETHYL KETONE	78-93-3	2000	EPA RfC(1)	1266	48	1	120.0	364	0	ND	ND	117	1	5.0	30.0	785	47	1.7	120.0
Methyl isobutyl ketone	108-10-1	700	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Methyl tert-butyl ether	1634-04-4	700	ATSDR Chr. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
METHYLENE CHLORIDE	75-09-2	300	ATSDR Chr. MRL(1)	1266	18	1	9.0	364	0	ND	ND	117	0	ND	ND	785	18	1.0	9.0
NAPHTHALENE, 2-(1,1-DIMETHYLETHY…*	54934-96-2	NA	NA	1266	1	7.8	7.8	364	0	ND	ND	117	0	ND	ND	785	1	7.8	7.8
NAPHTHALENE, DECAHYDRO-1,6-DIMET…*	1750-51-2	NA	NA	1266	1	7.2	7.2	364	0	ND	ND	117	0	ND	ND	785	1	7.2	7.2
NAPHTHALENE, DECAHYDRO-2,6-DIMETHYL-*	1618-22-0	NA	NA	1266	2	6.8	6.9	364	0	ND	ND	117	0	ND	ND	785	2	6.8	6.9
NAPHTHALENE, DECAHYDRO-2-METHYL-*	2958-76-1	NA	NA	1266	4	10	23.0	364	0	ND	ND	117	0	ND	ND	785	4	10.0	23.0
NONANAL*	124-19-6	NA	NA	1266	17	3.5	13.0	364	1	13.0	13.0	117	1	9.1	9.1	785	15	2.4	9.1
NONANE, 2,2,3-TRIMETHYL-*	55499-04-2	NA	NA	1266	1	1.1	1.1	364	0	ND	ND	117	0	ND	ND	785	1	1.1	1.1
NONANE, 2-METHYL-*	871-83-0	NA	NA	1266	1	16	16.0	364	0	ND	ND	117	0	ND	ND	785	1	16.0	16.0
NONANE, 3-METHYL-5-PROPYL-*	31081-18-2	NA	NA	1266	2	4.4	5.6	364	0	ND	ND	117	0	ND	ND	785	2	4.4	5.6
OCTADECANE, 2,6-DIMETHYL-*	75163-97-2	NA	NA	1266	1	7.8	7.8	364	0	ND	ND	117	0	ND	ND	785	1	7.8	7.8
OCTANAL*	124-13-0	NA	NA	1266	1	1.1	1.1	364	0	ND	ND	117	0	ND	ND	785	1	1.1	1.1
OCTANE, 2,2-DIMETHYL-*	15869-87-1	NA	NA	1266	1	2.5	2.5	364	0	ND	ND	117	0	ND	ND	785	1	2.5	2.5
OCTANE, 2,3,3-TRIMETHYL-*	62016-30-2	NA	NA	1266	1	5.7	5.7	364	0	ND	ND	117	0	ND	ND	785	1	5.7	5.7
OCTANE, 2,6-DIMETHYL-*	2051-30-1	NA	NA	1266	3	12.3	25.0	364	0	ND	ND	117	0	ND	ND	785	3	12.3	25.0
OCTANE, 2,7-DIMETHYL-*	1072-16-8	NA	NA	1266	1	4.8	4.8	364	0	ND	ND	117	0	ND	ND	785	1	4.8	4.8
OCTANE, 4-ETHYL-*	15869-86-0	NA	NA	1266	1	14	14.0	364	0	ND	ND	117	0	ND	ND	785	1	14.0	14.0
o-Veratramide*	1521-39-7	NA	NA	1266	1	24	24.0	364	0	ND	ND	117	0	ND	ND	785	1	24.0	24.0
PENTADECANE, 2,6,10,14-TETRAMETHYL-*	1921-70-6	NA	NA	1266	1	1.1	1.1	364	0	ND	ND	117	0	ND	ND	785	1	1.1	1.1
PENTANE*	109-66-0	300	EPA RfC(1)	1266	59	21.2	180.0	364	12	10.5	51.0	117	0	ND	ND	785	47	23.9	180.0
PENTANE, 2,3-DIMETHYL-*	565-59-3	850	MDEQ(1)	1266	2	9.2	16.0	364	0	ND	ND	117	0	ND	ND	785	2	9.2	16.0
PENTANE, 3-ETHYL-2,2-DIMETHYL-*	16747-32-3	NA	NA	1266	1	4.6	4.6	364	0	ND	ND	117	0	ND	ND	785	1	4.6	4.6
PENTANE, 3-METHYL-*	96-14-0	1000	MDEQ(1)	1266	1	1.4	1.4	364	0	ND	ND	117	0	ND	ND	785	1	1.4	1.4
PROPANE*	74-98-6	NA	NA	1266	10	4.4	25.0	364	1	7.0	7.0	117	0	ND	ND	785	9	4.1	25.0
PROPANOIC ACID, 2-OXO-*	127-17-3	NA	NA	1266	1	5.5	5.5	364	0	ND	ND	117	0	ND	ND	785	1	5.5	5.5
PROPYLENE	115-07-1	2000	EPA RfC(1)	1266	18	1	1.0	364	0	ND	ND	117	0	ND	ND	785	18	1.0	1.0
STYRENE	100-42-5	200	ATSDR Chr. MRL(1)	1266	2	1	5.0	364	0	ND	ND	117	0	ND	ND	785	2	1.0	5.0
SULFUROUS ACID, BUTYL HEPTADECYL…*	1000309-18-4	NA	NA	1266	1	6.1	6.1	364	0	ND	ND	117	0	ND	ND	785	1	6.1	6.1
TETRACHLOROETHYLENE	127-18-4	40	ATSDR Chr. MRL(1)	1266	1	1	2.0	364	0	ND	ND	117	0	ND	ND	785	1	1.0	2.0
TETRADECANE*	629-59-4	NA	NA	1266	1	1.3	1.3	364	0	ND	ND	117	0	ND	ND	785	1	1.3	1.3
TETRADECANE, 2,2-DIMETHYL-*	59222-86-5	NA	NA	1266	1	34	34.0	364	0	ND	ND	117	0	ND	ND	785	1	34.0	34.0
TETRAHYDROFURAN	109-99-9	6	MDEQ(1)	1266	4	1	44.0	364	1	5.0	44.0	117	0	ND	ND	785	3	1.0	3.0
TRANS,TRANS-1,8-DIMETHYLSPIRO[4....*	1000111-72-8	NA	NA	1266	1	6.3	6.3	364	0	ND	ND	117	0	ND	ND	785	1	6.3	6.3
trans-1,2-Dichloroethene	156-60-5	15	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
trans-1,3-Dichloropropene	10061-01-5	0.5	MDEQ(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
TRANS-DECALIN, 2-METHYL-*	1000152-47-3	NA	NA	1266	1	11	11.0	364	0	ND	ND	117	0	ND	ND	785	1	11.0	11.0
Trichloroethene	79-01-6	2	EPA RfC(1)	1266	1	1	1.0	364	0	ND	ND	117	0	ND	ND	785	1	1.0	1.0
Trichlorofluoromethane	75-69-4	130	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
TRICOSYL PENTAFLUOROPROPIONATE*	1000351-81-0	NA	NA	1266	1	1.9	1.9	364	0	ND	ND	117	0	ND	ND	785	1	1.9	1.9
TRIDECANE*	629-50-5	NA	NA	1266	1	10	10.0	364	0	ND	ND	117	0	ND	ND	785	1	10.0	10.0
TRIDECANE, 4,8-DIMETHYL-*	55030-62-1	NA	NA	1266	1	4.8	4.8	364	0	ND	ND	117	0	ND	ND	785	1	4.8	4.8
TRIDECANE, 6-METHYL-*	13287-21-3	NA	NA	1266	1	45	45.0	364	0	ND	ND	117	0	ND	ND	785	1	45.0	45.0
TRIDECYL HEPTAFLUOROBUTYRATE*	1000351-82-8	NA	NA	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
TRIETHYLAMINE*	121-44-8	2	EPA RfC(1)	1266	2	12.9	18.0	364	0	ND	ND	117	0	ND	ND	785	2	12.9	18.0
TRISULFIDE, DIMETHYL*	3658-80-8	NA	NA	1266	1	5.1	5.1	364	0	ND	ND	117	0	ND	ND	785	1	5.1	5.1

Non-Target Analytes (including TICs)	CAS NO	Human Health Air Screening Level (ppbv)	Source	All Sample Durations†				8-hour Target Period				12-hour Target Period				24-hour Target Period			
				N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)	N	Ndet	Average Level**	Max (ppbv)
UNDECANE, 2,2-DIMETHYL-*	17312-64-0	NA	NA	1266	1	2.7	2.7	364	0	ND	ND	117	0	ND	ND	785	1	2.7	2.7
UNDECANE, 2,6-DIMETHYL-*	17301-23-4	NA	NA	1266	6	13.4	52.0	364	0	ND	ND	117	0	ND	ND	785	6	13.4	52.0
UNDECANE, 3,6-DIMETHYL-*	17301-28-9	NA	NA	1266	2	8.7	16.0	364	0	ND	ND	117	0	ND	ND	785	2	8.7	16.0
UNDECANE, 3,9-DIMETHYL-*	17301-31-4	NA	NA	1266	1	4.9	4.9	364	0	ND	ND	117	0	ND	ND	785	1	4.9	4.9
UNDECANE, 5-METHYL-*	1632-70-8	NA	NA	1266	1	1.2	1.2	364	0	ND	ND	117	0	ND	ND	785	1	1.2	1.2
UNKNOWN*	78-99-9	NA	NA	1266	1	1.6	1.6	364	0	ND	ND	117	0	ND	ND	785	1	1.6	1.6
UNKNOWN*	288-47-1	NA	NA	1266	1	1.2	1.2	364	0	ND	ND	117	0	ND	ND	785	1	1.2	1.2
UNKNOWN*	62-55-5	NA	NA	1266	2	1.4	1.4	364	0	ND	ND	117	0	ND	ND	785	2	1.4	1.4
Vinyl acetate	108-05-4	10	ATSDR Int. MRL(1)	1266	3	1	2.0	364	0	ND	ND	117	0	ND	ND	785	3	1.0	2.0
Vinyl bromide	593-60-2	1	EPA RfC(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND
Vinyl chloride	75-01-4	30	ATSDR Int. MRL(1)	1266	0	ND	0.0	364	0	ND	ND	117	0	ND	ND	785	0	ND	ND

PPBV - Parts Per Billion Volume

*** -** TIC (tentatively identified compound)

** - Average Levels for compounds that were detected in <5% of samples are the median value using the detection limit for non-detects. Average Levels for compounds that were detected in >5% of samples are the mean using the detection limit for non-detects. Average Levels for tentatively identified compounds are the mean of detects.
†Samples reported do not include instantaneous 'grab' samples. Samples with 8-24 hour target sample periods are included.
NA - Not Available/**ND** - Not Detected

N - Number of samples analyzed/**NDET** - Number of detections

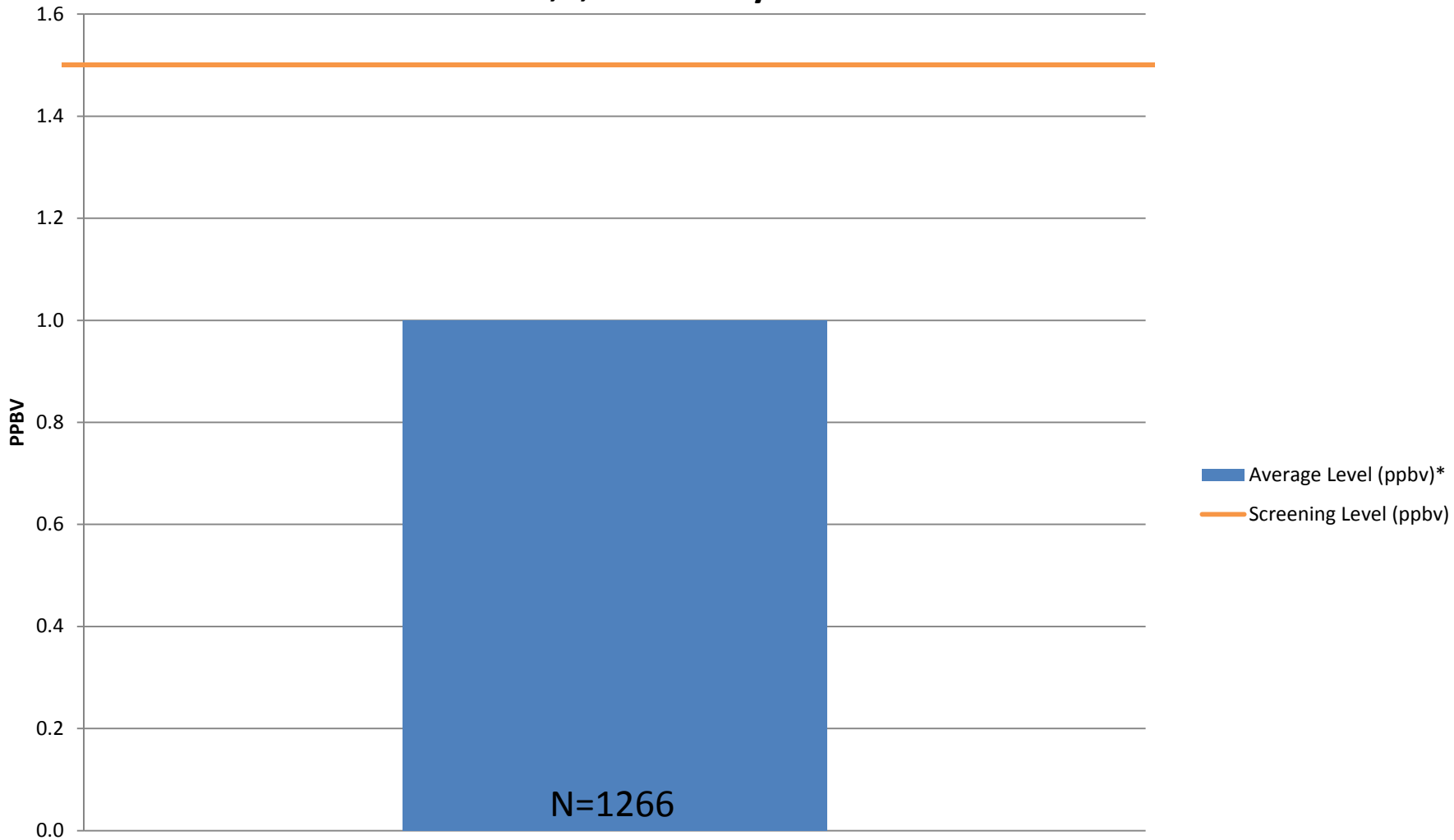
(1) - Unless otherwise noted, the screening level was obtained from Enbridge Oil Spill Human Health Air Screening Levels, August 31, 2011.
ATSDR Chr. MRL - Agency for Toxic Substances and Disease Registry - Chronic Minimal Risk Level for Inhalation

EPA RfC - If no Chronic MRL is available, the screening level is the EPA Chronic Reference Concentration (RfC). For 2 chemicals, vinyl acetate and vinyl chloride, the ATSDR Intermediate (Int.) MRL was selected. These were developed more recently than the EPA RfC and were lower than the EPA RfC.

EPA RSL - If none of the above are available, the EPA Regional Screening Level (RSL) is used.

MDEQ - If none of the above are available, the Michigan DEQ Air Quality Division, Air Toxics Screening Level is the screening level.

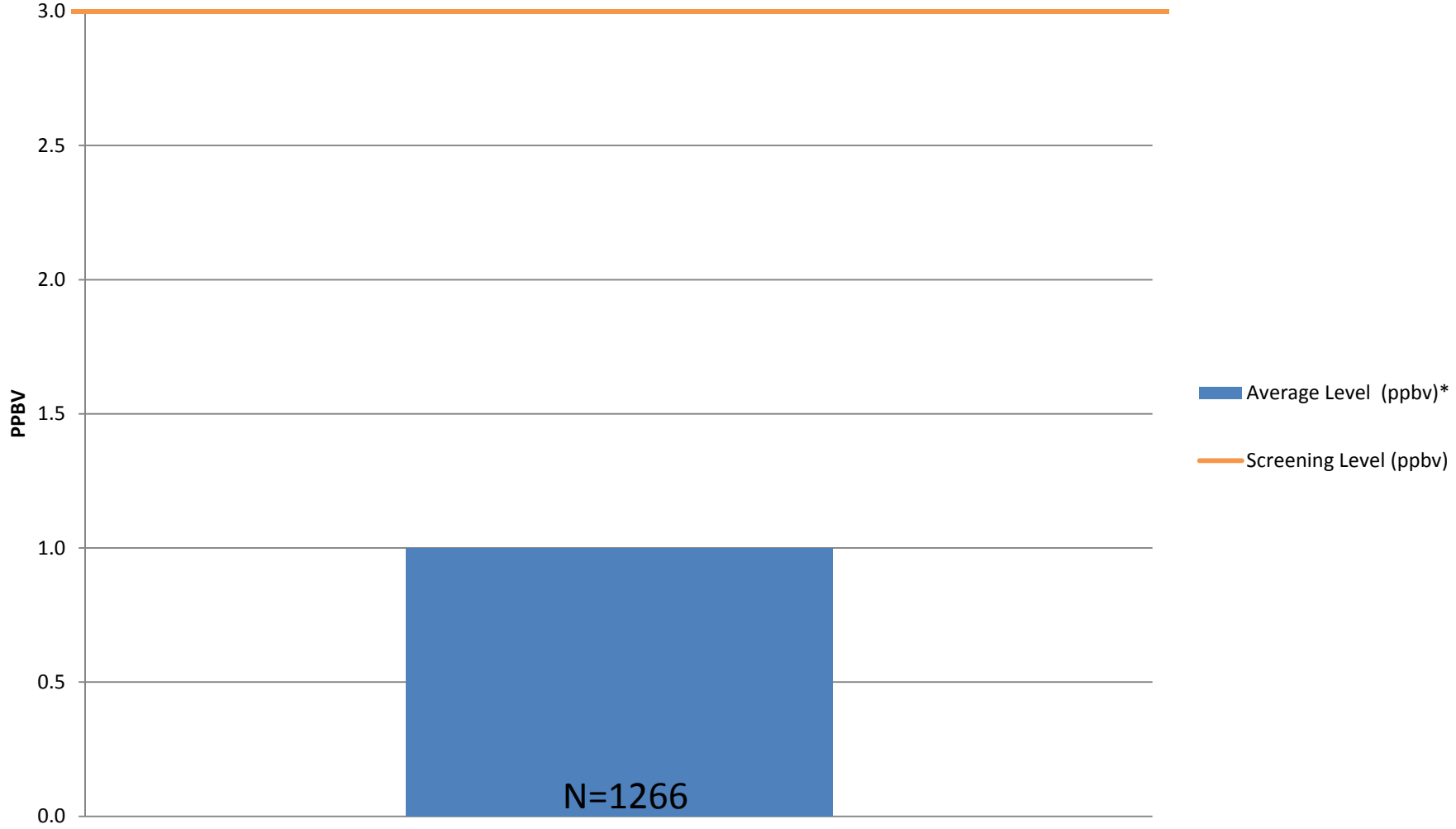
Comparison of Average Air Levels with Human Health Screening Levels
1,2,4-Trimethylbenzene



PPBV - Parts Per Billion Volume

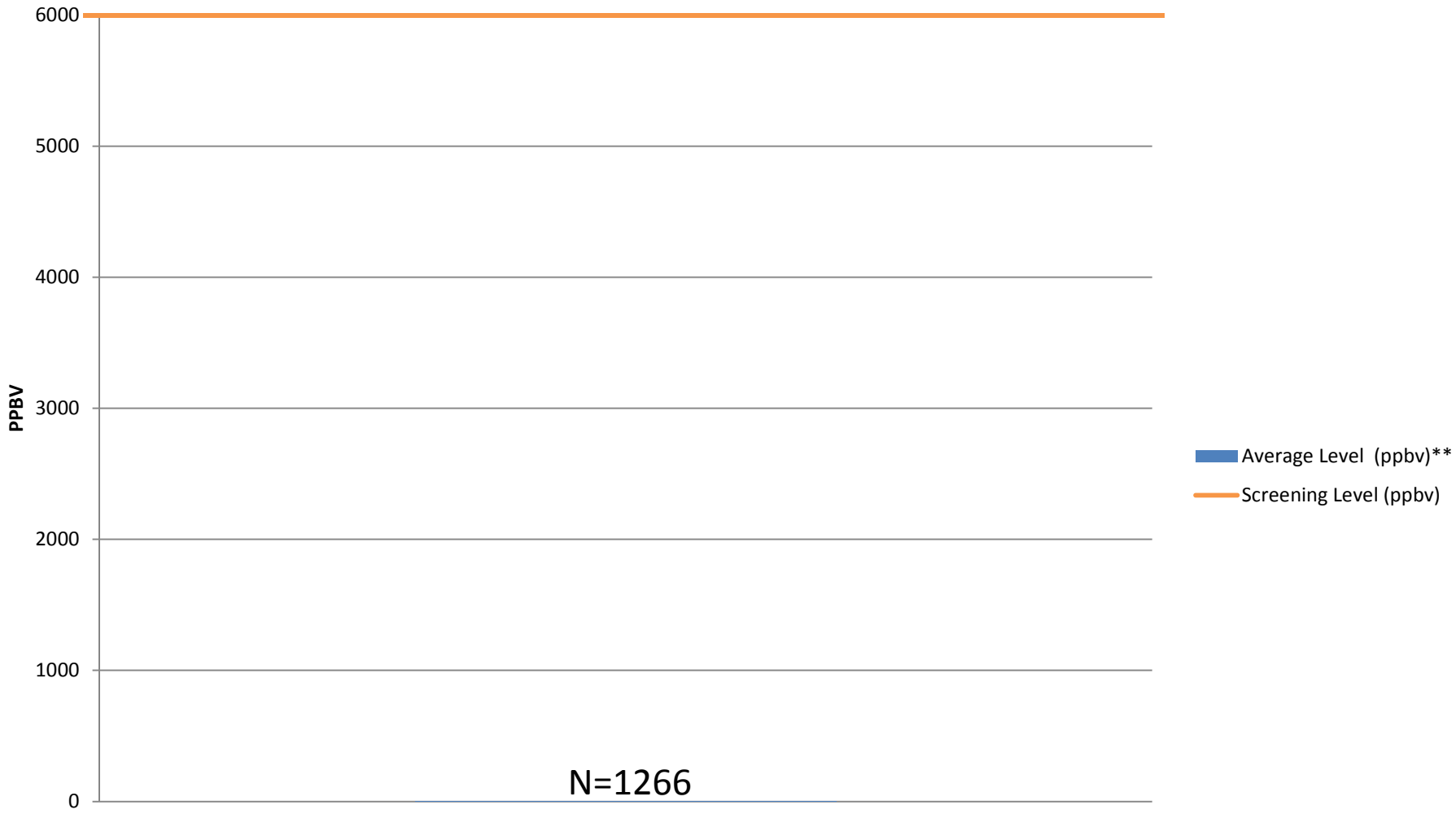
* - Average Levels for compounds that were detected in <5% of samples are the median value using the detection limit for non-detects.
Average Levels for compounds that were detected in >5% of samples are the mean using the detection limit for non-detects.
Average Levels for tentatively identified compounds are the mean of detects.

Comparison of Average Air Levels with Human Health Screening Levels
Benzene



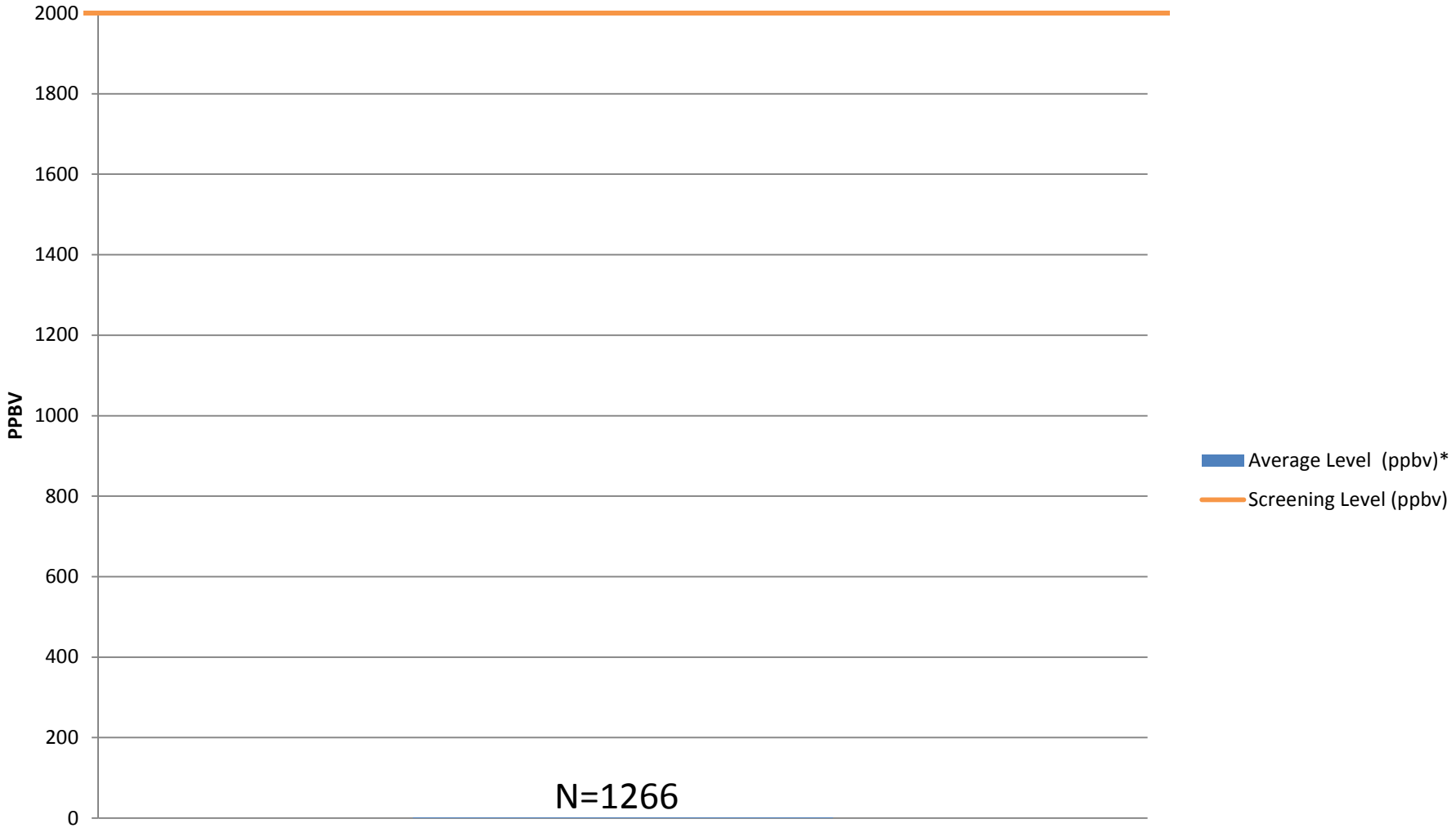
PPBV - Parts Per Billion Volume
* - Average Levels for compounds that were detected in <5% of samples are the median value using the detection limit for non-detects.
Average Levels for compounds that were detected in >5% of samples are the mean using the detection limit for non-detects.
Average Levels for tentatively identified compounds are the mean of detects.

Comparison of Average Air Levels with Human Health Screening Levels
2-Methylbutane*



PPBV - Parts Per Billion Volume
* - TIC (tentatively identified compound)
** - Average Levels for compounds that were detected in <5% of samples are the median value using the detection limit for non-detects.
Average Levels for compounds that were detected in >5% of samples are the mean using the detection limit for non-detects.
Average Levels for tentatively identified compounds are the mean of detects.

Comparison of Average Air Levels with Human Health Screening Levels
Cyclohexane



PPBV - Parts Per Billion Volume

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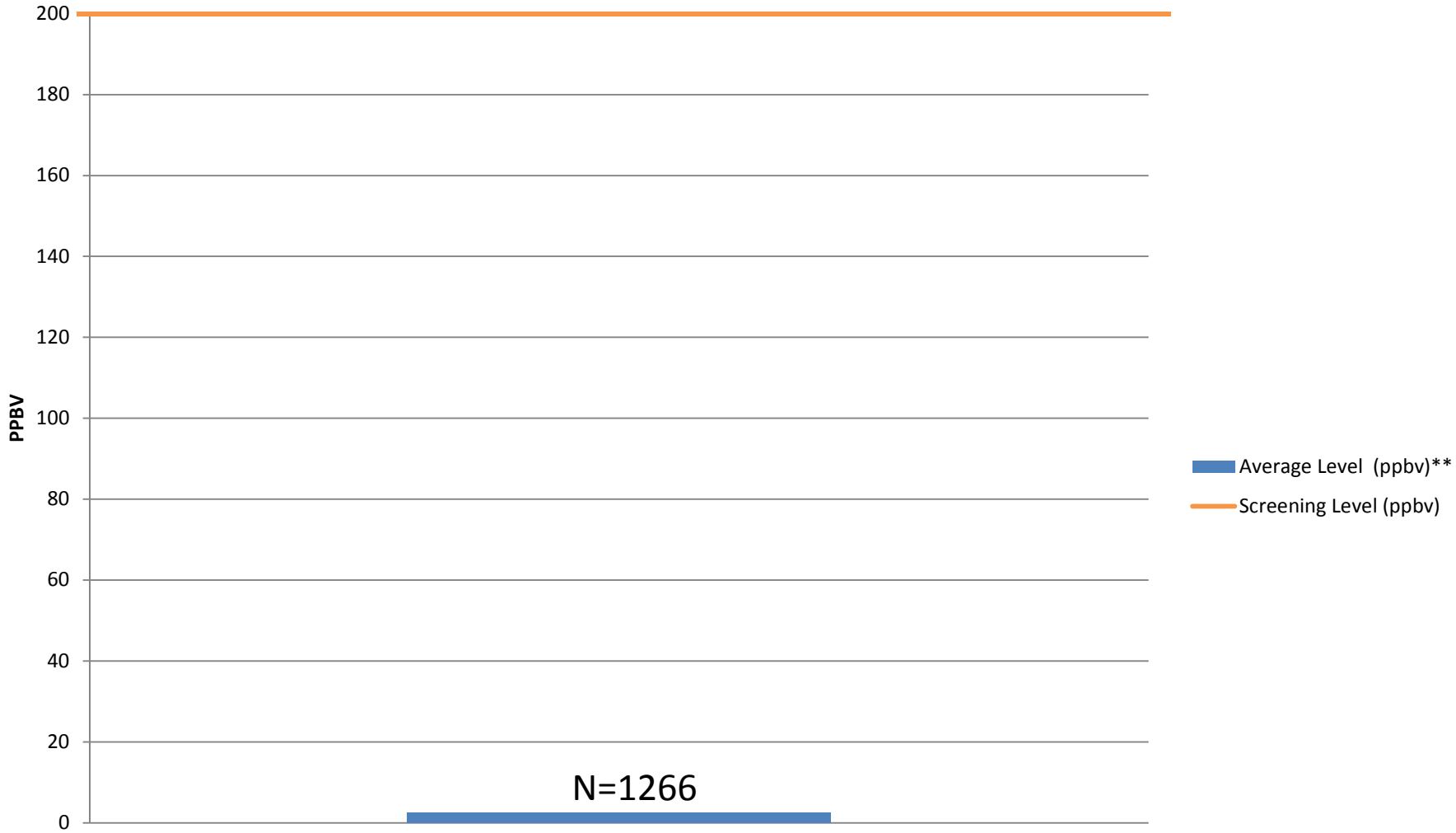
Average Levels for tentatively identified compounds are the mean of detects.

Comparison of Average Air Levels with Human Health Screening Levels
Methylcyclopentane*



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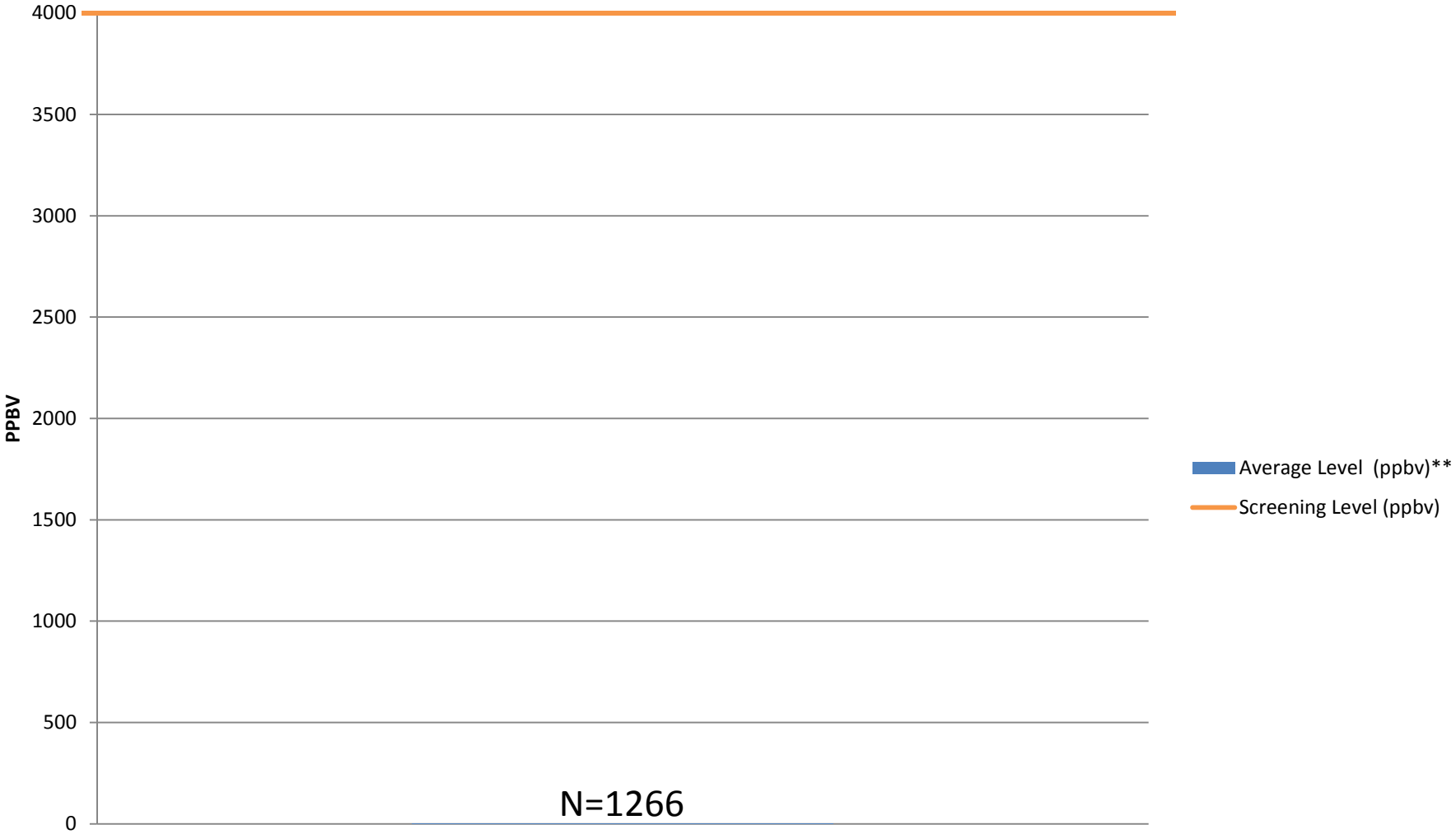
Comparison of Average Air Levels with Human Health Screening Levels
Methylcyclohexane*



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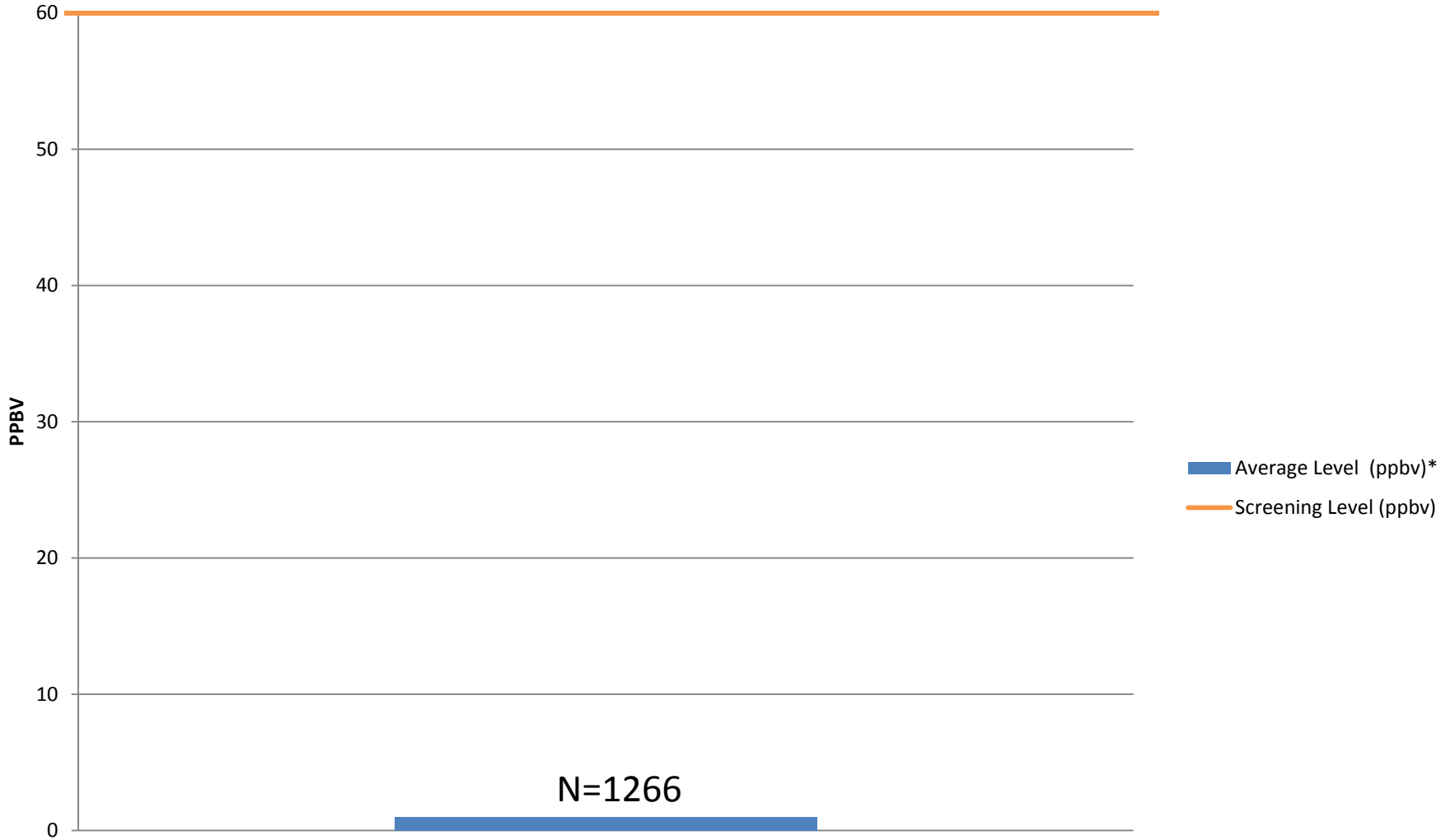
Comparison of Average Air Levels with Human Health Screening Levels
Ethylbenzene



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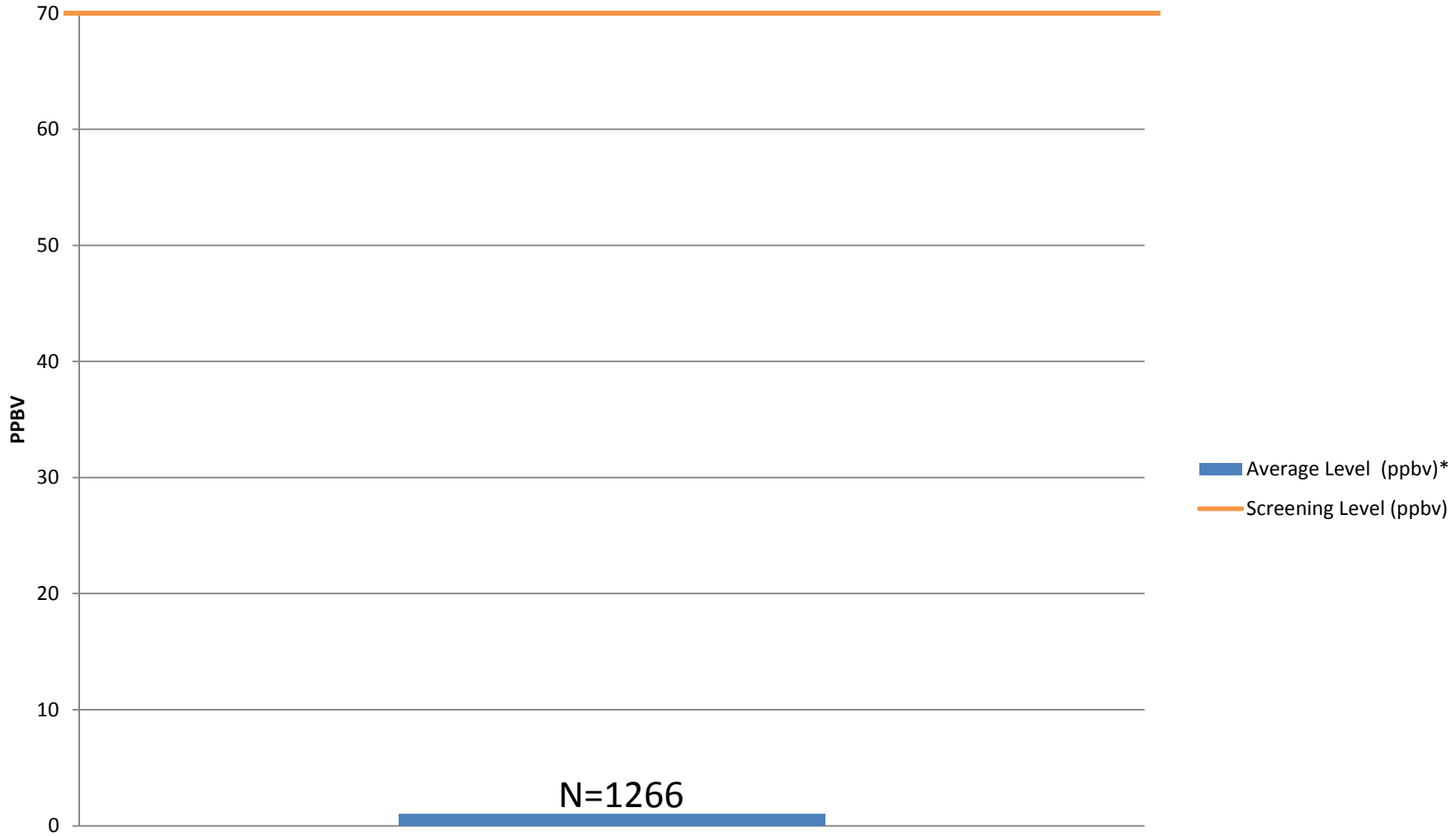
Comparison of Average Air Levels with Human Health Screening Levels
4-Ethyltoluene



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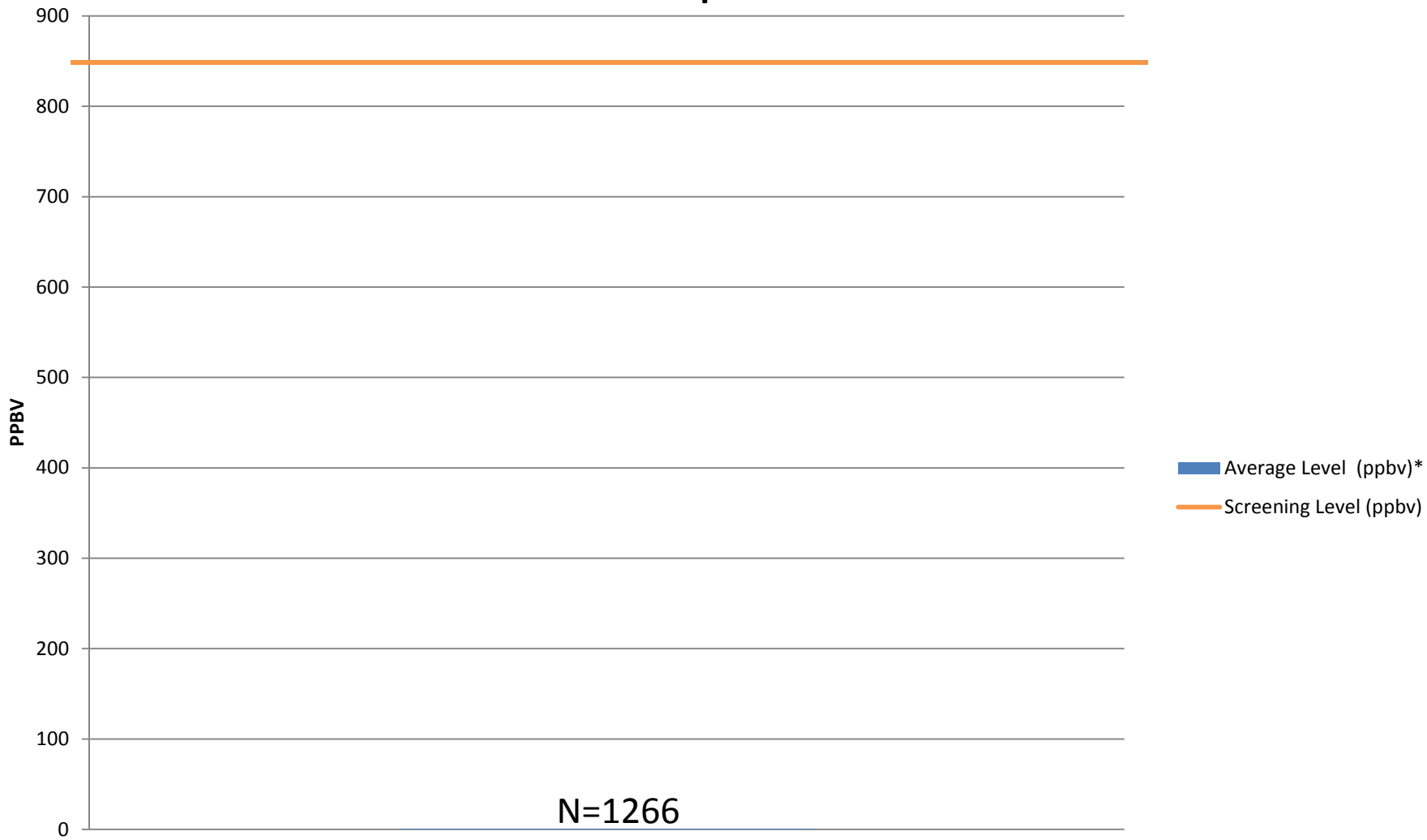
Comparison of Average Air Levels with Human Health Screening Levels
n-Heptane



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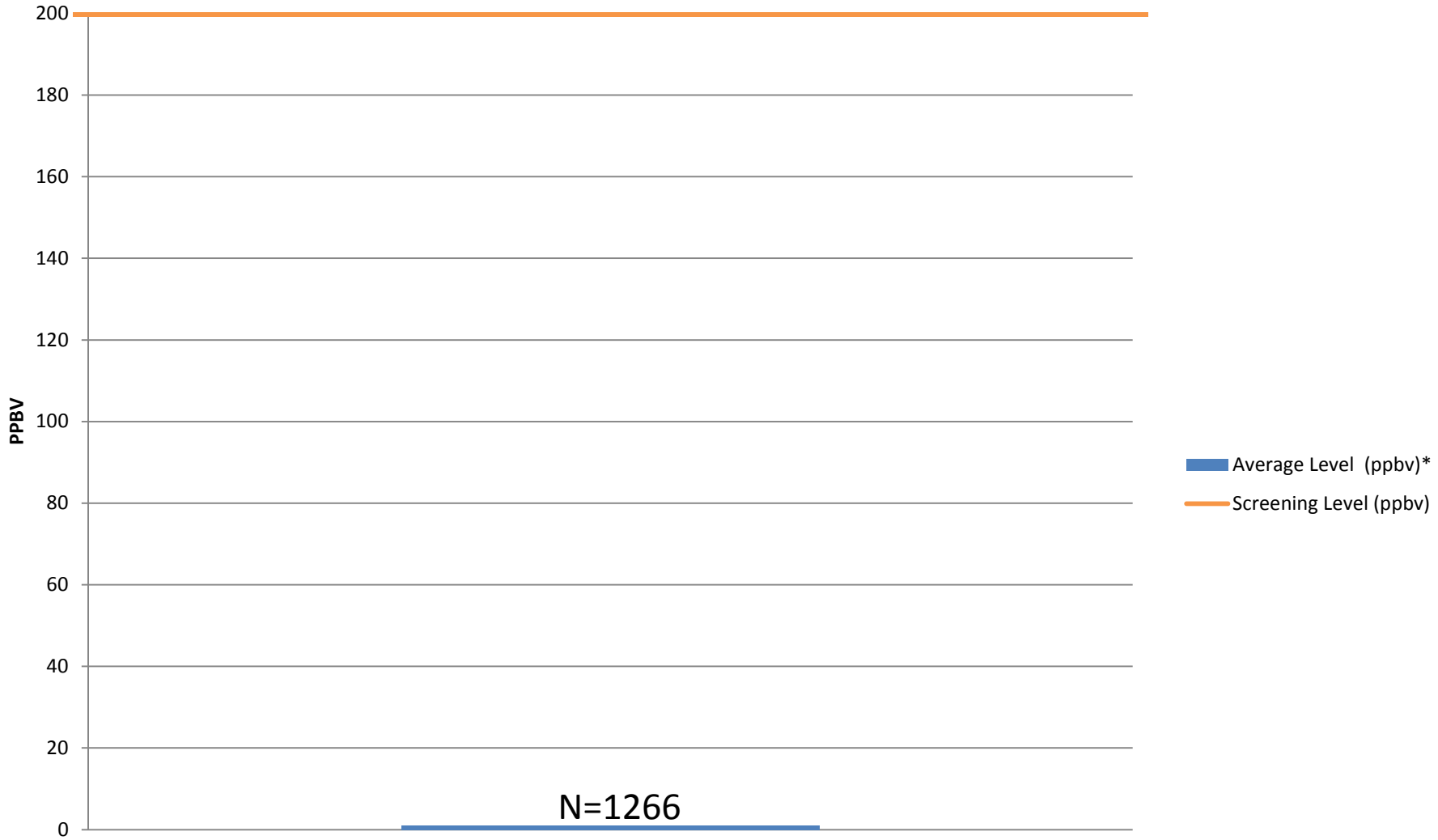
Comparison of Average Air Levels with Human Health Screening Levels
n-Hexane



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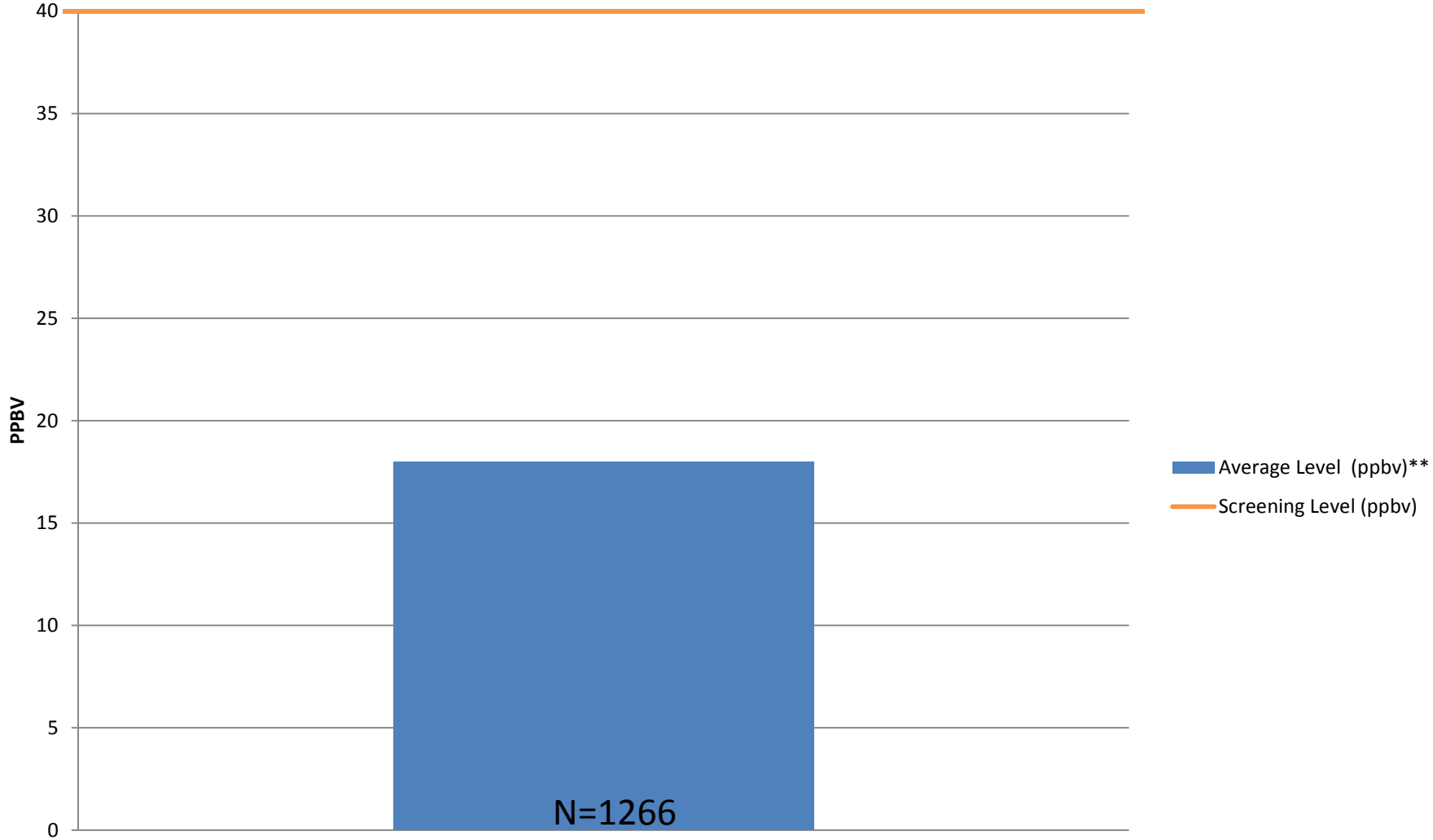
Comparison of Average Air Levels with Human Health Screening Levels
Nonane*



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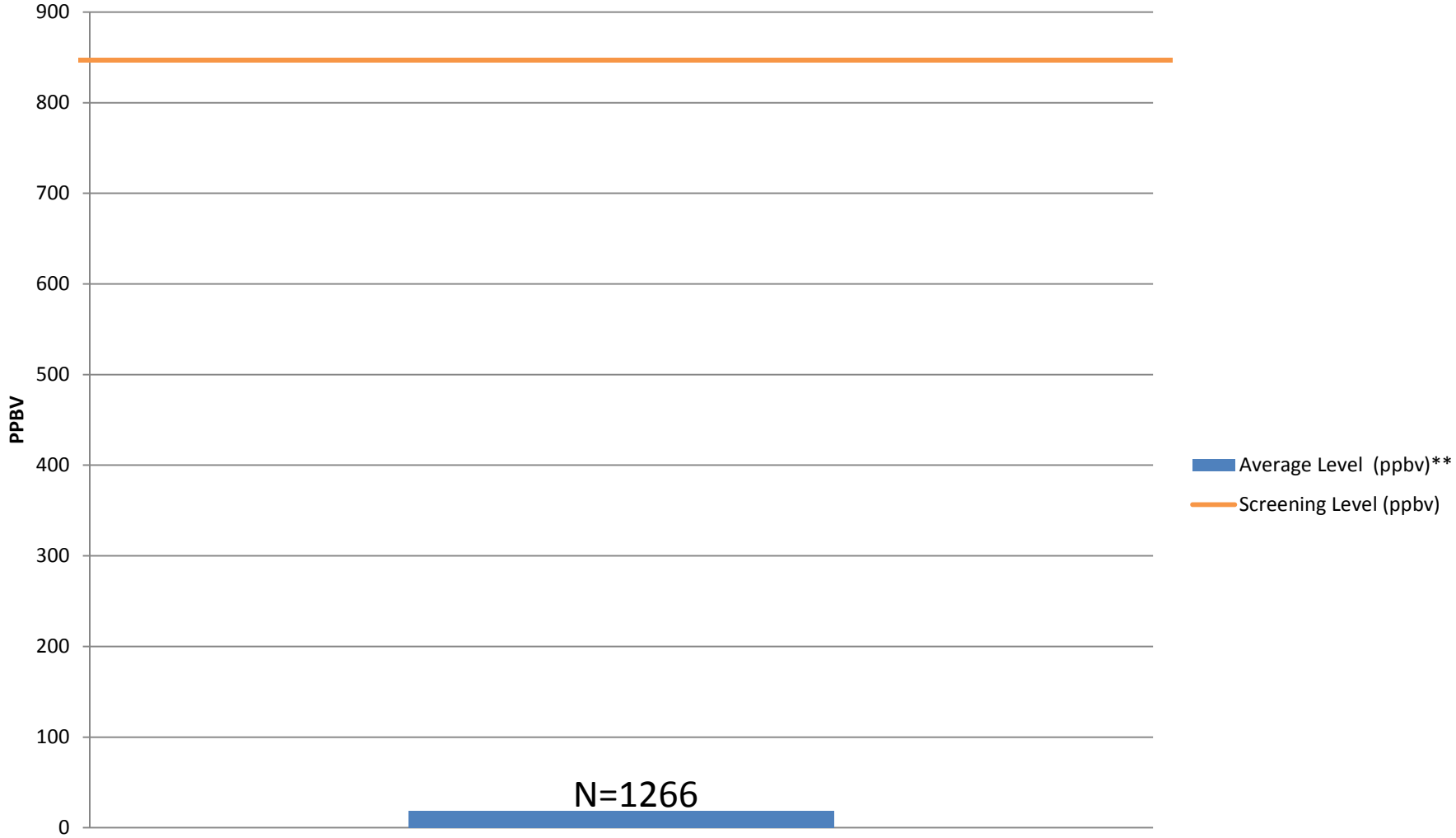
Comparison of Average Air Levels with Human Health Screening Levels
2-Methylhexane*



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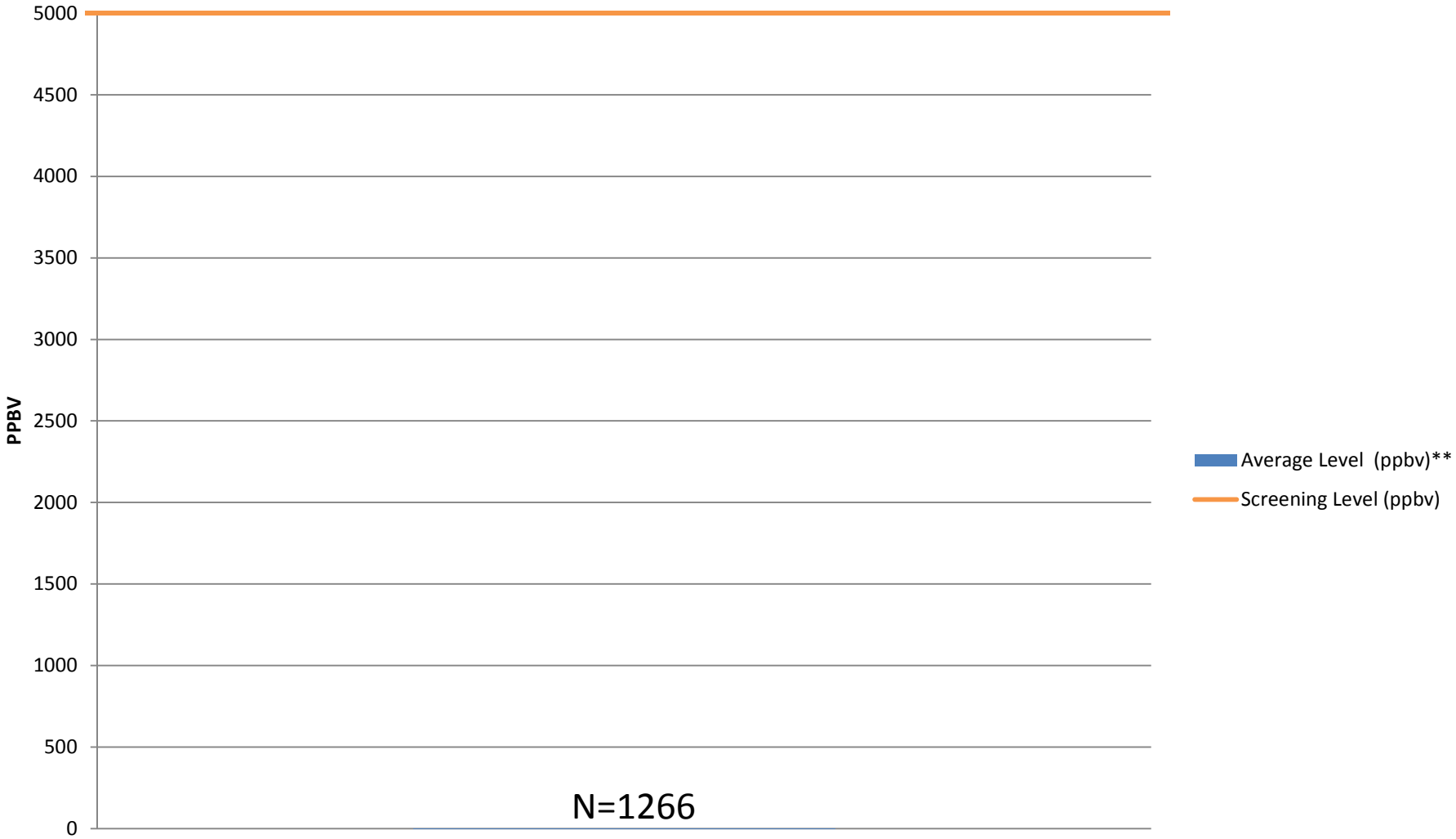
2-Methylpentane*



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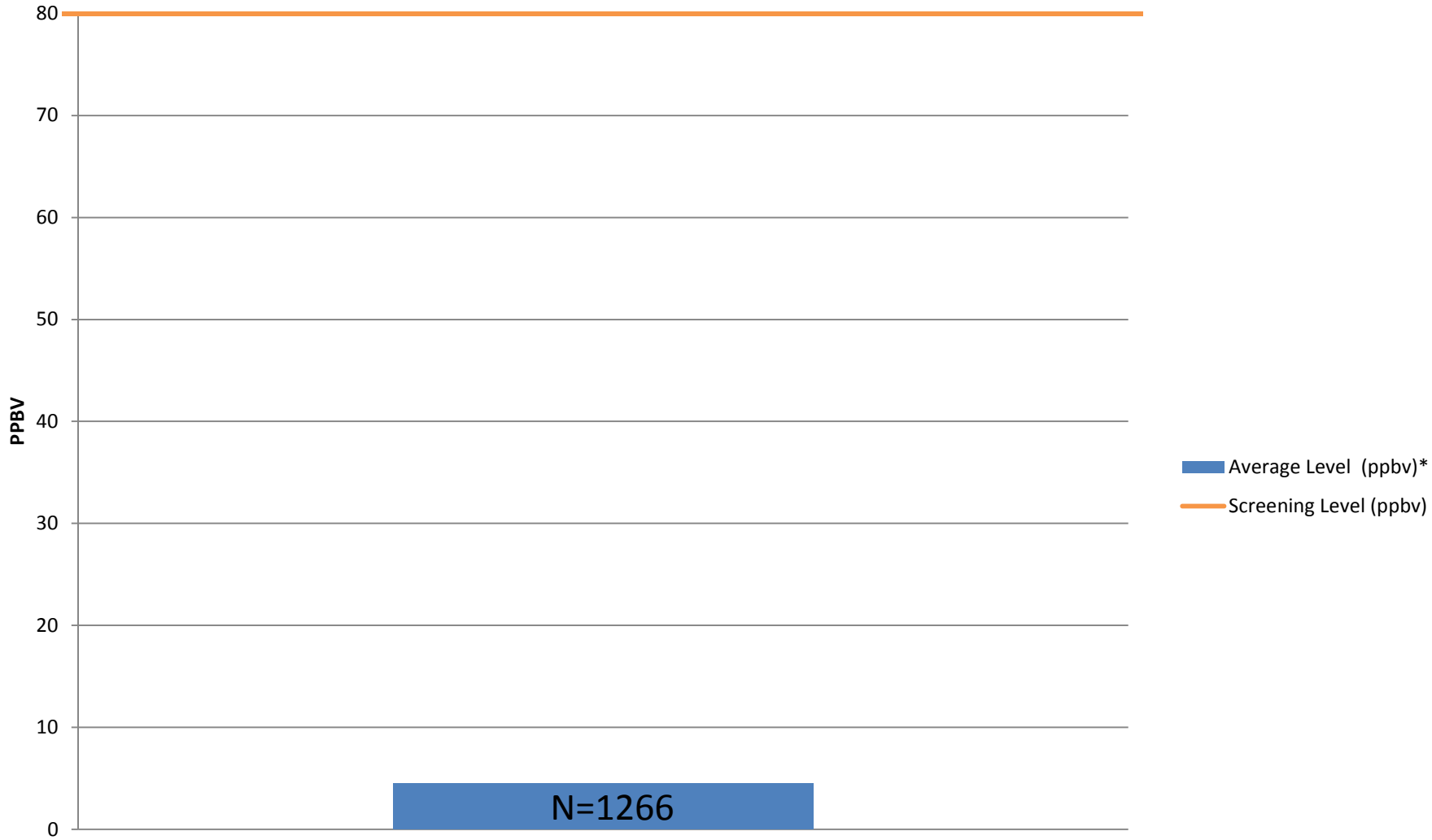
Comparison of Average Air Levels with Human Health Screening Levels
Toluene



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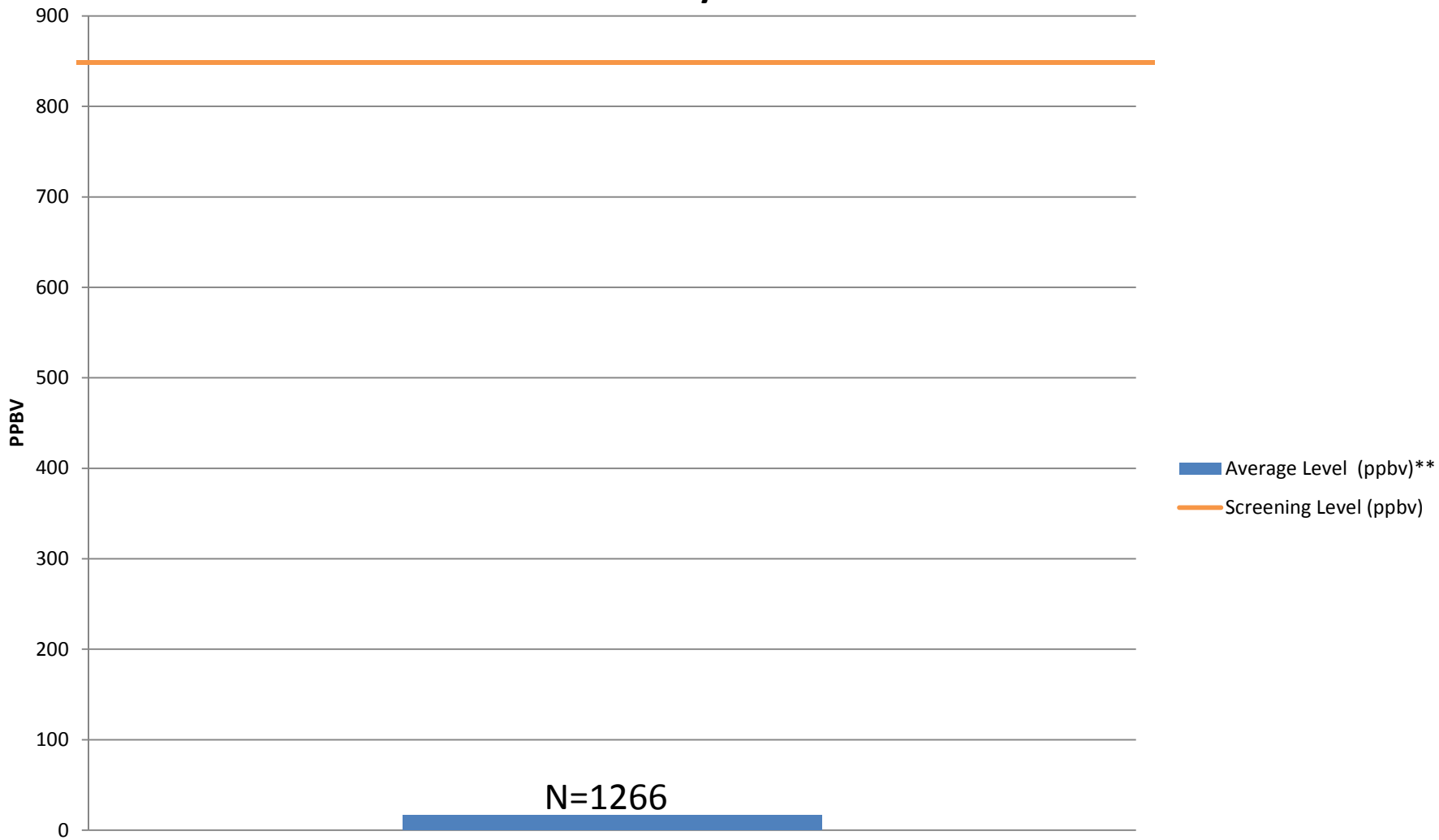
Comparison of Average Air Levels with Human Health Screening Levels
3-Methylhexane*



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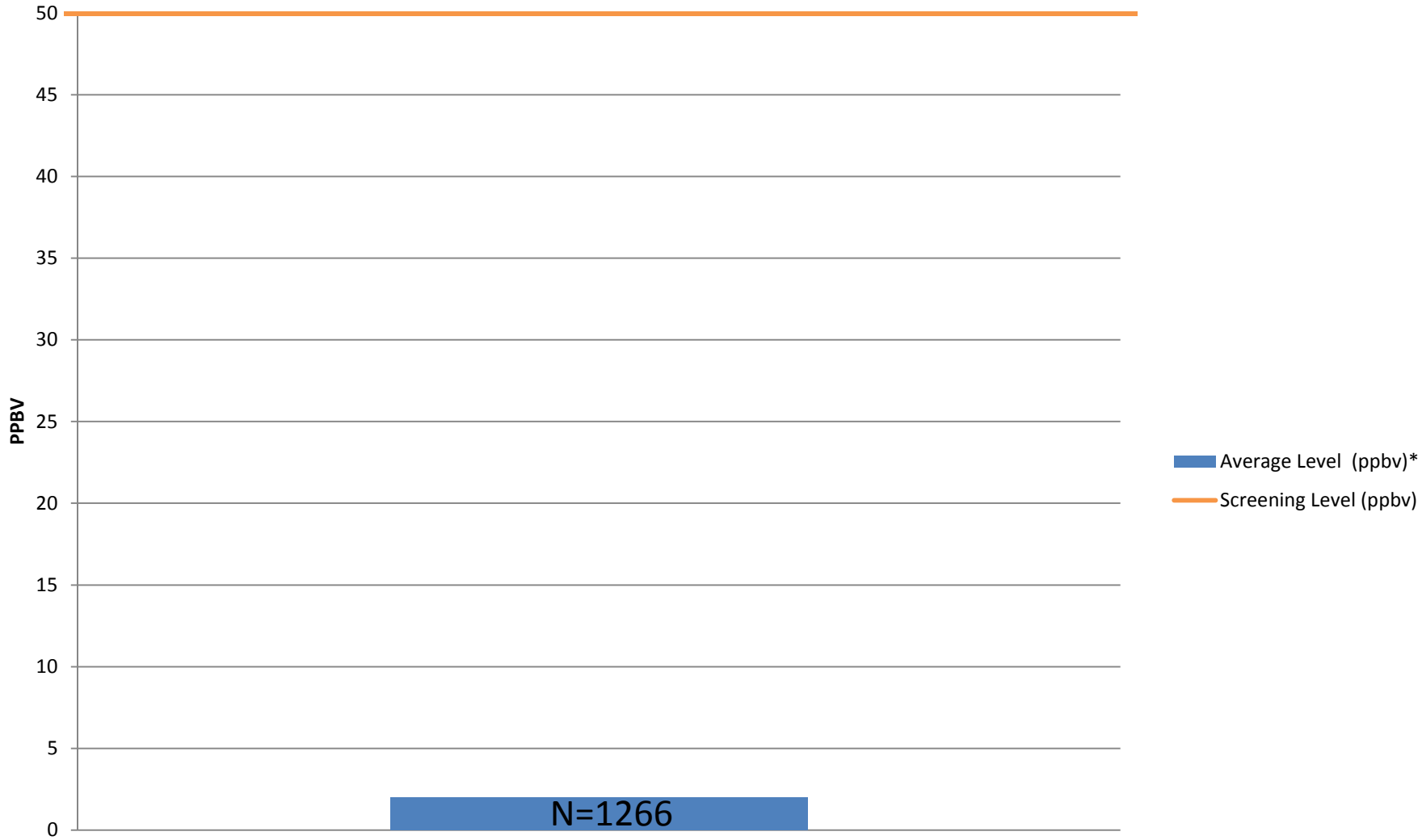
Comparison of Average Air Levels with Human Health Screening Levels
m&p-Xylene



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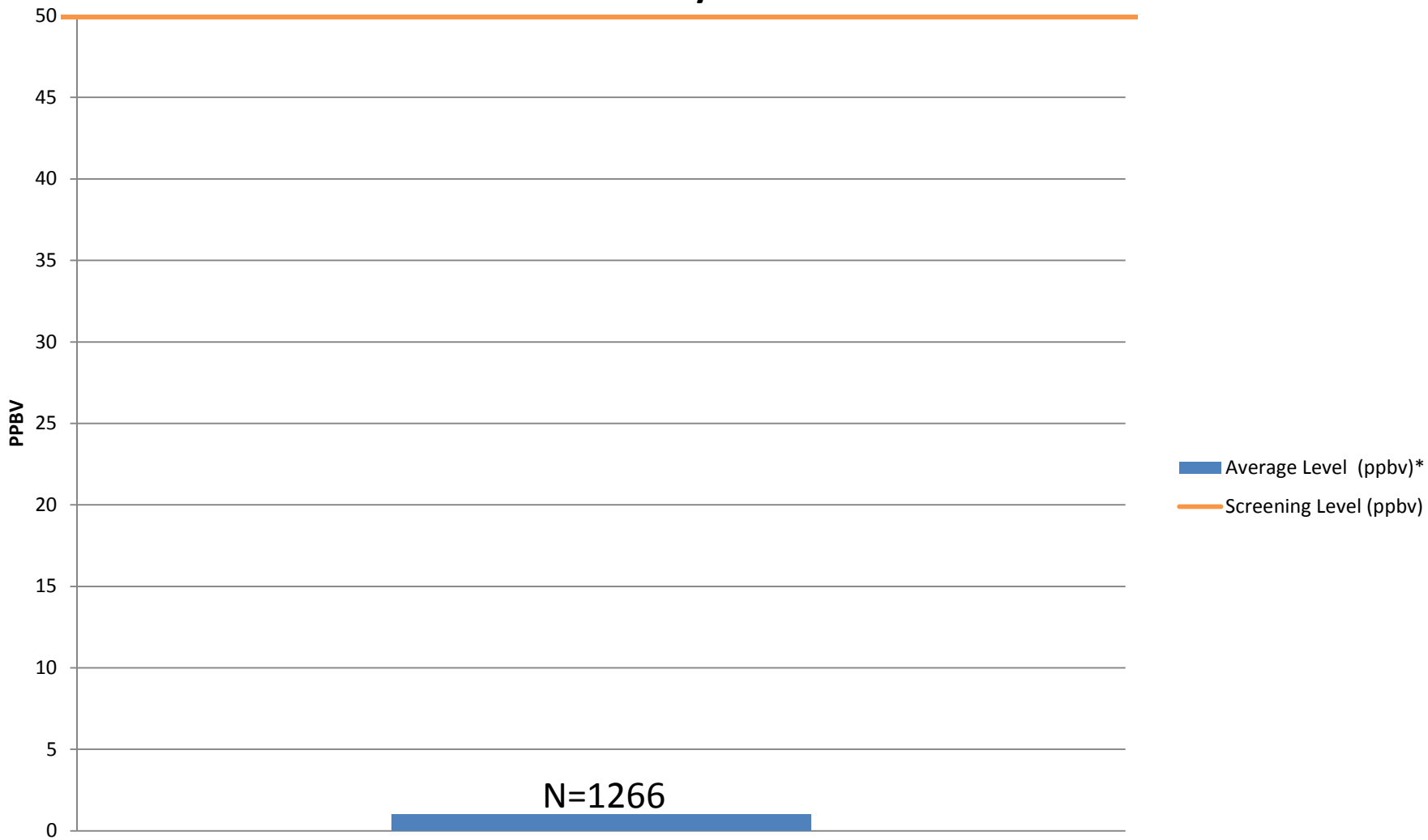
Comparison of Average Air Levels with Human Health Screening Levels
o-Xylene



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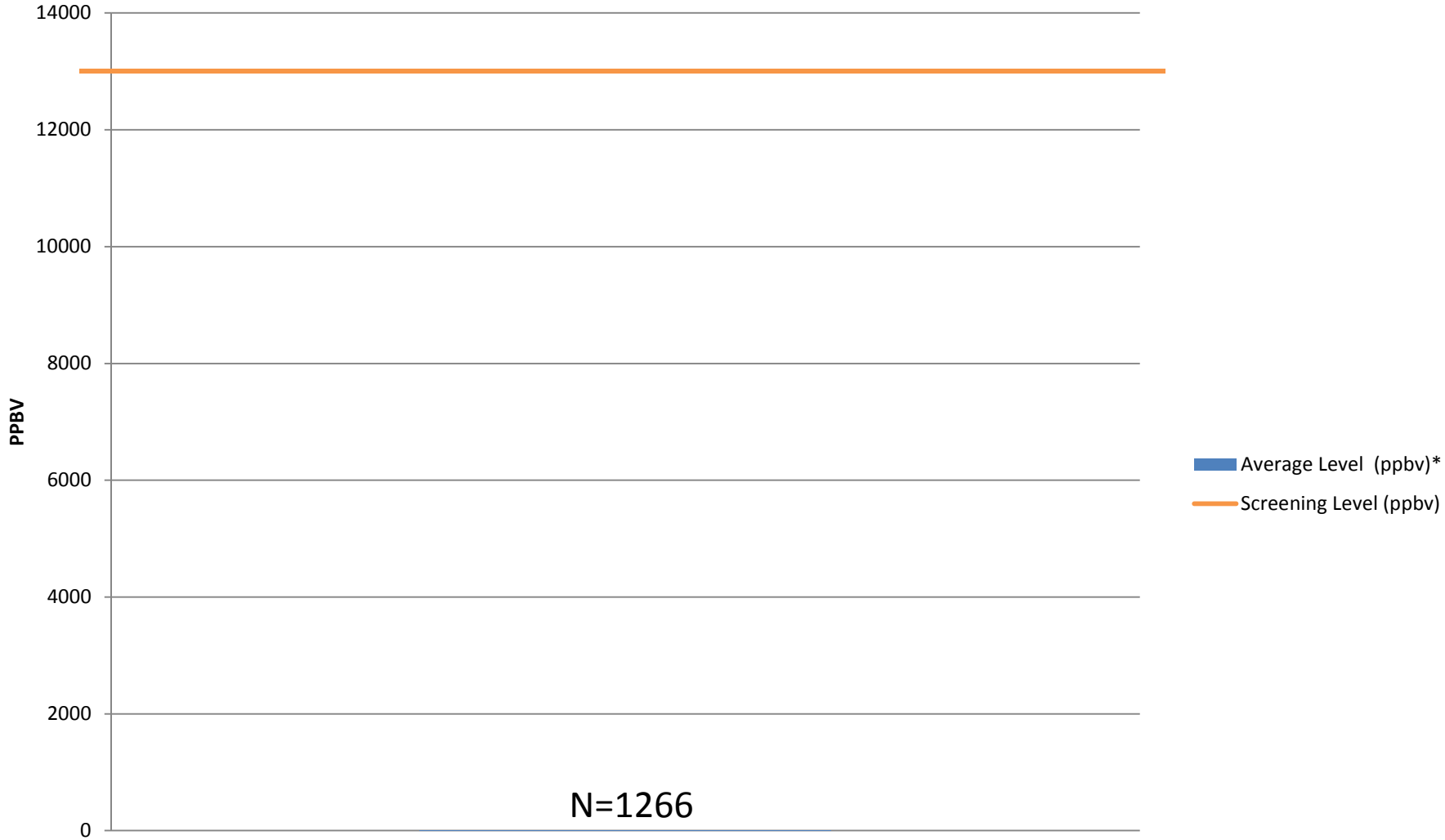
Comparison of Average Air Levels with Human Health Screening Levels
Acetone



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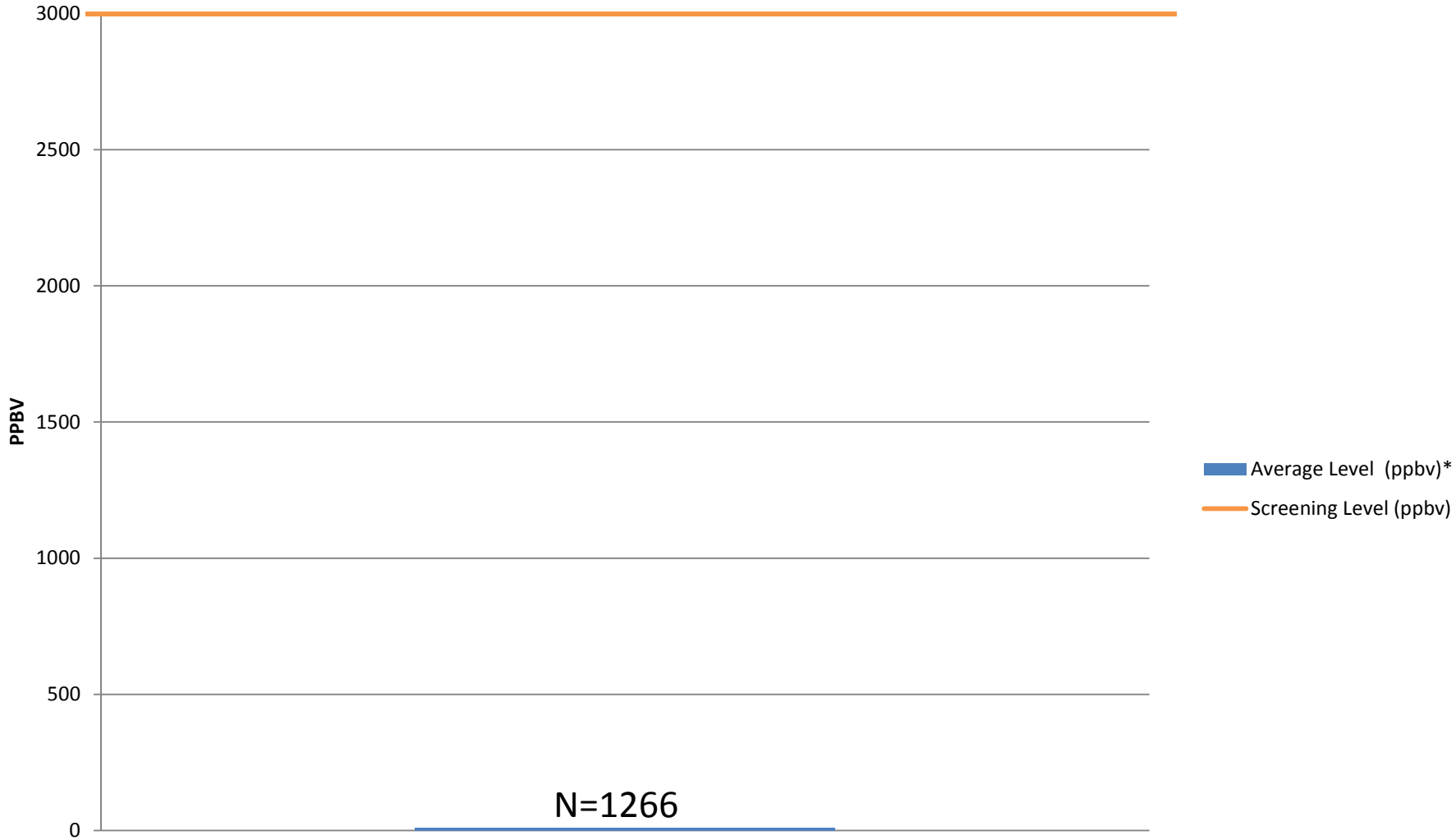
Comparison of Average Air Levels with Human Health Screening Levels
Isopropyl Alcohol



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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

September 20, 2011

Enbridge Energy, Limited Partnership
c/o Mr. Rich Adams
Vice President, Operations
Superior City Centre
Second Floor
1409 Hammond Ave.
Superior, Wisconsin 54880

Re: Approval of Enbridge Energy, Limited Partnership's September 9, 2011 requested modification of the 2011 Air Monitoring and Sampling Addendum dated June 21, 2011 submitted in response to the Administrative Order issued by U.S. EPA on July 27, 2010 and Supplement to the Administrative Order issued by U.S. EPA on September 23, 2010, pursuant to §311(c) of the Clean Water Act (Docket No. CWA 1321-5-10-001).

Dear Mr. Adams:

On September 9, 2011 Enbridge Energy, Limited Partnership, Enbridge Pipelines (Lakehead) L.L.C., Enbridge Pipelines (Wisconsin), and Enbridge Energy Partners, L.P. (herein collectively referred to as "Enbridge") submitted a letter to U.S. EPA requesting a modification of the 2011 Air Monitoring and Sampling Addendum dated June 21, 2011.

U.S. EPA has completed its review of the requested modification; specifically to modify the laboratory turn-around time (TAT) for Community Air Sampling from a 24-hour TAT to a 5-day TAT.

Pursuant to Paragraph 18 of the Order and Paragraph 6 of the Supplement, this letter provides written confirmation of my September 16, 2011 verbal approval of Enbridge's request.

If you have any questions regarding this approval, please contact me immediately at (231) 301-0559.

Sincerely,

Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. EPA, Region 5

cc: L. Kirby-Miles, U.S. EPA, ORC

J. Cahn, U.S. EPA, ORC
J. Kimble, U.S. EPA
M. Durno, U.S. EPA
T. Edwards, U.S. EPA
S. Wolfe, U.S. EPA
S. Vega, U.S. EPA
M. Ducharme, MDEQ
M. Alexander, MDEQ
L. Dykema, MDCH
Records Center, U.S. EPA, Reg. V

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

October 26, 2011

Enbridge Energy, Limited Partnership
c/o Mr. Rich Adams
Vice President, Operations
Superior City Centre
Second Floor
1409 Hammond Ave.
Superior, Wisconsin 54880

Re: Approval with Modifications of Enbridge Energy, Limited Partnership's October 13, 2011 requested modification of the 2011 Air Monitoring and Sampling Addendum dated June 21, 2011 submitted in response to the Administrative Order issued by U.S. EPA on July 27, 2010 and Supplement to the Administrative Order issued by U.S. EPA on September 23, 2010, pursuant to §311(c) of the Clean Water Act (Docket No. CWA 1321-5-10-001).

Dear Mr. Adams:

On October 13, 2011 Enbridge Energy, Limited Partnership, Enbridge Pipelines (Lakehead) L.L.C., Enbridge Pipelines (Wisconsin), and Enbridge Energy Partners, L.P. (herein collectively referred to as "Enbridge") submitted a letter to U.S. EPA requesting a modification of the 2011 Air Monitoring and Sampling Addendum dated June 21, 2011.

U.S. EPA has completed its review of the requested modification; specifically to "indefinitely suspend all Community Air Sampling and Monitoring activities, Work Area Monitoring, and eliminate River Opening Sampling, effective immediately."

Although EPA does not agree with Enbridge's justification for the requested suspension of air monitoring and sampling, EPA agrees that a decrease in the prescribed level of air monitoring and sampling under the current plan is warranted based on EPA's own review of the daily air monitoring and sampling data. Therefore, pursuant to Paragraph 18 of the Order and Paragraph 6 of the Supplement, U.S. EPA approves the Enbridge request with modifications described below.

- Remove the term "indefinitely". Air monitoring and sampling will be required when work ramp-up in the spring occurs, as approved by U.S. EPA.
- Air monitoring must be continued in current work areas to ensure that workers are not exposed to unacceptable levels of oil-related contaminants; specifically during excavations such as Talmadge Creek MP 0.5, MP 2.75 and 6.0, the island at MP 15.0, and any other pending work areas.

- Work area perimeter sampling must be performed in areas in close proximity to residential areas as directed by U.S.EPA.
- The plans to assess acetaldehyde air levels must still be completed as requested by the Michigan Department of Community Health in a letter dated August 23, 2011 and discussed during the 29 August meeting with U.S. EPA and MDCH representatives.
- Odor complaint response capability must be maintained as required in the *2011 Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan, Submitted: June 15, 2011, Approved: June 21, 2011*

If you have any questions regarding this approval, please contact me immediately at (231) 301-0559.

Sincerely,

Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. EPA, Region 5

cc: L. Kirby-Miles, U.S. EPA, ORC
J. Cahn, U.S. EPA, ORC
J. Kimble, U.S. EPA
M. Durno, U.S. EPA
T. Edwards, U.S. EPA
S. Wolfe, U.S. EPA
S. Vega, U.S. EPA
M. Ducharme, MDEQ
M. Alexander, MDEQ
L. Dykema, MDCH
Records Center, U.S. EPA, Reg. V

Approved

Enbridge Line 6B MP 608
Marshall, MI Pipeline Release

Air Monitoring and Sampling
Addendum to the Sampling and Analysis Plan

Prepared for United States Environmental Protection Agency

Enbridge Energy, Limited Partnership

Originally Submitted: December 9, 2011

Resubmitted: January 31, 2012

Resubmitted: March 28, 2012

Resubmitted: May 3, 2012

Approved

1.0 INTRODUCTION AND PURPOSE 1

2.0 ADAPTIVE MANAGEMENT 1

3.0 AIR SAMPLING METHODS 2

4.0 METEOROLOGICAL DATA 2

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ATTACHMENTS

Attachment A VOCs Detected by TO-15 Analysis

Attachment B Enbridge Oil Spill Human Health Screening Levels

Attachment C Field Standard Operating Procedures

Attachment D Galson Laboratories SOP for VOCs by OSHA PV-2120 & EPA TO-15

Approved

LIST OF ACRONYMS

COC	Chain of Custody
Enbridge	Enbridge Energy, Limited Partnership
GPS	global positioning system
H_2S	hydrogen sulfide
Line 6B	The pipeline owned by Enbridge Energy, Limited Partnership that runs just south of Marshall, Michigan
MDCH	Michigan Department of Community Health
MP	Mile Post
NWS	National Weather Service
OSHA	Occupational Safety and Health Administration
ppm	parts per million
QA/QC	Quality Assurance/Quality Control
SCRIBE	SCRIBE is a software tool developed by EPA to assist in the process of managing environmental data.
SOP	Standard Operating Procedure
TIC	Tentatively Identified Compound
U.S. EPA	United States Environmental Protection Agency
U.S. EPA Order	U.S. EPA Removal Administrative Order Under Section 311(c) of the Clean Water Act, issued on July 27, 2010 to Enbridge Energy Partners, L.P., Docket Number: CWA 1321-5-10-001
VOCs	Volatile Organic Compounds

Approved

1.0 INTRODUCTION AND PURPOSE

Enbridge Energy, Limited Partnership (Enbridge) will conduct air monitoring and sampling to evaluate worker safety and public health during assessment and recovery operations. Enbridge was given verbal direction on June 2, 2011, verified in a letter dated June 17, 2011 by United States Environmental Protection Agency (U.S. EPA) to conduct real-time air monitoring and/or air sampling in the following areas:

- Real-time air monitoring in work areas where oil recovery activities occur;
- Real-time air monitoring for work area perimeters, if elevated volatile organic compounds (VOCs) or benzene are detected during work area air monitoring, within close proximity to residential areas;
- Air sampling for work area perimeters, if continuous elevated VOCs or benzene levels are detected during work area perimeter air monitoring, within close proximity to residential areas as directed by U.S. EPA, and
- Air monitoring and sampling in other areas in response to odor complaints.

The real-time air monitoring will include VOCs, hydrogen sulfide (H_2S), and benzene. Air sampling will only be conducted for VOCs.

Data gathered in the above mentioned areas will be used to assess the potential for worker and community exposures associated with oil and oil recovery efforts. All field work and data collection will be conducted in accordance with approved work plans and standard operating procedures (SOPs). More detailed discussions of air sampling and real-time air monitoring and air sampling can be found in the following sections.

2.0 ADAPTIVE MANAGEMENT

Many of the activities described in this Addendum are investigative in nature and are designed to provide scientific information that can be used to further evaluate worker safety and public health. Therefore, future findings of assessment activities may affect the viability and/or effectiveness of activities described herein. Findings of air monitoring and sampling activities shall be evaluated and considered in an iterative fashion when determining tactics and strategies to accomplish the overall objectives of the work. However, any changes to the activities described must be approved by the U.S. EPA prior to changing this Addendum and/or implementation of activities.

3.0 AIR SAMPLING METHODS

Air samples for VOCs will be collected by subatmospheric sampling using evacuated canisters in accordance with the field SOP included in *Attachment C*. The collected whole-air samples will be analyzed according to modified U.S. EPA Method TO-15 and Occupational Safety and Health Administration (OSHA) PV-2120. *Attachment D* presents the laboratory SOP for this sampling. The compounds detected by TO-15 analysis are presented in *Attachment A*. The laboratory will also provide a report of Tentatively Identified Compounds (TICs) detected in each canister sample. Please note that acetaldehyde will be included as a calibrated laboratory standard analyte, and not as a TIC as in previous analysis.

Canister samples will consist of either grab (instantaneous) or 24-hour collections. The collection time will be based on sampling objectives. For instance, a grab sample may be collected in response to odor complaints. A 24-hour sample will be collected for evaluating the potential for long-term exposure at work area perimeter sites. The 24-hour samples will be positioned both upwind (one sample) and downwind (two samples) of oil recovery work areas near residential areas to evaluate VOC vapors on-site and as background (further described in *Section 5.1* below). All extended duration samples will be collected using critical flow orifices and pressure regulators calibrated by the laboratory to collect a specified target volume into the canister over the desired period. Details of the flow rate settings and pressure limits of the flow controllers are contained in the applicable SOP.

Samples will be sent to Galson Laboratories, an American Industrial Hygiene Association accredited laboratory, in Syracuse, NY. Samples will be analyzed on a five-day turnaround time for sample results.

4.0 METEOROLOGICAL DATA

Meteorological data is an important consideration for deploying canisters and for interpreting air sampling results. National Weather Service (NWS) data will be used to support air sampling.

In areas where work area perimeter air sampling is conducted, NWS data from Battle Creek (call sign KBTL) or Kalamazoo (call sign KAZO), whichever is in closer physical proximity, will be used to produce wind roses and classify upwind/downwind samples. The

observations of meteorological data (specifically temperature, wind speed, and wind direction) will be downloaded from the internet daily.

Forecasts issued by the NWS, accessed via the NWS web site, will be used to plan sample deployment. Samples will be placed in patterns so as to capture (as best possible) conditions both upwind and downwind of an oil recovery work area based on these forecasts. Predicted shifts in winds due to frontal passages will be taken into consideration in sample placement.

5.0 WORK AREA & PERIMETER EVALUATIONS

5.1 Work Area Real-Time Monitoring

Real-time air monitoring for VOCs, H_2S, and benzene, will be conducted using a MultiRAE Plus (or similar) and UltraRAE or Gastec Pump with benzene colorimetric tubes within all the work zones. Enbridge Safety or safety designee will coordinate work area air monitoring activities. Air monitoring readings will be documented once each hour. If the Health and Safety monitoring indicates a VOC alarm above applicable action levels, benzene checks will be initiated with a real-time benzene monitor along with appropriate protective action as described in the *Health and Safety Plan*. The benzene checks will be recorded on an air monitoring log form or by entry into a handheld data collection device.

5.2 Work Area Perimeter Real-Time Monitoring

In the event work area real-time air monitoring reveals a detection of VOCs in exceedance of 300 parts per million (ppm) for two consecutive 1-minute readings or benzene in exceedance of 0.5 ppm (American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV)), work area perimeter real-time air monitoring will be initiated if the work area is in close proximity to residential areas. Close proximity to residential areas shall be determined through a review by Enbridge of oil recovery activities on the GIS mapping system. Enbridge will document distances between oil recovery activities and residential dwellings and review factors including, but not limited to: natural and man-made features, topography, and prevailing wind direction to make a determination on whether the oil recovery activity is in close proximity to a residential area. This determination and supporting documentation will be e-mailed to U.S. EPA air support staff for final determination. Air monitoring will be conducted as outlined in *Section 5.1* in a

minimum of three locations to ensure both upwind (one location) and downwind (two locations) capture zones from work operations to evaluate VOC vapors on-site and as background. Air monitoring will be conducted by means of one MultiRAE Plus monitor (or similar), moving between each of the three locations, during periods of active oil recovery. The air monitoring will be conducted at a rate of approximately 30 minutes at each location commencing at the initiation of oil recovery activities and ending at the completion of oil recovery activities for a single work day (i.e. one full work day of air monitoring). If the air monitoring indicates a sustained VOC alarm (i.e. two consecutive 1-minute readings) above the detection limit (i.e. 0.1 ppm), a benzene check will be initiated with a real-time benzene monitor (i.e. UltraRAE or Gastec Pump with benzene colorimetric tubes). Work area monitoring will continue during work area perimeter air monitoring. Work area perimeter air monitoring will be discontinued and revert back to only work area air monitoring, if no sustained detections, as defined above, are revealed.

5.3 Work Area Perimeter Sampling

Work area perimeter air samples will be collected at work sites involving submerged oil recovery, dredged sediment recovery, and overbank excavation, if both the following conditions exist:

1. Work area perimeter air monitoring (triggered by work area air monitoring) reveals two consecutive 1-minute sustained detections of VOCs in exceedance of 300 ppm or benzene in exceedance of 0.5 ppm, and
2. Work area is in close proximity to residential areas.

Within 24-hours of the existence of the above two conditions, three canister samples will be collected simultaneously over a 24-hour period along the perimeter work areas, coinciding with work activity (e.g. 0700 to 0700 sampling period). Sample locations will be selected based on anticipated activities and forecast wind directions. The purpose is to select locations with the greatest opportunity to detect volatile organic compounds, if any, that are present during recovery activities. Work area samples will be positioned to ensure both upwind (one sample) and downwind (two samples) capture zones from work operations to evaluate VOC vapors on-site and as background. Sample canisters will be placed as close as practical to the actual removal activities, without compromising site safety or work efforts. All sample locations will be documented using global positioning system (GPS) devices.

Following the initial response, perimeter air sampling will continue at identified work locations (i.e. work locations where the above two conditions exist), as directed by U.S. EPA for a period of 12 work days, or until results can be evaluated for an initial 6-day period, or until completion of work (whichever is the shorter duration). Enbridge and U.S. EPA will review all sampling results from the initial period, and determine the perimeter sampling frequency and strategy needed for ongoing operations.

6.0 ODOR INVESTIGATIONS

Enbridge will provide an Odor Response Team. During periods of active oil recovery, the Odor Response Team will be contacted and response initiated by contacting the complainant within 30 minutes (maximum) after receiving odor complaints/concerns from the Enbridge Hotline between 0700 and 1900 Monday through Saturday. The initial complaint information will be collected through the Hotline and evaluated for response. Complaints received during periods when there is no active oil recovery, or on weekends or holidays, will be addressed on the next scheduled working day, and will be communicated as such to the complainant via the Hotline answering service. Nuisance complaints or complaints logged from areas outside of the geographic areas reasonably expected to be impacted will be addressed. Enbridge will relay all initial odor reports to U.S. EPA and Michigan Department of Community Health (MDCH) and the three entities will work together (corresponding via e-mail or phone) within a timely manner to determine if a response is appropriate. U.S. EPA will make the final ruling on response if the parties cannot agree.

Personnel responding to the odor event will attempt to contact the complainant and schedule sampling and monitoring at the location where the report originated. Real-time air monitoring data and analytical "grab" canister sample data will be collected at the reported location. Short-term real-time readings will be taken for VOCs, H_2S, and sulfur dioxide (SO_2) using a MultiRAE Plus monitor (or similar) and benzene using an UltraRAE monitor or Gastec pump with benzene specific colorimetric tubes. These readings will be reported to the complainant if present, and recorded in log books. At least one canister sample will be obtained, with additional long term (24 hour) canisters possible depending on the situation encountered. The canister samples will be analyzed using the same analytical approach and target compound list as routine samples (*Attachment A*), with an expedited 24-hour turn-around-time for odor response. In addition, at the time of sampling, the Odor Response

Team will document the presence or absence of odors and the subjective quality of the odors. The odor event location will also be documented using GPS.

After completion of the field visit, the Odor Response Team will relay the collected information to Enbridge. Enbridge will provide U.S. EPA with a summary of all Odor Response Team activities utilizing the *Odor Complaint Response Action Tracker*. Upon receipt of canister sampling results, Enbridge contractor will prepare a follow-up letter report, to be transmitted to the complainant, MDCH, and U.S. EPA.

7.0 DATA QUALITY AND MANAGEMENT

Air samples will be sent to Galson Laboratories located in Syracuse, N.Y or other approved laboratory. Preliminary results will be provided to Enbridge's designated representative and to any other designated representative or organization within five days of receipt by the laboratory. Analytical results will be flagged in instances where the contaminant is also detected in the laboratory blanks. Data will be submitted to the U.S. EPA SCRIBE database through Enbridge data management system. In addition, Enbridge will provide daily sampling and monitoring summaries to U.S. EPA, when such activities are being conducted, as outlined in *Section 8.0*.

Duplicate samples will be collected at a frequency of 1 per 10 (10%).

8.0 AIR MONITORING AND SAMPLING REPORTING

Enbridge will provide on a weekly basis (every Monday) the following deliverables, during periods of air sampling:

- An overview of air sampling activities conducted each day.
- The overview for air sampling will consist of a map of the oil recovery work area perimeter and community area, or the geographical extent of air sampling activities. The map will include the following layers:
    - Locations of discrete analytical samples collected the previous day. Labels will include a common name (e.g. Ceresco) or project marker name (e.g. MP 24.75), discrete sample identifiers, and identification of work area (e.g. polygon showing approximate excavation area).

- Windrose(s) generated from meteorological data downloaded the previous day.

Air monitoring data for work areas will be submitted weekly (every Monday) summarized from the previous day(s) in a table format identifying the work area location, number of sampling points recorded, and detections as applicable.

An overview of the latest full day of air sampling laboratory results received. The overview will consist of one map of the area(s) encompassing all locations where samples were collected and any compounds were detected. The map will include the following layers:

- Locations of all discrete analytical samples. Labels will include a unique location code for each symbol, as well as common name or project marker name.
- Chart listing concentrations and applicable screening levels of all analytes detected in the locations included in the extent of the map.
- Windrose(s) generated from meteorological data collected the day of sampling.

These deliverables will be provided following an internal Quality Assurance/Quality Control (QA/QC) process. The analytical data is received and reviewed by a qualified individual (project manager/industrial hygienist and/or toxicologist). The data will be reviewed on a daily basis to ensure that necessary actions are implemented if required (such as the need for: additional real-time air monitoring, air sampling, or additional canister placement and/or real-time monitoring). Deliverables will be disseminated to the air group, including U.S. EPA representative and MDCH representative, via e-mail following the internal QA/QC process. Raw analytical data will be available through the SCRIBE database following data validation.

A final report will be produced upon completion of air monitoring/sampling activities detailed in this plan. The final report will consist of a compilation of real-time and analytical data, physical parameters such as wind direction, and geographical area. An evaluation of the results will be conducted to determine if “target analytes” were present during the oil recovery operations and if those “target analyte” concentrations exceeded applicable Human Health Air Screening Levels included in *Attachment B*.

9.0 PROJECT ORGANIZATION

Enbridge will utilize Environmental Consultants for responsibility of the following:

- Toxicological support,
- Air sampling,
- Air monitoring for odor response,
- Air data quality assurance/quality control, and
- Data evaluation and reporting.

Enbridge Safety will be utilized for real-time air monitoring activities in work areas where oil recovery activities occur.

10.0 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 Enbridge's or Consultant's calibration logs. All field real-time air monitoring instruments or equipment will be calibrated prior to use in the field. Real-time instruments will be calibrated daily or as needed, according to manufacturer recommendations. Specifically, MultiRAE Plus (or similar meter with photoionization detector) will be calibrated with a known concentration of isobutylene gas or zeroed using zero-grade air or at background site locations. Gastec chemical specific colorimetric detector tubes are hermetically sealed and are calibrated by the manufacturer, and therefore, do not require field calibration. Calibrations will be conducted in accordance with user manuals included in the *2011 Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan*, approved by the U.S. EPA on June 21, 2011 (Enbridge, 2011).

11.0 CHAIN OF CUSTODY (COC)

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

12.0 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 the sample was collected, and
- Unique identifier.

13.0 PACKAGING AND SHIPPING

Packaging and shipping of air samples will be conducted following method recommendations. Canisters will be shipped in a box via carrier service (e.g. FedEx). Air samples do not require sample preservation in the field. However, caps will be placed on canisters and regulators or critical orifices will be detached during shipment. The person packaging the samples is responsible to ensure that the sample packaging is in suitable condition for shipping.

14.0 REFERENCES

Enbridge, 2011. Enbridge Line 6B Pipeline Release, Marshall, Michigan*; 2011 Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan.* June 21, 2011.

Attachment A
VOCs Detected by TO-15 Analysis

Predominant Crude Oil VOCs Detected by TO-15 Analysis[1]		
Target Analyte	**CAS No.**	**Laboratory LOQ (ppbv)**
Benzene	71-43-2	5
Butane, 2-methyl-*	78-78-4	NA
Cyclohexane	110-82-7	5
Cyclohexane, 1,3-dimethyl*	591-21-9	NA
Cyclopentane, methyl-*	96-37-7	NA
Cyclohexane, 1,3-dimethyl-, cis-*	638-04-0	NA
Cyclohexane, butyl-*	1678-93-9	NA
Cyclohexane, ethyl-*	1678-91-7	NA
Cyclohexane, methyl-*	108-87-2	NA
Cyclohexane, propyl-*	1678-92-8	NA
Cyclopentane, 1,1-dimethyl*	1638-26-2	NA
Cyclopentane, 1,3-dimethyl-, trans*	1759-58-6	NA
Cyclopentane, 1,2-dimethyl-, trans*	822-50-4	NA
Heptane, 3-methyl-*	589-81-1	NA
2-Octene, 2,6-dimethyl-*	4057-42-5	NA
Decane*	124-18-5	NA
Dodecane*	112-40-3	NA
Ethylbenzene	100-41-4	5
Ethyltoluene, 4-	622-96-8	5
Heptane, n-	142-82-5	5
Hexane, n-	110-54-3	5
Naphthalene*	91-20-3	NA
Nonane*	111-84-2	NA
Hexane, 2-methyl*	591-76-4	NA
Octane*	111-65-9	NA
Octane, 3-methyl-*	2216-33-3	NA
Pentane, 2-methyl-*	107-83-5	NA
Toluene	108-88-3	5
Benzene, 1,2,4-trimethyl	95-63-6	5
Hexane, 3-methyl*	589-34-4	NA
Heptane, 2-methyl-*	592-27-8	NA
Cyclohexane-1,1,3-trimethyl*	3073-66-3	NA
Benzene, 1,3,5-trimethyl	108-67-8	5
Undecane*	1120-21-4	NA
Xylene, m&p-	179601-23-1	10
Xylene, o-	95-47-6	5

[1]The laboratory will also be asked to report on all analytes included in their TO-15 method standard analyte list.

*****Tentatively identified compound (TIC)

NA – Not Applicable

Predominant Crude Oil VOCs Detected by TO-15 Analysis[1]		
Non-Target Analyte	**CAS NO**	**Laboratory LOQ (ppbv)**
ALPHA-PINENE*	80-56-8	NA
1,1,1-TRICHLOROETHANE	71-55-6	5
1,1,2,2-TETRACHLOROETHANE	79-34-5	5
1,1,2-TRICHLOROETHANE	79-00-5	5
1,1-DICHLOROETHANE	75-34-3	5
1,1-DICHLOROETHENE	75-35-4	5
1,2-DIBROMOETHANE	106-93-4	5
1,2-DICHLOROBENZENE	95-50-1	5
1,2-DICHLOROETHANE	107-06-2	5
1,2-DICHLOROPROPANE	78-87-5	5
1,3-BUTADIENE	106-99-0	5
1,3-BUTADIENE, 2-METHYL-*	78-79-5	NA
1,3-DICHLOROBENZENE	541-73-1	5
1,4-DICHLOROBENZENE	106-46-7	5
1,4-DIOXANE	123-91-1	20
1-HEPTANOL, 2-PROPYL-*	10042-59-8	NA
2,2,4-TRIMETHYLPENTANE	540-84-1	5
2,2,7,7-TETRAMETHYLOCTANE*	1071-31-4	NA
2,3,4,5-TETRAHYDROPYRIDAZINE*	694-06-4	NA
2-HEPTANONE*	110-43-0	NA
2-PENTANONE*	107-87-9	NA
2-PROPANOL, 2-METHYL-*	75-65-0	NA
3-HEPTANONE*	106-35-4	NA
ACETALDEHYDE[2]	75-07-0	1
ACETIC ACID, 2-ETHYLHEXYL ESTER*	103-09-3	NA
ACETONITRILE*	75-05-8	NA
ALLYL CHLORIDE	107-05-1	5
BENZENE, 1-METHYL-4-(1-METHYLETHYL)*	99-87-6	NA
BENZYL CHLORIDE	100-44-7	5
BROMODICHLOROMETHANE	75-27-4	5
BROMOFORM	75-25-2	5
BROMOMETHANE	74-83-9	5
BUTANE*	106-97-8	NA
BUTANOIC ACID, 2-METHYLPROPYL ESTER*	539-90-2	NA
BUTANOIC ACID, BUTYL ESTER*	109-21-7	NA
BUTANOIC ACID, ETHYL ESTER*	105-54-4	NA
BUTANOIC ACID, METHYL ESTER*	623-42-7	NA
BUTANOIC ACID, PROPYL ESTER*	105-66-8	NA
CARBON DISULFIDE	75-15-0	10
CARBON TETRACHLORIDE	56-23-5	5
CARBONYL SULFIDE*	463-58-1	NA
CHLOROBENZENE	108-90-7	5
CHLOROETHANE	75-00-3	5
CHLOROFORM	67-66-3	5
CHLOROMETHANE	74-87-3	5

[1]The laboratory will also be asked to report on all analytes included in their TO-15 method standard analyte list.

[2]Acetaldehyde was added as a standard analyte in 2011 based on continuous detections of this compound as a TIC in community air samples

*****Tentatively identified compound (TIC)

NA – Not Applicable

Predominant Crude Oil VOCs Detected by TO-15 Analysis[1]		
Non-Target Analyte	**CAS NO**	**Laboratory LOQ (ppbv)**
CIS-1,2-DICHLOROETHYLENE	156-59-2	5
CIS-1,3-DICHLOROPROPENE	10061-01-5	5
CYCLOPENTANE, 1,1'-ETHYLIDENEBIS-*	4413-21-2	NA
DECANE, 2,2,4-TRIMETHYL-*	62237-98-3	NA
DECANE, 2,3,4-TRIMETHYL-*	62238-15-7	NA
DECANE, 2,3,5-TRIMETHYL-*	62238-11-3	NA
DIACETYL*	431-03-8	NA
DIBROMOCHLOROMETHANE	124-48-1	5
DISULFIDE, DIMETHYL*	624-92-0	NA
DISULFIDE, FLUOROMETHYL METHYL*	60307-49-5	NA
ETHANE, 1,1-DIFLUORO-*	75-37-6	NA
ETHYL ACETATE	141-78-6	5
ETHYL ALCOHOL*	64-17-5	NA
EUCALYPTOL*	470-82-6	NA
FREON 11	75-69-4	5
FREON 113	76-13-1	5
FREON 114	76-14-2	5
FREON 12	75-71-8	5
FURAN, 2,3-DIHYDRO-3-METHYL-*	1708-27-6	NA
HEPTANE, 2,2,3,4,6,6-HEXAMETHYL-*	62108-32-1	NA
HEPTANE, 2,2,4,6,6-PENTAMETHYL-*	13475-82-6	NA
HEPTANE, 2,2-DIMETHYL-*	1071-26-7	NA
HEPTANE, 4-ETHYL-2,2,6,6-TETRAMER*	62108-31-0	NA
HEXADECANE, 2,6,10,14-TETRAMETHYL-*	638-36-8	NA
HEXANAL*	66-25-1	NA
HEXANE, 2,2,5-TRIMETHYL-*	3522-94-9	NA
HEXANE, 2,4-DIMETHYL-*	589-43-5	NA
HEXANOIC ACID, METHYL ESTER*	106-70-7	NA
HEXYL N-VALERATE*	1117-59-5	NA
ISOBUTANE*	75-28-5	NA
LIMONENE*	138-86-3	NA
METHYL 3-BUTENOATE*	3724-55-8	NA
METHYL BUTYL KETONE	591-78-6	20

[1]The laboratory will also be asked to report on all analytes included in their TO-15 method standard analyte list.

[2]Acetaldehyde was added as a standard analyte in 2011 based on continuous detections of this compound as a TIC in community air samples

*****Tentatively identified compound (TIC)

NA – Not Applicable

Attachment B

Enbridge Oil Spill Human Health Screening Levels

Enbridge Oil Spill
Human Health Air Screening Levels
August 31, 2011

Chemical Name	Chemical Abstract Service Number	Screening Level in parts per billion by volume (ppbv)	Source of Screening Level
1,1,1-trichloroethane	71-55-6	1,000	EPA RfC
1,1,2,2-Tetrachloroethane	79-34-5	0.006	EPA RSL
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4,000	EPA RSL
1,1,2-Trichloroethane	79-00-5	0.04	EPA RfC
1,1-Dichloroethane	75-34-3	0.4	EPA RSL
1,1-Dichloroethene	75-35-4	50	EPA RfC
1,2,4-Trichlorobenzene	120-82-1	0.3	EPA RfC
1,2,4-Trimethylbenzene	95-63-6	1.5	EPA RfC
1,2-Dibromoethane	106-93-4	1	EPA RfC
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9,900	MDEQ
1,2-Dichlorobenzene	95-50-1	30	EPA RfC
1,2-Dichloroethane	107-06-2	600	ATSDR Chr. MRL
1,2-Dichloropropane	78-87-5	1	EPA RfC
1,3-Butadiene	106-99-0	1	EPA RfC
1,3,5-Trimethylbenzene	108-67-8	45	MDEQ
1,3-Dichlorobenzene	541-73-1	0.5	MDEQ
1,4-Dichlorobenzene	106-46-7	10	ATSDR Chr. MRL
1,4-Dioxane	123-91-1	1,000	ATSDR Chr. MRL
2,2,4-Trimethylpentane	540-84-1	750	MDEQ
2-Chloro-1,3-butadiene	126-99-8	6	EPA RfC
2-Propanol	67-63-0	3,000	EPA RfC
3-Chloropropene	107-05-1	32	EPA RfC
Acetaldehyde	75-07-0	5	EPA RfC
Acetone	67-64-1	13,000	ATSDR Chr. MRL
Acetonitrile	75-05-8	36	EPA RfC
Acrylonitrile	107-13-1	1	EPA RfC
Benzene	71-43-2	3	ATSDR Chr. MRL
Benzyl chloride	100-44-7	0.2	EPA RfC
Bromodichloromethane	75-27-4	0.01	EPA RSL
Bromoform	75-25-2	0.2	EPA RSL
Bromomethane	74-83-9	5	ATSDR Chr. MRL
Butane	106-97-8	10,000	MDEQ
Carbon disulfide	75-15-0	200	EPA RfC
Carbon tetrachloride	56-23-5	30	ATSDR Chr. MRL
Chlorobenzene	108-90-7	10	EPA RfC
Chloroethane	75-00-3	4,000	EPA RfC
Chloroform	67-66-3	20	ATSDR Chr. MRL
Chloromethane	74-87-3	50	ATSDR Chr. MRL
cis-1,2-dichloroethene	156-59-2	9	MDEQ
cis-1,3-Dichloropropene*	10061-02-6	4	MDEQ
Cumene	98-82-8	80	EPA RfC
Cyclohexane	110-82-7	2,000	EPA RfC
Cyclohexane,methyl	108-87-2	4,000	MDEQ

Chemical Name	Chemical Abstract Service Number	Screening Level in parts per billion by volume (ppbv)	Source of Screening Level
Cyclopentane	287-92-3	6,000	MDEQ
Dibromochloromethane	124-48-1	0.01	EPA RSL
Dichlorodifluoromethane	75-71-8	20	EPA RfC
Ethyl Acetate	141-78-6	890	MDEQ
Ethyl benzene	100-41-4	60	ATSDR Chr. MRL
Heptane	142-82-5	850	MDEQ
Hexachlorobutadiene	87-68-3	0.01	EPA RSL
Hexane	110-54-3	200	EPA RfC
Isobutane	75-28-5	10,000	MDEQ
Methyl butyl ketone	591-78-6	10	EPA RfC
Methyl ethyl ketone	78-93-3	2,000	EPA RfC
Methyl isobutyl ketone	108-10-1	700	EPA RfC
Methyl tert-butyl ether	1634-04-4	700	ATSDR Chr. MRL
Methylene chloride	75-09-2	300	ATSDR Chr. MRL
Napthalene	91-20-3	1	ATSDR Chr. MRL
Nonane	111-84-2	40	EPA RfC
Pentane	109-66-0	300	EPA RfC
Propene	115-07-1	2,000	EPA RfC
Styrene	100-42-5	200	ATSDR Chr. MRL
Tetrachloroethene	127-18-4	40	ATSDR Chr. MRL
Tetrahydrofuran	109-99-9	6	MDEQ
Toluene	108-88-3	80	ATSDR Chr. MRL
trans-1,2-Dichloroethene	156-60-5	15	EPA RfC
trans-1,3-Dichloropropene*	10061-01-5	0.5	MDEQ
Trichloroethene	79-01-6	2	EPA RfC
Trichlorofluoromethane	75-69-4	130	EPA RfC
Vinyl acetate	108-05-4	10	ATSDR Int. MRL
Vinyl bromide	593-60-2	1	EPA RfC
Vinyl chloride	75-01-4	30	ATSDR Int. MRL
Xylenes	1330-20-7	50	EPA RfC

* MDEQ provisional screening value for Dichloropropene based on a 1 in 100,000 cancer risk

ATSDR Chr. MRL - The Agency for Toxic Substances and Disease Registry Chronic Minimal Risk Level (MRL) is the preferred screening level. The MRL is protective of daily human inhalation exposure for longer than a year, including sensitive individuals such as children, the elderly, and those with pre-existing illnesses.

EPA RfC - If no Chronic MRL is available, the screening level is the EPA Reference Concentration (RfC). The RfC is protective of daily human inhalation exposure over a lifetime, including sensitive individuals. For 2 chemicals, vinyl acetate and vinyl chloride, the ATSDR Intermediate (Int.) MRL was selected. These were developed more recently than the EPA RfC and were lower than the EPA RfC.

EPA RSL - If none of the above are available, the EPA Regional Screening Level (RSL) is used. The RSLs are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

MDEQ - If none of the above are available, the Michigan DEQ Air Quality Division, Air Toxics Screening Level is the screening level. The MDEQ screening levels are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

Attachment C
Field Standard Operating Procedures

Standard Operation Procedure:

6L SUMMA Canister Sampling

METHOD SUMMARY

Sub atmospheric pressure sampling uses an initially cleaned and evacuated stainless steel canister. The canister has a hand valve and fixed orifice to regulate flow. Sub atmospheric pressure sampling is performed with a 24-hr critical orifice and low pressure regulator for 24-hour sampling or without the flow metering for taking grab samples. With this configuration, a grab sample of ambient air is drawn into a pre-evacuated Summa passivated canister. The canister is placed in the Breathing Zone (between 3 and 6 feet above ground surface). For 24-hour sampling the hand valve is opened to full and the canister allowed to fill as regulated by the metering equipment. With the grab sample, the hand valve is opened a quarter turn until the sound changes as it nears atmospheric pressure, and the hand valve is then closed. Normal documentation, chain of custody and sealing of the sample(s) are completed and the package is readied for shipping.

SAMPLE PRESERVATION, CONTAINERS HANDLING, AND STORAGE

After the air sample is collected, the canister valve is closed, flow regulator removed, cap is installed, an identification tag is attached to the canister, and the canister is transported to a laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded. Sample holding times and expiration are to be determined prior to initiating field activities.

Care must be taken not to exceed 40 psi in the canister (do not heat canister above 140^{o}F). Canisters should not be dented or punctured. They should be stored in a cool dry place and always be placed in their cardboard shipping boxes or similar protective carrier during transport and storage.

EQUIPMENT/MATERIALS REQUIRED

The following equipment/apparatus is required:

- Sub atmospheric Pressure Sampling Equipment

- VOC canister sampler – whole air sampler capable of filling an initially evacuated canister by action of the hand valve from vacuum to near atmospheric pressure.

PROCEDURE

1. Prior to sampling collection, the appropriate information is completed on the Field Data Sheet and brass cap is removed with 9/16 inch end wrench.

2. Place canister at the “Breathing Zone height”.

3. A canister, (which is evacuated to at least 26 inches Hg) hand valve is opened to the atmosphere containing the air to be sampled. The pressure differential causes the sample to flow into the canister.

4. The sampling duration depends on the degree to which the flow is restricted.

5. A fixed orifice flow restrictor will have a decrease in the flow rate as the vacuum canister approaches atmospheric (which is indicated by a change in pitch or sound level). Shut off hand valve following completion of sampling interval.

6. Upon sample completion at the location, the appropriate information is recorded on the Field Data Sheet and labels (Note the final vacuum reading on canister by separate gauge on each canister. Separate gauge will need to be attached and removed. Cap the SUMMA Canister with the cap and tighten with wrench slightly to seal vacuum.

7. Place canister into a cardboard box labeled for shipping with the Field Data Sheet information, chain of custody, and labels.

QUALITY ASSURANCE/QUALITY CONTROL

The following general quality assurance procedures apply:

1. All data must be documented on standard chain of custody records, field data sheets, or site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

3. Duplicate samples will be taken as 1 in 10 samples.

4. Blank samples or “zero air,” (sample not taken) will be returned at a rate of 1 per week of air sampling.

Attachment D

Galson Laboratories SOP for VOCs by OSHA PV-2120 & EPA TO-15

SUBJECT: **VOLATILE ORGANIC COMPOUNDS BY OSHA PV2120 & EPA TO-15**

SOP ID: IN-VOCS
AUTHOR: Justin Palmer/ Rob Wilson
SECTION SUPERVISOR: Justin Palmer
QA OFFICER: Wendy Ferro
COPYRIGHT
LABORATORY DIRECTOR: Mary Unangst

1.0 PURPOSE

1.1 This SOP describes the procedure for determining contaminants in whole air samples collected in a fused silica-lined stainless steel canister (following OSHA method PV2120 and Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method TO-15). This method utilizes GC/MS for the determination of a wide range of volatile and semi-volatile organic compounds (as listed in Table 1).

2.0 RESPONSIBILITIES

2.1 All GC/MS analysts performing this method are required to read and understand the method as written in OSHA PV2120, and are required to meet all QC requirements (as described in EPA TO-15) before attempting analysis of samples.

2.2 The section supervisor is required to read and understand the method as written, but is also responsible for the training and continued education of technicians performing this method.

2.3 The section supervisor is required to review reports and packages to ensure that all data are valid prior to client receipt.

3.0 DEFINITIONS

3.1 GC/MS: Gas Chromatography/Mass Spectrometry

3.2 Capillary: Analytical column with an internal diameter less than or equal to 0.32 mm

3.3 EICP: Extracted ion current profile: Plot of ion abundance vs. GC retention time for a single characteristic mass (amu)/charge ratio.

3.4 AMU: Atomic Mass Unit

3.5 ppbv: part per billion by volume for component concentration in the gas phase.

3.6 Mini Can: Canisters ranging from 400mL to 1000mL in volume; these are associated with an injection volume of 100mL.

3.7 Summa Canisters: Canisters with a 6L volume; these are associated with an injection volumes of ***500cc to 1000cc.***

3.8 SCAN: Normal MS acquisition mode where mass ranges from 35 to 300 amu are scanned to produce a Total Ion Chromatogram.

3.9 SIM: Selective Ion Mode; only scans certain ions per sample to increase sensitivity. Used for only certain projects that require low level analysis.

4.0 METHOD SUMMARY

4.1 The sample is prepared for analysis by pre-concentration, which removes potential interference and dries the sample. After the pre-concentration and drying steps are completed, the analytes are cryo-focused onto the head of the GC column via reduced temperature trapping, followed by rapid thermal desorption.

4.2 Separation of the analytes is achieved by temperature programming of the GC oven.

4.3 The eluent from the capillary column is introduced directly to the mass spectrometer, which is operated in the electron impact mode. Identification of target analytes is accomplished by comparing sample mass spectra with reference spectra generated from purchased standards on the GC/MS system used to analyze the samples. Quantitation is achieved using the internal standard technique. The response of a selected quantitation ion for each analyte relative to the quantitation ion of the designated internal standard (relative response factor, or RRF) is determined over a minimum five-point calibration range.

5.0 INTERFERENCES

5.1 Raw GC/MS data from all samples and blanks must be evaluated for interference. Determine if the source of interference is in the sample introduction system. If so, take corrective action to eliminate the problem.

5.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Each auto-sampler port is flushed with nitrogen after use (prior to set-up of the next batch of samples).

5.3 Interferences are minimal by GC/MS as this type of detector allows the determination if compounds are co-eluting in the chromatographic system. Quantification can be done on alternate ions so interferences are eliminated in most cases. In other instances, a dilution may be performed to allow better separation or results may be considered estimated if the interference cannot be removed.

6.0 SAFETY

6.1 Most volatile compounds are considered hazardous. Always wear gloves and a lab coat when handling stock standards.

6.2 Safety glasses with side-shields are required whenever working in the laboratory.

6.3 It is very important that special precaution be used when working with liquid nitrogen,

as it can cause serious burns.

6.4 Be sure that only radiation worker trained personnel handle Mini Cans that have been screened for radiation. These cans will have an orange dot on them.

7.0 MATERIALS AND APPARATUS

7.1 Agilent (previously Hewlett Packard (HP)- may be used interchangeably) 5890, 6890, or 7890 Series GC, in conjunction with an HP model 5972, 5973, or 5975 mass spectrometer (capable of scanning from 35 to 300 amu every 1-second or less using 70 volts (nominal) electron energy in the electron impact ionization mode).

7.2 Entech 7032, 7032L, 7032A, or 7016CA autosampler models with the Entech 7100 or 7100A three stage Preconcentrator.

7.2.1 Microscale Purge and Trap (MPT) analysis is performed by utilizing a glass bead trap in module 1 and a Tenax sorbent trap in module 2. Module 3 contains an empty trap.

7.2.2 Cold Trap Dehydration analysis (CTD) employs an empty trap in module 1 and a Tenax trap in module 2. Module 3 contains an empty trap.

7.3 Analytical Chromatography column: 0.32mm ID x 60m length silicone-coated capillary column with a 1 um film thickness – Restek RTX-1 or equivalent.

7.4 GC/MS Interface - The GC column is directly coupled to the mass spectrometer ion source. Acceptable tuning and calibration performance must be demonstrated on a daily basis.

7.5 Data System – The data system used is the HP Chemstation G1701BA with (at minimum) Revision B.01.00 software package for the HP5972, 5973, or 5975 MS. This system allows continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software allows for searching any GC/MS data file for ions of a specific mass, and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile. The software allows integration of the abundance in any EICP between specified time or scan number limits. The NIST 129K version mass spectral library is being used for a reference library.

8.0 REAGENTS AND STANDARDS

8.1 Helium @ 99.9999% purity

8.2 Liquid nitrogen

8.3 Stock standards

8.3.1 Stock standard solutions are purchased as certified solutions.

8.3.1.1 TO-15 Subset standard is purchased from Spectra gases

8.3.1.1.1 (Catalogue # ENT15-25S-6A-1M***)*** or Scott gases (item# 0104AZ00025).

8.3.1.2 TO-14 standard is purchased from Spectra gases

8.3.1.2.1 (Catalogue # ENT14/39S/6A1M) or Scott gases (item# 01049Z90001).

8.3.1.3 Ethylene oxide standard is purchased from Spectra gases

8.3.1.3.1 (ETOX/CGA3501M) or Scott gases (item# 08020001310PAL).

8.3.1.4 4-Phenylcyclohexene standard is purchased from Scott gases (item# 0104P200046).

8.3.1.5 TO-15 100-ppbv 75 compound standard Vapor Intrusion stock standard is purchased from Scott gases (item# MAZ00090-Z-7AL). Two different lots are purchased for calibration and alternate source. This stock contains Naphthalene.

8.3.1.6 TO-15 10-ppbv project specific compound list

8.3.1.6.1 Used for ultra low level SIM analysis.

8.3.2 Stock standard solutions must be stored at room temperature, or as recommended by the manufacturer.

8.3.3 Stock standard solutions must be replaced after 1 year, or sooner depending on manufacturer's expiration date.

8.4 Internal Standard and Surrogate

8.4.1 The internal standards are Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5.

8.4.2 The surrogate is Bromofluorobenzene.

8.4.3 Each sample undergoing analysis, as well as all calibration standards must be spiked with 50 ppbvof each internal standard and surrogate ***(based on a 100cc injection volume). For a 500cc injection volume this equates to 10 ppbv and 1000cc injection volume gives 5 ppbv.***

8.4.4 A certified stock internal and surrogate standard mixture must be purchased every 12 months (or sooner, if degradation is observed). (Spectra Gases, TO-14 IS/Surr. mix, catalogue # ENT14ITS-6A-1M) or (Scott Gases, TO-14 IS/Surr. Mix, P/N 24087828)

8.4.5 Store the internal/surrogate standard at room temperature.

8.5 GC/MS Tuning standard

8.5.1 In a 6L Summa canister, prepare a 100-ppbv standard of Bromofluorobenzene (BFB). This standard contains the internal standard compounds as well.

8.5.2 The tuning standard is stored at room temperature when not in use. When using premixed certified gases, store according to the manufacturer's documented holding time and storage temperature recommendations.

8.6 Intermediate (working) standards

8.6.1 A working standard of the target compounds is prepared at 5-ppbv, 25-ppbv, and 100-ppbv for both 100cc and 500cc injection methods. This is used to generate the instrument calibration curve. The working standard must contain all of the analytes of interest. Target compound working standards expire one month after preparation. ***Standards may be prepared at lower concentrations to meet project specific detection limits. For 75 compound list with 0.2 ppbv reporting limit, working standards are currently prepared at 2 and 10 ppbv.***

8.6.2 The internal / surrogate working standard is prepared at 100 ppbv. This is also used as the tuning standard. Working internal standards expire two months from preparation date.

8.7 Calibration standards

8.7.1 Calibration standards must be analyzed at a minimum of five different concentrations. One of the calibration standards must correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards must correspond to the range of concentrations expected to be found in the actual samples. The typical calibration curve range for TO15 (Minican) list is 5-ppbv to 150-ppbv for most analytes. TO-15 (6L Summa can) list is from 1-ppbv to 30-ppbv. ***TO-15 low level list is from 0.2-ppbv up to 30-ppbv. TO-15 SIM is dependent on project specific reporting limits.*** Ethylene Oxide ranges from 20-400-ppbv and 4-Phenylcyclohexene ranges from 1-20-ppbv.

8.7.2 Internal standards and surrogate are added to all calibration standards during analysis.

9.0 PROCEDURES

9.1 Sample collection, preservation and handling

9.1.1 Whole air samples are collected in 400cc or 1000cc fused silica lined stainless steel canisters (Mini Cans) or 6-liter Summa canisters that are stored at room temperature until analysis. Sample stability is unknown, therefore samples should be analyzed as soon as possible.

9.2 Sample Preparation

9.2.1 Once the GCMS group has received the samples, the vacuum in the can is measured to verify the amount of sample collected. If the vacuum reading is > 5 inches of Hg, the project manager must notify the customer. This can be caused by either improper sample collection or a malfunction of the regulator. A full canister will read < 5 inches of Mercury. ***There should be a partial vacuum remaining (@ 1 to < 5 inches of Mercury) to evidence that a full sampling event took place. No measurable vacuum may be an indication that the canister was not collecting the sample over the full duration of the sampling period or that the canister was leaking during sampling. The customer must be notified if there is no measurable vacuum. Pump group will set regulators to leave a partial vacuum for the specified sampling time (8 hrs, 24 hrs, or week).*** A volume of Nitrogen can be added to bring the volume above 5" Mercury with the use of the Entech 7100 sample diluter. The initial and final pressure readings must be recorded in the can dilution logbook. The dilution factor is calculate according to the equation:

$$DF = \frac{PSIA_f}{PSIAi}$$ Where $PSIA_f$ = final pressure reading, $PSIA_I$ = initial pressure reading

Detection limits will be raised proportionately.

9.3 Analytical Procedure

9.3.1 Instrument Maintenance

9.3.1.1 Appropriate instrument maintenance must be performed as necessary prior to initial calibration. Indications of the need for maintenance include poor peak shape, inadequate sensitivity, and inability to pass BFB tune. Steps that may be required to address these problems include replacing one or both traps in the Entech 7100, baking the transfer line and GC column, trimming or replacing the column, and/or cleaning the ion source.

9.3.2 Instrument conditions for TO-15 regular list, ***TO-15 0.2 ppbv reporting level,*** and Hydrocarbon analysis:

The following GC/MS instrument conditions are used:

Mass range:	35-300 amu
Scan time:	2.82 scan/sec
Initial temperature:	34 ^{0}C, hold for 5.5 minutes
Temperature program	increase at 5 ^{0}C /minute to 70^{0}C, then increase at 15^{0}C /minute to 170^{0}C, then increase at 25^{0}C/ minute to 240^{0}C, holding there for 1-10 minutes.
Final temperature:	240 ^{0}C, hold 1-10 minutes after Hexachloro-1,3-Butadiene elutes.
Injector temperature:	150 ^{0}C
Injection volume:	100cc
Carrier gas:	Helium at 20 cm/sec

9.3.3 Instrument conditions for Ethylene Oxide analysis:

Mass range:	28-250 for Ethylene oxide then at 6.9 min. 29-250 amu
Initial temperature:	34 ^{0}C, hold for 5.5 minutes,
Temperature program	increase at 15 ^{0}C /minute to
Final temperature:	240 ^{0}C, hold 1-10 minutes
Injector temperature:	150 ^{0}C
Injection volume:	100cc
Carrier gas:	Helium at 20 cm/sec

9.3.4 Instrument conditions for 4-Phenylcyclohexene analysis:

Mass range:	SIM Mode (4PCH 74, 108, 158 amu)
Initial temperature:	50 ^{0}C
Temperature program	increase at 10 ^{0}C /minute to 200^{0}C, then increase at 25 ^{0}C /minute.
Final temperature:	250 ^{0}C, hold 1-10 minutes.
Injector temperature:	150 ^{0}C
Injection volume:	100cc
Carrier gas:	Helium at 20 cm/sec

9.4 Instrument Calibration

9.4.1 Instrument Performance Check: At the beginning of a 24-hour analysis sequence it is necessary to show that the GC/MS system meets the instrument performance criteria. This is accomplished by the analysis of a 50-ppbv injection of BFB to demonstrate correct mass calibration, mass resolution, and mass transmission. Any injection containing 50-ppbv of BFB can be used for this purpose ***(based on 100cc injection volume).***

9.4.1.1 BFB must meet the criteria listed in 9.4.1.2 before standards and samples are analyzed. An acceptable BFB tune is demonstrated once at the beginning of each 24-hour period during which samples or standards are analyzed. The 24-hour period begins with the injection time of the BFB and ends after 24 hours according to the system clock. The following abundance criteria are required to establish instrument tune compliance:

9.4.1.2 Tune acceptance criteria:

Mass	Ion Abundance Criteria
50	8.0-40.0 percent of mass 95
75	30.0-66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95
173	Less than 2.0 percent of mass 174
174	50.0 - 120 percent of mass 95
175	4.0-9.0 percent of mass 174
176	Greater than 93.0 percent but less than 101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

9.4.1.3 For demonstrating an acceptable tune, the mass spectrum of BFB must be obtained. This is can be performed by the HP/Agilent Chemstation Software using the Auto-find BFB function. This function works as follows: three scans are taken (the peak apex scan, and the scans immediately preceding and following the apex) and then averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of BFB. The background subtraction is designed to eliminate column bleed and instrument background ions. Alternately, the BFB spectrum can be obtained/performed manually.

9.4.2 Calibration standards are analyzed concurrently or once BFB meets acceptance criteria.

9.4.3 Initial Calibration

9.4.3.1 For use with 100cc-sample injection volume TO15 analysis (i.e. 400-1000cc canisters): A minimum 5-point calibration curve must be analyzed prior to sample analysis. The internal standards must be added at 50-ppbv to each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from the 25 and/or 50-ppbv working standard canister to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. A 5-ppbv standard is utilized (100-cc injection volume) for the 5-ppbv level on some instruments. A blank should be run in-between the three highest standards (for example, between the 100 and 150-ppbv standards).

Standard Level	25-ppbv working standard	50-ppbv working standard
5-ppbv standard	Use 20cc	Use 10cc
20-ppbv standard	Use 80cc	Use 40cc
50-ppbv standard	Use 200cc	Use 100cc
100-ppbv standard	Use 400cc	Use 200cc
150-ppbv standard	Use 600cc	Use 300cc
200-ppbv standard	N/A	Use 400cc

9.4.3.2 For use with 500cc-sample injection volume analysis (i.e. 6-liter canisters): A minimum 5-point calibration curve must be analyzed prior to sample analysis. The internal standards must be added at 10-ppbv for each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from the 25-ppbv working standard canister to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. Blanks should be run in-between the three highest standards (for example, between the 20 & 30-ppbv standards).

Standard Level	1-ppbv working standard	5-ppbv working standard	25-ppbv working standard
0.2-ppbv standard	Use 100cc	Use 500cc	N/A

1-ppbv standard	N/A	Use 100cc	Use 20cc
5-ppbv standard	N/A	N/A	Use 100cc
10-ppbv standard	N/A	N/A	Use 200cc
20-ppbv standard	N/A	N/A	Use 400cc
30-ppbv standard	N/A	N/A	Use 600cc

9.4.3.3 For use with 1000cc sample injection volume analysis (i.e. 6-liter canisters): A minimum 5-point calibration curve must be analyzed prior to sample analysis. The internal standards must be added at 5-ppbv for each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from the 2 and 10-ppbv working standard canisters to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. Blanks may need to be run in-between the highest standards (for example, between the 4 & 6-ppbv standards).

Standard Level	*2-ppbv working standard*	*10-ppbv working standard*
0.2-ppbv standard	***Use 100cc***	***N/A***
1-ppbv standard	***N/A***	***Use 100cc***
2-ppbv standard	***N/A***	***Use 200cc***
3-ppbv standard	***N/A***	***Use 300cc***
4-ppbv standard	***N/A***	***Use 400cc***
6-ppbv standard	***N/A***	***Use 600cc***

9.4.3.4 For use with 1000cc sample injection volume analysis (6 liter SIM): A minimum 5-point calibration curve must be analyzed prior to sample analysis. The internal standards must be added at midpoint for each curve concentration level. Analyze to determine the instrument sensitivity and linearity of the GC/MS response for the target compounds. Analyze the following volumes from either 0.05-ppbv working standard canister or 1-ppbv working standard canister to obtain the desired concentration. Other standard levels can be used as needed to meet calibration range criteria. Blanks should be run in-between the highest standards (for example, between the 0.4 & 0.6-ppbv standards) and blanks should be run after the calibration to clean out the system.

Standard Level	0.05-ppbv working standard	1-ppbv working standard
0.005-ppbv standard	Use 100cc	N/A
0.025-ppbv standard	Use 500cc	N/A
0.1-ppbv standard	N/A	Use 100cc
0.2-ppbv standard	N/A	Use 200cc
0.4-ppbv standard	N/A	Use 400cc
0.6-ppbv standard	N/A	Use 600cc

9.4.3.5 Calculate the relative response factor for each compound using the following equation:

$$RRF = \frac{A_x}{} * \frac{C_{is}}{}$$

$$\frac{A_{is}}{C_x}$$

Where:

A_x = Area of the characteristic quant ion for the compound to be measured (see *Table 1 and 2*).

A_{is} = Area of the characteristic quant ion for the designated internal standard (see *Table 1*).

C_{is} = Concentration of the internal standard (ppbv).
C_x = Concentration of the compound to be measured (ppbv).

9.4.3.6 Calculate the average RRF for each analyte in the curve.

9.4.3.7 Calculate the % Relative Standard Deviation (%RSD) of RRF values for the initial calibration curve using the following equation:

$$\%RSD = \frac{\text{Standard Deviation (n-1)}}{\text{Average RRF}} * 100$$

9.4.3.8 Calculate the average RT for each internal standard over the initial calibration range.

9.4.4 Calibration acceptance criteria

9.4.4.1 The BFB must meet the specified criteria

9.4.4.2 The %RSD is calculated and must be less than or equal to 30% for all compounds. This criterion must be met for the initial calibration to be valid. However, an exception can be made for up to 2 compounds that may exceed 30% RSD, but the RSD for these compounds must be <40.0%. Refer to QC-SOP-12 (current revision) for calibration level rejection criteria.

9.4.4.3 Evaluation of IS retention time: The retention time shift for each of the internal standards at each calibration level must be within 20s of the mean retention time over the initial calibration range.

9.4.4.4 Evaluation of target compound retention time: The relative retention time (RRT) of each target analyte in each calibration level must be within 0.06 RRT units of the mean RRT for that compound

9.5 Calibration verification

9.5.1 Instrument Performance Check: Prior to sample analysis, a 10/50-ppbv injection of BFB must meet the criteria listed in 9.4.1.2.

9.5.2 Calibration verification standard: The initial calibration must be verified on a daily basis prior to the analysis of any samples. Analyze a mid-level (10/50-ppbv)-calibration standard at the beginning and end of each 24-hour working

period after meeting BFB tune criteria.

9.5.2.1 Calculate the % Difference between the average response factor from the calibration curve and the response factor from the daily standard using the equation below:

$$\% \text{ Difference} = \frac{|RRF_i - RRF_c|}{RRF_i} * 100$$

Where:

RRF_i = Average relative response factor from initial calibration.

RRF_c = Relative response factor from the current calibration check standard.

The %D in the daily standard must be +/-30% for all compounds.

The %D report is monitored daily to evaluate instrument performance and watch for trends that might indicate the need for corrective action.

9.6 Method Blank

9.6.1 A Method blank is a volume of a clean reference matrix (Nitrogen @ 99.9999% purity) carried through the entire analytical procedure. The volume of the method blank must be approximately equal to the volume of the associated samples.

9.7 Laboratory Control Sample and Duplicate (LCS/LCSD)

9.7.1 A laboratory control sample and duplicate (consisting of a representative list of target analytes prepared near the mid-level of the calibration curve) are analyzed daily. The LCS/LCSD are spiked into Mini Cans or 6 liter canisters and are analyzed in the same manner as client samples. The LCS/LCSD standard must be from a separate source than that of the calibration standards. Sub-sampling for an LCS or LCSD from a 6 liter standard stock canister requires the 6 liter canister to be > or = 10 psig to minimize any sub-sampling biases for the wide variety of volatile compounds analyzed by this method.

9.8 Detection Limit Standard (DLS)

9.8.1 The lower limit of quantitation is verified daily by the analysis of a standard at the detection limit (5-ppbv for most compounds in Minican, 0.2-ppbv or 1-ppbv for 6 liter) in the TO15 list analysis. ***The lower limit of quantitation for SIM analysis will depend on client specifications and targets.*** Recovery of all compounds with the DLS should be within the range of 60-140%. The Ethylene Oxide DLS is analyzed at 20-ppbv and the 4-Phenylcyclohexene DLS is at 1-ppbv (limits are also 60-140%).

9.9 Sample analysis

9.9.1 Once the instrument check and calibration verification standards have passed the acceptance criteria, samples may be analyzed.

9.9.2 Add 50cc of the 100-ppbv internal standard/surrogate mixture (for a level of 50-ppbv for a 100cc-sample injection and 10-ppbv for a 500cc-sample injection) to the sample extract obtained from the sample mini-canister. ***For 1000cc sample injection this equates to 5 ppbv.***

9.9.3 Analyze the sample on the GC/MS system using the same operating conditions that were used for the calibration.

9.9.4 If the concentration of any target analyte in the sample exceeds the initial calibration range of the GC/MS system, the sample must be diluted and reanalyzed.

9.9.4.1 Dilutions can be automated by using the Entech 7100 system. However, the smallest sample size that can be analyzed reliably is 10cc. If greater than a 10X dilution is needed on the can, the analyst must pressurize the canister with nitrogen to further dilute the sample. The pressurization factor is multiplied by the instrument dilution to obtain the total dilution factor:

$$\text{Total Df} = \frac{P_{sia}\ \text{final} \times 100\text{cc}}{P_{sia}\ \text{initial} \quad \text{inj vol}} \times \text{(split factor for loop injector, if used)}$$

Once the canister is pressurized above atmospheric pressure, or 14.7 P_{sia}, the Entech 7032 loop injector may be used to withdraw a 1-cc injection volume. Automated splitting of the sample stream can further dilute this volume up to a factor of 10x. If the sample is to be reanalyzed via normal injection, it must be vented to ambient pressure by depressing the quick-connect pin on the Mini Can.

9.10 Qualitative analysis

9.10.1 Identification of Target Compounds

The qualitative identification of compounds is based on retention time and comparison of the sample spectrum with characteristic ions in a reference mass spectrum. The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The list of characteristic ions for each analyte is presented in *Table 1*. Target compounds are positively identified when the following criteria are met:

9.10.1.1 The EICPs of the characteristic ions of an analyte must maximize within one scan of each other.

9.10.1.2 The RRT of the sample component is within +/- 0.06 RRT units of the RRT of the standard component.

9.10.1.3 The relative intensities of the characteristic ions in the sample analyte must agree within 30 percent of the relative intensities of these ions in the

reference spectrum from the most recent calibration verification standard. The analyst must account for deviations from this criterion such as in the case of interference/co-elution.

9.10.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 percent of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs (for example, m- & p-xylene).

9.10.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component, appropriate selection of analyte spectra and background spectra is important. When analytes coelute the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

9.10.2 Identification of Non-Target Compounds

For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. Up to 20 organic compounds with greatest concentration excluding surrogate and internal standards will be identified and reported. ***Non-Target compounds identification is not possible in SIM analysis.***

9.10.2.1 Major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

9.10.2.2 The relative intensities of the major ions should agree within +/-20 percent. For example: an ion with an absolute abundance of 50 percent in the standard spectrum must be between 30 and 70 percent in the corresponding sample spectrum.

9.10.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

9.11 Quantitative identification

9.11.1 Once a target compound has been identified, the quantitation of that compound is based on the total abundance, or EICP integration area, of the primary characteristic ion.

9.11.2 The concentration of a compound in the sample is determined using the mean relative response factor determined from the initial calibration.

9.11.3 Concentration is calculated from the equation:

$$ppbv = \frac{(Ax)(Is)(Df)}{\quad}$$

$$\frac{(Ax)(Is)(Df)}{(Ais)(RRF_i)}$$

Where: Ax = Area of the compound characteristic ion in the sample.
Ais = Area of the characteristic ion for the corresponding internal standard.
Is = Concentration of internal standard in ppbv
RRF_i = Mean relative response factor (from initial calibration) for the compound being measured.
Df = Dilution factor

9.11.4. In all instances where the quantitation report has been edited, or where manual integration or quantitation has been performed, the GC/MS operator must identify edits or manual procedures by initialing and dating the changes made to the report. The data system flags a manual integration on the quantitation report by placing the symbol "m" next to the area. The analyst who performed the integration should initial and date this flag.

9.11.5 Samples that contain target analytes above the linear range of the curve must be diluted to bring the analytes within the curve range. If a dilution was initially performed and no target analytes are detected above the LOQ, the sample must be reanalyzed at a more concentrated level.

9.12 Technical Acceptance Criteria for Sample analysis

9.12.1 The samples must be analyzed on a system meeting BFB, initial calibration and calibration verification criteria.

9.12.2 The sample must have an associated method blank meeting acceptance criteria (see section 11.2).

9.12.3 Surrogate recovery must fall within default limits of 80-120% for all samples and blanks.

9.12.4 The retention time of each internal standard must be within ±20s of the retention time in the most recent calibration verification standard.

9.12.5 The instrumental response (EICP area) for each of the internal standards must be within ± 40% of the area response in the most recent calibration verification standard. If analyzed within the same sequence a calibration curve, then the average of the area responses for all calibration standards can be used for this criteria comparison.

9.12.6 Concentration of all analytes must be within the calibration range determined from the initial calibration.

9.12.7 Control Sample/Duplicate must be evaluated to determine if recoveries (and RPDs) are within control limits.

9.13 Hydrocarbon Analysis

9.13.1 Initial Calibration

9.13.1.1 A copy of the day's data folder is made and renamed "InstID+date+HC." For example, if the date is 02/25/2011 on instrument J, the new folder will be named J022511HC. Load the previous hydrocarbon calibration curve, rename with the current date and save the method.

9.13.1.2 With the global detection limit set to zero, re-quantitate the same data files used for the TO-15 calibration curve. Q-Edit the files to ensure that all of the hydrocarbon peaks are correct, using the following table.

Name	Major Peak
Bromochloromethane	130
1,4-Difluorobenzene	114
Chlorobenzene-d5	117
Bromofluorobenzene	174
Total VOC's as n-Heptane	43,57,71,100
Trimethyl Siloxanol	75
Hexmethyl Cyclotrisiloxane	207
Octomethyl Cyclotetrasiloxane	281
Siloxane	267

Note: In standards and blanks, the Trimethyl Siloxanol and Siloxane may not be present. Highlight the peak around the retention time of where it should be, with the lowest level present. This is usually the beginning of the peak found.

9.13.1.3 Once the peaks have been selected correctly, clear the calibration responses in the curve. Update all the levels of the calibration using the same data files that were used for the TO-15 curve. Ensure that you select "Quantitate Using Initial Cal RF's" under the "Quant" menu before saving the method.

9.13.1.4 Repeat steps 9.4.3.2 – 9.4.3.5 for n-Heptane only. An additional conversion may be necessary, depending on client, to convert n-Heptane to Gasoline (M.W. Gasoline divided by M.W. of n-Heptane). Siloxanes are not calibrated compounds. RSD for siloxanes should be crossed out and marked "Not calibrated for these compounds." Update the Custom Report Response factor using the Average of the Total VOC's as n-Heptane.

9.14 SIM Analysis

9.14.1 SIM analysis is a technique used to increase sensitivity with GCMS for for target compounds using only specific ions. The only ions scanned for are those that are characteristic of target compounds only. As a result non target compounds are not able to be detected using SIM analysis.

9.14.2 SIM analysis can be done upon client request for compounds that require lower detection limits than the low level 0.2-ppbv standard.

9.14.3 Target compounds will depend on client target list and will be ordered at a

lower level primary standard if needed (example: Order a 10-ppbv standard if client requests detection limit of 0.005-ppbv)

9.14.4 If the detection limits can be meet with a standard SCAN TO-15 method but client requests SIM analysis, the same stock and working standards used for SCAN analysis can be used.

9.14.5 Target compounds will be quantitated from the primary ion for each respective compound with at least 1 secondary ion for qualitative identification. Retention time will be the primary method of identification per 9.10.1.

9.14.6 SIM analysis will be set up using a separate chemstation method using only the ions for compounds that require SIM analysis. This will keep from scanning non target compound ions which will increase sensitivity. Target ions will depend on client request and the ions used should be seen in regular TO-15 SCAN ECIP.

9.14.7 SIM methods will be made per client project to maximize sensitivity by minimizing dwell time by the mass spectrometer. See section supervisor or alternate for any questions.

9.14.8 Blank should be run after any QC until system is fully cleaned out before running any client samples. This will ensure that client samples are free from any possible carry over effects from working standards used for QC. Blanks should be run at the end of client sample batch to ensure that there is no carry over. Blanks should be run in between any client samples with a hit at or greater than the mid point calibration level, to ensure that subsequent client samples are not contaminated with carry over.

9.15 Corrective Action

9.15.1 Corrective Action for sample analysis: the sample technical acceptance criteria must be met. If any samples do not meet acceptance criteria, consult with the section supervisor to determine whether reanalysis is required.

9.15.2 Corrective Action for surrogate recovery failure: check calculations and examine the chromatogram for interference. If no interference is noted, reanalyze any sample that exceeds criteria. If the sample meets criteria upon reanalysis, report the reanalysis only. If the sample produced similar results upon reanalysis, the problem may be matrix-related. Contact the project manager so the client may be notified.

9.15.3 Corrective Action for Internal Standard Response failures: if any internal standard exceeds acceptance criteria, check calculations. Verify that the standard concentration is accurate, and that the instrument did not malfunction. Reanalyze the sample to see if the problem was matrix related. If the reanalysis meets criteria, report the reanalysis only. If the reanalysis produced similar results, consult with the section supervisor and project manager to determine the best course of action.

9.15.4 Corrective Action for Internal Standard Retention Time: if any internal standard exceeded retention time criteria, follow the same guidelines used in Section 9.14.3.

9.15.5 Corrective Action for Instrument Contamination: if an instrument has come into contact with a PPM level of analytes, the instrument might need extra cleaning to ensure that there is no carry-over to other client samples. Block access to the ports affected on the Entech autosampler until they go through at least 5 flush and bake cycles. Test the ports, as room air blanks, to see if there is carry-over. If there no carry-over, go ahead and use the ports during the next run. If there is carry-over, see section supervisor for other possible actions, which may include cleaning the source.

10.0 DOCUMENTATION

10.1 The raw data is archived to CD-ROM and is stored in a secured area. Hard copies of raw data are kept for a period of ~1 year in the laboratory and then stored for a total time of 5 years before disposal.

10.2 Chain of custody forms, instrument maintenance logs, standards preparation logs, analytical run logs, and corrective action logs must be filled out in a timely manner**.** These records are maintained in the laboratory for five years.

11.0 CALCULATIONS

All calculations are covered in Section 9.

12.0 QUALITY CONTROL CHECKS & CRITERIA

12.1 Instrument performance must be monitored to ensure that all of the tuning, initial calibration and calibration verification criteria requirements are met.

12.2 Method blanks

12.2.1 A method blank is a volume of a clean reference matrix (nitrogen @ 99.9999% purity) carried through the entire analytical procedure. The volume of the method blank must be approximately equal to the volume of the associated samples. The purpose of the method blank is to determine the level of contamination associated with the preparation and analysis of samples.

12.2.2 Method blanks must be analyzed with each batch of samples, or at a minimum frequency of 1 for every 20 samples.

12.2.3 A method blank is analyzed following the calibration verification standard under the same conditions as the standards and samples before any samples may be analyzed.

12.2.4 The method blank must contain no targets above the LOQ of 5-ppbv (100cc injection for Minican) and 0.2-ppbv (500cc injection ***or 1000cc*** for 6-L Summa canisters) for the TO15 list. ***They should contain no targets above client specific detection limits for SIM analysis.*** The LOQ for Ethylene Oxide is 20-ppbv and the 4-Phenylcyclohexene LOQ is 1-ppbv.

12.2.5 If the method blank does not meet this criterion, repeat the analysis until an acceptable blank is obtained. Sample analysis may not begin until a method blank meeting criteria has been successfully analyzed.

12.2.6 If the surrogate recovery in the method blank does not meet control limits, reanalyze the method blank. If the surrogate recovery is still outside control limits, it may be necessary to re-prepare the internal standard/surrogate mixture or recalibrate the instrument.

12.3 Laboratory Control Sample/ Laboratory Control Sample Duplicate

12.3.1 A laboratory control sample & duplicate (LCS/LCSD) consist of an aliquot of a clean reference matrix (UHP nitrogen), spiked with a representative list of the target analytes at the mid-level of the calibration curve. The spiking standard must be from a source different from that of the calibration standards.

12.3.2 The LCS & LCSD must be analyzed with each analytical run. The recoveries should fall within the range of 70-130%. For compounds 1,2,4-Trichlorobenzene and Hexachloro-1, 3-Butadiene, separate limits have been established based on historical laboratory data (these compounds are no longer in the TO-15 regular list). RPD method default limits of 25% are used to assess analytical precision. If recovery and/or RPD are not within this range, the possible effect(s) on the sample data must be determined. The data may be qualified or the LCS/LCSD sample may be reanalyzed.

12.4 Surrogate Recoveries

12.4.1 All samples, including quality control samples, are spiked with 50ppbv Bromofluorobenzene as a surrogate ***for 100cc sample injection volume (this equates to 10 and 5 ppbv for 500cc and 1000cc injection volumes).***

12.4.2 The surrogate (BFB) recovery control limits are 80-120%. All samples should meet the surrogate recovery criterion. If BFB recovery falls outside control limits for any sample, the sample must be reanalyzed. If the reanalysis produces similar results, contact the project manager.

12.5 Duplicate analysis.

12.5.1 A sample is analyzed in duplicate to assess precision. Duplicates must be analyzed with each batch of samples, or at a minimum frequency of 1 for every 24-hour analytical sequence. The relative percent difference (RPD) between measurements should be 25% or less.

12.6 Initial Demonstration of Proficiency (IDP)

12.6.1 Demonstration of proficiency is established by generating data of acceptable accuracy and precision for target analytes for each preparative method and matrix by analyzing reference samples. On-going demonstration is performed on a semiannual basis.

12.6.2 Four reference samples are prepared so that each analyst tests 4 samples of unknown concentration containing all analytes of interest. Analyst One prepares two different stock standards independently and fills two sample canisters from each. The preparing analyst labels the canisters with the injection volume to use and gives them a sample ID. This results in 4 different concentrations for each analyst. A second analyst repeats the process for any other analysts. The standards must be made from stock standards prepared independently from those used for calibration. The concentration of targets in the four reference samples may be anywhere within the current calibration range of the instrument.

12.6.3 Analyze the four reference samples by the same procedure used for analyzing actual samples. Calculate both the average recoveries in ppbv and the relative standard deviations of the recovery for each analyte of interest. The average recovery should fall within the in-house generated control limits for each analyte.

12.6.4 IDP procedures must be repeated whenever new staff is trained or significant changes in preparative or analytical methods are made.

12.7 Verification of Method Detection Limit

12.7.1 Instrument reporting limits are verified (at least) annually by analyzing 7 replicates at the reporting limit. All compounds must be within 60-140% recovery for the detection limit standard (DLS) when using a nominal sample injection volume of 100-cc for MiniCan, ***500cc-1000cc fo***r Summa Canisters ***or 1000cc for SIM analysis***.

12.7.2 Alternatively, an MDL study can be performed if needed. MDL is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined by the analysis of seven replicate injections of each compound of interest at a level near the expected detection limit. The standard deviation of the seven measurements multiplied by 3.14 (Student's *t* value for 99% confidence for seven values) defines the MDL for each analyte.

12.7.3 MDLs are determined only if needed for each instrument, as the detection limit studies (described in 12.7.1) are used to verify instrument-reporting limits.

12.7.4 ***For SIM analysis, detection limits should meet or exceed client specifications.***

12.8 Additional Control Procedures

12.8.1 Logbook Review Procedure:
The supervisor or designee will review GCMS run logs and maintenance logs

weekly. The logbooks will be reviewed for content and for the absence of cross outs. All forms will be verified to be the most recent approved version. Logbooks will be initialed and dated as to the date of review. MS-Form-6 will be used to document that all logbooks are reviewed as per their set schedule. The preventative maintenance log will be reviewed as the maintenance is done (some is weekly, some monthly and also some at 6-12 month intervals). The standards logbooks are reviewed each time a standard is made. Can cleaning logbooks and canister dilution logbooks will be reviewed weekly.

12.8.2 Forms Control Procedure:
In addition to forms being reviewed on a weekly basis new forms once approved (notification through email) will be printed and a new logbook made by the end of the next business day. Previous logbooks will be closed out and archived.

12.8.3 Preventative Action Plan Initiation/Review Policy:
A PAP should be initiated whenever an action can be initiated to prevent a future problem. Consultation with the QC group will be used to determine if a PAP is required. PAPs will be reviewed at least weekly until completed.

12.8.4 Entech auto-sampler ports are flushed before use and this is indicated on system injection log.

12.8.5 All working standard numbers (IH numbers) will be verified on hard copy reports and in LIMS to ensure accuracy and traceability for standard documentation.

12.8.6 Sample Canister Cleaning Approval Procedure.
This procedure is used to ensure sample analysis is complete before sample canisters are cleaned. After a sample analysis sequence is complete, canisters are placed in project holding bin (red or purple) waiting for approval of all Quality control and sample results. If any re-analysis is required, those samples are kept in this bin until re-analysis is performed. When approval is given by supervisor and/or designee to clean sample canisters, canisters are then transferred to the "approved for cleaning bin" (black or blue) by verifying sample identification using Galson Login number and individual sample number. This bin is then taken to the sample cleaning area.

13.0 CORRECTIVE ACTION

13.1 See section 9.14 for corrective actions.

14.0 WASTE DISPOSAL

14.1 Refer to Galson Laboratories SOP LF-DISPO (current revision).

15.0 REFERENCES

15.1 Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) In Air Collected I Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Second Edition, U. S. Environmental

Protection Agency, Research Triangle Park, NC 27711, EPA/626/R-96/010b, January 1999.

15.2 PV2120: Volatile Organic Compounds in Air, U. S. Department of Labor – Occupational Safety & Health Administration, Control Number T-PV2120-01-0305-ACT, May 2003

16.0 METHOD MODIFICATIONS

Method PV2120:

The samples arrive in the lab at ~ 15 psia (atmospheric pressure, 0 psig) and this is adequate to sample without pressurizing (diluting) the sample up to 30 psig (45 psia).

Method TO-15: (parentheses denote method-referenced sections)

(10.7.5)
Daily blank limit is set at 5-ppbv for TO15 list (the normal reporting limit for most compounds), not 3x the MDL.

(8.4.1.2)
Can leak-checks are done by evacuating cans to ~ 30" of Mercury (vacuum reading), and then checking them before sample shipment. If vacuum falls to <28" of Mercury within 24 hours, a can is considered to be leaking (TO-15 leak-checks by pressurizing cans to 30 psig and has pass/fail criteria of <+/- 2 psig) in 24 hours.

(8.4.1.6)
Cans containing less than 2-ppm of individual contaminants are cleaned in batches where a representative can is tested to demonstrate cleanliness of the batch. For cans containing analytes greater than 2-ppm, these cans are tested individually to verify cleanliness. Can cleaning limits are higher (refer to section 9.2.2.2). For MiniCans: the representative can cleaning blank limit (or individual can) for TO-15 list is set at 5-ppbv, the normal reporting limit. The warning limit is 2.5-ppbv. Quantitation in general is not reliable below 5-ppbv. Cans are generally re-cleaned if above 2.5-ppbv for any analyte. For 6-L Summa Canisters: the cleaning blank limit is 0.2-ppbv (LOQ for most compounds), anything less than 0.2-ppbv is considered clean. Correspondingly, for Ethylene Oxide the limit is 20-ppbv and for 4-Phenylcyclohexene the limit is 1 ppbv.

(10.8.1)
For Minican analysis: 100cc sample injection volume is used when sampling is done with 400mL and 1-liter canisters rather than 6-liter summa canisters. Therefore, MDL limits, etc. are ~ 5x higher because the sample injection volume is 5x less.

(9.2.2.3)
For Minican analysis: Internal standard/surrogate levels are spiked at 50-ppbv rather than 10-ppbv to be consistent with calibration levels for TO15 list analyses.

(10.7.2)
A blank is not always analyzed after a high level sample. If the compound that was high

is detected in samples injected after the high level sample, those samples would be reanalyzed after the system was shown to be clean.

(10.7.5)

Internal standard area limit of +/- 40% is calculated versus the daily standard for all injections that day (24 hour window) not versus the most recent calibration curve average areas.

Table 1
Characteristic Ions, PQLs

COMPOUND	EI PRIMARY	EI SECONDARY	EI TERTIARY	PQL ppb	
				Summa	Minican
Propylene	41	39		0.2	5
Freon-12	85	87		0.2	5
Chloromethane	50	52		0.2	5
Freon-114	85	135	87	0.2	5
Vinyl Chloride	62	64		0.2	5
1,3-Butadiene	39	54		0.2	5
Bromomethane	94	96		0.2	5
Chloroethane	64	66		0.2	5
Vinyl Bromide	106	108		0.2	5
Freon-11	101	103	105	0.2	5
Isopropyl Alcohol	45	43		0.2	5
Acetone	43	58		0.2	5
1,1-Dichloroethene	96	61	98	0.2	5
Methylene Chloride	84	86	49	0.2	5
Freon-113	101	101	151	0.2	5
Allyl chloride	76	41	39	0.2	5
Carbon Disulfide	76	78		0.2	5
Trans-1,2-Dichloroethene	61	96	98	0.2	5
Methyl Tert-Butyl Ether	73	41	57	0.2	5
1,1-Dichloroethane	63	65		0.2	5
Vinyl Acetate	43	86		0.2	5
Methyl Ethyl Ketone	43	57	72	0.2	5
cis-1,2-Dichloroethylene	61	96	98	0.2	5
Hexane	57	41	43	0.2	5
Ethyl Acetate	43	45	61	0.2	5
Chloroform	83	85	47	0.2	5
Tetrahydrofuran	42	71	72	0.2	5
COMPOUND	**EI PRIMARY**	**EI SECONDARY**	**EI TERTIARY**	**PQL ppb**	
				Summa	**Minican**

1,2-Dichloroethane	62	64		0.2	5
1,1,1-Trichloroethane	97	99	61	0.2	5
Cyclohexane	56	41	84	0.2	5
Carbon Tetrachloride	117	119		0.2	5
Benzene	78	77	50	0.2	5
1,4-Dioxane	88	58		0.8	20
2,2,4-Trimethylpentane	57	41	56	0.2	5
Heptane	43	57	71	0.2	5
1,2-Dichloropropane	63	41	62	0.2	5
Trichloroethylene	130	132	95	0.2	5
Bromodichloromethane	83	85		0.2	5
cis-1,3-Dichloropropene	75	39	77	0.2	5
Trans-1,3-Dichloropropene	75	39	77	0.2	5
1,1,2-Trichloroethane	97	83	61	0.2	5
Toluene	92	91	92	0.2	5
Dibromochloromethane	129	127		0.2	5
Methyl Isobutyl Ketone	43	57	58	0.8	20
Methyl Butyl Ketone	43	57	58	0.8	20
1,2-Dibromomethane	107	109		0.2	5
Tetrachloroethylene	164	166	131	0.2	5
Chlorobenzene	112	77	114	0.2	5
Ethylbenzene	91	106		0.2	5
Bromoform	173	175		0.2	5
Styrene	104	78	103	0.2	5
o-xylene	91	106		0.2	5
m- & p-xylene (co-elute)	91	106		0.4	10
1,1,2,2-Tetrachloroethane	83	85		0.2	5
4-Ethyltoluene	105	120		0.2	5
1,3,5-Trimethylbenzene	105	120		0.2	5
1,2,4-Trimethylbenzene	105	120		0.2	
1,3-Dichlorobenzene	146	148	111	0.2	
COMPOUND	**EI PRIMARY**	**EI SECONDARY**	**EI TERTIARY**	**PQL ppb**	
				Summa	**Minican**
Benzyl Chloride	91	126		0.2	5
1,4-Dichlorobenzene	146	148	111	0.2	5
1,2-Dichlorobenzene	146	148	111	0.2	5

1,2,4-Trichlorobenzene	180	182	184	0.2	5
Hexachloro-1,3-Butadiene	225	227	223	0.2	5
Ethylene Oxide	44	29	NA		20
4-Phenylcyclohexene	104	158	78		1
Naphthalene	128	102	NA	0.2	5
Bromofluorobenzene (surrogate)	95			-	
*Bromochloromethane	128			-	
*1,4-Difluorobenzene	114			-	
*Chlorobenzene-d5	117			-	

*Indicates internal standard

Table 2

Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

*Bromochloromethane	*1,4-Difluorobenzene	*Chlorobenzene-d5
Propylene	1,1,1-Trichloroethane	Toluene
Freon-12	Cyclohexane	Dibromochloromethane
Chloromethane	Carbon Tetrachloride	Methyl Isobutyl ketone
Freon-114	Benzene	Methyl Butyl ketone
Vinyl Chloride	1,4-Dioxane	1,2-Dibromoethane
1,3-Butadiene	2,2,4-Trimethylpentane	Tetrachloroethylene
Bromomethane	Heptane	Chlorobenzene
Chloroethane	1,2-Dichloropropane	Ethylbenzene
Vinyl bromide	Trichloroethylene	m- & p-xylene (co-elute)
Freon-11	Bromodichloromethane	Styrene
Isopropyl alcohol	cis-1,3-Dichloropropene	o-xylene
Acetone	trans-1,3-Dichloropropene	Bromoform
1,1-Dichloroethene	1,1,2-Trichloroethane	1,1,2,2-Tetrachloroethane
Methylene Chloride		4-Ethyltoluene
Freon-113		1,3,5-Trimethylbenzene
Allyl chloride		1,2,4-Trimethylbenzene
Carbon disulfide		Benzyl chloride
Trans-1,2-Dichloroethene		1,3-Dichlorobenzene
Methyl tert-butyl ether		1,4-Dichlorobenzene
1,1-Dichloroethane		1,2-Dichlorobenzene
Vinyl acetate		1,2,4-Trichlorobenzene
Methyl ethyl ketone (2-butanone)		Hexachloro-1,3-Butadiene
Cis-1,2-Dichloroethylene		Bromofluorobenzene (surrogate)
Hexane		4-Phenylcyclohexene
Ethyl acetate		**Naphthalene**
Chloroform		
Tetrahydrofuran		
1,2-Dichloroethane		
Ethylene Oxide		

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August 17, 2012

Mr. Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. Environmental Protection Agency
801 Garfield Avenue, #229
Traverse City, MI 49686

RE: Request for Modification of the Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan,
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release

Dear Mr. Dollhopf:

Enbridge Energy, Limited Partnership (Enbridge) is requesting the United States Environmental Protection Agency (U.S. EPA) approve the following modification to the *Air Monitoring and Sampling Addendum to the Sampling and Analysis Plan* (AMSA) approved by the U.S. EPA on January 31, 2012. The proposed modifications are being requested for immediate implementation.

Enbridge continues to meet obligations related to air monitoring and sampling under the current AMSA, which specifically requires work area air monitoring for all oil recovery activities, and the ability to respond to odor complaints. Enbridge is requesting a suspension of all work area air monitoring activities and odor response requirements effective immediately.

As you are aware, the air monitoring and sampling program was designed to protect worker safety and public health during assessment and oil recovery activities. Enbridge has been conducting, collecting, and reporting air monitoring and sampling since July 27, 2010. This has been a comprehensive and collaborative effort that has involved not only real-time and analytical data collection, but at minimum weekly reviews and discussion of data involving an air sampling and monitoring group that includes: Enbridge, U.S. EPA, and Michigan Department of Community Health (MDCH). In addition, Enbridge has supported and provided extensive scientific studies as informally requested by U.S. EPA and MDCH to ensure air sampling activities support the safety of workers and public health.

Air monitoring and sampling conducted in 2010, 2011, and 2012 for the Line 6B release has resulted in the compilation of robust data sets from all types of oil recovery activities including, but not limited to, free product recovery, overbank surface oil recovery, overbank excavation, and submerged oil recovery. These activities were conducted over a broad range of atmospheric conditions and through degradation of the released oil from free product to weathered tar patties and submerged oil. As a result, a negative exposure assessment for potential inhalation exposure has been derived from which Enbridge is confident that there is not an inhalation exposure risk to their workers or the community with respect to remaining oil recovery activities.

The following summarizes pertinent data with respect to air monitoring and sampling to support the suspension of the air monitoring and sampling program for the Line 6B release.

Air Monitoring Data

Air monitoring has been utilized as a screening tool throughout the Line 6B release to assess potential exposures to workers and the community. Real-time air monitoring included the collection of data for concentrations of airborne volatile organic compounds (VOCs), benzene, hydrogen sulfide (H_2S), and sulfur dioxide (SO_2) associated with oil recovery activities.

Work Zone

Throughout 2010, 2011, and 2012, work zones (also known as 'work areas') were monitored to assess potential exposures to airborne concentrations of chemicals of potential concern, which are a subset of "target analytes" (a list of crude oil related constituents, specifically related to Enbridge Line 6B crude oil, and enclosed as *Table 1*). Real-time air monitoring conducted in work zones is compared to Occupational Exposure Standards and Guidelines that were compiled by the Enbridge Public Health Unit during initial response activities. The exposure criteria, presented in the enclosed *Table 2*, outline the applicable occupational exposure standards and guidelines established by the Occupational Safety & Health Administration (OSHA), Michigan OSHA, and American Conference of Governmental Industrial Hygienists. In 2011, a total of 21,169 real-time work zone monitoring readings were collected which resulted in a total of 44 detections (27 SO_2 and 17 VOC detections) all linked through field notes to boat motor exhaust odors. 6,378 real-time work zone monitoring readings were collected in 2012 (through July 31, 2012). There were 28 VOC detections and 16 carbon monoxide (CO) detections during 2012 work area monitoring. The VOC detections were not sustained readings, were indicative of boat motors, and coincide with the CO detections. All detections of CO were attributed to boat motors.

Community

As a screening tool for determining air sampling locations and in addition to work zone air monitoring, community air monitoring (which also included work zone perimeter air monitoring) was conducted in 2010 and 2011. A total of 66,922 real-time community air monitoring readings were collected in 2010, with no detections. From June 3, 2011 through and including October 27, 2011 a total of 33,424 real-time community air monitoring readings were also collected with no detections.

Enbridge has made an undeniable commitment to the communities and people affected by the Line 6B release, which is further supported by the community air sampling program. Specifically between August 16, 2010 through and including November 10, 2010, a total of 1,531 24-hour duration community air samples were collected. Enbridge continued the community air sampling program with the collection of another 1,702 24-hour duration community air samples between June 3, 2011 through and including January 23, 2012 during oil recovery activities.

Community Air Sampling

To evaluate potential exposures during oil recovery activities, a list of target analytes was developed based on modified U.S. EPA Method TO-15 laboratory analysis of volatiles which could potentially be released from Line 6B crude oil. All other chemicals are referred to as "non-target analytes". Developed as a baseline for comparison to assess potential community exposure to VOCs from the Line 6B crude oil, the 2011 Enbridge Oil Spill Human Health Air Screening Levels (HHASLs), included as *Attachment A*, were compiled by local and state health

departments and regulatory agencies using State and Federal exposure criteria. It's important to note that these HHASLs are concentrations that are likely to be without appreciable risk of deleterious non-cancer effects during a long term continuous exposure at or greater than the reference concentrations. They are not a direct estimator of risk but rather a reference point to gauge potential effects. At exposures to a chemical increasingly greater than the HHASL, the potential for adverse health effects increases. A long term continuous exposure above the HHASLs does not imply that an adverse health effect would necessarily occur, just that risk increases.

Enbridge has utilized the above referenced HHASLs to compare the subset of air sampling data from 2010, 2011, and 2012 filtered, specifically to include only 24-hour duration samples and target analytes, to evaluate potential community exposure to chemicals that may be related to Enbridge crude oil and associated oil recovery activities. An initial assessment of this data revealed that, when segregated by target analytes, greater than 99% of the air sampling data set is below the method detection limit (MDL) for their respective analytes, with the exception of toluene which showed greater than 85% of samples below the MDL. The air sampling data set was evaluated through the use of U.S. EPA ProUCL Version 4.00.02 (ProUCL) statistical analysis software to adequately evaluate all results, including those below the MDL. Based on a general statistical analysis through ProUCL for each of the target analytes with MDLs (i.e. not including tentatively identified compounds), the Kaplan-Meier (KM) method was recommended for a more refined statistical evaluation of the analytical data set. Copies of the ProUCL statistical analysis outputs for these target analytes are included as *Attachment B*.

In conjunction with the use of statistical analysis to evaluate data in comparison to HHASLs, Enbridge developed charts for select target analytes (target analytes with at least one detection and a comparable HHASL) and one non-target analyte (acetaldehyde) that has been of interest to the air sampling and monitoring group. These charts display a chronology of detections for each of the analytes from August 16, 2010 through and including January 23, 2012, including: a depiction of the KM calculated mean (where applicable for analytes with MDLs), respective HHASL, number of detections, analyte concentrations, and number of samples analyzed. It is important to note that the charts only reflect analyte concentrations above the MDL. However, for select parameters analyzed in 2010 the MDL may be higher than the current HHASL and is noted as such on the respective charts. These charts are also enclosed with this correspondence.

As shown in these charts, the detection frequency of target analytes is low and mean values, where appropriate, are well below respective HHASLs. In addition, the total number of detections above HHASLs for each of the contaminants in comparison to the total number of samples analyzed is significant.

Odor Response Monitoring & Sampling

The Odor Response Team responded to 11 odor complaints between June 3, 2011 through and including October 13, 2011 at which a combination of real-time air monitoring data and canister air samples (grab and/or 24-hour canister samples) were collected. Real-time readings were collected for VOCs, benzene, H_2S, and SO_2 at each response. There were no detections above the instrument detection limits on any occasion. Grab and 24-hour duration samples collected during the response were analyzed for VOCs by U.S. EPA Method TO-15. Laboratory results indicated no detections for target analytes above HHASLs.

Supported by limited number of odor complaints (the last complaint occurring on October 13, 2011) and air monitoring and sampling data collected to date, Enbridge is requesting to discontinue the current odor response requirements.

Enbridge understands that there are a variety of ways to sort, analyze, and present the air sampling and monitoring data from the Line 6B release and all parties may not all agree on the selected technical approach. Data has been presented in multiple formats for review and comment by the U.S. EPA including, but not limited to: daily deliverables, SCRIBE.net, Monthly Reports, and Report of Findings Air Monitoring and Sampling reports. In the professional opinion of our engineers and scientists, there is conclusive evidence to support suspension of the air monitoring and sampling program. Enbridge is certainly open to the opportunity to present additional information and is willing to accept comments and/or suggestions regarding the analysis of data collected through our air monitoring and sampling program.

If you have any questions regarding this request, please do not hesitate to contact Jim Snider at (269)781–1195.

Sincerely,

ENBRIDGE ENERGY, LIMITED PARTNERSHIP
By Enbridge Pipelines (Lakehead) L.L.C.
Its General Partner

Richard Adams
Vice President, U.S. Field Operations

Enclosures: Table 1: Predominant Crude Oil VOCs Detected by TO-15 Analysis
Table 2: Occupational Exposure Standards and Guidelines
Attachment A. 2011 Enbridge Oil Spill Human Health Air Screening Levels
Attachment B. ProUCL Statistical Output for Target Analytes
Attachment C. Charts for Select Analytes

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Tables

Table 1. Predominant Crude Oil VOCs Detected by TO-15 Analysis
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release
Enbridge Energy, Limited Partnership

Predominant Crude Oil VOCs Detected by TO-15 Analysis[1]		
Target Analyte	**CAS No.**	**Laboratory LOQ (ppbv)**
Benzene	71-43-2	1.0
Butane, 2-methyl-*	78-78-4	NA
Cyclohexane	110-82-7	1.0
Cyclohexane, 1,3-dimethyl*	591-21-9	NA
Cyclopentane, methyl-*	96-37-7	NA
Cyclohexane, 1,3-dimethyl-, cis-*	638-04-0	NA
Cyclohexane, butyl-*	1678-93-9	NA
Cyclohexane, ethyl-*	1678-91-7	NA
Cyclohexane, methyl-*	108-87-2	NA
Cyclohexane, propyl-*	1678-92-8	NA
Cyclopentane, 1,1-dimethyl*	1638-26-2	NA
Cyclopentane, 1,3-dimethyl-, trans*	1759-58-6	NA
Cyclopentane, 1,2-dimethyl-, trans*	822-50-4	NA
Heptane, 3-methyl-*	589-81-1	NA
2-Octene, 2,6-dimethyl-*	4057-42-5	NA
Decane*	124-18-5	NA
Dodecane*	112-40-3	NA
Ethylbenzene	100-41-4	1.0
Ethyltoluene, 4-	622-96-8	1.0
Heptane, n-	142-82-5	1.0
Hexane, n-	110-54-3	1.0
Naphthalene*	91-20-3	NA
Nonane*	111-84-2	NA
Hexane, 2-methyl*	591-76-4	NA
Octane*	111-65-9	NA
Octane, 3-methyl-*	2216-33-3	NA
Pentane, 2-methyl-*	107-83-5	NA
Toluene	108-88-3	1.0
Benzene, 1,2,4-trimethyl	95-63-6	1.0
Hexane, 3-methyl*	589-34-4	NA
Heptane, 2-methyl-*	592-27-8	NA
Cyclohexane-1,1,3-trimethyl*	3073-66-3	NA
Benzene, 1,3,5-trimethyl	108-67-8	1.0
Undecane*	1120-21-4	NA
Xylene, m&p-	179601-23-1	2.0
Xylene, o-	95-47-6	1.0

Table 1. Predominant Crude Oil VOCs Detected by TO-15 Analysis
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release
Enbridge Energy, Limited Partnership

Non-Target Analyte	CAS NO	Laboratory LOQ (ppbv)
ALPHA-PINENE*	80-56-8	NA
1,1,1-TRICHLOROETHANE	71-55-6	1.0
1,1,2,2-TETRACHLOROETHANE	79-34-5	1.0
1,1,2-TRICHLOROETHANE	79-00-5	1.0
1,1-DICHLOROETHANE	75-34-3	1.0
1,1-DICHLOROETHENE	75-35-4	1.0
1,2-DIBROMOETHANE	106-93-4	1.0
1,2-DICHLOROBENZENE	95-50-1	1.0
1,2-DICHLOROETHANE	107-06-2	1.0
1,2-DICHLOROPROPANE	78-87-5	1.0
1,3-BUTADIENE	106-99-0	1.0
1,3-BUTADIENE, 2-METHYL-*	78-79-5	NA
1,3-DICHLOROBENZENE	541-73-1	1.0
1,4-DICHLOROBENZENE	106-46-7	1.0
1,4-DIOXANE	123-91-1	4.0
1-HEPTANOL, 2-PROPYL-*	10042-59-8	NA
2,2,4-TRIMETHYLPENTANE	540-84-1	1.0
2,2,7,7-TETRAMETHYLOCTANE*	1071-31-4	NA
2,3,4,5-TETRAHYDROPYRIDAZINE*	694-06-4	NA
2-HEPTANONE*	110-43-0	NA
2-PENTANONE*	107-87-9	NA
2-PROPANOL, 2-METHYL-*	75-65-0	NA
3-HEPTANONE*	106-35-4	NA
ACETALDEHYDE*	75-07-0	NA
ACETIC ACID, 2-ETHYLHEXYL ESTER*	103-09-3	NA
ACETONITRILE*	75-05-8	NA
ALLYL CHLORIDE	107-05-1	1.0
BENZENE, 1-METHYL-4-(1-METHYLETHYL)*	99-87-6	NA
BENZYL CHLORIDE	100-44-7	1.0
BROMODICHLOROMETHANE	75-27-4	1.0
BROMOFORM	75-25-2	1.0
BROMOMETHANE	74-83-9	1.0
BUTANE*	106-97-8	NA
BUTANOIC ACID, 2-METHYLPROPYL ESTER*	539-90-2	NA
BUTANOIC ACID, BUTYL ESTER*	109-21-7	NA
BUTANOIC ACID, ETHYL ESTER*	105-54-4	NA
BUTANOIC ACID, METHYL ESTER*	623-42-7	NA
BUTANOIC ACID, PROPYL ESTER*	105-66-8	NA
CARBON DISULFIDE	75-15-0	2.0
CARBON TETRACHLORIDE	56-23-5	1.0
CARBONYL SULFIDE*	463-58-1	NA

Table 1. Predominant Crude Oil VOCs Detected by TO-15 Analysis
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release
Enbridge Energy, Limited Partnership

Non-Target Analyte	CAS NO	Laboratory LOQ (ppbv)
CHLOROBENZENE	108-90-7	1.0
CHLOROETHANE	75-00-3	1.0
CHLOROFORM	67-66-3	1.0
CHLOROMETHANE	74-87-3	1.0
CIS-1,2-DICHLOROETHYLENE	156-59-2	1.0
CIS-1,3-DICHLOROPROPENE	10061-01-5	1.0
CYCLOPENTANE, 1,1'-ETHYLIDENEBIS-*	4413-21-2	NA
DECANE, 2,2,4-TRIMETHYL-*	62237-98-3	NA
DECANE, 2,3,4-TRIMETHYL-*	62238-15-7	NA
DECANE, 2,3,5-TRIMETHYL-*	62238-11-3	NA
DIACETYL*	431-03-8	NA
DIBROMOCHLOROMETHANE	124-48-1	1.0
DISULFIDE, DIMETHYL*	624-92-0	NA
DISULFIDE, FLUOROMETHYL METHYL*	60307-49-5	NA
ETHANE, 1,1-DIFLUORO-*	75-37-6	NA
ETHYL ACETATE	141-78-6	1.0
ETHYL ALCOHOL*	64-17-5	NA
EUCALYPTOL*	470-82-6	NA
FREON 11	75-69-4	1.0
FREON 113	76-13-1	1.0
FREON 114	76-14-2	1.0
FREON 12	75-71-8	1.0
FURAN, 2,3-DIHYDRO-3-METHYL-*	1708-27-6	NA
HEPTANE, 2,2,3,4,6,6-HEXAMETHYL-*	62108-32-1	NA
HEPTANE, 2,2,4,6,6-PENTAMETHYL-*	13475-82-6	NA
HEPTANE, 2,2-DIMETHYL-*	1071-26-7	NA
HEPTANE, 4-ETHYL-2,2,6,6-TETRAMER*	62108-31-0	NA
HEXADECANE, 2,6,10,14-TETRAMETHYL-*	638-36-8	NA
HEXANAL*	66-25-1	NA
HEXANE, 2,2,5-TRIMETHYL-*	3522-94-9	NA
HEXANE, 2,4-DIMETHYL-*	589-43-5	NA
HEXANOIC ACID, METHYL ESTER*	106-70-7	NA
HEXYL N-VALERATE*	1117-59-5	NA
ISOBUTANE*	75-28-5	NA
LIMONENE*	138-86-3	NA
METHYL 3-BUTENOATE*	3724-55-8	NA
METHYL BUTYL KETONE	591-78-6	4.0
METHYL ETHYL KETONE	78-93-3	1.0
METHYL ISOBUTYL KETONE	108-10-1	4.0
METHYL TERTIARY BUTYL ETHER	1634-04-4	1.0
METHYLENE CHLORIDE	75-09-2	1.0

Table 1. Predominant Crude Oil VOCs Detected by TO-15 Analysis
Enbridge Line 6B MP 608 Marshall, MI Pipeline Release
Enbridge Energy, Limited Partnership

Non-Target Analyte	CAS NO	Laboratory LOQ (ppbv)
NONANAL*	124-19-6	NA
NONANE, 3-METHYL-5-PROPYL-*	31081-18-2	NA
OCTANE, 2,2-DIMETHYL-*	15869-87-1	NA
OCTANE, 2,7-DIMETHYL-*	1072-16-8	NA
o-Veratramide*	1521-39-7	NA
PENTANE*	109-66-0	NA
PENTANE, 3-METHYL-*	96-14-0	NA
PROPANE*	74-98-6	NA
PROPANOIC ACID, 2-OXO-*	127-17-3	NA
PROPYLENE	115-07-1	1.0
STYRENE	100-42-5	1.0
TETRACHLOROETHYLENE	127-18-4	1.0
TETRADECANE*	629-59-4	NA
TETRADECANE, 2,2-DIMETHYL-*	59222-86-5	NA
TETRAHYDROFURAN	109-99-9	1.0
TRANS-1,2-DICHLOROETHENE	156-60-5	1.0
TRANS-1,3-DICHLOROPROPENE	10061-02-6	1.0
TRICHLOROETHYLENE	79-01-6	1.0
TRIDECANE, 6-METHYL-*	13287-21-3	NA
TRISULFIDE, DIMETHYL*	3658-80-8	NA
UNDECANE, 2,2-DIMETHYL-*	17312-64-0	NA
UNDECANE, 2,6-DIMETHYL-*	17301-23-4	NA
UNDECANE, 3,6-DIMETHYL-*	17301-28-9	NA
THIAZOLE*	288-47-1	NA
THIOACETAMIDE*	62-55-5	NA
1,1-DICHLOROPROPANE*	78-99-9	NA
VINYL ACETATE	108-05-4	1.0
VINYL BROMIDE	593-60-2	1.0
VINYL CHLORIDE	75-01-4	1.0

[1]The laboratory will also be asked to report on all analytes included in their TO-15 method standard analyte list.

*****Tentatively identified compound (TIC)

NA – Not Applicable

ppbv – parts per billion by volume

Chemical	OSHA PEL-TWA[(a)]	OSHA PEL-STEL[(b)]	OSHA PEL-Ceiling[(c)]	ACGIH TLV-TWA[(d)]	ACGIH TLV-STEL[(e)]	MIOSHA PEL-TWA[(f)]	MIOSHA PEL-STEL[(g)]
Benzene	1 ppm	5 ppm	NE	0.5 ppm	2.5 ppm	1 ppm	5 ppm
Ethyl Benzene	100 ppm	NE	NE	20 ppm	125 ppm	NE	NE
n-Hexane	500 ppm	NE	NE	50 ppm	NE	NE	NE
Toluene	200 ppm	NE	300 ppm	20 ppm	NE	NE	NE
Xylene	100 ppm	NE	NE	100 ppm	NE	NE	NE

a. OSHA PEL-TWA = The permissible concentration in air of a substance that shall not be exceeded in an 8-hour work shift or a 40-hour work week (OSHA, 1989).

b. OSHA PEL-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (OSHA, 1989).

c. OSHA PEL-Ceiling = The exposure limit that shall at no time be exceeded. If instantaneous monitoring is not feasible, then the ceiling shall be assessed as a 15-minute time-weighted average exposure, which shall not be exceeded at any time during the workday (OSHA, 1989).

d. ACGIH TLV-TWA = The Threshold Limit Value-TWA is the concentration for a normal 8-hour workday and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (ACGIH, 2011).

e. ACGIH TLV-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (ACGIH, 2011).

f. MIOSHA PEL-TWA = The permissible concentration in air of a substance that shall not be exceeded in an 8-hour work shift or a 40-hour work week (R 325.77103 Rule 3 (1) MIOSHA Reference of OSHA Permissible Exposure Limits).

g. MIOSHA PEL-STEL = The time-weighted average exposure that should not be exceeded for any 15-minute period (R 325.77103 Rule 3 (2) MIOSHA Reference of OSHA Permissible Exposure Limits).

NE – Not Established
ppm – parts per million

Attachment A

2011 Enbridge Oil Spill Human Health Air Screening Levels

Enbridge Oil Spill
Human Health Air Screening Levels
August 31, 2011

Chemical Name	Chemical Abstract Service Number	Screening Level in parts per billion by volume (ppbv)	Source of Screening Level
1,1,1-trichloroethane	71-55-6	1,000	EPA RfC
1,1,2,2-Tetrachloroethane	79-34-5	0.006	EPA RSL
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4,000	EPA RSL
1,1,2-Trichloroethane	79-00-5	0.04	EPA RfC
1,1-Dichloroethane	75-34-3	0.4	EPA RSL
1,1-Dichloroethene	75-35-4	50	EPA RfC
1,2,4-Trichlorobenzene	120-82-1	0.3	EPA RfC
1,2,4-Trimethylbenzene	95-63-6	1.5	EPA RfC
1,2-Dibromoethane	106-93-4	1	EPA RfC
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	9,900	MDEQ
1,2-Dichlorobenzene	95-50-1	30	EPA RfC
1,2-Dichloroethane	107-06-2	600	ATSDR Chr. MRL
1,2-Dichloropropane	78-87-5	1	EPA RfC
1,3-Butadiene	106-99-0	1	EPA RfC
1,3,5-Trimethylbenzene	108-67-8	45	MDEQ
1,3-Dichlorobenzene	541-73-1	0.5	MDEQ
1,4-Dichlorobenzene	106-46-7	10	ATSDR Chr. MRL
1,4-Dioxane	123-91-1	1,000	ATSDR Chr. MRL
2,2,4-Trimethylpentane	540-84-1	750	MDEQ
2-Chloro-1,3-butadiene	126-99-8	6	EPA RfC
2-Propanol	67-63-0	3,000	EPA RfC
3-Chloropropene	107-05-1	32	EPA RfC
Acetaldehyde	75-07-0	5	EPA RfC
Acetone	67-64-1	13,000	ATSDR Chr. MRL
Acetonitrile	75-05-8	36	EPA RfC
Acrylonitrile	107-13-1	1	EPA RfC
Benzene	71-43-2	3	ATSDR Chr. MRL
Benzyl chloride	100-44-7	0.2	EPA RfC
Bromodichloromethane	75-27-4	0.01	EPA RSL
Bromoform	75-25-2	0.2	EPA RSL
Bromomethane	74-83-9	5	ATSDR Chr. MRL
Butane	106-97-8	10,000	MDEQ
Carbon disulfide	75-15-0	200	EPA RfC
Carbon tetrachloride	56-23-5	30	ATSDR Chr. MRL
Chlorobenzene	108-90-7	10	EPA RfC
Chloroethane	75-00-3	4,000	EPA RfC
Chloroform	67-66-3	20	ATSDR Chr. MRL
Chloromethane	74-87-3	50	ATSDR Chr. MRL
cis-1,2-dichloroethene	156-59-2	9	MDEQ
cis-1,3-Dichloropropene*	10061-02-6	4	MDEQ
Cumene	98-82-8	80	EPA RfC
Cyclohexane	110-82-7	2,000	EPA RfC
Cyclohexane,methyl	108-87-2	4,000	MDEQ

Chemical Name	Chemical Abstract Service Number	Screening Level in parts per billion by volume (ppbv)	Source of Screening Level
Cyclopentane	287-92-3	6,000	MDEQ
Dibromochloromethane	124-48-1	0.01	EPA RSL
Dichlorodifluoromethane	75-71-8	20	EPA RfC
Ethyl Acetate	141-78-6	890	MDEQ
Ethyl benzene	100-41-4	60	ATSDR Chr. MRL
Heptane	142-82-5	850	MDEQ
Hexachlorobutadiene	87-68-3	0.01	EPA RSL
Hexane	110-54-3	200	EPA RfC
Isobutane	75-28-5	10,000	MDEQ
Methyl butyl ketone	591-78-6	10	EPA RfC
Methyl ethyl ketone	78-93-3	2,000	EPA RfC
Methyl isobutyl ketone	108-10-1	700	EPA RfC
Methyl tert-butyl ether	1634-04-4	700	ATSDR Chr. MRL
Methylene chloride	75-09-2	300	ATSDR Chr. MRL
Napthalene	91-20-3	1	ATSDR Chr. MRL
Nonane	111-84-2	40	EPA RfC
Pentane	109-66-0	300	EPA RfC
Propene	115-07-1	2,000	EPA RfC
Styrene	100-42-5	200	ATSDR Chr. MRL
Tetrachloroethene	127-18-4	40	ATSDR Chr. MRL
Tetrahydrofuran	109-99-9	6	MDEQ
Toluene	108-88-3	80	ATSDR Chr. MRL
trans-1,2-Dichloroethene	156-60-5	15	EPA RfC
trans-1,3-Dichloropropene*	10061-01-5	0.5	MDEQ
Trichloroethene	79-01-6	2	EPA RfC
Trichlorofluoromethane	75-69-4	130	EPA RfC
Vinyl acetate	108-05-4	10	ATSDR Int. MRL
Vinyl bromide	593-60-2	1	EPA RfC
Vinyl chloride	75-01-4	30	ATSDR Int. MRL
Xylenes	1330-20-7	50	EPA RfC

* MDEQ provisional screening value for Dichloropropene based on a 1 in 100,000 cancer risk

ATSDR Chr. MRL - The Agency for Toxic Substances and Disease Registry Chronic Minimal Risk Level (MRL) is the preferred screening level. The MRL is protective of daily human inhalation exposure for longer than a year, including sensitive individuals such as children, the elderly, and those with pre-existing illnesses.

EPA RfC - If no Chronic MRL is available, the screening level is the EPA Reference Concentration (RfC). The RfC is protective of daily human inhalation exposure over a lifetime, including sensitive individuals. For 2 chemicals, vinyl acetate and vinyl chloride, the ATSDR Intermediate (Int.) MRL was selected. These were developed more recently than the EPA RfC and were lower than the EPA RfC.

EPA RSL - If none of the above are available, the EPA Regional Screening Level (RSL) is used. The RSLs are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

MDEQ - If none of the above are available, the Michigan DEQ Air Quality Division, Air Toxics Screening Level is the screening level. The MDEQ screening levels are protective of daily human inhalation exposure over a lifetime, including sensitive individuals.

Attachment B

ProUCL Statistical Output for Target Analytes

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

1,2,4-TMB

General Statistics

Number of Valid Data	3232	Number of Detected Data	10
Number of Distinct Detected Data	5	Number of Non-Detect Data	3222
		Percent Non-Detects	99.69%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	9	Maximum Detected	2.197
Mean of Detected	3.32	Mean of Detected	1.009
SD of Detected	2.432	SD of Detected	0.625
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended
For all methods (except KM, DL/2, and ROS Methods),
Observations < Largest ND are treated as NDs

Number treated as Non-Detect	3232
Number treated as Detected	0
Single DL Non-Detect Percentage	100.00%

UCL Statistics

Normal Distribution Test with Detected Values Onl	
Shapiro Wilk Test Statistic	0.75
5% Shapiro Wilk Critical Value	0. 42
Data not Normal at 5% Significance Level	

Lognormal Distribution Test with Detected Values Onl	
Shapiro Wilk Test Statistic	0.907
5% Shapiro Wilk Critical Value	0. 42
Data appear Lognormal at 5% Significance Level	

ssuming Normal Distribution	
DL/2 Substitution Method	
Mean	1.515
SD	1.069
95% DL/2 (t) UCL	1.546
Maximum Likelihood stimate(ML) Method	N/
ML method failed to converge properl	

ssuming Lognormal Distribution	
DL/2 Substitution Method	
Mean	0.117
SD	0. 06
95% -Stat (DL/2) UCL	N/
Log ROS Method	
Mean in Log Scale	-4.20
SD in Log Scale	1.7
Mean in Original Scale	0.0716
SD in Original Scale	0.276
95% Percentile Bootstrap UCL	0.0 01
95% BC Bootstrap UCL	0.0 15

Gamma Distribution Test with Detected Values Onl	
k star (bias corrected)	2.00
Theta Star	1.653
nu star	40.17
-D Test Statistic	0.74
5% -D Critical Value	0.733
K-S Test Statistic	0.733
5% K-S Critical Value	0.269
Data not Gamma Distributed at 5% Significance Level	

Data Distribution Test with Detected Values Onl
Data appear Lognormal at 5% Significance Level

ssuming Gamma Distribution	
Gamma ROS Statistics using xtrapolated Data	
Minimum	0.00676
Maximum	103.3
Mean	67.69
Median	72.06
SD	25.07
k star	4.4 4
Theta star	15.1
Nu star	2 9 3
ppChi2	2 5
95% Gamma pproximate UCL	6 .62
95% djusted Gamma UCL	6 .62

Nonparametric Statistics	
Kaplan-Meier (KM) Method	
Mean	1.01
SD	0.195
S of Mean	0.00404
95% KM (t) UCL	1.017
95% KM ( ) UCL	1.017
95% KM (lackknife) UCL	1.652
95% KM (bootstrap t) UCL	1.01
95% KM (BC) UCL	2.01
95% KM (Percentile Bootstrap) UCL	2.009
95% KM (Cheb shev) UCL	1.02
97.5% KM (Cheb shev) UCL	1.035
99% KM (Cheb shev) UCL	1.05
Potential UCLs to Use	
95% KM (t) UCL	1.017
95% KM (% Bootstrap) UCL	2.009

Note: DL/2 is not a recommended method.

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

1,3,5-TMB

General Statistics

Number of Valid Data	3232	Number of Detected Data	3
Number of Distinct Detected Data	2	Number of Non-Detect Data	3229
		Percent Non-Detects	99.91%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	2	Maximum Detected	0.693
Mean of Detected	1.333	Mean of Detected	0.231
SD of Detected	0.577	SD of Detected	0.4
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended
For all methods (except KM, DL/2, and ROS Methods),
Observations < Largest ND are treated as NDs

Number treated as Non-Detect	3232
Number treated as Detected	0
Single DL Non-Detect Percentage	100.00%

Warning: Data set has only 2 Distinct Detected Values.
This may not be adequate enough to compute meaningful and reliable test statistics and estimates.
The Project Team may decide to use alternative site specific values to estimate environmental parameters (e.g., EPC, BTV).

Unless Data Quality Objectives (DQOs) have been met, it is suggested to collect additional observations.

The number of detected data may not be adequate enough to perform GOF tests, bootstrap, and ROS methods.
Those methods will return a 'N/A' value on your output display!

It is necessary to have 4 or more Distinct Values for bootstrap methods.
However, results obtained using 4 to 9 distinct values may not be reliable.
It is recommended to have 10 to 15 or more observations for accurate and meaningful results and estimates.

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.75
5% Shapiro Wilk Critical Value	0.767

Data not Normal at 5% Significance Level

Assuming Normal Distribution

DL/2 Substitution Method

Mean	1.507
SD	1.05
95% DL/2 (t) UCL	1.53

Maximum Likelihood Estimate(MLE) Method	N/A

MLE method failed to converge properly

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	N/A
Theta Star	N/A
nu star	N/A
A-D Test Statistic	N/A
5% A-D Critical Value	N/A
K-S Test Statistic	N/A
5% K-S Critical Value	N/A

Data not Gamma Distributed at 5% Significance Level

Assuming Gamma Distribution

Gamma ROS Statistics using Extrapolated Data

Minimum	N/A
Maximum	N/A
Mean	N/A
Median	N/A
SD	N/A
k star	N/A
Theta star	N/A
Nu star	N/A
AppChi2	N/A
95% Gamma Approximate UCL	N/A
95% Adjusted Gamma UCL	N/A

Note: DL/2 is not a recommended method.

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.75
5% Shapiro Wilk Critical Value	0.767

Data not Lognormal at 5% Significance Level

Assuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.113
SD	0.04
95% H-Stat (DL/2) UCL	N/A

Log ROS Method

Mean in Log Scale	-5.032
SD in Log Scale	1.652
Mean in Original Scale	0.025
SD in Original Scale	0.0754
95% Percentile Bootstrap UCL	0.0273
95% BCA Bootstrap UCL	0.027

Data Distribution Test with Detected Values Only

Data do not follow a Discernable Distribution (0.05)

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.001
SD	0.0247
SE of Mean	0.000747
95% KM (t) UCL	1.002
95% KM (z) UCL	1.002
95% KM (jackknife) UCL	1.002
95% KM (bootstrap t) UCL	N/A
95% KM (BCA) UCL	N/A
95% KM (Percentile Bootstrap) UCL	2
95% KM (Chebyshev) UCL	1.004
97.5% KM (Chebyshev) UCL	1.005
99% KM (Chebyshev) UCL	1.00

Potential UCLs to Use

95% KM (t) UCL	1.002
95% KM (% Bootstrap) UCL	2

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

4-Ethyltoluene

General Statistics

Number of Valid Data	3232	Number of Detected Data	3
Number of Distinct Detected Data	2	Number of Non-Detect Data	3229
		Percent Non-Detects	99.91%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	2	Maximum Detected	0.693
Mean of Detected	1.333	Mean of Detected	0.231
SD of Detected	0.577	SD of Detected	0.4
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended	Number treated as Non-Detect	3232
For all methods (except KM, DL/2, and ROS Methods),	Number treated as Detected	0
Observations < Largest ND are treated as NDs	Single DL Non-Detect Percentage	100.00%

Warning: Data set has only 2 Distinct Detected Values.

This may not be adequate enough to compute meaningful and reliable test statistics and estimates.

The Project Team may decide to use alternative site specific values to estimate environmental parameters (e.g., EPC, BTV).

Unless Data Quality Objectives (DQOs) have been met, it is suggested to collect additional observations.

The number of detected data may not be adequate enough to perform GOF tests, bootstrap, and ROS methods.

Those methods will return a 'N/A' value on your output display!

It is necessary to have 4 or more Distinct Values for bootstrap methods.

However, results obtained using 4 to 9 distinct values may not be reliable.

It is recommended to have 10 to 15 or more observations for accurate and meaningful results and estimates.

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.75
5% Shapiro Wilk Critical Value	0.767

Data not Normal at 5% Significance Level

Assuming Normal Distribution

DL/2 Substitution Method

Mean	1.507
SD	1.05
95% DL/2 (t) UCL	1.53

Maximum Likelihood Estimate(MLE) Method	N/A

MLE method failed to converge properly

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.75
5% Shapiro Wilk Critical Value	0.767

Data not Lognormal at 5% Significance Level

Assuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.113
SD	0. 04
95% H-Stat (DL/2) UCL	N/A

Log ROS Method

Mean in Log Scale	-5.032
SD in Log Scale	1.652
Mean in Original Scale	0.025
SD in Original Scale	0.0754
95% Percentile Bootstrap UCL	0.0273
95% BCA Bootstrap UCL	0.0274

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	N/A
Theta Star	N/A
nu star	N/A
A-D Test Statistic	N/A
5% A-D Critical Value	N/A
K-S Test Statistic	N/A
5% K-S Critical Value	N/A

Data not Gamma Distributed at 5% Significance Level

Assuming Gamma Distribution

Gamma ROS Statistics using Extrapolated Data

Minimum	N/A
Maximum	N/A
Mean	N/A
Median	N/A
SD	N/A
k star	N/A
Theta star	N/A
Nu star	N/A
AppChi2	N/A
95% Gamma Approximate UCL	N/A
95% Adjusted Gamma UCL	N/A

Note: DL/2 is not a recommended method.

Data Distribution Test with Detected Values Only

Data do not follow a Discernable Distribution (0.05)

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.001
SD	0.0247
SE of Mean	0.000747
95% KM (t) UCL	1.002
95% KM ( ) UCL	1.002
95% KM (jackknife) UCL	1.002
95% KM (bootstrap t) UCL	N/A
95% KM (BCA) UCL	2
95% KM (Percentile Bootstrap) UCL	2
95% KM (Chebyshev) UCL	1.004
97.5% KM (Chebyshev) UCL	1.005
99% KM (Chebyshev) UCL	1.00

Potential UCLs to Use

95% KM (t) UCL	1.002
95% KM (% Bootstrap) UCL	2

General UCL Statistics for Data Sets with Non-Detects

User Selected Options

From File	C:\Users\loppor\Desktop\acetaldehyde.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

Acetaldehyde

General Statistics

Number of Valid Data	104	Number of Detected Data	15
Number of Distinct Detected Data	7	Number of Non-Detect Data	89
		Percent Non-Detects	85.58%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	15	Maximum Detected	2.708
Mean of Detected	5.533	Mean of Detected	1.101
SD of Detected	5.878	SD of Detected	1.157
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	4	Maximum Non-Detect	1.386

Note: Data have multiple DLs - Use of KM Method is recommended
For all methods (except KM, DL/2, and ROS Methods),
Observations < Largest ND are treated as NDs

Number treated as Non-Detect	99
Number treated as Detected	5
Single DL Non-Detect Percentage	95.19%

UCL Statistics

Normal Distribution Test with Detected Values Only	
Shapiro Wilk Test Statistic	0.724
5% Shapiro Wilk Critical Value	0.881
Data not Normal at 5% Significance Level	

Lognormal Distribution Test with Detected Values Only	
Shapiro Wilk Test Statistic	0.793
5% Shapiro Wilk Critical Value	0.881
Data not Lognormal at 5% Significance Level	

Assuming Normal Distribution	
DL/2 Substitution Method	
Mean	1.24
SD	2.803
95% DL/2 (t) UCL	1.697
Maximum Likelihood Estimate(MLE) Method	N/A
MLE yields a negative mean	

Assuming Lognormal Distribution	
DL/2 Substitution Method	
Mean	-0.421
SD	0.771
95% H-Stat (DL/2) UCL	0.886
Log ROS Method	
Mean in Log Scale	-3.18
SD in Log Scale	2.691
Mean in Original Scale	0.877
SD in Original Scale	2.899
95% Percentile Bootstrap UCL	1.381
95% BCA Bootstrap UCL	1.482

Gamma Distribution Test with Detected Values Only	
k star (bias corrected)	0.807
Theta Star	6.86
nu star	24.2
A-D Test Statistic	1.469
5% A-D Critical Value	0.765
K-S Test Statistic	0.765
5% K-S Critical Value	0.228
Data not Gamma Distributed at 5% Significance Level	

Assuming Gamma Distribution	
Gamma ROS Statistics using Extrapolated Data	
Minimum	1E-09
Maximum	150.8
Mean	57.95
Median	50.57
SD	47.44
k star	0.48
Theta star	120.6
Nu star	99.93
AppChi2	77.87
95% Gamma Approximate UCL	74.36
95% Adjusted Gamma UCL	74.62

Note: DL/2 is not a recommended method.

Data Distribution Test with Detected Values Only
Data do not follow a Discernable Distribution (0.05)

Nonparametric Statistics	
Kaplan-Meier (KM) Method	
Mean	1.654
SD	2.681
SE of Mean	0.272
95% KM (t) UCL	2.106
95% KM (z) UCL	2.102
95% KM (jackknife) UCL	2.093
95% KM (bootstrap t) UCL	2.342
95% KM (BCA) UCL	2.106
95% KM (Percentile Bootstrap) UCL	2.135
95% KM (Chebyshev) UCL	2.841
97.5% KM (Chebyshev) UCL	3.354
99% KM (Chebyshev) UCL	4.362
Potential UCLs to Use	
95% KM (BCA) UCL	2.106

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

Benzene

General Statistics

Number of Valid Data	3234	Number of Detected Data	5
Number of Distinct Detected Data	4	Number of Non-Detect Data	3229
		Percent Non-Detects	99.85%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	4	Maximum Detected	1.386
Mean of Detected	2.2	Mean of Detected	0.636
SD of Detected	1.304	SD of Detected	0.63
Minimum Non-Detect	0.2	Minimum Non-Detect	-1.609
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended
For all methods (except KM, DL/2, and ROS Methods),
Observations < Largest ND are treated as NDs

Number treated as Non-Detect	3234
Number treated as Detected	0
Single DL Non-Detect Percentage	100.00%

Warning: There are only 4 Distinct Detected Values in this data

Note: It should be noted that even though bootstrap may be performed on this data set
the resulting calculations may not be reliable enough to draw conclusions

It is recommended to have 10-15 or more distinct observations for accurate and meaningful results.

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.902
5% Shapiro Wilk Critical Value	0.□62

Data appear Normal at 5% Significance Level

□ssuming Normal Distribution

DL/2 Substitution Method

Mean	1.509
SD	1.059
95% DL/2 (t) UCL	1.539

Maximum Likelihood □stimate(ML□) Method	N/□

ML□ method failed to converge properly

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.886
5% Shapiro Wilk Critical Value	0.□62

Data appear Lognormal at 5% Significance Level

□ssuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.113
SD	0.806
95% □-Stat (DL/2) UCL	N/□

Log ROS Method	
Mean in Log Scale	-6.315
SD in Log Scale	2.2□8
Mean in Original Scale	0.0223
SD in Original Scale	0.133
95% Percentile Bootstrap UCL	0.0263
95% BC□ Bootstrap UCL	0.02□3

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	1.505
Theta Star	1.462
nu star	15.05
□-D Test Statistic	0.365
5% □-D Critical Value	0.682
K-S Test Statistic	0.682
5% K-S Critical Value	0.359

Data appear Gamma Distributed at 5% Significance Level

□ssuming Gamma Distribution

Gamma ROS Statistics using □xtrapolated Data

Minimum	0.151
Maximum	4
Mean	1.101
Median	1.028
SD	0.621
k star	2.635
Theta star	0.418
Nu star	1□046
□ppChi2	16□43
95% Gamma □pproximate UCL	1.121
95% □d□usted Gamma UCL	1.121

Data Distribution Test with Detected Values Only

Data appear Normal at 5% Significance Level

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.004
SD	0.092
S□ of Mean	0.00253
95% KM (t) UCL	1.008
95% KM (z) UCL	1.008
95% KM (□ackknife) UCL	1.00□
95% KM (bootstrap t) UCL	1.009
95% KM (BC□) UCL	3.001
95% KM (Percentile Bootstrap) UCL	2.004
95% KM (Chebyshev) UCL	1.015
9□.5% KM (Chebyshev) UCL	1.019
99% KM (Chebyshev) UCL	1.029

Potential UCLs to Use

95% KM (t) UCL	1.008
95% KM (Percentile Bootstrap) UCL	2.004

Note: DL/2 is not a recommended method.

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

Cyclohexane

General Statistics

Number of Valid Data	3234	Number of Detected Data	30
Number of Distinct Detected Data	10	Number of Non-Detect Data	3204
		Percent Non-Detects	99.07%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	20	Maximum Detected	2.996
Mean of Detected	4.333	Mean of Detected	0.979
SD of Detected	5.208	SD of Detected	0.941
Minimum Non-Detect	0.5	Minimum Non-Detect	-0.693
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended
For all methods (except KM, DL/2, and ROS Methods),
Observations < Largest ND are treated as NDs

Number treated as Non-Detect	3234
Number treated as Detected	0
Single DL Non-Detect Percentage	100.00%

UCL Statistics

Normal Distribution est with Detected Values Only

Shapiro Wilk est Statistic	0.654
5% Shapiro Wilk Critical Value	0.927

Data not Normal at 5% Significance Level

 ssuming Normal Distribution

DL/2 Substitution Method

Mean	1.541
SD	1.195
95% DL/2 (t) UCL	1.575

Maximum Likelihood stimate(ML) Method	N/

ML method failed to converge properly

Lognormal Distribution est with Detected Values Only

Shapiro Wilk est Statistic	0.871
5% Shapiro Wilk Critical Value	0.927

Data not Lognormal at 5% Significance Level

 ssuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.126
SD	0.81
95% -Stat (DL/2) UCL	N/

Log ROS Method	
Mean in Log Scale	-5.355
SD in Log Scale	2.441
Mean in Original Scale	0.0876
SD in Original Scale	0.667
95% Percentile Bootstrap UCL	0.108
95% BC Bootstrap UCL	0.114

Gamma Distribution est with Detected Values Only

k star (bias corrected)	1.07
heta Star	4.05
nu star	64.2

-D est Statistic	1.822
5% -D Critical Value	0.771
K-S est Statistic	0.771
5% K-S Critical Value	0.164

Data not Gamma Distributed at 5% Significance Level

 ssuming Gamma Distribution

Gamma ROS Statistics using xtrapolated Data

Minimum	0.783
Maximum	20
Mean	2.577
Median	2.536
SD	1.154
k star	5.118
heta star	0.504
Nu star	33102
ppChi2	32680
95% Gamma pproximate UCL	2.611
95% dusted Gamma UCL	2.611

Note: DL/2 is not a recommended method.

Data Distribution est with Detected Values Only

Data do not follow a Discernable Distribution (0.05)

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.037
SD	0.599
S of Mean	0.0111
95% KM (t) UCL	1.055
95% KM ( ) UCL	1.055
95% KM (ackknife) UCL	1.055
95% KM (bootstrap t) UCL	1.063
95% KM (BC) UCL	1.056
95% KM (Percentile Bootstrap) UCL	1.056
95% KM (Chebyshev) UCL	1.086
97.5% KM (Chebyshev) UCL	1.107
99% KM (Chebyshev) UCL	1.148

Potential UCLs to Use

95% KM (t) UCL	1.055
95% KM (% Bootstrap) UCL	1.056

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

Ethylbenzene

General Statistics

Number of Valid Data	3232	Number of Detected Data	6
Number of Distinct Detected Data	4	Number of Non-Detect Data	3226
		Percent Non-Detects	99.81%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	6	Maximum Detected	1.792
Mean of Detected	2.667	Mean of Detected	0.78
SD of Detected	1.862	SD of Detected	0.7
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended	Number treated as Non-Detect	3232
For all methods (except KM, DL/2, and ROS Methods),	Number treated as Detected	0
Observations < Largest ND are treated as NDs	Single DL Non-Detect Percentage	100.00%

Warning: There are only 4 Distinct Detected Values in this data

Note: It should be noted that even though bootstrap may be performed on this data set
the resulting calculations may not be reliable enough to draw conclusions

It is recommended to have 10-15 or more distinct observations for accurate and meaningful results.

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.861
5% Shapiro Wilk Critical Value	0.788

Data appear Normal at 5% Significance Level

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.913
5% Shapiro Wilk Critical Value	0.788

Data appear Lognormal at 5% Significance Level

 ssuming Normal Distribution

DL/2 Substitution Method

Mean	1.511
SD	1.061
95% DL/2 (t) UCL	1.541

Maximum Likelihood Estimate(MLE) Method N/

MLE method failed to converge properly

 ssuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.114
SD	0.805
95% -Stat (DL/2) UCL	N/

Log ROS Method

Mean in Log Scale	-5.605
SD in Log Scale	2.079
Mean in Original Scale	0.0308
SD in Original Scale	0.165
95% Percentile Bootstrap UCL	0.0361
95% BC Bootstrap UCL	0.0369

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	1.436
Theta Star	1.858
nu star	17.23
-D Test Statistic	0.343
5% -D Critical Value	0.702
K-S Test Statistic	0.702
5% K-S Critical Value	0.335

Data appear Gamma Distributed at 5% Significance Level

 ssuming Gamma Distribution

Gamma ROS Statistics using Extrapolated Data

Minimum	0.274
Maximum	306.4
Mean	179.5
Median	188.2
SD	81.72
k star	2.947
Theta star	60.92
Nu star	19047
ppChi2	18727
95% Gamma pproximate UCL	182.6
95% djusted Gamma UCL	182.6

Note: DL/2 is not a recommended method.

Data Distribution Test with Detected Values Only

Data appear Normal at 5% Significance Level

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.005
SD	0.115
SE of Mean	0.00263
95% KM (t) UCL	1.009
95% KM (z) UCL	1.009
95% KM (ackknife) UCL	1.009
95% KM (bootstrap t) UCL	1.009
95% KM (BC) UCL	3.002
95% KM (Percentile Bootstrap) UCL	2.005
95% KM (Chebyshev) UCL	1.016
97.5% KM (Chebyshev) UCL	1.021
99% KM (Chebyshev) UCL	1.031

Potential UCLs to Use

95% KM (t) UCL	1.009
95% KM (Percentile Bootstrap) UCL	2.005

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

m,p-Xylene

General Statistics

Number of Valid Data	3232	Number of Detected Data	11
Number of Distinct Detected Data	7	Number of Non-Detect Data	3221
		Percent Non-Detects	99.66%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	2	Minimum Detected	0.693
Maximum Detected	19	Maximum Detected	2.944
Mean of Detected	5.818	Mean of Detected	1.445
SD of Detected	5.4	SD of Detected	0.794
Minimum Non-Detect	2	Minimum Non-Detect	0.693
Maximum Non-Detect	50	Maximum Non-Detect	3.912

Note: Data have multiple DLs - Use of KM Method is recommended	Number treated as Non-Detect	3232
For all methods (except KM, DL/2, and ROS Methods),	Number treated as Detected	0
Observations < Largest ND are treated as NDs	Single DL Non-Detect Percentage	100.00%

UCL Statistics

Normal Distribution est with Detected Values Only

Shapiro Wilk est Statistic	0.752
5% Shapiro Wilk Critical Value	0.85

Data not Normal at 5% Significance Level

 ssuming Normal Distribution

DL/2 Substitution Method

Mean	3.028
SD	2.131
95% DL/2 (t) UCL	3.089

Maximum Likelihood stimate(ML) Method	N/

ML method failed to converge properly

Lognormal Distribution est with Detected Values Only

Shapiro Wilk est Statistic	0.869
5% Shapiro Wilk Critical Value	0.85

Data appear Lognormal at 5% Significance Level

 ssuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.809
SD	0.805
95% -Stat (DL/2) UCL	N/

Log ROS Method

Mean in Log Scale	-5.698
SD in Log Scale	2.448
Mean in Original Scale	0.062
SD in Original Scale	0.488
95% Percentile Bootstrap UCL	0.0769
95% BC Bootstrap UCL	0.0804

Gamma Distribution est with Detected Values Only

k star (bias corrected)	1.32
heta Star	4.408
nu star	29.04

-D est Statistic	0.752
5% -D Critical Value	0.741
K-S est Statistic	0.741
5% K-S Critical Value	0.259

Data follow ppr. Gamma Distribution at 5% Significance Level

 ssuming Gamma Distribution

Gamma ROS Statistics using xtrapolated Data

Minimum	1 -09
Maximum	694.8
Mean	391.7
Median	408
SD	190.2
k star	2.356
heta star	166.3
Nu star	15227
ppChi2	14941
95% Gamma pproximate UCL	399.2
95% dusted Gamma UCL	399.2

Note: DL/2 is not a recommended method.

Data Distribution est with Detected Values Only

Data Follow ppr. Gamma Distribution at 5% Significance Level

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	2.015
SD	0.382
S of Mean	0.00731
95% KM (t) UCL	2.027
95% KM ( ) UCL	2.027
95% KM (ackknife) UCL	2.027
95% KM (bootstrap t) UCL	2.037
95% KM (BC) UCL	2.034
95% KM (Percentile Bootstrap) UCL	2.03
95% KM (Chebyshev) UCL	2.047
97.5% KM (Chebyshev) UCL	2.061
99% KM (Chebyshev) UCL	2.088

Potential UCLs to Use

95% KM (t) UCL	2.027

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

n-Heptane

General Statistics

Number of Valid Data	3232	Number of Detected Data	17
Number of Distinct Detected Data	6	Number of Non-Detect Data	3215
		Percent Non-Detects	99.47%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	14	Maximum Detected	2.639
Mean of Detected	3.118	Mean of Detected	0.708
SD of Detected	3.551	SD of Detected	0.885
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended		Number treated as Non-Detect	3232
For all methods (except KM, DL/2, and ROS Methods),		Number treated as Detected	0
Observations < Largest ND are treated as NDs		Single DL Non-Detect Percentage	100.00%

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.666
5% Shapiro Wilk Critical Value	0.892

Data not Normal at 5% Significance Level

Assuming Normal Distribution

DL/2 Substitution Method

Mean	1.52
SD	1.091
95% DL/2 (t) UCL	1.552

Maximum Likelihood Estimate(MLE) Method	N/A

MLE method failed to converge properly

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.793
5% Shapiro Wilk Critical Value	0.892

Data not Lognormal at 5% Significance Level

Assuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.119
SD	0.806
95% H-Stat (DL/2) UCL	N/A

Log ROS Method

Mean in Log Scale	-5.995
SD in Log Scale	2.417
Mean in Original Scale	0.0439
SD in Original Scale	0.354
95% Percentile Bootstrap UCL	0.0549
95% BCA Bootstrap UCL	0.0583

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	1.117
Theta Star	2.792
nu star	37.96

A-D Test Statistic	1.627
5% A-D Critical Value	0.76
K-S Test Statistic	0.76
5% K-S Critical Value	0.214

Data not Gamma Distributed at 5% Significance Level

Assuming Gamma Distribution

Gamma ROS Statistics using Extrapolated Data

Minimum	1E-09
Maximum	545.4
Mean	284.4
Median	290.4
SD	154.9
k star	1.697
Theta star	167.6
Nu star	10969
AppChi2	10727
95% Gamma Approximate UCL	290.8
95% Adjusted Gamma UCL	290.8

Note: DL/2 is not a recommended method.

Data Distribution Test with Detected Values Only

Data do not follow a Discernable Distribution (0.05)

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.013
SD	0.3
SE of Mean	0.00567
95% KM (t) UCL	1.023
95% KM (z) UCL	1.023
95% KM (jackknife) UCL	1.022
95% KM (bootstrap t) UCL	1.03
95% KM (BCA) UCL	1.023
95% KM (Percentile Bootstrap) UCL	1.023
95% KM (Chebyshev) UCL	1.038
97.5% KM (Chebyshev) UCL	1.049
99% KM (Chebyshev) UCL	1.07

Potential UCLs to Use

95% KM (t) UCL	1.023
95% KM (% Bootstrap) UCL	1.023

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

n-Hexane

General Statistics

Number of Valid Data	3234	Number of Detected Data	21
Number of Distinct Detected Data	3	Number of Non-Detect Data	3213
		Percent Non-Detects	99.35%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	3	Maximum Detected	1.099
Mean of Detected	1.619	Mean of Detected	0.388
SD of Detected	0.74	SD of Detected	0.437
Minimum Non-Detect	0.5	Minimum Non-Detect	-0.693
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended	Number treated as Non-Detect	3234
For all methods (except KM, DL/2, and ROS Methods),	Number treated as Detected	0
Observations < Largest ND are treated as NDs	Single DL Non-Detect Percentage	100.00%

Warning: There are only 3 Distinct Detected Values in this data set

The number of detected data may not be adequate enough to perform GOF tests, bootstrap, and ROS methods.

Those methods will return a 'N/A' value on your output display!

It is necessary to have 4 or more Distinct Values for bootstrap methods.

However, results obtained using 4 to 9 distinct values may not be reliable.

It is recommended to have 10 to 15 or more observations for accurate and meaningful results and estimates.

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.755
5% Shapiro Wilk Critical Value	0.908

Data not Normal at 5% Significance Level

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.75
5% Shapiro Wilk Critical Value	0.908

Data not Lognormal at 5% Significance Level

Assuming Normal Distribution

DL/2 Substitution Method

Mean	1.514
SD	1.057
95% DL/2 (t) UCL	1.544

Maximum Likelihood □ stimate(ML□) Method	N/A

ML□ method failed to converge properly

Assuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.118
SD	0.803
95% H-Stat (DL/2) UCL	N/A

Log ROS Method

Mean in Log Scale	-3.074
SD in Log Scale	1.338
Mean in Original Scale	0.112
SD in Original Scale	0.224
95% Percentile Bootstrap UCL	0.119
95% BCA Bootstrap UCL	0.119

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	4.737
Theta Star	0.342
nu star	198.9
A-D Test Statistic	2.411
5% A-D Critical Value	0.745
K-S Test Statistic	0.745
5% K-S Critical Value	0.19

Data not Gamma Distributed at 5% Significance Level

Assuming Gamma Distribution

Gamma ROS Statistics using □ xtrapolated Data

Minimum	1
Maximum	3
Mean	1.963
Median	1.993
SD	0.128
k star	211.5
Theta star	0.00928
Nu star	1367784
AppChi2	1365064
95% Gamma Approximate UCL	1.967
95% Ad□usted Gamma UCL	1.967

Note: DL/2 is not a recommended method.

Data Distribution Test with Detected Values Only

Data do not follow a Discernable Distribution (0.05)

Nonparametric Statistics

Kaplan-Meier (KM) Method

Mean	1.008
SD	0.107
S□ of Mean	0.00271
95% KM (t) UCL	1.012
95% KM (□) UCL	1.012
95% KM (□ackknife) UCL	1.012
95% KM (bootstrap t) UCL	1.014
95% KM (BCA) UCL	1.012
95% KM (Percentile Bootstrap) UCL	1.012
95% KM (Chebyshev) UCL	1.02
97.5% KM (Chebyshev) UCL	1.025
99% KM (Chebyshev) UCL	1.035

Potential UCLs to Use

95% KM (t) UCL	1.012
95% KM (% Bootstrap) UCL	1.012

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

Toluene

General Statistics

Number of Valid Data	3234	Number of Detected Data	457
Number of Distinct Detected Data	62	Number of Non-Detect Data	2777
		Percent Non-Detects	85.87%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	270	Maximum Detected	5.598
Mean of Detected	8.492	Mean of Detected	1.088
SD of Detected	24.39	SD of Detected	1.169
Minimum Non-Detect	0.4	Minimum Non-Detect	-0.916
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended
For all methods (except KM, DL/2, and ROS Methods),
Observations < Largest ND are treated as NDs

Number treated as Non-Detect	3206
Number treated as Detected	28
Single DL Non-Detect Percentage	99.13%

UCL Statistics

Normal Distribution Test with Detected Values Onl	
Lilliefors Test Statistic	0.379
5% Lilliefors Critical Value	0.0414
Data not Normal at 5% Significance Level	

Lognormal Distribution Test with Detected Values Onl	
Lilliefors Test Statistic	0.19
5% Lilliefors Critical Value	0.0414
Data not Lognormal at 5% Significance Level	

ssuming Normal Distribution	
DL/2 Substitution Method	
Mean	2.609
SD	9.515
95% DL/2 (t) UCL	2.885
Maximum Likelihood stimate(ML) Method	N/
ML ields a negative mean	

ssuming Lognormal Distribution	
DL/2 Substitution Method	
Mean	0.342
SD	0.912
95% -Stat (DL/2) UCL	N/
Log ROS Method	
Mean in Log Scale	-1.799
SD in Log Scale	2.044
Mean in Original Scale	1.517
SD in Original Scale	9.611
95% Percentile Bootstrap UCL	1.803
95% BC Bootstrap UCL	1.863

Gamma Distribution Test with Detected Values Onl	
k star (bias corrected)	0.587
Theta Star	14.46
nu star	536.6
-D Test Statistic	47.5
5% -D Critical Value	0.814
K-S Test Statistic	0.814
5% K-S Critical Value	0.0447
Data not Gamma Distributed at 5% Significance Level	

Data Distribution Test with Detected Values Onl
Data do not follow a Discernable Distribution (0.05)

ssuming Gamma Distribution	
Gamma ROS Statistics using xtrapolated Data	
Minimum	1 -09
Maximum	301.8
Mean	79.61
Median	52.68
SD	81.73
k star	0.23
Theta star	345.6
Nu star	1490
ppChi2	1401
95% Gamma pproximate UCL	84.65
95% djusted Gamma UCL	84.65

Note: DL/2 is not a recommended method.

Nonparametric Statistics	
Kaplan-Meier (KM) Method	
Mean	2.146
SD	9.522
S of Mean	0.168
95% KM (t) UCL	2.422
95% KM ( ) UCL	2.422
95% KM (jackknife) UCL	2.422
95% KM (bootstrap t) UCL	2.505
95% KM (BC) UCL	2.438
95% KM (Percentile Bootstrap) UCL	2.445
95% KM (Cheb shev) UCL	2.878
97.5% KM (Cheb shev) UCL	3.195
99% KM (Cheb shev) UCL	3.817
Potential UCLs to Use	
95% KM (BC) UCL	2.438

General UCL Statistics for Data Sets with Non-Detects

User Selected Options	
From File	WorkSheet.wst
Full Precision	OFF
Confidence Coefficient	95%
Number of Bootstrap Operations	2000

o-Xylene

General Statistics

Number of Valid Data	3232	Number of Detected Data	6
Number of Distinct Detected Data	4	Number of Non-Detect Data	3226
		Percent Non-Detects	99.81%

Raw Statistics		Log-transformed Statistics	
Minimum Detected	1	Minimum Detected	0
Maximum Detected	4	Maximum Detected	1.386
Mean of Detected	2.5	Mean of Detected	0.828
SD of Detected	1.049	SD of Detected	0.486
Minimum Non-Detect	1	Minimum Non-Detect	0
Maximum Non-Detect	25	Maximum Non-Detect	3.219

Note: Data have multiple DLs - Use of KM Method is recommended	Number treated as Non-Detect	3232
For all methods (except KM, DL/2, and ROS Methods),	Number treated as Detected	0
Observations < Largest ND are treated as NDs	Single DL Non-Detect Percentage	100.00%

Warning: There are only 4 Distinct Detected Values in this data

Note: It should be noted that even though bootstrap may be performed on this data set
the resulting calculations may not be reliable enough to draw conclusions

It is recommended to have 10-15 or more distinct observations for accurate and meaningful results.

UCL Statistics

Normal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.96
5% Shapiro Wilk Critical Value	0.□88

Data appear Normal at 5% Significance Level

□ssuming Normal Distribution

DL/2 Substitution Method

Mean	1.51
SD	1.059
95% DL/2 (t) UCL	1.541

Maximum Likelihood □stimate(ML□) Method	N/□

ML□ method failed to converge properly

Lognormal Distribution Test with Detected Values Only

Shapiro Wilk Test Statistic	0.918
5% Shapiro Wilk Critical Value	0.□88

Data appear Lognormal at 5% Significance Level

□ssuming Lognormal Distribution

DL/2 Substitution Method

Mean	0.115
SD	0.805
95% □-Stat (DL/2) UCL	N/□

Log ROS Method

Mean in Log Scale	-3.959
SD in Log Scale	1.598
Mean in Original Scale	0.06□4
SD in Original Scale	0.189
95% Percentile Bootstrap UCL	0.0□32
95% BC□ Bootstrap UCL	0.0□35

Gamma Distribution Test with Detected Values Only

k star (bias corrected)	3.033
Theta Star	0.824
nu star	36.4
□-D Test Statistic	0.316
5% □-D Critical Value	0.698
K-S Test Statistic	0.698
5% K-S Critical Value	0.333

Data appear Gamma Distributed at 5% Significance Level

□ssuming Gamma Distribution

Gamma ROS Statistics using □xtrapolated Data

Minimum	0.93□
Maximum	36.96
Mean	26.96
Median	28.68
SD	□.68□
k star	8.382
Theta star	3.216
Nu star	541□8
□ppChi2	53638
95% Gamma □pproximate UCL	2□.23
95% □d□usted Gamma UCL	2□.23

Note: DL/2 is not a recommended method.

Data Distribution Test with Detected Values Only

Data appear Normal at 5% Significance Level

Nonparametric Statistics

Kaplan-Meier (KM) Method

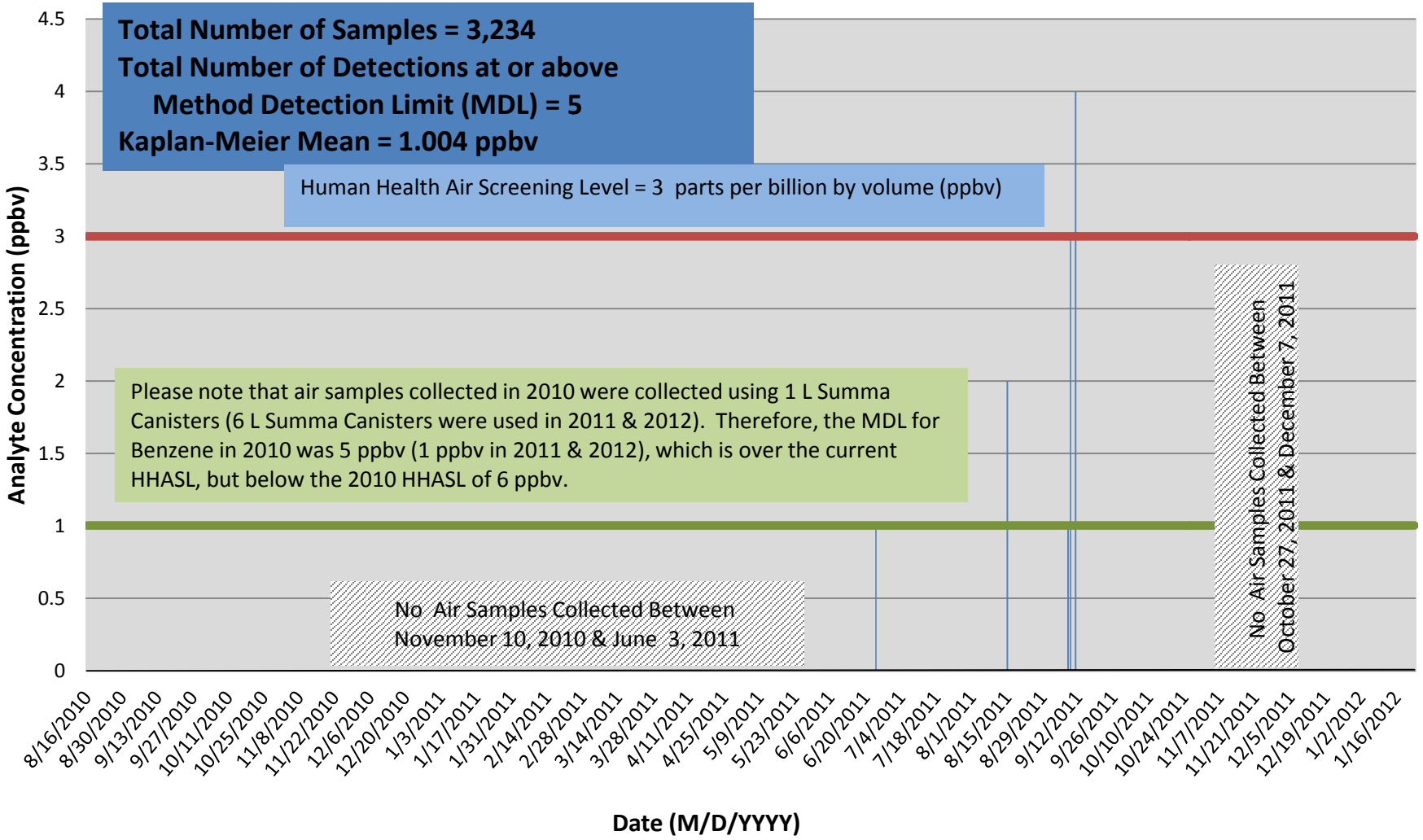
Mean	1.005
SD	0.10□
S□ of Mean	0.00289
95% KM (t) UCL	1.01
95% KM (□) UCL	1.01
95% KM (□ackknife) UCL	1.649
95% KM (bootstrap t) UCL	1.01
95% KM (BC□) UCL	3.001
95% KM (Percentile Bootstrap) UCL	2.00□
95% KM (Chebyshev) UCL	1.018
9□.5% KM (Chebyshev) UCL	1.024
99% KM (Chebyshev) UCL	1.034

Potential UCLs to Use

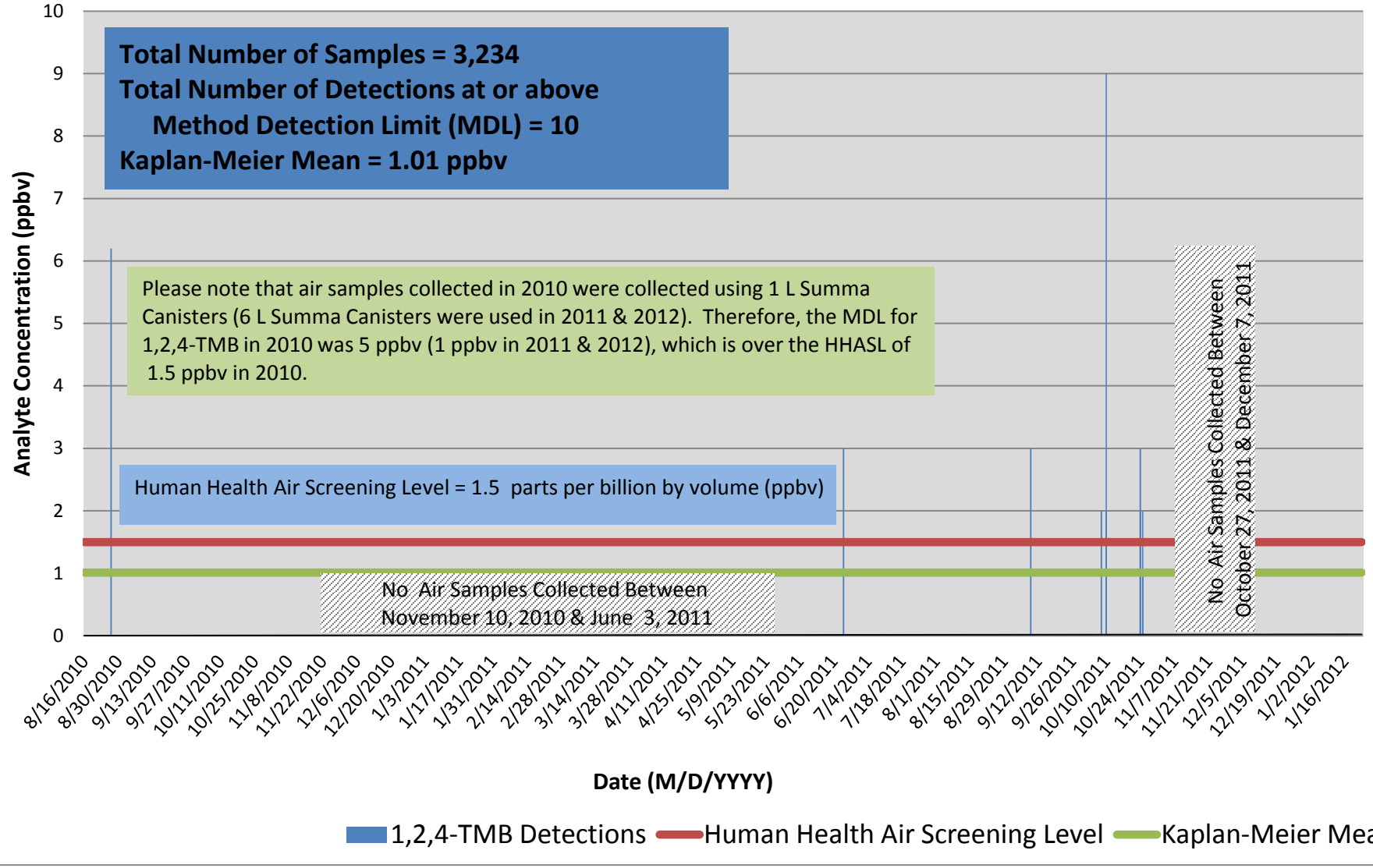
95% KM (t) UCL	1.01
95% KM (Percentile Bootstrap) UCL	2.00□

Attachment C
Charts for Select Analytes

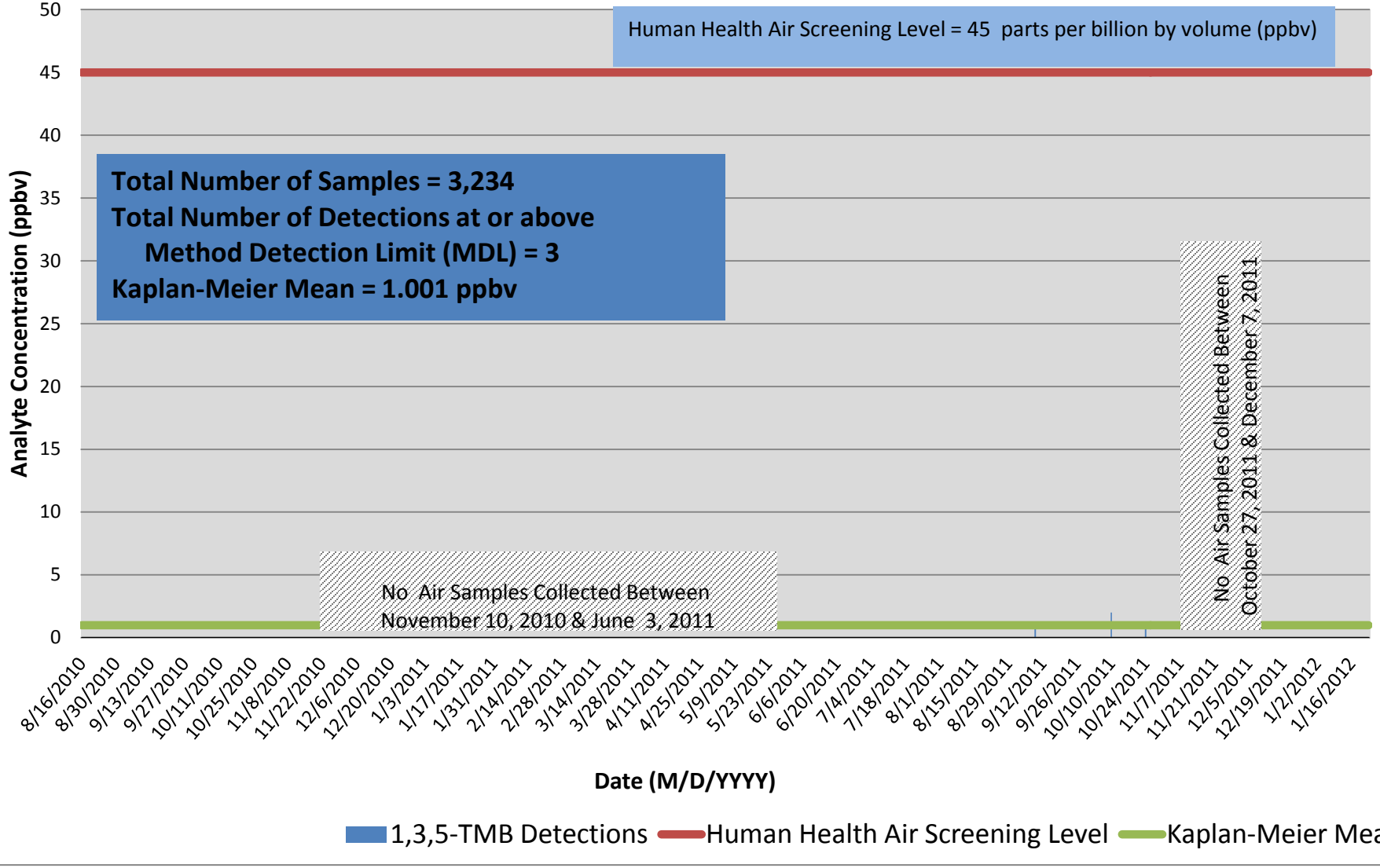
24-Hour Community Air Sampling Data
Benzene Detections
Time Period: 8/16/2010 - 1/23/2012



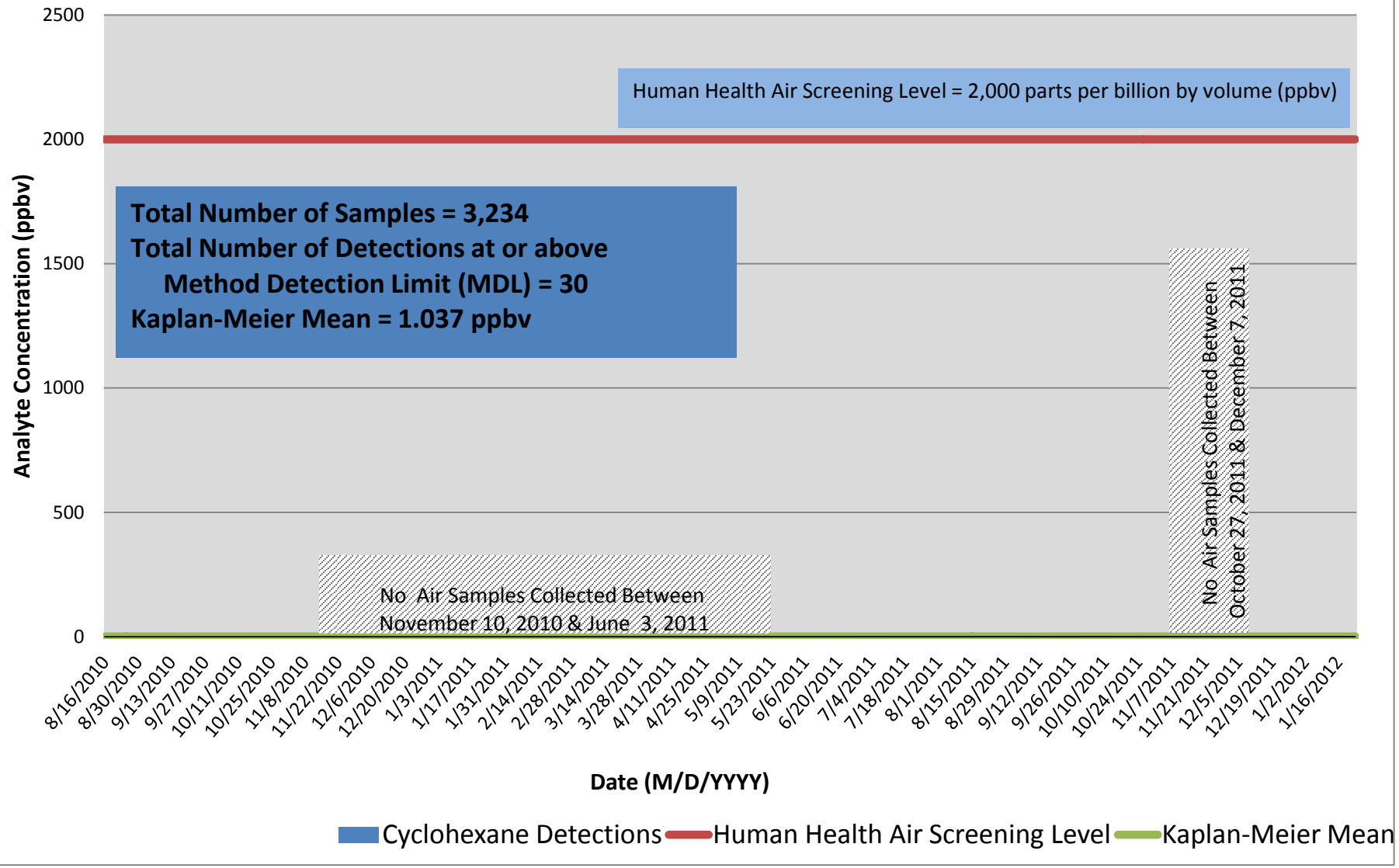
24-Hour Community Air Sampling Data
1,2,4-TMB Detections
Time Period: 8/16/2010 - 1/23/2012



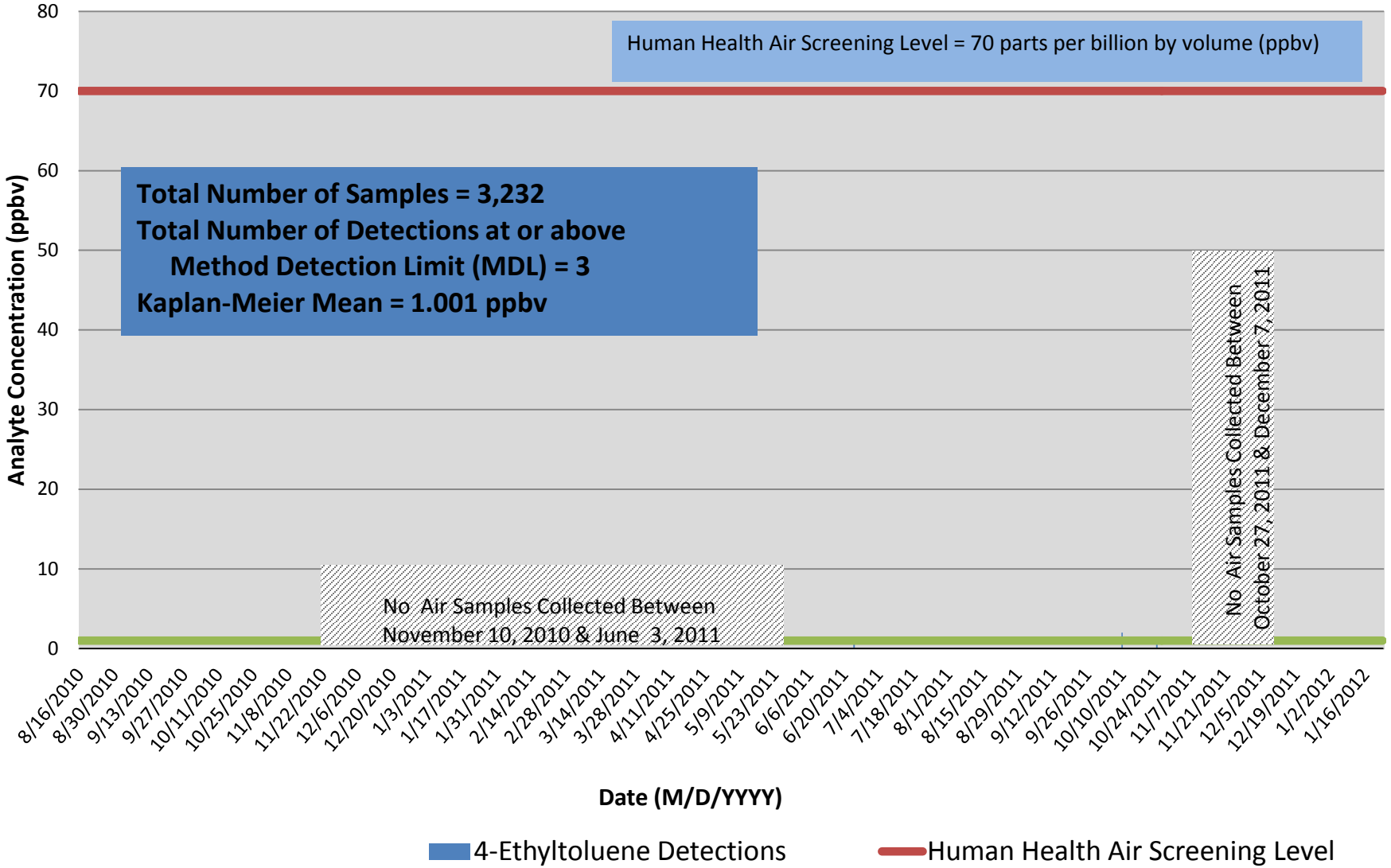
24-Hour Community Air Sampling Data
1,3,5-TMB Detections
Time Period: 8/16/2010 - 1/23/2012



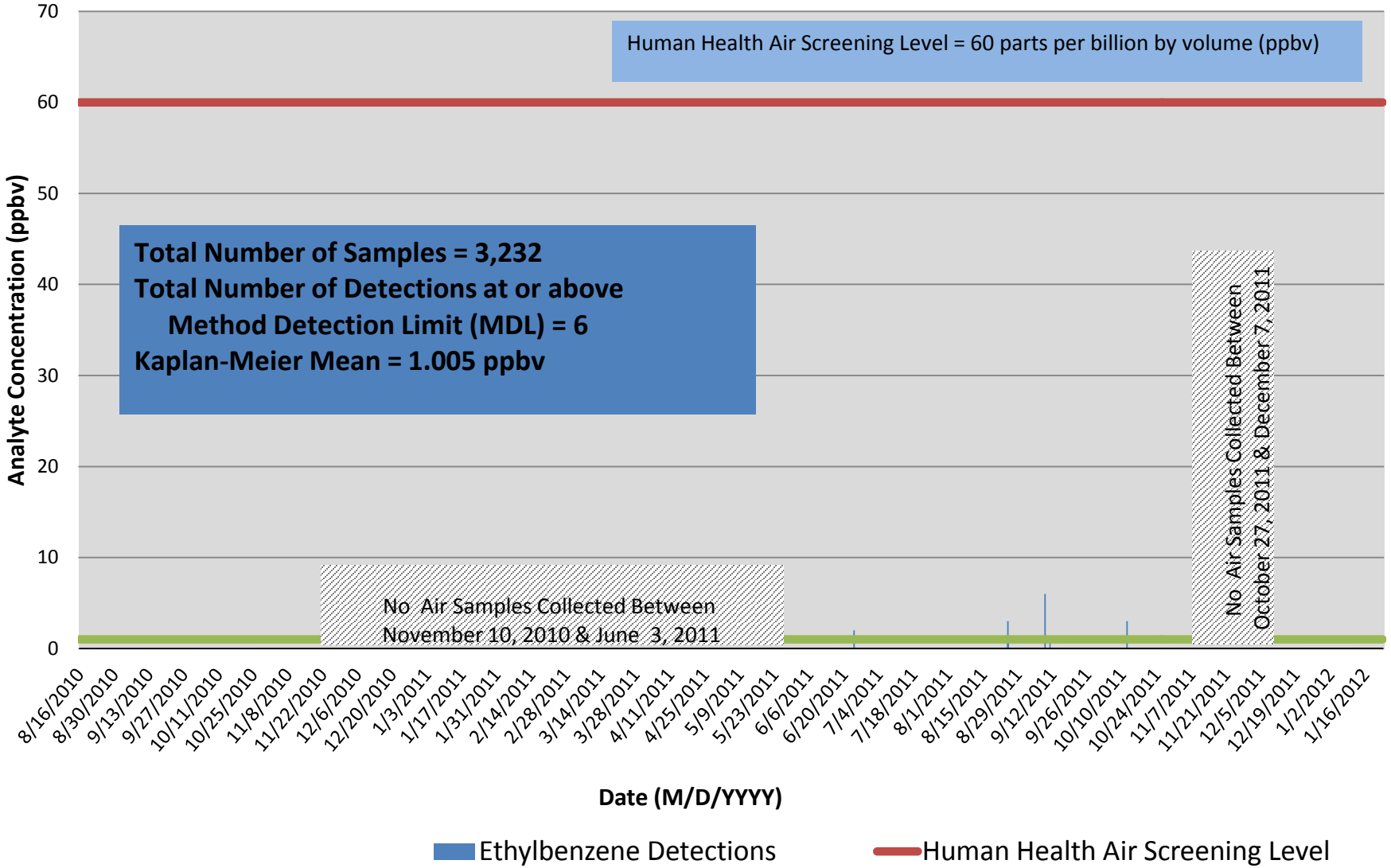
24-Hour Community Air Sampling Data
Cyclohexane Detections
Time Period: 8/16/2010 - 1/23/2012



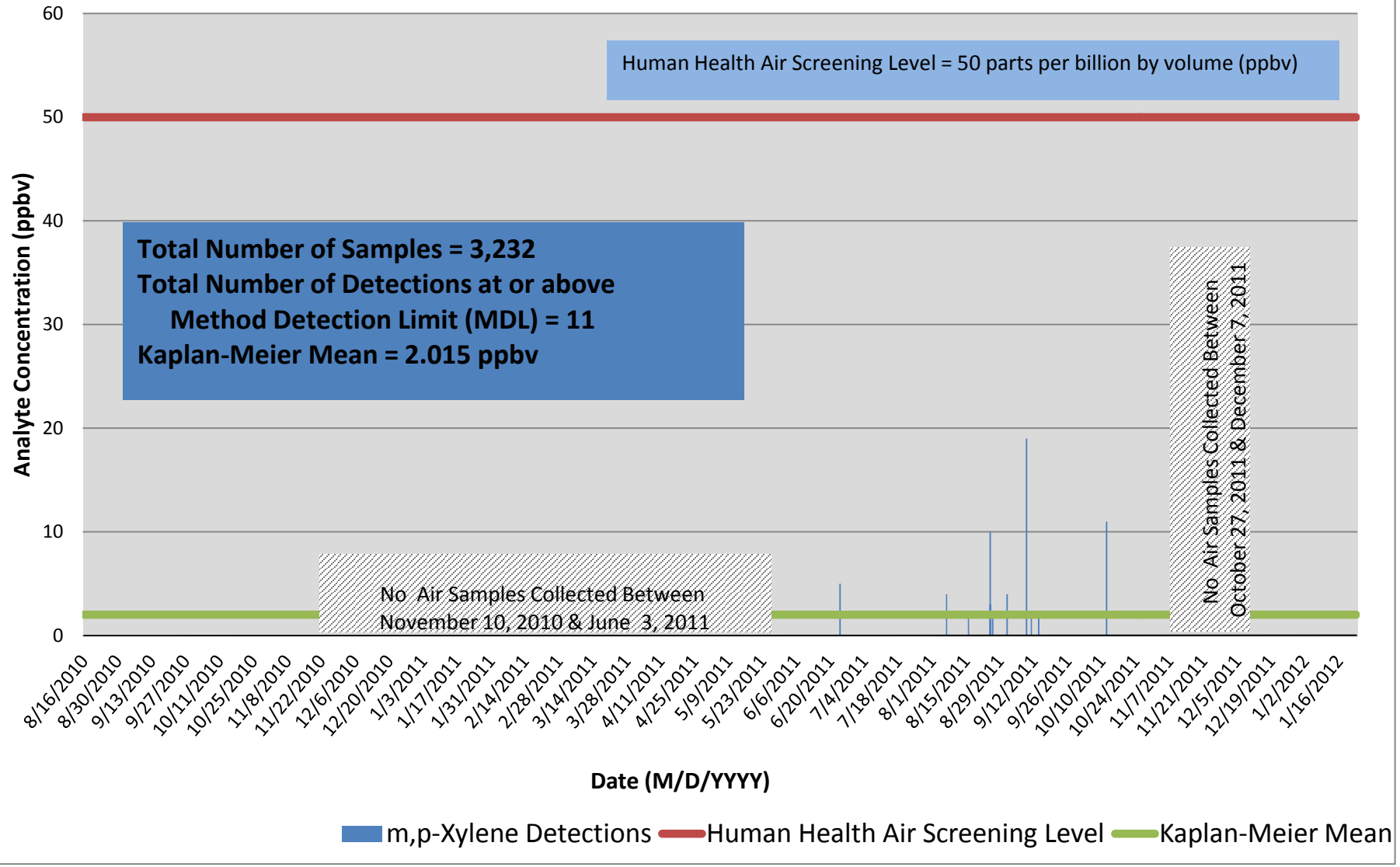
24-Hour Community Air Sampling Data
4-Ethyltoluene Detections
Time Period: 8/16/2010 - 1/23/2012



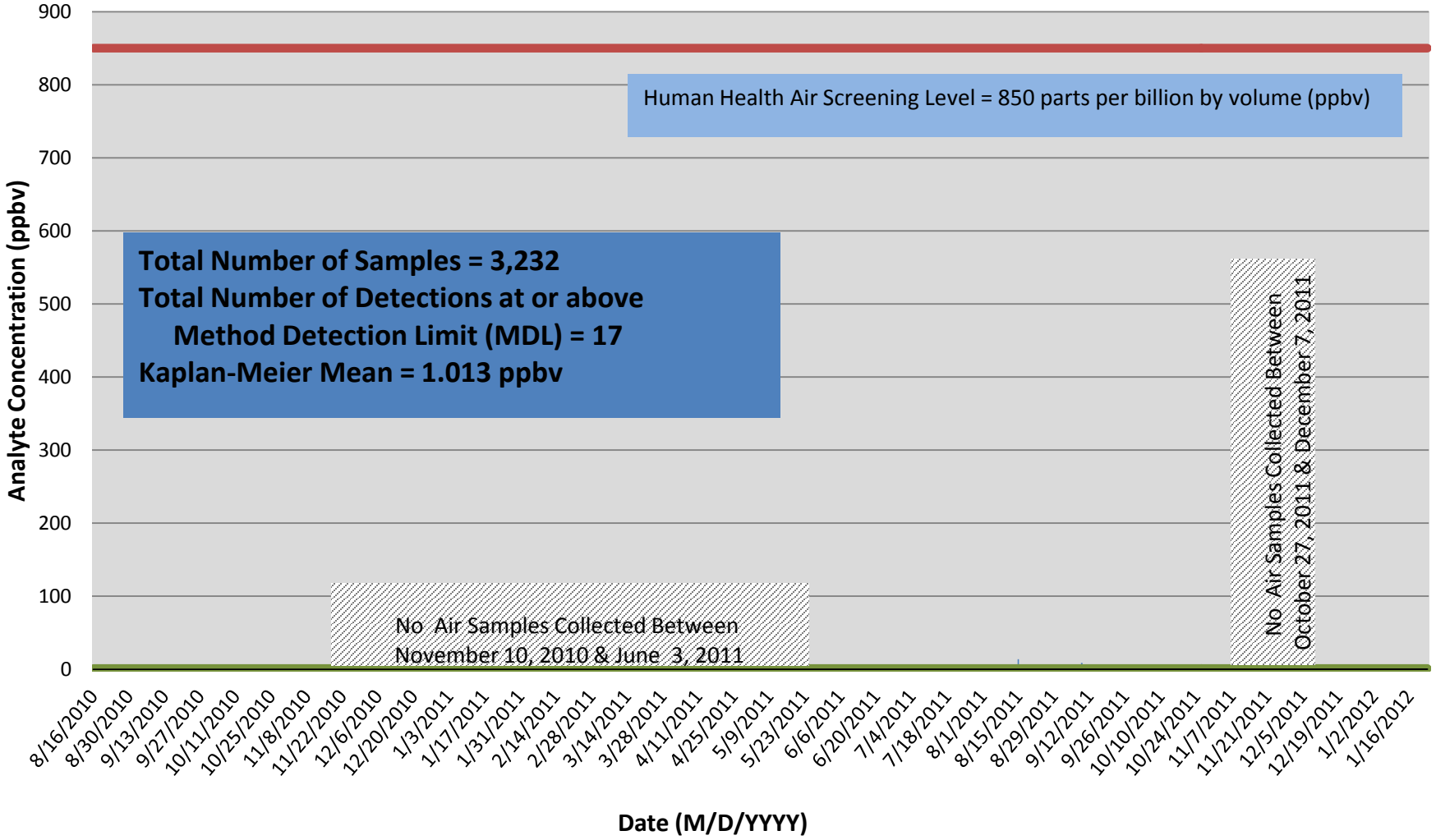
24-Hour Community Air Sampling Data
Ethylbenzene Detections
Time Period: 8/16/2010 - 1/23/2012



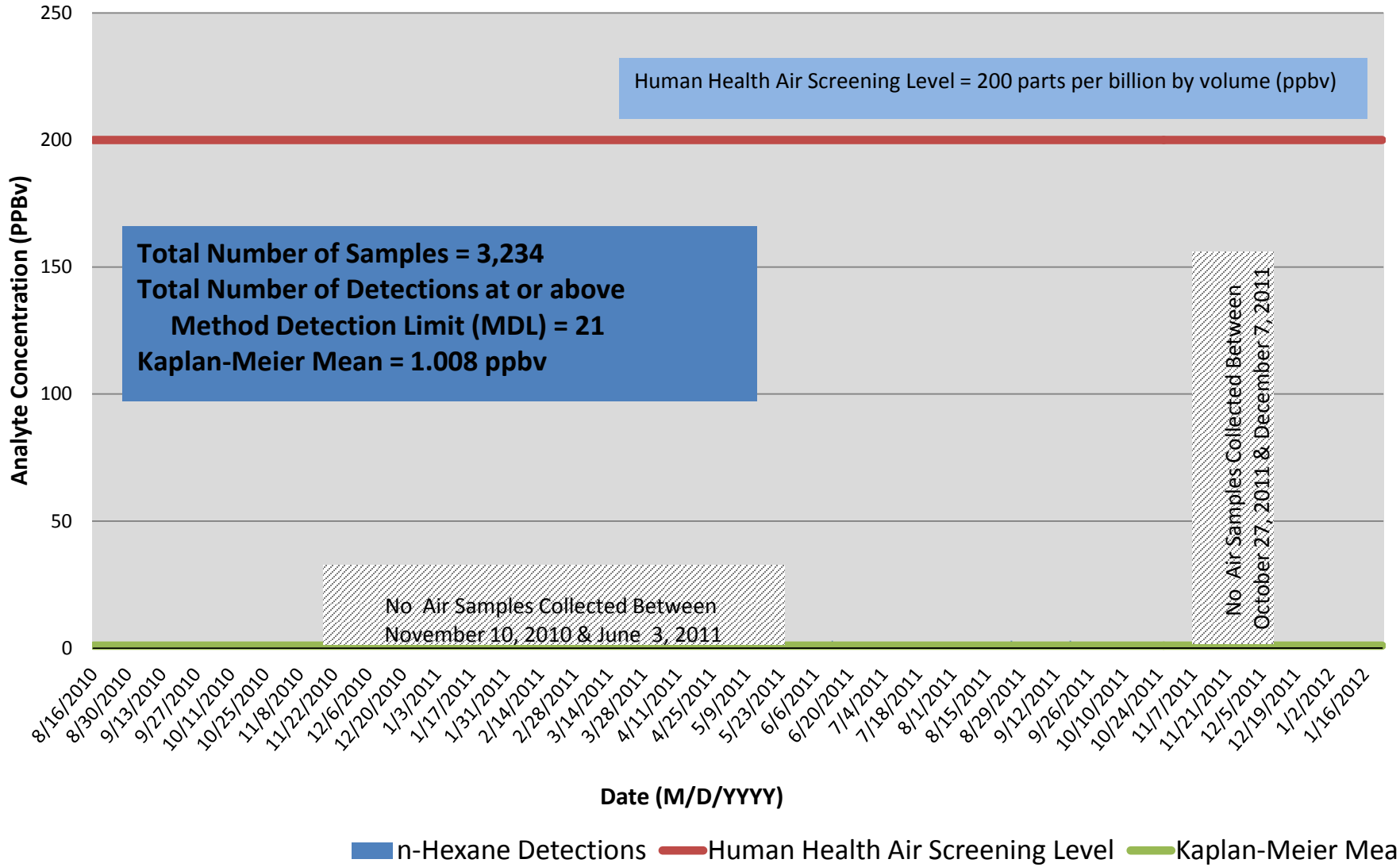
24-Hour Community Air Sampling Data
m,p-Xylene Detections
Time Period: 8/16/2010 - 1/23/2012



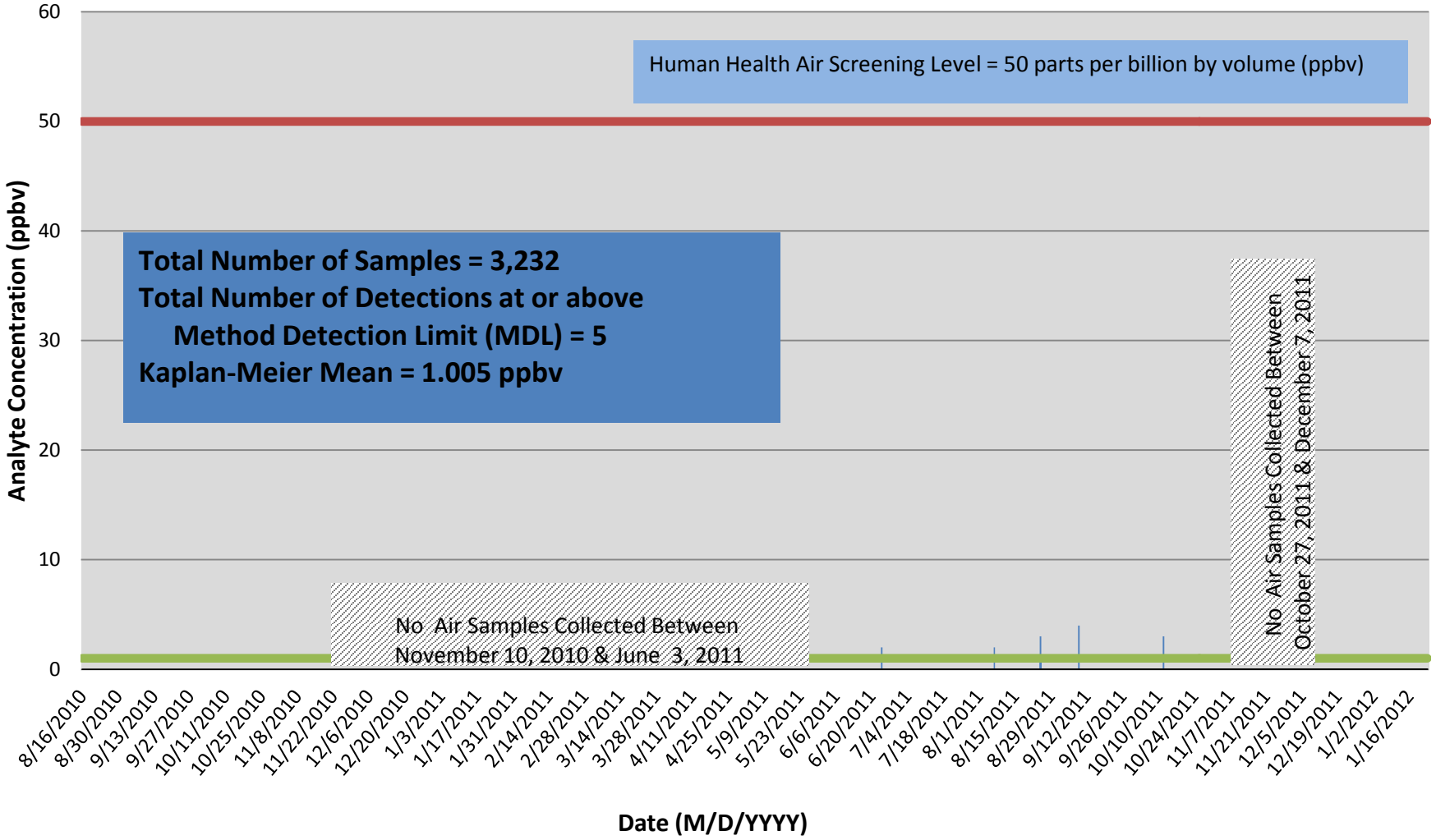
24-Hour Community Air Sampling Data
n-Heptane Detections
Time Period: 8/16/2010 - 1/23/2012



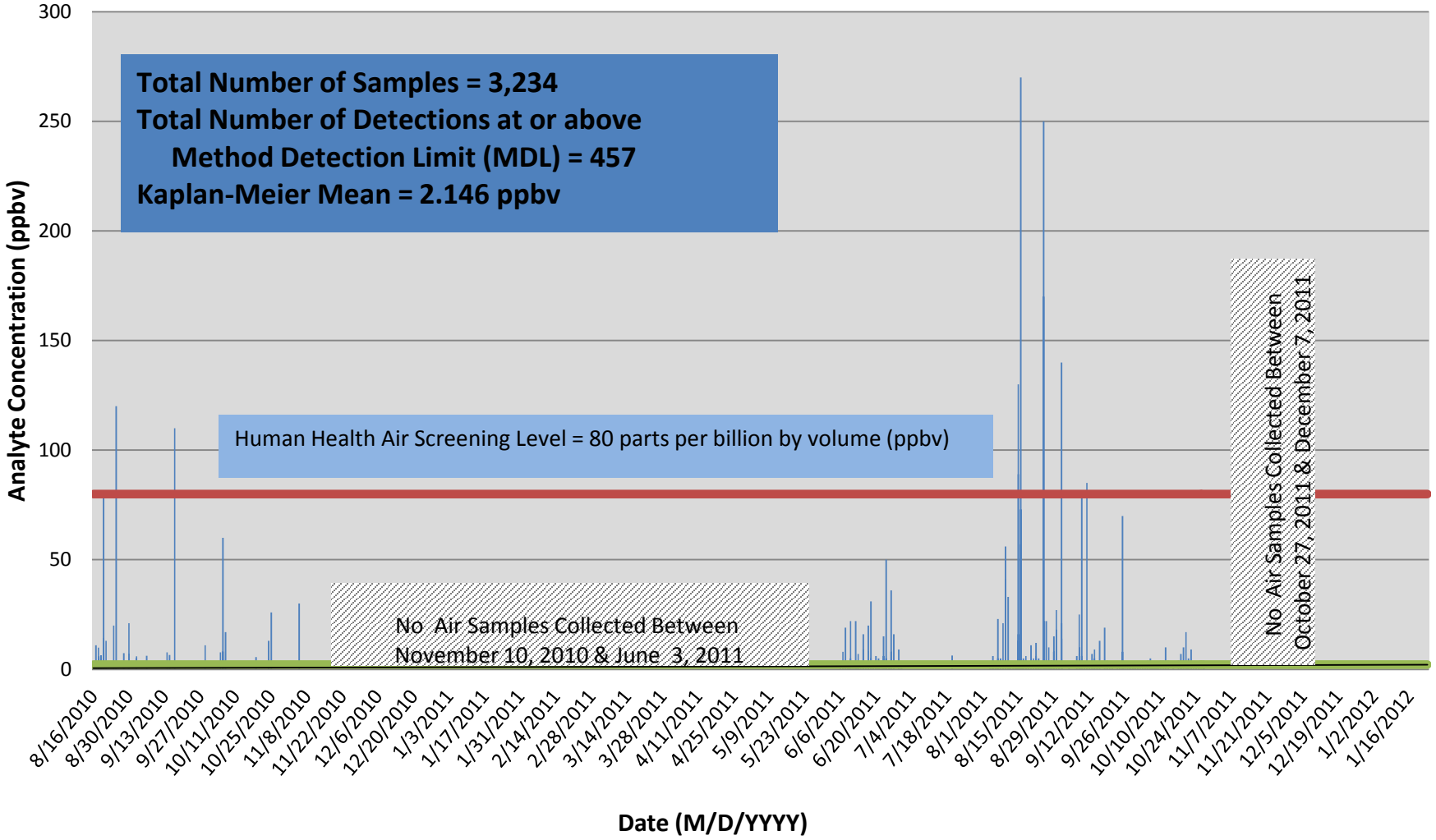
24-Hour Community Air Sampling Data
n-Hexane Detections
Time Period: 8/16/2010 - 1/23/2012



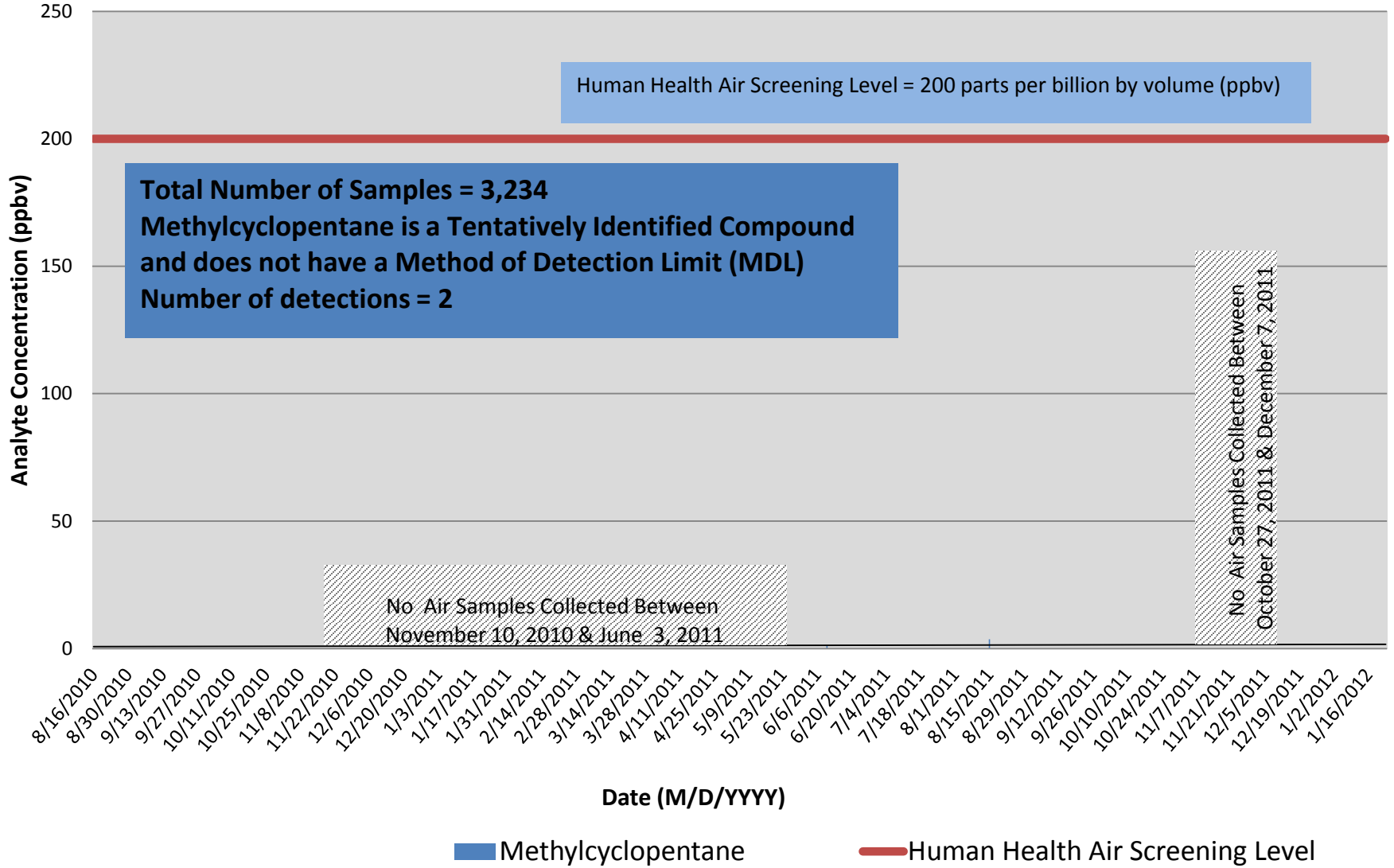
24-Hour Community Air Sampling Data
o-Xylene Detections
Time Period: 8/16/2010 - 1/23/2012



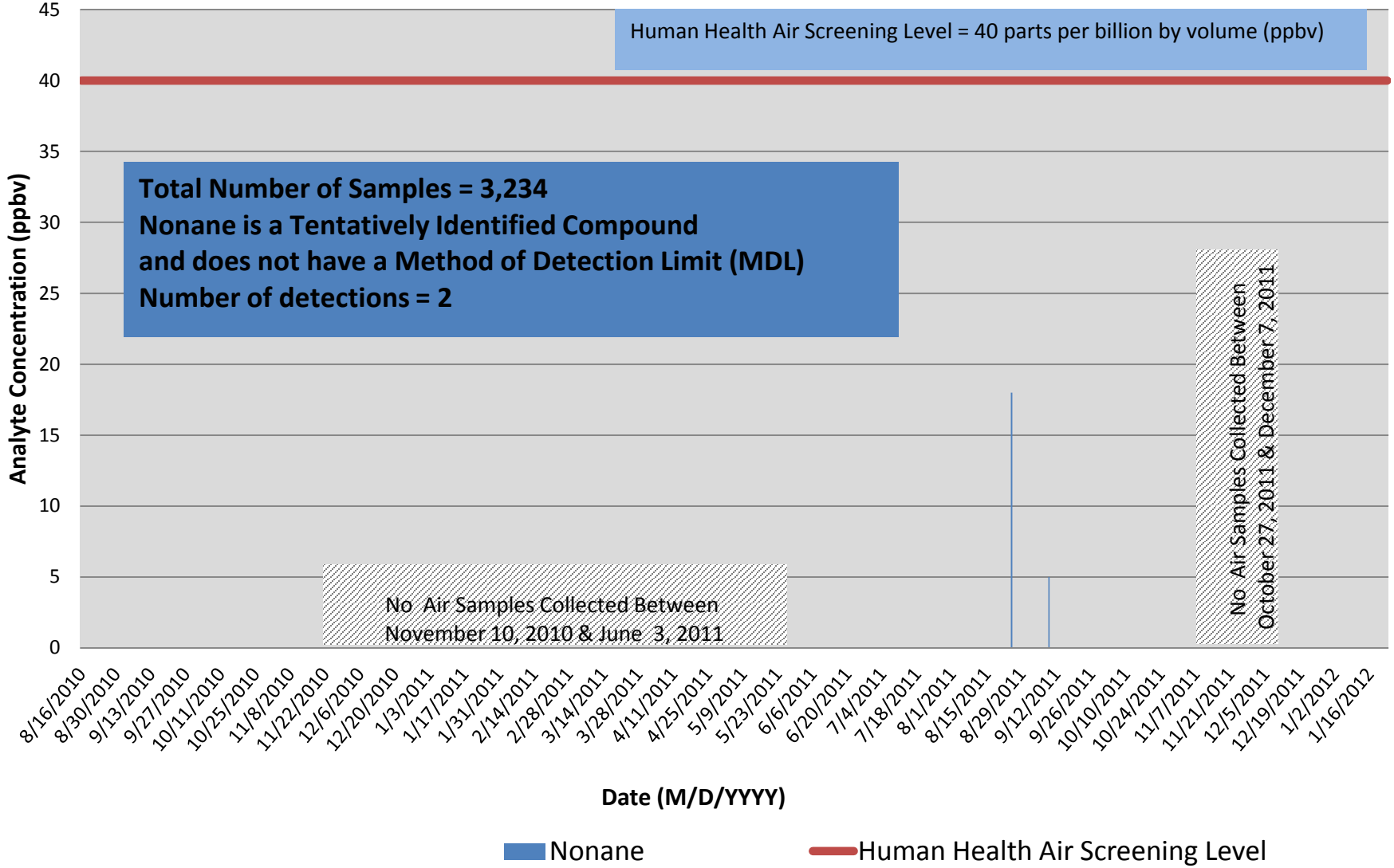
24-Hour Community Air Sampling Data
Toluene Detections
Time Period: 8/16/2010 - 1/23/2012



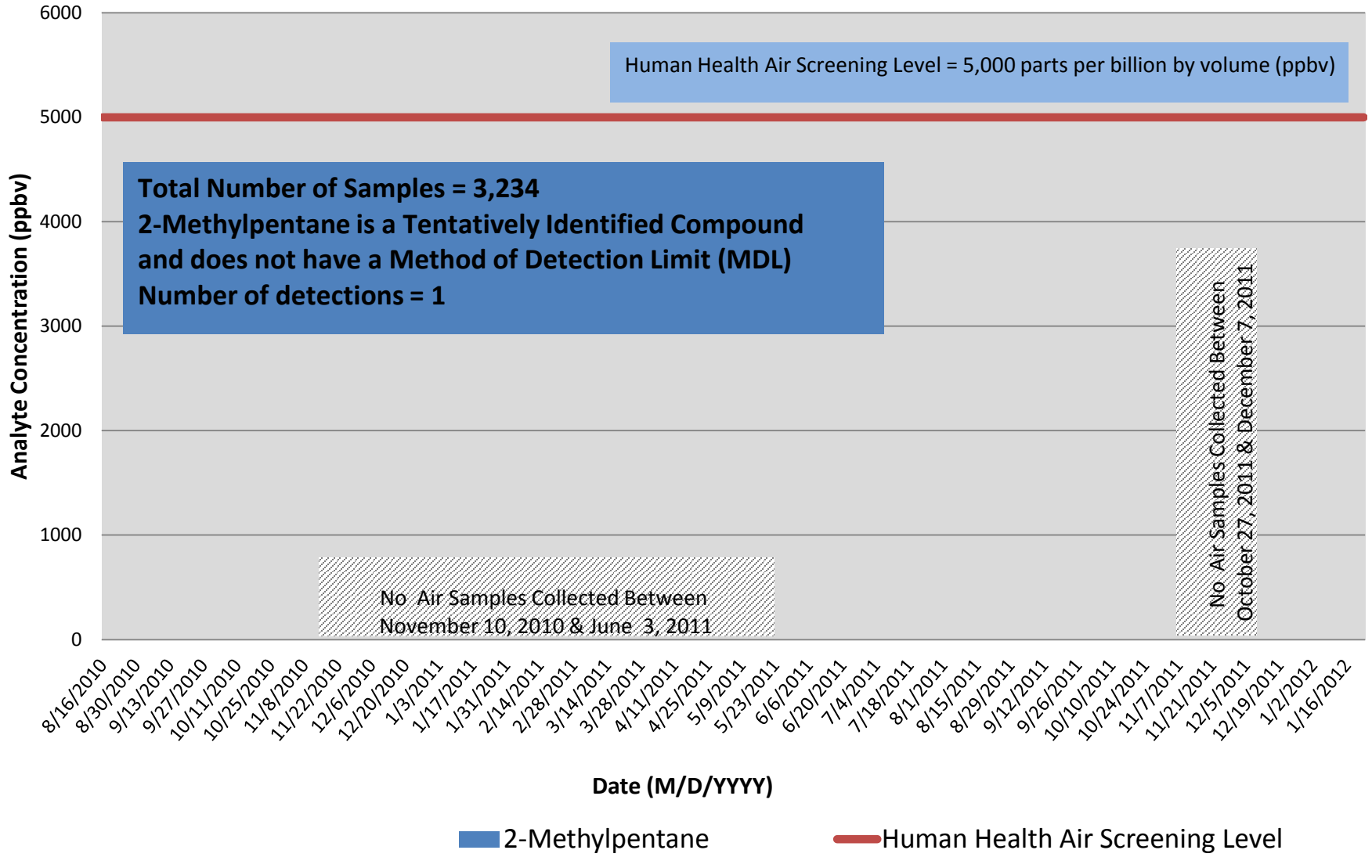
24-Hour Community Air Sampling Data
Methylcyclopentane Detections
Time Period: 8/16/2010 - 1/23/2012



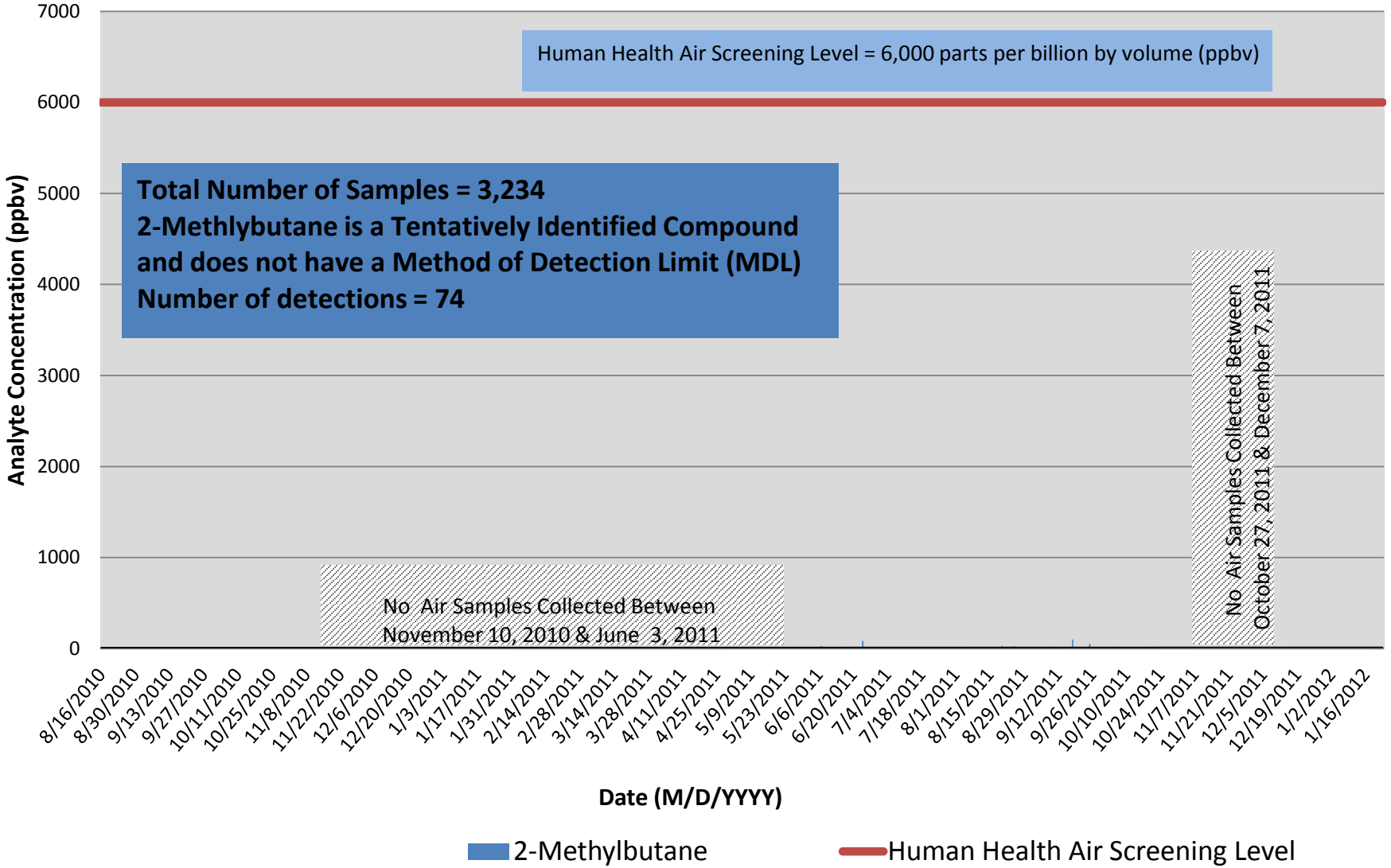
24-Hour Community Air Sampling Data
Nonane Detections
Time Period: 8/16/2010 - 1/23/2012



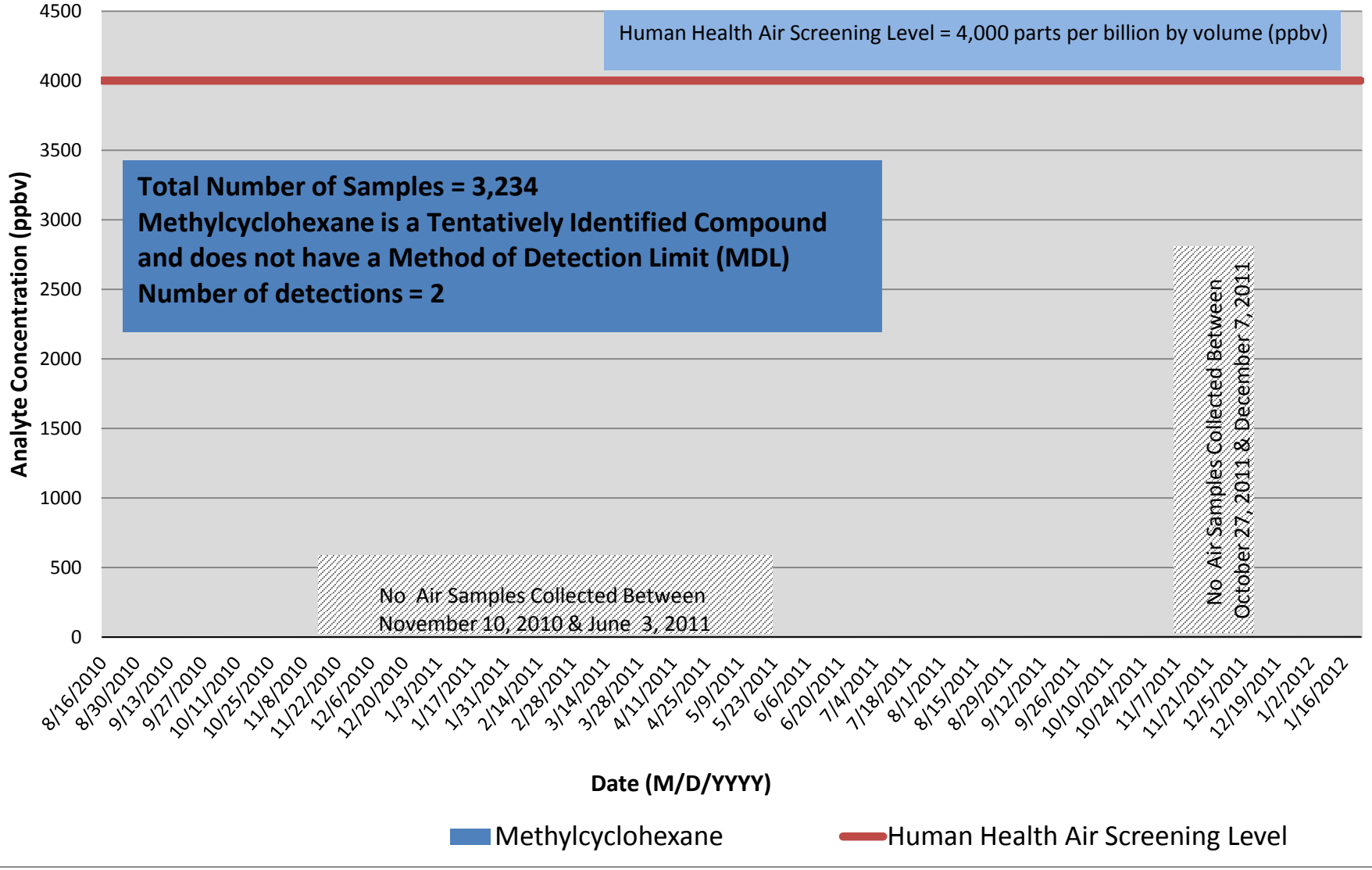
24-Hour Community Air Sampling Data
2-Methylpentane Detections
Time Period: 8/16/2010 - 1/23/2012

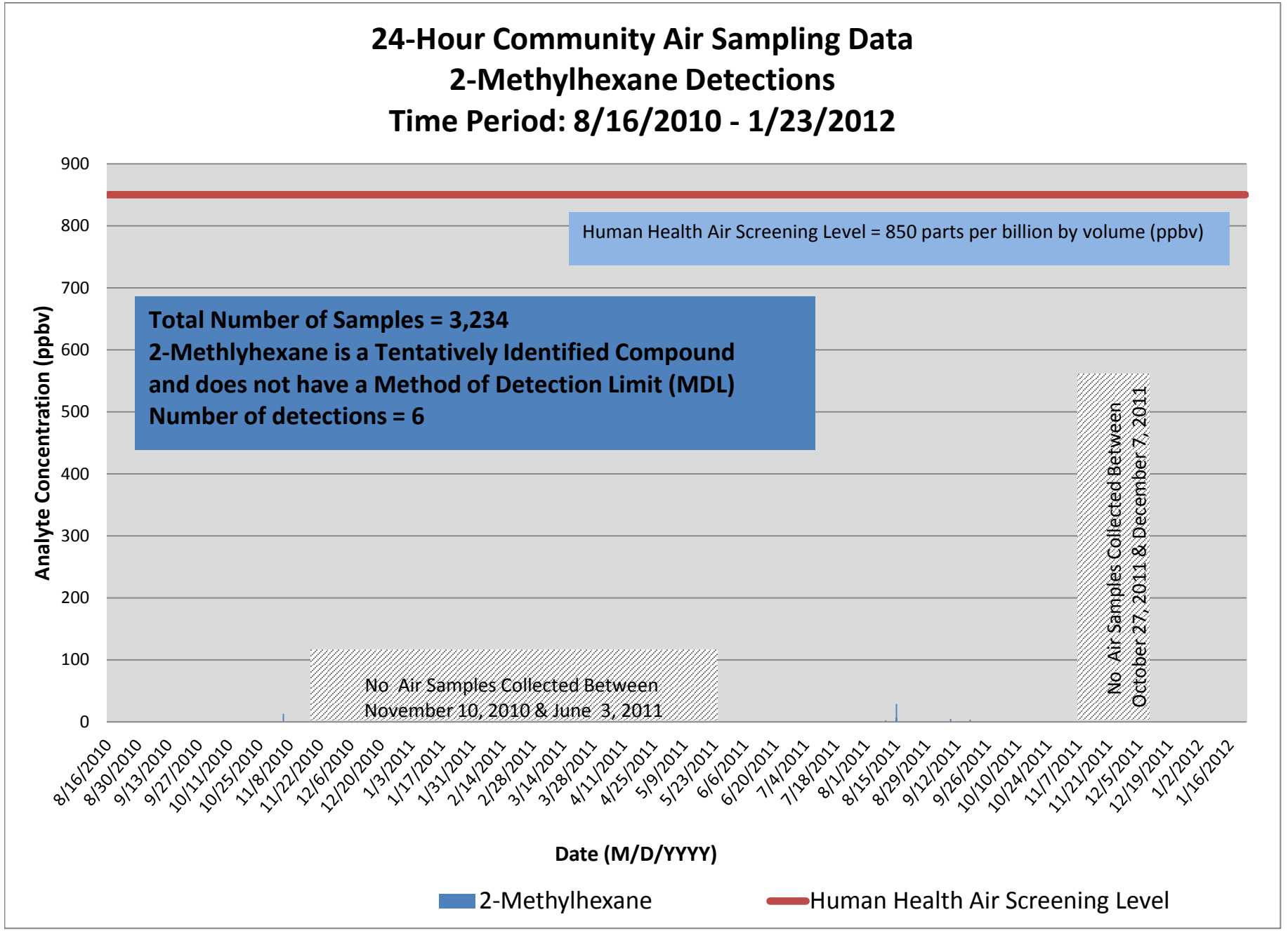


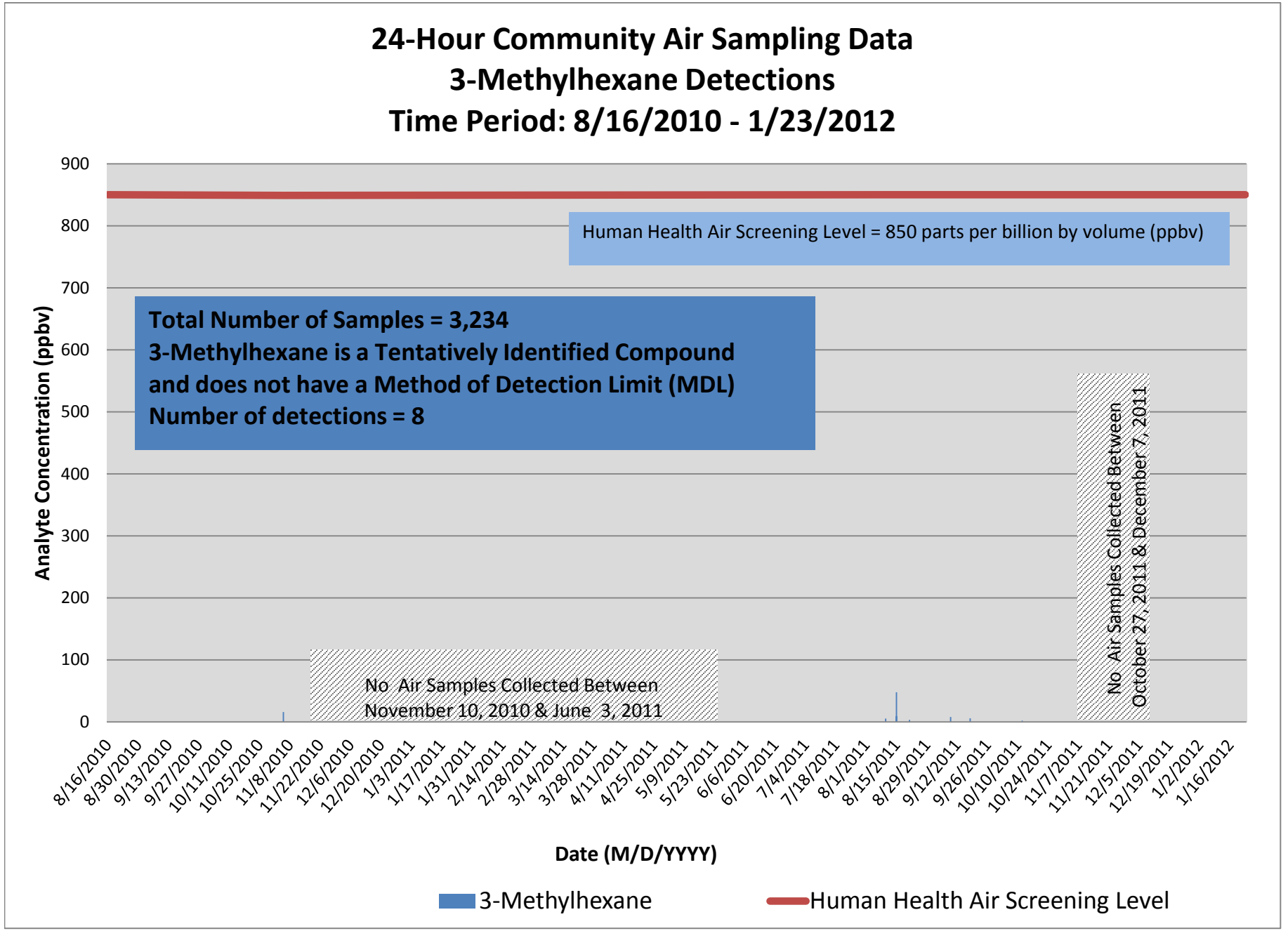
24-Hour Community Air Sampling Data
2-Methylbutane Detections
Time Period: 8/16/2010 - 1/23/2012



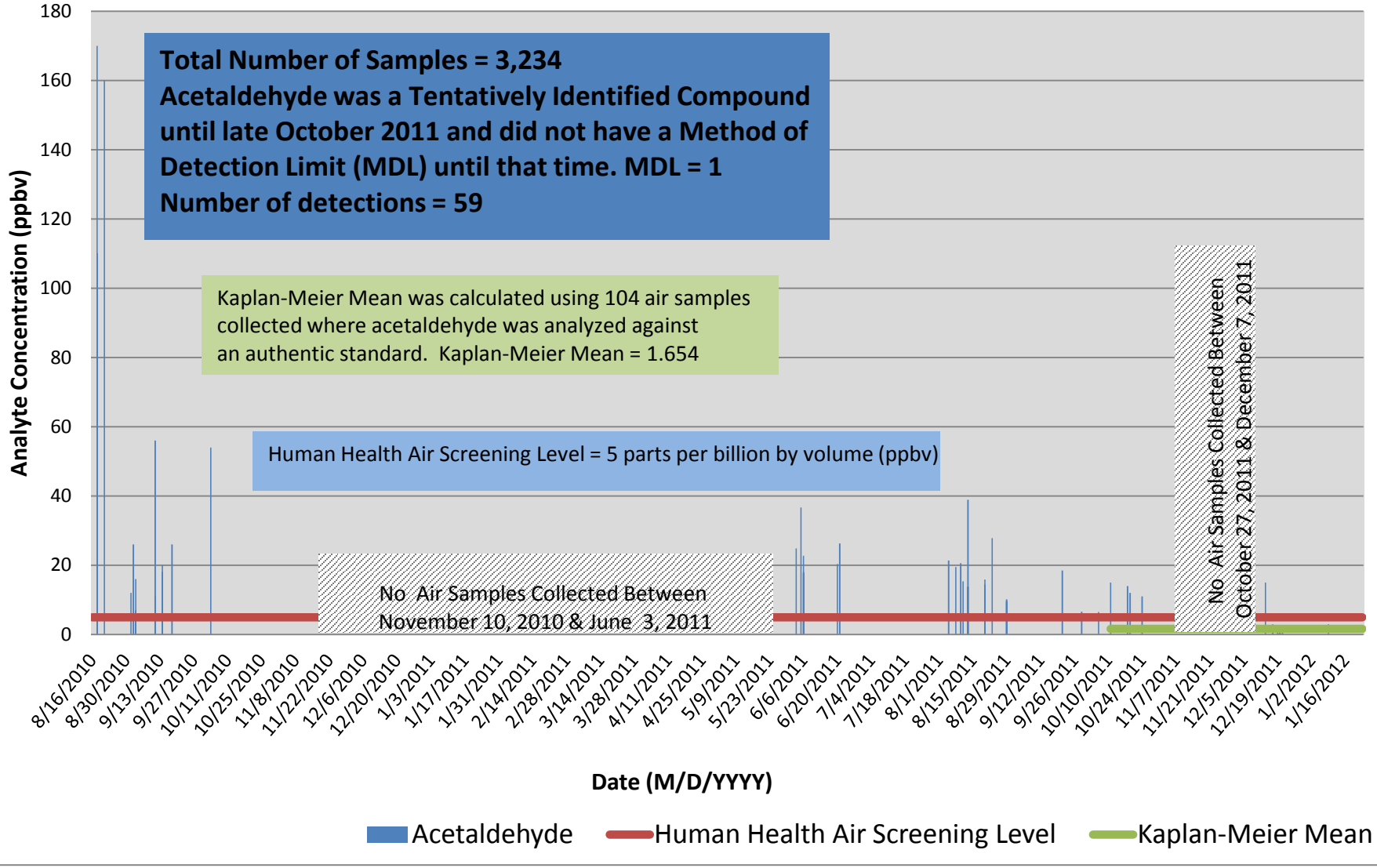
24-Hour Community Air Sampling Data
Methylcyclohexane Detections
Time Period: 8/16/2010 - 1/23/2012




24-Hour Community Air Sampling Data
2-Methylhexane Detections
Time Period: 8/16/2010 - 1/23/2012
Analyte Concentration (ppbv)
900
800
700
600
500
400
300
200
100
0
Human Health Air Screening Level = 850 parts per billion by volume (ppbv)
Total Number of Samples = 3,234
2-Methlyhexane is a Tentatively Identified Compound
and does not have a Method of Detection Limit (MDL)
Number of detections = 6
No Air Samples Collected Between
November 10, 2010 & June 3, 2011
No Air Samples Collected Between
October 27, 2011 & December 7, 2011
8/16/2010
8/30/2010
9/13/2010
9/27/2010
10/11/2010
10/25/2010
11/8/2010
11/22/2010
12/6/2010
12/20/2010
1/3/2011
1/17/2011
1/31/2011
2/14/2011
2/28/2011
3/14/2011
3/28/2011
4/11/2011
4/25/2011
5/9/2011
5/23/2011
6/6/2011
6/20/2011
7/4/2011
7/18/2011
8/1/2011
8/15/2011
8/29/2011
9/12/2011
9/26/2011
10/10/2011
10/24/2011
11/7/2011
11/21/2011
12/5/2011
12/19/2011
1/2/2012
1/16/2012
Date (M/D/YYYY)
2-Methylhexane
Human Health Air Screening Level


24-Hour Community Air Sampling Data
3-Methylhexane Detections
Time Period: 8/16/2010 - 1/23/2012
Analyte Concentration (ppbv)
900
800
700
600
500
400
300
200
100
0
Human Health Air Screening Level = 850 parts per billion by volume (ppbv)
Total Number of Samples = 3,234
3-Methylhexane is a Tentatively Identified Compound
and does not have a Method of Detection Limit (MDL)
Number of detections = 8
No Air Samples Collected Between
November 10, 2010 & June 3, 2011
No Air Samples Collected Between
October 27, 2011 & December 7, 2011
8/16/2010
8/30/2010
9/13/2010
9/27/2010
10/11/2010
10/25/2010
11/8/2010
11/22/2010
12/6/2010
12/20/2010
1/3/2011
1/17/2011
1/31/2011
2/14/2011
2/28/2011
3/14/2011
3/28/2011
4/11/2011
4/25/2011
5/9/2011
5/23/2011
6/6/2011
6/20/2011
7/4/2011
7/18/2011
8/1/2011
8/15/2011
8/29/2011
9/12/2011
9/26/2011
10/10/2011
10/24/2011
11/7/2011
11/21/2011
12/5/2011
12/19/2011
1/2/2012
1/16/2012
Date (M/D/YYYY)
3-Methylhexane
Human Health Air Screening Level

24-Hour Community Air Sampling Data
AcetaldehydeDetections
Time Period: 8/16/2010 - 1/23/2012



C) 00-20

Enbridge Line 6B MP 608 Pipeline Release

Supplement to Sampling and Analysis Plan

Air Sampling and Monitoring Plan

Ceresco Dam Dredging Operations

Ceresco, Michigan

Enbridge Energy

Revised: October 7, 2010

612773

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Quality Assurance Project Plan ..... Appendix 2

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 26, 2010. CTEH® is providing air monitoring, air sampling, and toxicology support to address public health concerns resulting from the crude oil spill and subsequent dredging operations. CTEH® has been conducting community air monitoring and sampling in communities to protect human health.

This work plan addresses air monitoring and sampling in the Ceresco community, and surrounding areas to ensure air quality is not adversely impacted by the dredging activities. The purpose of this sampling includes the following:

- Air monitoring and sampling in the community potentially impacted by the presence of crude oil and suspended particulates during work activities.
- Air monitoring and sampling throughout the community during remediation 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 the USEPA, on a daily basis.

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

CTEH personnel will perform continuous air monitoring in and around the Ceresco community (Figure 1) using the MultiRAE Plus, UltraRAE, UltraRAE 3000, Gastec pump with benzene specific colorimetric tubes, and the TSI AM510. Real-time data using these instruments will be collected for volatile organic

compounds (VOCs), hydrogen sulfide (H_2S), benzene, and particulate matter (2.5um and 10um). A summary of the air monitoring equipment to be used is listed in Table 1.

Figure 1

Ceresco Community

Table 1

Real-Time Air Monitoring Equipment

AM510 with 2.5um impactor	Particulate	0.001 mg/m3
AM510 with 10um impactor	Particulate	0.001 mg/m3
MultiRAE 10.6 PID	VOCs	0.1 ppm
MultiRAE H_2S electrochemical sensor	H_2S	1 ppm
UltraRAE 3000 PID with benzene sep filters	Benzene	0.05 ppm
UltraRAE PID with benzene sep filters	Benzene	0.01 ppm
Gastec detector tube with pump	Benzene	0.05 ppm*

* Gastec detection limits are based upon detector tubes used

2.1 Monitoring Frequency and Coverage

CTEH personnel will conduct air monitoring within the Ceresco community, and surrounding areas, for the duration of dredging operations. Monitoring emphasis will be placed on community areas along the effected portion of the waterway, areas located downwind of the dewatering/soil staging area, and within the work zone.

Real-Time readings will be taken at various locations in and around the Ceresco community, as well as within the work zone. At each location a VOC, H2S, PM10, and PM2.5 reading will be recorded. Multiple readings in the same location will be used as one method to determine if detects from instantaneous readings from real-time instrumentation are due to transient elevations, spikes in air concentration, or if the concentrations are sustained. If sustained, further air monitoring and/or sampling would be initiated. In the case of benzene, readings will be taken in all areas with detectable VOCs or where odor is present.

3. Noise Monitoring

Noise monitoring will be conducted within the community as well as the work area.
The Questpro DX noise dosimeter will be utilized to determine real-time noise expose levels. The detection limit for this instrument is 40 dB. Noise readings will be used by Enbridge as well as various regulators to determine what, if any, actions should be taken to reduce community and/or worker noise exposure. Exposure values are listed in Table 2.

Table 2

Noise Exposure Levels

Sound Pressure Level (SPL)	90 dBA (100% dose)	85 dBA

Analytical air sampling will be conducted in community areas near the Ceresco Dam dredging operations. Analytical samples will be taken in fixed community locations near dredging operations (Figure 2), around the de-watering/soil staging area (Figure 2), and as needed due to changing site conditions, odor complaints, wind direction, and in areas where elevated reading are recorded.

Air samples will be collected once at each location during a 12-hour period (5um Polyvinyl Chloride cassette), and once during a 24-hour period (evacuated canisters) each day. The criteria used in selecting sampling locations include proximity of residences to the Kalamazoo River, location of dredging operations, and location of potential receptors surrounding the de-watering/soil staging area. Air samples collected using 5um PVC cassettes will be analyzed for total dust according to NIOSH 0500, as well as for metals using NIOSH 7300 (Table 3). Evacuated canister samples will be analyzed for VOCs using EPA Method TO-15 (Table 4). Air Sampling Methods are summarized in Table 5. Each analytical method can be found in Appendix 1.

Figure 2

Analytical Air Sampling Locations

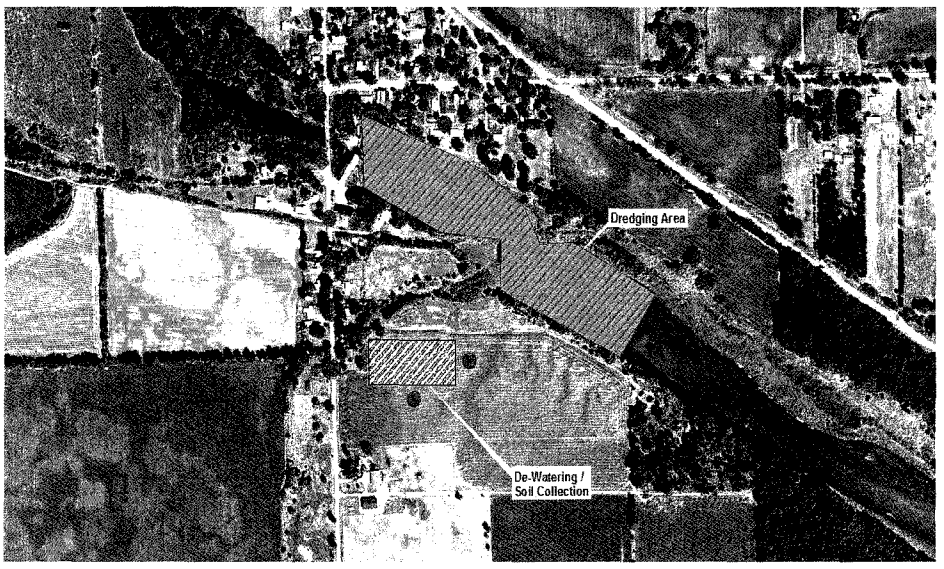

Table 3

Metal Analysis NIOSH 7300

NIOSH 7300 – Metals	
Aluminium	Molybdenum
Antmony	Nickel
Arsenic	Potassium
Barium	Phosphorus
Beryllium	Selenium
Cadmium	Silver
Calcium	Strontium
Chromium	Tellurium
Cobat	Tin
Copper	Thallium
Iron	Titanium
Lead	Tungsten
Lanthanum	Vanadium
Lithium	Yittarium
Magnesium	Zinc
Manganese	Zirconium

Table 4

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 5

Summary of Analytical Air Sampling Methods

VOCs	EPA TO-15	Canisters	NA
Total Dust	NIOSH 0500	37mm PVC 5um	2000
Metals	NIOSH 7300	37mm PVC 5um	2000

Evacuated canisters will also be used to collect air samples to address community concerns about odors. Canister samples will consist of either grab 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. For example, 24-hour sampling would be appropriate for evaluating the potential for exposure at certain receptor sites like homes and schools.

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 day turnaround is anticipated for data is anticipated.

5. Air Sampling 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. Manually logged real-time data will be collected and uploaded to the CTEH® data management system using MC55 handheld data collection devices.

6. Odor Investigations

A CTEH team will be available as an 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/or 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.

7. Response to Detections

A decision process has been developed for the evaluation of air monitoring results for dust, VOCs, TO-15, 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, and HAP analysis (Tedlar bag collection). 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. For particulates, additional engineering controls will be utilized if real-time instrumentation detect concentrations that meet or exceed 75% of the National Ambient Air Quality Standards (NAAQS) for PM2.5 and/or PM10 (Table 5).

Table 5
National Ambient Air Quality Standards (NAAQS) for PM2.5 and PM10

	Primary Standard	
	Level	Averaging Time
Particulate Matter (PM_{10})	150 $\mu g/m^3$	24-hour [1]
Particulate Matter ($PM_{2.5}$)	35 $\mu g/m^3$	24-hour

[1] Not to be exceeded more than once per year on average over 3 years.

8. 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 air sampling and air monitoring data will be provided to Unified Command in a format compatible with SCRIBE. The Quality Assurance Project Plan can be found in Appendix 2.

9. 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.

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

13. 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.

PARTICULATES NOT OTHERWISE REGULATED, TOTAL 0500

DEFINITION: total aerosol mass CAS: NONE RTECS: NONE

METHOD: 0500, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA: 15 mg/m^3
NIOSH: no REL
ACGIH: 10 mg/m^3, total dust less than 1% quartz

PROPERTIES: contains no asbestos and quartz less than 1%

SYNONYMS: nuisance dusts; particulates not otherwise classified

SAMPLING

SAMPLER:	FILTER (tared 37-mm, 5-μm PVC filter)
FLOW RATE:	1 to 2 L/min
VOL-MIN:	7 L @ 15 mg/m^3
-MAX:	133 L @ 15 mg/m^3
SHIPMENT:	routine
SAMPLE STABILITY:	indefinitely
BLANKS:	2 to 10 field blanks per set
BULK SAMPLE:	none required

ACCURACY

RANGE STUDIED:	8 to 28 mg/m^3
BIAS:	0.01%
OVERALL PRECISION ($\hat{S}_{rT}$):	0.056 [1]
ACCURACY:	±11.04%

MEASUREMENT

TECHNIQUE:	GRAVIMETRIC (FILTER WEIGHT)
ANALYTE:	airborne particulate material
BALANCE:	0.001 mg sensitivity; use same balance before and after sample collection
CALIBRATION:	National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights
RANGE:	0.1 to 2 mg per sample
ESTIMATED LOD:	0.03 mg per sample
PRECISION ($\bar{S}_r$):	0.026 [2]

APPLICABILITY: The working range is 1 to 20 mg/m^3 for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [3] in addition to the other ACGIH particulates not otherwise regulated [4].

INTERFERENCES: Organic and volatile particulate matter may be removed by dry ashing [3].

OTHER METHODS: This method is similar to the criteria document method for fibrous glass [3] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

EQUIPMENT:

1. Sampler: 37-mm PVC, 2- to 5-μm pore size membrane or equivalent hydrophobic filter and supporting pad in 37-mm cassette filter holder.
2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
3. Microbalance, capable of weighing to 0.001 mg.
4. Static neutralizer: e.g., Po-210; replace nine months after the production date.
5. Forceps (preferably nylon).
6. Environmental chamber or room for balance (e.g., 20 °C ± 1 °C and 50% ± 5% RH).

SPECIAL PRECAUTIONS: None.

PREPARATION OF FILTERS BEFORE SAMPLING:

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h. NOTE: An environmentally controlled chamber is desirable, but not required.
2. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
3. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight, W_1 (mg).
   a. Zero the balance before each weighing.
   b. Handle the filter with forceps. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
4. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

SAMPLING:

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1 to 2 L/min for a total sample volume of 7 to 133 L. Do not exceed a total filter loading of approximately 2 mg total dust. Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure.

SAMPLE PREPARATION:

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.
9. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust. NOTE: If the filter adheres to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

CALIBRATION AND QUALITY CONTROL:

10. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.
11. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same

equipment, procedures, and personnel used in the routine field samples. The relative standard deviation calculated from these replicates should be recorded on control charts and action taken when the precision is out of control [7].

MEASUREMENT:

12. Weigh each filter, including field blanks. Record the post-sampling weight, W_2 (mg). Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.)

CALCULATIONS:

13. Calculate the concentration of total particulate, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \times 10^3, \text{ mg/m}^3,$$

where: W_1 = tare weight of filter before sampling (mg),
W_2 = post-sampling weight of sample-containing filter (mg),
B_1 = mean tare weight of blank filters (mg),
B_2 = mean post-sampling weight of blank filters (mg).

EVALUATION OF METHOD:

Lab testing with blank filters and generated atmospheres of carbon black was done at 8 to 28 mg/m^3 [2,6]. Precision and accuracy data are given on page 0500-1.

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METHOD REVISED BY:

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ELEMENTS by ICP (Nitric/Perchloric Acid Ashing) 7300

MW: Table 1 CAS: Table 2 RTECS: Table 2

METHOD: 7300, Issue 3 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

OSHA: Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

ELEMENTS:

aluminum*	calcium	lanthanum	nickel	strontium	tungsten*
antimony*	chromium*	lithium*	potassium	tellurium	vanadium*
arsenic	cobalt*	magnesium	phosphorus	tin	yittrium
barium	copper	manganese*	selenium	thallium	zinc
beryllium*	iron	molybdenum*	silver	titanium	zirconium*
cadmium	lead*				

*Some compounds of these elements require special sample treatment.

SAMPLING

SAMPLER: FILTER (0.8-µm, cellulose ester membrane, or 5.0-µm, polyvinyl chloride membrane)

FLOWRATE: 1 to 4 L/min

VOL-MIN: Table 1
-MAX: Table 1

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not determined

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rt}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: elements above

ASHING REAGENTS: conc. HNO_3/ conc. $HClO_4$ (4:1), 5 mL; 2mL increments added as needed

CONDITIONS: room temperature, 30 min; 150 °C to near dryness

FINAL SOLUTION: 4% HNO_3, 1% $HClO_4$, 25 mL

WAVELENGTH: depends upon element; Table 3

BACKGROUND CORRECTION: spectral wavelength shift

CALIBRATION: elements in 4% HNO_3, 1% $HClO_4$

RANGE: varies with element [1]

ESTIMATED LOD: Tables 3 and 4

PRECISION ($\bar{S}$): Tables 3 and 4

APPLICABILITY: The working range of this method is 0.005 to 2.0 mg/m^3 for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.

INTERFERENCES: Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1-4].

OTHER METHODS: This issue updates issues 1 and 2 of Method 7300, which replaced P&CAM 351 [3] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.

REAGENTS:

1. Nitric acid (HNO_3), conc., ultra pure.
2. Perchloric acid ($HClO_4$), conc., ultra pure.*
3. Ashing acid: 4:1 (v/v) HNO_3:$HClO_4$. Mix 4 volumes conc. HNO_3 with 1 volume conc. $HClO_4$.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO_3, 1% $HClO_4$. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled,deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size; or polyvinyl chloride membrane, 5.0-µm pore size; 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.**
6. Volumetric flasks, 10-, 25-,100-mL., and 1-L**
7. Assorted volumetric pipets as needed.**
8. Hotplate, surface temperature 150 °C.

** Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

SPECIAL PRECAUTIONS: All perchloric acid digestions are required to be done in a perchloric acid hood. When working with concentrated acids, wear protective clothing and gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.
   NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.
   NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.
   NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10]. For example, aqua regia may be needed for Mn [6,12].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.
    NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate the spectrometer according to the manufacturers recommendations.
    NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO_3/1% $HClO_4$:
    a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
    b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Tl, V, Y, Zn, Sc
    c. Mo, Sb, Sn, Te, Ti, W, Zr
    d. Acid blank
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked blank filters per ten samples.

MEASUREMENT:

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.
    NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.
18. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m^3), of each element in the air volume sampled, V (L):

$$C = \frac{CsVs - CbVb}{V}, mg/m^3$$

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

Issues 1 and 2
Method, 7300 was originally evaluated in 1981 [2,3]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The measurements used for the method evaluation in Issues 1 and 2 were determined with a Jarrell-Ash Model 1160 Inductively Coupled Plasma Spectrometer operated according to manufacturer's instructions.

Issue 3
In this update of NIOSH Method 7300, the precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. Tables 3 and 4 list the precision and recovery data, instrumental detection limits, and analytical wavelengths for mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters. PVC Filters which can be used for total dust measurements and then digested for metals measurements were tested and found to give good results. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments Model End On Plasma (EOP)(axial) operated according to manufacturer's instructions.

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METHOD REVISED BY:

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Method originally written by Mark Millson, NIOSH/DART, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS, James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Labortories, Salt Lake City, UT.

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m³ (Ca = carcinogen) OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--	--	--	--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	–	–	–	--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW240000	--	C 0.05	--
Tungsten	7440-33-7	–	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	–	--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3. MEASUREMENT PROCEDURES AND DATA [1].
Mixed Cellulose Ester Filters (0.45 µm)

Element (a)	wavelength nm	Est. LOD µg/ Filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	102.9	2.64	3.21	98.3	1.53
Al	167	0.115	4.6	1.54	105.4	11.5	6.40	101.5	1.98
As	189	0.140	5.6	3.08	94.9	2.28	12.9	93.9	1.30
Ba	455	0.005	0.2	0.31	101.8	1.72	1.29	97.7	0.69
Be	313	0.005	0.2	0.31	100.0	1.44	1.29	98.4	0.75
Ca	317	0.908	36.3	15.4	98.7	6.65	64.0	100.2	1.30
Cd	226	0.0075	0.3	0.31	99.8	1.99	1.29	97.5	0.88
Co	228	0.012	0.5	0.31	100.8	1.97	1.29	98.4	0.90
Cr	267	0.020	0.8	0.31	93.4	16.3	1.29	101.2	2.79
Cu	324	0.068	2.7	1.54	102.8	1.47	6.40	100.6	0.92
Fe	259	0.095	3.8	1.54	103.3	5.46	6.40	98.0	0.95
K	766	1.73	69.3	23.0	90.8	1.51	96.4	97.6	0.80
La	408	0.048	1.9	0.77	102.8	2.23	3.21	100.1	0.92
Li	670	0.010	0.4	0.31	110.0	1.91	1.29	97.7	0.81
Mg	279	0.098	3.9	1.54	101.1	8.35	6.40	98.0	1.53
Mn	257	0.005	0.2	0.31	101.0	1.77	1.29	94.7	0.73
Mo	202	0.020	0.8	0.31	105.3	2.47	1.29	98.6	1.09
Ni	231	0.020	0.8	0.31	109.6	3.54	1.29	101.2	1.38
P	178	0.092	3.7	1.54	84.4	6.19	6.40	82.5	4.75
Pb	168	0.062	2.5	1.54	109.4	2.41	6.40	101.7	0.88
Sb	206	0.192	7.7	3.08	90.2	11.4	12.9	**41.3**	32.58
Se	196	0.135	5.4	2.3	87.6	11.6	9.64	84.9	4.78
Sn	189	0.040	1.6	0.77	90.2	18.0	3.21	**49**	21.79
Sr	407	0.005	0.2	0.31	101.0	1.55	1.29	97.3	0.65
Te	214	0.078	3.1	1.54	102.0	2.67	6.40	97.4	1.24
Ti	334	0.050	2.0	0.77	98.4	2.04	3.21	93.4	1.08
Tl	190	0.092	3.7	1.54	100.9	2.48	6.40	99.1	0.80
V	292	0.028	1.1	0.77	103.2	1.92	3.21	98.3	0.84
W	207	0.075	3.0	1.54	**72.2**	10.1	6.40	**57.6**	14.72
Y	371	0.012	0.5	0.31	100.5	1.80	1.29	97.4	0.75
Zn	213	0.310	12.4	4.60	102.2	1.87	19.3	95.3	0.90
Zr	339	0.022	0.9	0.31	88.0	19.4	1.29	**25**	57.87

(a) Bold values are qualitative only because of low recovery.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].
Polyvinyl Chloride Filter (5.0 µm)

Element (c)	wavelength nm	Est. LOD µg per filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (a)	Percent RSD (N=25)	Certified[17] 10x LOD (b)	% Recovery (a)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	104.2	8.20	3.18	81.8	18.9
Al	167	0.115	4.6	1.56	77.4	115.24	6.40	92.9	20.9
As	189	0.140	5.6	3.10	100.7	5.13	12.70	96.9	3.2
Ba	455	0.005	0.2	0.31	102.4	3.89	1.270	99.8	2.0
Be	313	0.005	0.2	0.31	106.8	3.53	1.270	102.8	2.1
Ca	317	0.908	36.3	15.6	**68.1**	12.66	64.00	96.8	5.3
Cd	226	0.0075	0.3	0.31	105.2	5.57	1.27	101.9	2.8
Co	228	0.012	0.5	0.31	109.3	4.67	1.27	102.8	2.8
Cr	267	0.020	0.8	0.31	109.4	5.31	1.27	103.4	4.1
Cu	324	0.068	2.7	1.56	104.9	5.18	6.40	101.8	2.4
Fe	259	0.095	3.8	1.56	88.7	46.82	6.40	99.1	9.7
K	766	1.73	69.3	23.4	96.4	4.70	95.00	99.2	2.2
La	408	0.048	1.9	0.78	**45.5**	4.19	3.18	98.8	2.6
Li	670	0.010	0.4	0.31	107.7	4.80	1.27	110.4	2.7
Mg	279	0.098	3.9	1.56	**54.8**	20.59	6.40	**64.5**	5.7
Mn	257	0.005	0.2	0.31	101.9	4.18	1.27	99.3	2.4
Mo	202	0.020	0.8	0.31	106.6	5.82	1.27	98.1	3.8
Ni	231	0.020	0.8	0.31	111.0	5.89	1.27	103.6	3.2
P	178	0.092	3.7	1.56	101.9	17.82	6.40	86.5	10.4
Pb	168	0.062	2.5	1.56	109.6	6.12	6.40	103.2	2.9
Sb	206	0.192	7.7	3.10	**64.6**	22.54	12.70	**38.1**	30.5
Se	196	0.135	5.4	2.30	83.1	26.23	9.50	76.0	17.2
Sn	189	0.040	1.6	0.78	85.7	27.29	3.18	**52.0**	29.4
Sr	407	0.005	0.2	0.31	**71.8**	4.09	1.27	81.2	2.7
Te	214	0.078	3.1	1.56	109.6	7.49	6.40	97.3	3.8
Ti	334	0.050	2.0	0.78	101.0	9.46	3.18	92.4	5.5
Tl	190	0.092	3.7	1.56	110.3	4.04	6.40	101.9	2.0
V	292	0.028	1.1	0.78	108.3	3.94	3.18	102.5	2.6
W	207	0.075	3.0	1.56	**74.9**	15.79	6.40	**44.7**	19.6
Y	371	0.012	0.5	0.31	101.5	3.63	1.27	101.4	2.5
Zn	213	0.310	12.4	4.70	91.0	68.69	19.1	101.0	9.6
Zr	339	0.022	0.9	0.31	**70.7**	54.20	1.27	**40.4**	42.1

(a) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD [12].
(c) Bold values are qualitative only because of low recovery. Other digestion techniques may be more appropriate for these elements and their compounds.

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Appendix 2

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
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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 project 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

QAPPs for each laboratory are attached.

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 is 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.

P500

Enbridge Line 6B MP 608 Pipeline Release

Marshall, Michigan

Supplement to Sampling and Analysis Monitoring Plan

Ceresco Dam River Dredging

Enbridge Energy

Revised: October 7, 2010

622922

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4.0 Water Quality Monitoring 2
5.0 Analysis 3

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Figures and Tables

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Figure 2: Equipment Areas Map ..... Attached
Figure 3: Sample and Dredge Locations Map ..... Attached
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1.0 BACKGROUND

Region 5 EPA directed Enbridge Energy to dredge the Kalamazoo River in the area directly upstream of the Ceresco Dam where submerged crude oil was identified on the stream bed. Dredging of the river bed to remove submerged oil collected in river bed sediment will be performed. The collected sediment will be pumped to a nearby de-watering bed and stored in a water permeable membrane. Water collected from the sediment will be analyzed for benzene, toluene, ethyl benzene, and xylenes (BTEX). When analysis of the water documents BTEX concentrations are below NPDES permit levels, the water will be discharged back into the Kalamazoo River.

The Work Plan for Permanent Recovery of Submerged Oil and Oil-Contaminated Sediments at Priority Locations and Ceresco Dam Dredging submitted as Attachment to the Supplemental Modification of the Response Plan for Downstream Impact Area and the Source Area Response Plan dated October 3, 2010 describes the method for dredging including equipment to be used for this effort. Figures 1 and 2 attached to this document show equipment areas.

Sampling requirements for NPDES permit compliance is as follows:

Parameter	Minimum Limits for Quality and Concentration	Maximum Limits for Quality and Concentration	Frequency of Analysis	Sample Type
Intermediate Total BTEX	-	(report)	Weekly	Grab
Final Effluent BTEX	-	20 ug/L	Weekly	Grab
Total Lead	-	(report)	Weekly	Grab
Dissolved Oxygen	4.0 mg/l	-	Weekly	Grab
pH	6.5	9.0	Weekly	Grab
Equipment and Outfall Inspections	-	(report)	3X Weekly	Visual

These test parameters are in accordance with, the NPDES Wastewater Discharge General Permit for Petroleum Contaminated Wastewater Permit Certificate of Coverage Number MIG081158.

2.0 PURPOSE

This supplement to the Sampling and Analysis Plan (SAP) approved on August 2, 2010, and revised August 17, 2010, serves to document the surface water sampling associated with the dredging operations. Surface water samples will be collected upstream of the dredging operation, near the operations, and downstream of the operation to assess water quality associated with the clean up operation. Samples will be submitted for analysis at the end of each operational day as a batch. Analysis will be conducted by Trace Analytical of Muskegon, Michigan. Identified sampling locations are included in Figure 3 attached to this document.

3.0 WATER SAMPLING

Surface water samples will be collected in laboratory supplied certified clean glassware with method appropriate preservatives as needed. Sample time, location, and conditions are recorded according to the approved Sampling and Analysis Plan. Each sample is given a unique identification number using the nomenclature outlined in the sampling plan.

A toal of three samples locations will include one sample 500 feet upstream of dredging operations, one sampledownstream of operations but upstream of the dam and one sample downstream of the dam just west of the final containment measures. Samples will be collected at stream mid-depth from boat or other means amenable to collection.

Samples will be collected at mid-operational shift during days 1 through 7 while active dredging activities are occurring. Analytical results turn around time (TAT) will be next day. Sampling frequency after seven (7) consecutive days will be determined by EPA OSC in consult with Enbridge..

Sample IDs and information are recorded on a Chain of Custody and sample custody is relinquished to the laboratory for analysis.

4.0 WATER QUALITY MONITORING

Water quality parameters (pH, dissolved oxygen, specific conductivity, and temperature) will also be measured and recorded during collection of each sample as prescribed in the Sampling and Analysis Plan. Parameters will be collected from the same depth and at the same time as each surface water sample during dredging operations and subject to the actionable values describe in Table 1. Oil sheen observed during surface water collection will be documented. In addition, oil sheen observed being generated from dredging operations will be immediately reported to Enbridge and Tetra Tech, who will determine the necessary actions to prevent further release of sheen from the dredge area.

In addition to the water quality parameters collected with each sample, water quality parameters will also be collected at one established location, downstream of dredging operations using a Eureka Environmental Manta 2 Multiprobe (Manta) or similar device. It is expected that a Manta will be deployed from a downstream location. Deployment locations and monitoring depth (shallow/surface, mid-depth, or deep) will be determined with input from Company personnel and state and federal agencies. The Manta will electronically log the water quality parameters at 15 minute intervals, 24 hours a day, and deliver the data through cellular telemetry to a web-based database accessible to the interested parties. The Manta will be calibrated in accordance with manufacturer's specifications and in accordance with the calibration SOP (included in Appendix A) and can be set to alert (via text and/or email) appropriate individuals should surface water quality parameters fall outside specified ranges established by state and federal agencies (i.e., "actionable" values). The proposed actionable background turbidity will be obtained daily from the upstream dredging operations.

Water quality parameters and proposed actionable values are presented in Table 1

Table 1
Water Quality Parameters and Proposed Actionable Values

Parameter	Proposed Actionable Value	Units
Temperature	NA[1]	°C
pH	6.5 < x > 9.0	
Specific Conductivity	NA[1]	S/cm
Dissolved Oxygen	4.0	mg/L
Turbidity	2x background levels	NTU

[1]NA-Not Applicable

Dredging areas are identified in Figure 3 attached to this document.

5.0 ANALYSIS

Trace Analytical will analyze each sample using EPA and Standard Methods listed in Table 2.

Table 2: Analysis Parameters and Methods

Parameter	Method
Volatile Organic Compounds (VOCs)	SW846 8260
Semi-Volatile Organic Compounds (SVOCs)	SW846 8270
Gasoline Range Organics (GRO)	SW846 8015
Diesel Range Organcis (DRO)	SW846 8015
Oil Range Organics (ORO)	SW846 8015
Polychlorinated Biphenyls (PCBs)	SW846 8280
Michigan Metals and Titanium	SW846 6010, 7470
Total Organic Carbon (TOC)	SM5310
Hardness	SM2340
Total Suspended Solids (TSS)	SM2540

Laboratory instrument calibration will be maintained in conformance with EPA standards with commercially produced standards.

Appropriate quality control samples will be periodically analyzed in accordance with the approved Data Quality Management plan to ensure data defensibility.

Appendix A

Manta 2 Multiprobe Calibration Procedures

Sensor Specific Calibrations

pH

Use a two-point calibration using two (2) buffers, 7.00 and 10.0.

1. Rinse the sensors in DI water, discarding rinse into the decon bucket.
2. Rinses sensors with the first buffer (7.00).
3. Fill cup with the 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 10.0 buffer and upright probe to immerse the sensors.
8. Follow the calibration instructions on the instrument calibration screen and discard the used solution into the decon bucket.

Specific Conductivity

Use a one (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 waters being sample). For our purposes, 12,586 S/cm is the standard to be used.
3. Follow the calibration instructions on the instrument calibration screen and discard the used solution into the decon bucket.

Turbidity

Use a two-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 on the instrument calibration screen and discard the used solution into the decon bucket. .

To set the second point, repeat the steps above using a 400 NTU standard solution. Discard used solutions into your decon bucket.

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 (1) minute.
2. Remove cap and let jar stand for one (1) minute. This lets the tiny air bubbles float out of the top.
3. Fill the calibration cup until the sensor is immersed in the aerated water, cap and upright.
4. Wait a few minutes for the temperature and reading to equilibrate.

5. Follow the calibration instructions on the instrument calibration screen and discard the used solution into the decon bucket.

Fluorometer CDOM

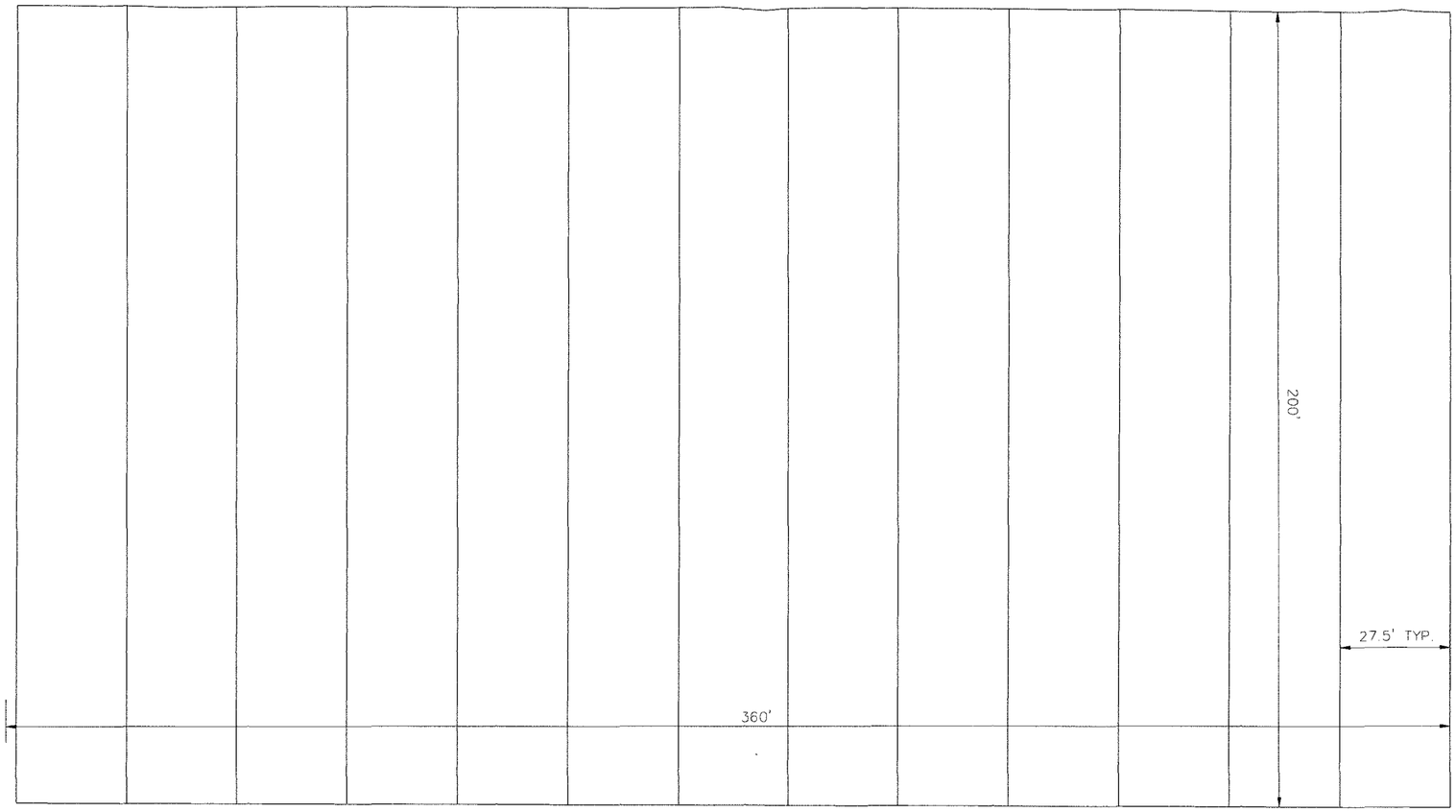
Use a two-point calibration.

To Zero;

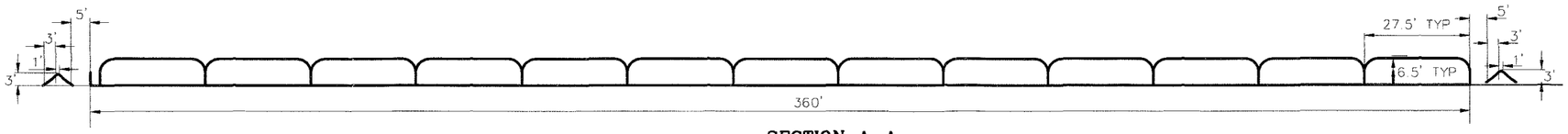
1. Rinse sensors twice with deionized water. Partially fill the calibrations cup with DI water, close and shake vigorously. Discard rinse into decon bucket.
2. Fill the calibration cup with the zero standard, replace lid and upright the Multiprobe to immerse the sensor in the solution.
3. Follow the calibration instructions on the instrument calibration screen and discard the used solution into the decon bucket.

To set the second point, repeat the steps above using a relative standard solution. Discard used solutions into your decon bucket.

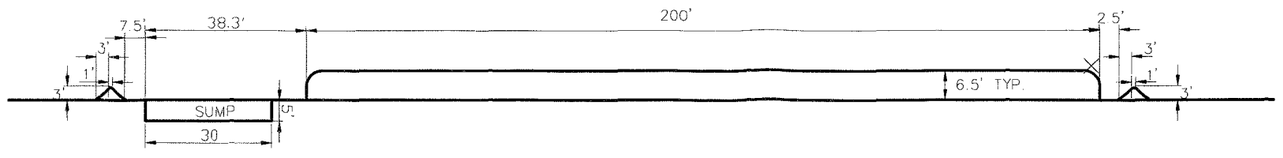
Figure 1: Equipment Areas Map



PROPOSED LAYDOWN AREA
SCALE: 1"=15'



SECTION A-A
NOT TO SCALE



SECTION B-B
NOT TO SCALE

INFRASTRUCTURE ALTERNATIVES
7005 CHURCHILL AVENUE NE, ROCKFORD, MICHIGAN 49341
phone: 616 866-1600 fax: 616 866-1611 web: www.INFRASTRUCTUREALTERNATIVES.com

NO.	REVISIONS	BY	DATE
5			
6			
7			
8			

REVISED IN ACCORDANCE WITH CONSTRUCTION RECORDS

NO.	REVISIONS	BY	DATE
1			
2			
3			
4			

Kalamazoo River

Figure 4 - Geotube Layout

DESIGNED BY AW	DATE 9/10
DRAWN BY AW	DATE 9/10
CHECKED BY	DATE
FILE	CDT
SCALE	1"=16'
DRAWING	1:1
PLOT	

PROJECT K-Zoo River

4

SHEET NO.

Figure 2: Equipment Areas Map

B
FIG. 4

A
FIG. 4

Install Silt fence

See Infrastructure Alternatives Drawings for Cross Section

SLOPE: 0.5%-1.0%

SUMP

30

65

55.0556

151.3038

B
FIG. 4

POLYMER INJECTION SPOOLS

Sediment line from Dredge

W.T.P. LOCATION
BAG FILTERS WITH OIL GRAB
OIL ABSORBING PRESSURE VESSELS
GAC VESSELS

SLOPE: 0.5%-1.0%

A
FIG. 4

DREDGE LINE

EFF TO RIVER

POLYMER INJECTION SPOOLS

POLYMER INJECTION DETAIL

NTS

INFRASTRUCTURE ALTERNATIVES

7986 CHILDSDALE AVENUE NE, ROCKFORD, MICHIGAN 49341
phone 616 866-1600 fax 616 866-1611 web www.INFRASTRUCTURE-ALTERNATIVES.com

NO	DATE	BY	REVISIONS
1			
2			
3			
4			
5			
6			
7			
8			

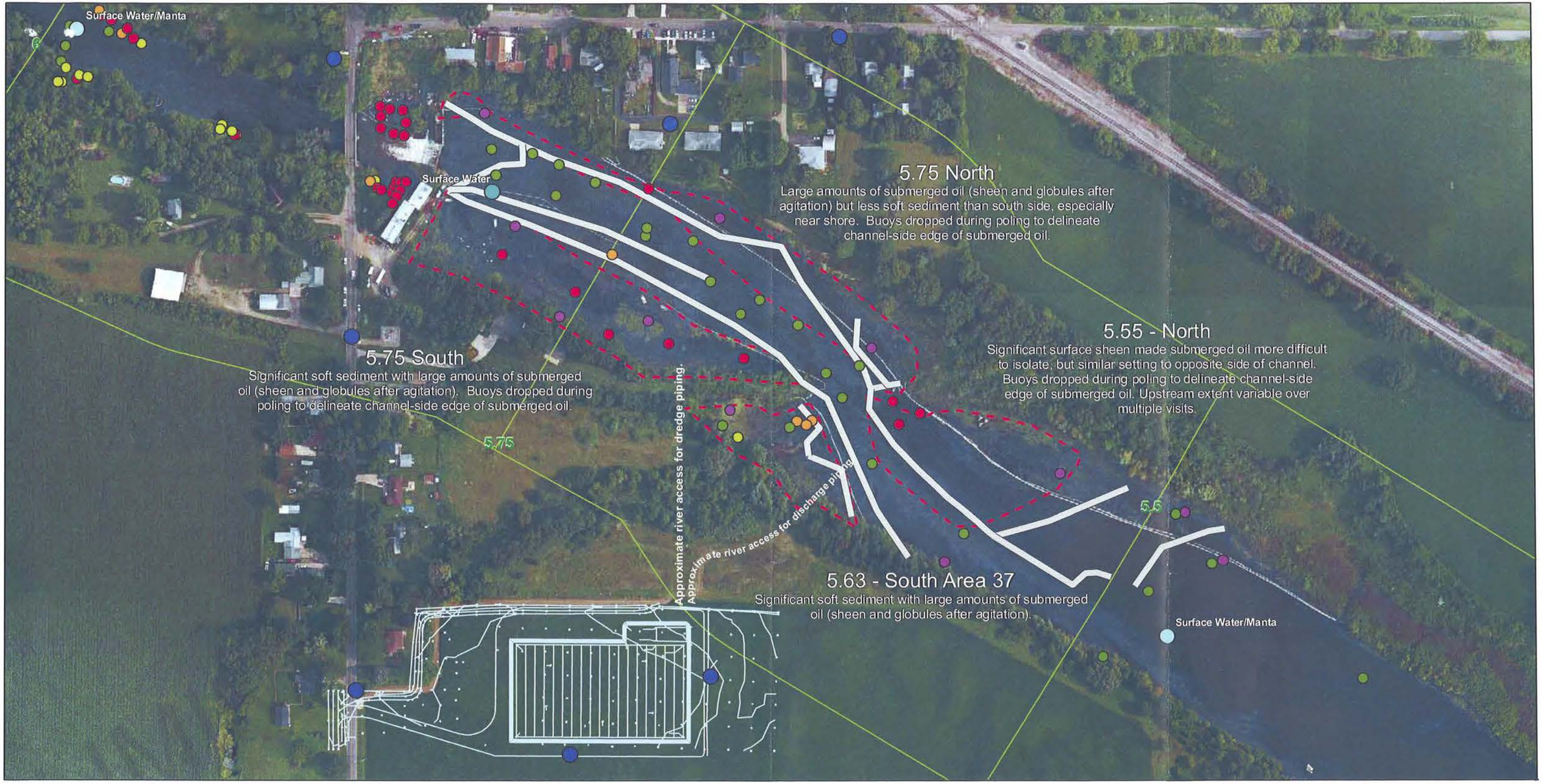
REVISED IN ACCORDANCE WITH CONSTRUCTION RECORDS

Kalamazoo River

Figure 2 – Sediment Handling Pad

DESIGNED BY AW	DATE 9/10
DRAWN BY AW	DATE 9/10
CHECKED BY	DATE
FILE	EDIT
SCALE 1"=16'	
DRAWING 1 1	
PLOT	
PROJECT K-Zoo River	
2	
SHEET NO.	

Figure 3: Sample and Dredge Locations Map



N
W E
S

0 200 400 Feet

1 inch = 150 feet

Legend

Observed Sheen/Globules After Poling
- None Observed
- Slight
- Moderate
- Heavy
- Observed But Quantity Not Noted

- Priority Areas
- Priority Area Approximate Containment (if known)
- Division Quarter Mile Grid
- Air Sample Locations
- Surface Water
- Surface Water/Manta

Coordinate System: Michigan State Plane South
Horizontal Datum: NAD83
Vertical Datum: NAVD88
Units: International Feet
Aerial Photography from August 26, 2010

SAMPLING ANALYSIS PLAN
FIGURE 3 DREDGE AND SAMPLE LOCATIONS
Ceresco Dam

SUBMERGED OIL TASK FORCE
KALAMAZOO AND CALHOUN COUNTIES
MICHIGAN
Oct 3, 2010

TETRA TECH EC, INC.

10/03/10 -- K. Bellrichard / D. Lutz

E:\ArcMap Project Files\ReportFigures\SAP_Figure3.mxd

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

August 16, 2011

Enbridge Energy, Limited Partnership
c/o Mr. Rich Adams
Vice President, Operations
Superior City Centre
Second Floor
1409 Hammond Ave.
Superior, Wisconsin 54880

Re: U.S. EPA Authorization to Discontinue Weekly Surface Water and Bi-Weekly Sediment Sampling Requirement pursuant to the Administrative Order issued by U.S. EPA on July 27, 2010, pursuant to §311(c) of the Clean Water Act (Docket No. CWA 1321-5-10-001) and Supplement to the Administrative Order issued by U.S. EPA on September 23, 2010

Dear Mr. Adams:

The United States Environmental Protection Agency (U.S. EPA) has directed Enbridge Energy, Limited Partnership, Enbridge Pipelines (Lakehead) L.L.C., Enbridge Pipelines (Wisconsin), and Enbridge Energy Partners, L.P. (herein collectively referred to as "Enbridge") to perform surface water and sediment sampling during the response and recovery of oil released from Enbridge Line 6B. U.S. EPA approved the requirements for surface water and sediment sampling in the Enbridge Sampling and Analysis Plan, August 18, 2010.

On October 22, 2010, U.S. EPA and MDEQ agreed that reductions in the surface water and sediment sampling may be appropriate (See Attachment 1) and that MDEQ should enter into a long-term surface water and sediment sampling program with Enbridge.

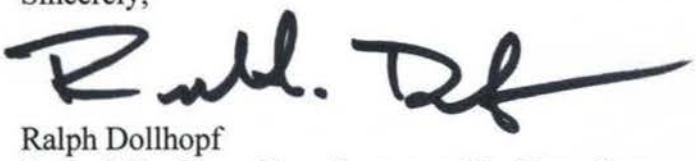
On Thursday, August 4, 2011 U.S. EPA determined that the State of Michigan and Enbridge have not yet agreed to a Sampling and Analysis Plan or a Surface Water and Sediment sampling program. Therefore, Enbridge has continued to conduct the surface water and sediment sampling pursuant to the U.S. EPA Order.

After review of the results obtained to date and the data objectives, Enbridge may discontinue the surface water and sediment sampling currently being conducted as outlined in Attachment 1.

By way of a copy of this letter, U.S. EPA will inform MDEQ of this decision and if MDEQ would like Enbridge to continue a surface water and sediment sampling program, MDEQ will direct you accordingly.

If you have any questions regarding this letter, please contact me immediately at (231) 301-0559.

Sincerely,



Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. EPA, Region 5

Attachment

cc: L. Kirby-Miles, U.S. EPA, ORC
J. Cahn, U.S. EPA, ORC
J. Kimble, U.S. EPA
M. Durno, U.S. EPA
T. Edwards, U.S. EPA
S. Wolfe, U.S.EPA
Records Center, U.S. EPA, Reg. V
M. Ducharme, MDEQ
M. Alexander, MDEQ

Attachment 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

MEMORANDUM

October 22, 2010

To: Ralph Dollhopf, U.S. EPA Incident Commander for RD

From: Steve Wolfe, U.S. EPA Monitoring Branch Director

Brian Schlieger, U.S. EPA Monitoring Branch Director

Thru: Brian Kelly, Operations Section Chief BK

RE: Recommendation for reduction in Surface Water and Sediment Sampling for the Enbridge Pipeline Release, Marshall, Calhoun County, Michigan

After review of the surface water (see attached pages for surface water summaries) and sediment sampling results and under consultation with the Michigan Department of Natural Resources and Environment (MDNRE), Water Resources Division, the following recommendations are made concerning surface water and sediment sampling (effective immediately):

SURFACE WATER SAMPLING DOWNSTREAM MORROW LAKE

On a weekly basis, Enbridge shall collect 1 surface water sample at the point nearest the Morrow Lake Dam (location SW-126). If oil-related compounds are detected, the next sampling event will include a sample from SW-126 and the next downstream location (SW-010).

This sample is being collected to show that oil from the Enbridge pipeline release has not gone past Morrow Dam.

SURFACE WATER SAMPLING MORROW LAKE

The every other day sampling of the former U.S. EPA "Mud Puppy" locations will be discontinued (locations ML-1 through ML-10).

Weekly sampling of 20 other locations within Morrow Lake are sufficient coverage for the Lake.

The Daily Mud Puppy sample results have not shown any changes over time during the course of 3 months of sampling. Enbridge has chosen 20 locations throughout Morrow Lake that will be sampled and provides ample coverage as discussed with MDNRE. All of the chosen locations (which includes the 10 former Mudpuppy locations) have historical data associated with them to show trends over time.

SURFACE WATER SAMPLING KALAMAZOO RIVER

Weekly sampling of 11 locations co-located with the collection/containment structures related to O&M will replace the current 23 sampling locations. The samples will be collected immediately downriver of the collection/containment points.

Co-locating the sample points with the O&M structures were chosen as these areas have petroleum contamination still associated with them and pose the greatest chance of ongoing petroleum releases into the environment.

SEDIMENT SAMPLING MORROW LAKE

The former U.S. EPA "Mud Puppy" locations will be discontinued (locations ML-1 through ML-10). Bi-weekly sampling of two locations will be sufficient coverage for Morrow Lake. The two locations will be one at the entrance to the lake from the Kalamazoo River and one near the Lake Morrow Dam from the deeper part of the lake.

These locations are recommended by MDNRE as the most likely to have deposition.

SEDIMENT SAMPLING KALAMAZOO RIVER

Sediment samples will be collected on a Bi-weekly basis along the Kalamazoo River. The sediment samples will be co-located with the 11 new surface water sampling locations.

The sediment sample locations were co-located with the surface water sampling locations in order to continue to monitor for submerged oil effects due to containing petroleum in discreet areas.

Enbridge will provide a map annotating all of the new sampling locations.

ANALYTES

All samples will be analyzed for the following analytes:

TPH- DRO, GRO, ORO	Benzene	o- xylene	Naphthalene
1,2,3-Trimethylbenzene	Cycloheaxane	n-propylbenzene	Phenanthrene
1,2,4-Trimethylbenzene	Ethylbenzene	p-Isopropyl toluene	Mercury
1,3,5 Trimethylbenzene	Isopropylbenzene	Sec-Butylbenzene	Beryllium
2-Methylnaphthalene	m & p Xylene	Toluene	Iron
Molybdenum	Nickel	Titanium	Vanadium

DURATION

This recommendation is being made with the understanding that Enbridge will enter into a long-term surface water and sediment sampling/monitoring program with MDNRE. New sampling plans for surface water and sediment sampling developed by Enbridge and approved by MDNRE will replace these recommendations.

NOTE: These recommendations do not affect any additional sampling that is being performed for the dredging project, aeration projects, or any other submerged oil project.

Surface Water Sampling Detections and Screening Summary
Monitoring Program Sample Locations
Enbridge Energy Pipeline 6B
Marshall, MI

Geographic Zone	Sample Location	Date	Sample ID	Analyte	Result µg/L	Source of Lowest Screening Criterion	Lowest Screening Crtierion µg/L
Downstream of Morrow Lake							
	SW-205	07-Aug-10	WS08071541GFG1	Lead	26	HNV-DW	14
	SW-201	16-Aug-10	WS08161122GAH1	Mercury	0.15 J	GSI	0.0013
	SW-009	17-Aug-10	WS08171225RTV1	Mercury	0.26	GSI	0.0013
	SW-202	11-Sep-10	WSF09111037JLS1	Mercury	0.16 J	GSI	0.0013
	SW-201	11-Sep-10	WSF09111314JLS1	Mercury	0.047 J	GSI	0.0013
	SW-131	13-Sep-10	WSF09131055RTV1	Mercury	0.13 J	GSI	0.0013
	SW-205	13-Sep-10	WSF09131204RRD1	Mercury	0.028 J	GSI	0.0013
	SW-200	21-Sep-10	WSF09211245JPN1	Mercury	0.01 J	GSI	0.0013
	SW-200	25-Sep-10	WSF09251015SDD1	Mercury	0.009 J	GSI	0.0013
	SW-008	27-Sep-10	WSF09270930RTV1	Mercury	0.012 J	GSI	0.0013
	SW-131	27-Sep-10	WSF09271035RTV1	Mercury	0.022 J	GSI	0.0013
	SW-205	27-Sep-10	WSF09271205RRD1	Mercury	0.016 J	GSI	0.0013
	SW-206	27-Sep-10	WSF09271310RRD1	Mercury	0.011 J	GSI	0.0013
	SW-206	27-Sep-10	WSF09271335RRD1	Mercury	0.01 J	GSI	0.0013
Zone Total Number of Exceedances					***= 14***		
Morrow Lake							
	SW-111	01-Aug-10	WS08012000PDS1	Vanadium	98	FCV/GSI	12
	SW-111	02-Aug-10	WS08021550PDS1	Vanadium	37	FCV/GSI	12
	SW-111	17-Aug-10	WS08170728RCM1	Mercury	0.079 J	GSI	0.0013
	ML-1	01-Sep-10	WSE09010950PML1	Mercury	0.06 J	GSI	0.0013
	SW-933	05-Sep-10	WSE09050915MHS1	Mercury	0.064 J	GSI	0.0013
	SW-934	07-Sep-10	WSE09071020JRP1	Mercury	0.022 J	GSI	0.0013
	SW-933	10-Sep-10	WSE09101433RCM1	Mercury	0.43	GSI	0.0013
	SW-938	15-Sep-10	WSE09151435JRP1	Lead	15	HNV-DW	14
	SW-935	22-Sep-10	WSE09220833RCM1	Mercury	0.096 J	GSI	0.0013
	SW-934	25-Sep-10	WSE09250930ARM1	Mercury	0.14 J	GSI	0.0013
	SW-937	27-Sep-10	WSE09271048RCM1	Mercury	0.025 J	GSI	0.0013
Zone Total Number of Exceedances					***= 12***		

Surface Water Sampling Detections and Screening Summary
Monitoring Program Sample Locations
Enbridge Energy Pipeline 6B
Marshall, MI

Geographic Zone	Sample Location	Date	Sample ID	Analyte	Result µg/L	Source of Lowest Screening Criterion	Lowest Screening Crtierion µg/L
Talmadge Creek							
	SW-107	27-Sep-10	WS009271100PMB1	Mercury	0.019 J	GSI	0.0013
Zone Total Number of Exceedances					***= 1***		
Upstream of Morrow Lake							
	SW-001	27-Jul-10	WS07270935TJV1	Benzene	27	HNV-DW	19
	SW-002	27-Jul-10	WS07271000TJV1	Benzene	39	HNV-DW	19
	SW-003	27-Jul-10	WS07271030TJV1	Benzene	32	HNV-DW	19
	SW-004	27-Jul-10	WS07271100TJV1	Benzene	28	HNV-DW	19
	SW-100	28-Jul-10	WS07282040TED1	Phenanthrene	2.4	FCV	1.4
	SW-116	03-Aug-10	WS08031510PDS1	Vanadium	24	FCV/GSI	12
	SW-115	03-Aug-10	WS08031600PDS1	Vanadium	140	FCV/GSI	12
	SW-108	17-Aug-10	WS08171455JRP1	Mercury	0.063 J	GSI	0.0013
	SW-103	25-Sep-10	WSB09251121JLS2	Mercury	0.023 J	GSI	0.0013
	SW-104	27-Sep-10	WSB09271230PMB1	Mercury	0.009 J	GSI	0.0013
	SW-002	02-Sep-10	WSC09021505JLS3	Mercury	0.2	GSI	0.0013
	SW-003	17-Sep-10	WSC09171616TDF1	Mercury	0.092 J	GSI	0.0013
	SW-003	27-Sep-10	WSC09271351JLS1	Mercury	0.01 J	GSI	0.0013
	SW-108	03-Sep-10	WSE09030905SWA1	Mercury	0.017 J	GSI	0.0013
Zone Total Number of Exceedances					***= 14***		

Notes:
µg/L = micrograms per liter
GSI = Groundwater Surface Water Interface Criterion (Table 2 of Attachment 1 of the RRD Op Memo No. 1, January 2006).
FCV = Final Cronic Value Criterion (Rule 57 Water Quality Values, December 2009).
HNV-DW = Human Noncancer Value Drining Water Criterion (Rule 57 Water Quality Values, December 2009).
NA - criterion or value is not available, or not applicable

Surface Water Sampling Detections and Screening Summary
Monitoring Program Sample Locations
Enbridge Energy Pipeline 6B
Marshall, MI

Compound	Analysis Summary			Sceening Summary				
	Maximum Detected Value	Number of Detects	Number of Results	Source of Lowest Screening Criteria	Lowest Screening Crtierion	Number of Exceedances	Date of Last Exceedance	Geographic Zone of Last Exceedance
Volatile Organics (µg/L):								
1,2,4-Trimethylbenzene	4.7	28	1546	FCV/GSI	17			
1,3,5-Trimethylbenzene	0.83	9	1546	FCV/GSI	45			
2-Methylnaphthalene	3.6	3	1546	FCV	19			
Benzene	39	28	1546	HNV-DW	19	4	7/27/2010	Upstream of Morrow Lake
Ethylbenzene	2.7	18	1546	FCV/GSI	18			
Isopropylbenzene	0.5	2	1143	FCV	28			
m,p-Xylene	14	36	1258	GSI	35			
Naphthalene	0.66	5	1449	FCV	11			
n-Propylbenzene	0.45	2	1305	NA	–			
o-Xylene	5.5	24	1546	GSI	35			
Toluene	34	170	1546	GSI	140			
Xylenes, Total	4.3	37	1402	GSI	35			
Semi-Volatile Organics (µg/L):								
2-Methylnaphthalene	4.4	6	1546	FCV	19			
Naphthalene	2.1	7	1546	FCV	11			
Phenanthrene	2.4	5	1546	FCV	1.4	1	28-Jul-10	Upstream of Morrow Lake
Metals (µg/L):								
Beryllium	1.7	88	1329	GSI	33			
Iron	11000	1306	1329	NA	–			
Lead	26	943	1167	HNV-DW	14	2	9/15/2010	Morrow Lake
Mercury	0.43	29	1329	GSI	0.0013	29	9/27/2010	Morrow Lake
Molybdenum	5.7	484	1010	HNV-DW	120			
Nickel	72	1021	1513	FCV	125			
Vanadium	140	749	1513	FCV/GSI	12	4	8/3/2010	Upstream of Morrow Lake

Notes:

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