October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: **<u>SAMPLING AND ANALYSIS - ATTACHMENT 5</u>**
COLLECTION OF SAMPLES FOR COMPARISON TO GENERIC CRITERIA

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
Low Flow:	Minimal drawdown groundwater sampling procedures as described in the United States Environmental Protection Agency, Office of Research and Development, Office of Solid Waste and Emergency Response, EPA/540/S-95/504, December, 1995, EPA Groundwater Issue
Response Actions:	Includes “response activities” as defined by Part 201 and “corrective action” as defined by Part 213

PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides direction for collection of groundwater and soil samples for comparison to generic criteria for site assessment, site investigation, and response actions under Part 201, Part 211, and Part 213.

Generic cleanup criteria for groundwater and soil have been developed pursuant to Sections 20120a(1) and 21304a of NREPA (see RRD Operational Memorandum No. 1). These criteria are the risk-based values the department has determined to be protective of the public health, safety, or welfare and the environment. The evaluation of sampling data to establish compliance with cleanup criteria under the provisions of Part 201, Part 211, and Part 213 requires data that reliably establish a representative concentration of the hazardous substance in a given environmental medium. The representativeness of the data can be maximized by using proven accurate and reproducible techniques and verified by using appropriate quality assurance and control procedures in the field and laboratory. This operational memorandum designates sampling, analysis, and quality assurance and control protocols for consistent data collection to facilitate gathering the information necessary for the department to determine compliance with the applicable provisions of Part 201, Part 211, or Part 213. Additional guidance regarding sampling strategies and methodology is available in RRD Operational Memorandum No. 4.

CALIBRATION OF FIELD EQUIPMENT

Instruments and equipment used to gather, generate, or measure environmental data should be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications. Equipment used for field sampling should be examined to certify that it is in operating condition. This includes checking the manufacturing's operating manual and the instructions for each instrument to ensure that all maintenance requirements are being observed. Calibration of field instruments should be performed in accordance with the manufacturer's recommendations and guidelines and at the intervals specified by the manufacturer or more frequently as conditions dictate. At a minimum, equipment should be calibrated prior to each sampling event. In the event that an internally calibrated field instrument fails to meet calibration/checkout procedures, it should not be used in the field until it is serviced and calibrated.

COLLECTION OF SOIL SAMPLES FOR COMPARISON TO THE GENERIC CRITERIA

<u>General Considerations</u>

The soil and groundwater terminology used for this discussion include the following:

- Unsaturated/Vadose Zone: a subsurface zone above the capillary fringe in which the soil pores are only partially filled with water. The moisture content is less than the porosity.
- Saturated Zone: contains two components
    - Capillary Fringe: a subsurface zone above the water table in which the soil pores are filled with water and the pressure heads are less than atmospheric.
    - Water Table: the water level surface below the ground at which a well screened in an unconfined aquifer would fill with water.
- Smear Zone: the vertical area over which groundwater fluctuates (thereby the contaminated water will smear floating and dissolved contamination into the soils in the zone).

Soil samples must be representative of the soils located in the area affected by the release of hazardous substances. The exposure assumptions for soil pathways are based on dry soil. For comparison to the applicable generic soil criteria soil samples must be collected from the vadose zone. The results must be reported by the laboratory on a dry weight basis (adjusted for the vadose zone soil moisture content). Soil analytical methods cannot be applied to saturated soils because they do not provide representative results.

Neither soil nor water sample analyses methods are appropriate for comparison of saturated "soils" samples to generic soil or groundwater cleanup criteria. The cleanup criteria are based upon exposure assumptions appropriate only for soil or water, individually, and are not applicable to exposure to saturated "soil" as a mixture of soil and water.

Contaminants present in the unsaturated soil zone shall be evaluated by comparison of soil sample analyses to the applicable soil criteria. If contaminants are present in a saturated soil zone a monitoring well should be properly installed and the groundwater sampled. These groundwater sample results shall be compared to the applicable groundwater criteria. If free product is suspected and/or a smear zone exists near the water table, a monitoring well shall be appropriately installed so that the water table is bisected by the well screen. Additional guidance regarding monitor well construction is available in RRD Operational Memorandum No. 4.

While analysis of saturated “soil” samples cannot be used to demonstrate compliance with generic cleanup criteria, laboratory analyses or field instrument readings of saturated soils may be of qualitative value for remedial evaluation and design purposes. For example indications of high concentrations in saturated soils may indicate a need to prevent construction worker exposure to shallow saturated soils. This information may also assist in determining the nature of the contaminant and in treatment evaluations. If such data are included as part of response actions under Part 201 or Part 213 rationale for the use must be provided.

If the water surface elevation drops significantly from the time that the original soil investigation was performed, samples should be collected from any former “smear zone” prior to site closure.

Evaluating Exposure Due To Lead In Soil

The amount of lead in soil has historically been evaluated by analyzing lead concentrations in the total soil sample. However, recent evidence indicates that the fine soil fraction, defined as less than 250 microns in size, is more appropriate for comparison to soil direct contact criteria (DCC) and particulate inhalation criteria (PSIC). Exposure to lead in ingested soil and dust is best represented by the lead concentration in the particle size fraction that sticks to hands or that is most likely to accumulate in the indoor environment as a result of wind-blown soil deposition and transport of soil on clothes, shoes, pets, toys and other objects. Additionally, exposure to lead in inhaled soil and dust is best represented by the lead concentration in the particle size fraction likely to enter the respiratory system and become lodged in the alveoli. The particle size fraction of soil and dust likely to be ingested or inhaled is the fine soil fraction. Generally the fine fraction has the higher concentration of lead, but it is possible that the coarse fraction may contain more lead. Therefore, when collecting soils for facility evaluation, both fine and coarse fraction analyses are necessary to determine lead exposure. MDEQ Laboratory SOP #213 provides appropriate procedures for sample preparation. To assure protectiveness, the concentration of lead in each fraction must be compared to the direct contact criteria separately. Only the concentration of lead in the fine fraction must be compared to particulate soil inhalation criteria. The concentration the total lead concentration must be compared to other lead soil criteria. For response actions under Part 201 and Part 213, if the direct contact and particulate inhalation pathways have been appropriately documented to be “not relevant” it is not necessary to analyze the fractions separately.

COLLECTION OF GROUNDWATER SAMPLES FOR COMPARISON TO THE GENERIC CRITERIA

General Considerations

Groundwater samples collected for analyses must be representative of the water moving in the aquifer, in the contaminant plume or in the target zone where contaminants are expected to be located or to migrate. Groundwater samples must represent the contaminant concentrations, including dissolved and naturally suspended particles. Stagnant water in monitor well casings is not representative of the groundwater. Purging of the stagnant water in monitor well casings is necessary but must minimize changes in groundwater chemistry to yield water samples that are representative of the groundwater. Indicator parameters including temperature, pH, dissolved oxygen, specific conductivity and turbidity must be monitored during the purging process to determine stabilization between the well casing waters and the formation waters. Turbidity is the most conservative indicator of stabilization as it is often the last to stabilize. Turbidity in groundwater samples may be naturally occurring, caused by the contamination, or a result of sampling disturbances such as accidental inclusion of aquifer matrix materials from disturbances or mixing that may occur while sampling. Knowledge of site geology, well design, and sampling methodology is helpful in determining the source of turbidity and the method of sampling. Turbidity due to sampling disturbances should be eliminated or minimized while naturally occurring turbidity or turbidity due to contamination should not.

A sampling methodology must be used that accounts for the effects of aquifer heterogeneities while minimizing alterations in water chemistry that could result from sampling disturbances. The MDEQ will accept properly conducted purging methods designed to minimize drawdown by controlling the flow from the well while monitoring stabilization indicator parameters, commonly referred to as Low-Flow methods. Available Low-Flow procedures include United States Environmental Protection Agency, Office of Research and Development, Office of Solid Waste and Emergency Response, EPA/540/S-95/504, December 1995, EPA Ground Water Issue, *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, Robert Puls and Michael Barcelona (http://www.solinst.com/Text/restext/407txt.html) and *Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells*, United States Environmental Protection Agency Region 1, July 30, 1996, Revision 2 (http://www.epa.gov/region01/measure/well/wellmon.html). If another sampling methodology is used, documentation must be submitted to the MDEQ with the data that demonstrates why it is as representative of aquifer conditions as low-flow methodologies. Careful use of the Low-Flow methods is essential in collection of groundwater samples from wells that contain non-aqueous phase liquids, as these substances may be stratified in the monitoring well. Where non-aqueous phase liquid is present, refer to additional guidance for sampling strategies for non-aqueous phase liquids available in RRD Operational Memorandum No. 4, Attachment 5.

Collection of Inorganic Groundwater Samples

Traditionally, the standard practice for collecting metals samples from monitoring wells to evaluate the drinking water pathway had prescribed that samples be filtered with a 0.45 micron filter before inorganic analysis. The practice minimizes the potential for artificially elevated particulate loading resulting in overestimation of metal concentrations. However, U.S. EPA has determined that contaminant concentrations and the potential human health risk may be drastically underestimated for filtered samples (*Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells*, U.S. EPA Region 1, July 30, 1996, Rev 2). Use of the Low-Flow sampling methodologies minimizes sampling disturbances, improves the data quality, and is the method recommended by the MDEQ.

Inorganic constituents must be measured as totals (i.e., unfiltered with appropriate preservation) unless groundwater samples cannot be collected without adequately minimizing the influence of sampling disturbances, in which case filtering may be necessary prior to preservation. The intent of the field-filtration is only to eliminate or minimize sampling disturbances or interference. Any necessary filtration should be accomplished using a filter with a large enough pore size to allow naturally suspended particles to pass through the filter. Some preliminary testing may be required to determine the appropriate filter size. Site-specific conditions may require that both a filtered and unfiltered sample be collected to adequately evaluate the contaminant concentrations. Documentation for the use of filtration and the evaluation of appropriate filter sizes must be provided to the MDEQ with the data.

Collection of Organic Groundwater Samples

Samples to be analyzed for organic substances should not be filtered regardless of sample turbidity except as described in the next paragraph. When response action under Part 201 or Part 213 requires evaluation of the dermal contact with groundwater for contaminants listed in R 299.5750 footnote (AA) an additional set of groundwater samples should be collected for organic substances analysis which should be filtered for analysis of the dissolved phase. The groundwater contact criteria equation estimates the dermal adsorption of hazardous substances that are in the dissolved phase. Therefore, when analyzing for contaminants that strongly adsorb to soil particles, those samples should be filtered so that contaminants in the dissolved phase can be estimated. Filters of appropriate material should be used to ensure the filter does not absorb dissolved contaminants that are not attached to particulates. Glass filters with no binders are acceptable and recommended. Some preliminary testing may be required to determine the appropriate filter medium and pore size. Documentation of the evaluation of appropriate filter medium and size must be provided to the MDEQ with the data.

GENERAL QUALITY ASSURANCE AND QUALITY CONTROL

In order to insure that representative data is used to evaluate facilities, quality assurance and quality control (QA/QC) procedures must be implemented to assure that the precision, accuracy, and representativeness of the data are known and documented. This includes appropriate sample distribution to evaluate the extent of contamination; appropriate sample collection, preservation, shipping, and analysis methodology; collection and analysis of collocated, replicate and split duplicate samples for evaluation of precision; and collection and analysis of field, equipment, and trip blanks as well as matrix spike, matrix spike/duplicate, and laboratory spike samples for analysis of accuracy. Sample distribution and collection are more completely discussed in Operational Memorandum No. 4. Sample handling, preservation, and holding times are discussed in Attachment 4 of this Operational Memorandum. Collection of duplicate, blank and spike samples is discussed below.

Collection of Duplicate Samples to Evaluate Precision

Precision estimates the reproducibility of measurements under a given set of conditions and is reflected in the field duplicate samples and laboratory duplicates analysis. Overall precision for a sampling set is a mixture of field sampling techniques and laboratory techniques. Three types of duplicate samples are relevant to this document: collocated, replicates, and split samples. Collocated samples should be collected and used to estimate the overall precision of a data collection activity. Sampling error can be estimated by inclusion of both collocated and replicated versions of the same samples. Definitions of these samples are listed below:

- Collocated samples are independent samples collected at the same location and at the same time and, for the purpose of these site assessments, processed and analyzed by the same laboratory. Collocated samples are not mixed together and then split into two or more samples. They are two separate samples from an identical site location. They provide a good estimate of precision information for the entire system, including transportation, sampling technique, homogeneity of the site, and laboratory analysis. Examples of collocated samples are samples taken from a moving stream, side by side soil core samples (nesting), two air quality samples taken from one common sample manifold, and two water samples taken from essentially the same point in a lake or lagoon. Collocated samples are used to estimate the overall precision of a data collection activity. Sampling error can be estimated by including a replicate sample with a collocated sample.

- Replicate samples are samples that have been divided into two or more portions at the same step in the measurement process. Examples of replicate samples include two samples taken from a single purged well, samples collected in a common container and then put into separate containers or a soil sample which is thoroughly mixed in a tray and divided into separate containers. Replicate samples are processed and analyzed by the same laboratory.
- Split samples are replicate samples divided into two portions, sent to different laboratories, and subjected to the same environmental conditions and steps in measurement process. They serve as an oversight function in assessing the analytical portion of a measurement system. Samples are often split between the MDEQ and a facility owner or liable party.

Collection of Blank and Spike Samples to Evaluate Accuracy

Accuracy estimates the bias in a measurement system. Accuracy is difficult to estimate for the entire data collection activity. Sources of error include: sampling procedure; field contamination; preservation handling; sample matrix; sample preparation; and analytical techniques. Sampling accuracy can be audited through field, equipment, and trip blanks, while analytical (or laboratory) accuracy can be audited through spike samples and the surrogate recovery results.

A field blank is prepared by pouring distilled/deionized water directly into sample containers. This preparation is performed in the area where sample handling and preservation operations occur. The field blank sample is handled and shipped in the same manner as other analytical samples. Field blank sample analytical results are used to evaluate sample handling, preservation, and shipping procedures.

An equipment blank can be prepared by pouring distilled/deionized water through or over a piece of sampling equipment and collecting rinsate in a sample container. Results of equipment blank analysis are used to evaluate field decontamination procedures and to determine the likelihood of cross contamination.

A trip blank, which normally applies only to volatiles, is a sample that is prepared before any sampling is performed. This sample is shipped from the warehouse to the field and then to the laboratory. Results of trip blank analysis are used to evaluate possible contamination of containers/samples from the time the sample containers are prepared through the field event to the time the samples are received and analyzed at the laboratory.

Laboratory blanks are used to estimate variabilities caused by technique, in-house contamination, and other laboratory problems. Laboratory blanks are prepared by the laboratory.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples and surrogates are samples that are spiked in the laboratory. MS/MSD samples for organic and inorganic water analyses require an extra sample volume. The actual MS/MSD sample is prepared by the laboratory to evaluate accuracy.

Field background, or upgradient samples may need to be collected on a site-specific basis and should be collected from a clean location and shipped with other samples from the site. These samples should be submitted to the laboratory as routine field samples and should not be defined as blanks.

To provide adequate QA/QC for site investigations, the following duplicate, blank and matrix spike samples should be taken. Duplicate and field blank samples should be taken at critical sampling locations, but not at the same location from which the matrix spike/duplicate sample is obtained. They should be sent to the laboratory as blind samples. Reduced QA/QC evaluations may be implemented on a case by case basis with approval of the MDEQ RRD Project Manager.

	Duplicate Samples[1]				**Blank Samples**		
QA/QC Sample Type	**Collocated**	**Replicate**	**Split**	**MS/MSD**	**Field**	**Equipment**	**Trip**
Recommended Number of QA/QC Samples	1 per 10 or fewer samples per matrix[2] and analytical group[3], at least 1 per day	When used: 1 per matrix and analytical group per day	When used: 1 per 1 for samples that will be split	1 per 20 or fewer samples per matrix and analytical group, at least 1 per day	1 per 20 or fewer samples per matrix and analytical group, at least 1 per day	1 per 10 or fewer samples per matrix and analytical group, at least 1 per day	1 per every volatile organic sample shipping container
QA/QC Sample Collection	Individual samples taken from the same location not mixed together and then split.	One sample divided into two or more portions then analyzed by the same laboratory	Replicate samples sent to different labs for analysis	Water samples require double volumes. Samples should be taken at critical locations but different from the field blank.	Fill the sample containers with deionized or distilled water in the area where sample handling and preserving operations occur. Handle and ship the field blank sample as other samples.	Pour deionized or distilled water over or through the sampling equipment and collect rinsate in the sample container. Handle and ship the field blank sample as other samples.	Fill the sample container with deionized water. This in prepared before any sampling is performed and travels to the field and the laboratory with the other sample containers.

1 Normally no field duplicate is required for samples of waste containers or other high concentration samples.

2 soil, groundwater, surface water, sediment, or drinking water, etc.

3 volatile organics, semi-volatiles. pesticides/PCBs, metals, cyanide, etc.

Note: Where method 8260+ volatile analysis for soils, sediments, sludges, and waste container samples is done, methanol blank samples should be collected by the laboratory for each methanol lot used. These lots should be tracked in the field and reported on the laboratory receipt form so laboratory correlations can be made.

SAMPLE CHAIN OF CUSTODY

An essential part of any sampling and analytical scheme is ensuring the integrity of the sample from collection to data reporting. The possession and handling of samples should be traceable from the time of collection through analysis and final disposition. This documentation, referred to as chain of custody, is particularly necessary if there is any possibility that the analytical data or conclusions based upon analytical data will be used in litigation. Regardless of the potential for litigation, these procedures are useful for routine control of sample flow.

A sample is under your custody if it is in your possession; is in your view, after being in your possession; was in your possession and you placed them in a secured location; or is in a designated secure area.

As few people as possible should handle the samples. The field sampler/sampling crew should track the chain of custody in the field on the individual sample data collection sheets and chain of custody tracking reports before shipment. Samples should be collected following the appropriate sampling procedures and documented on the sample data sheet. The equipment used to collect samples should be noted, along with the time of sampling, sample location, type and description, depth at which the sample was collected, and any other pertinent remarks. All bottles and jars should be properly labeled with sample number, date and time of collection, and location. Sample labels and tags should be affixed to the each sample container prior to or at the time of sampling. Sample seals should be used to detect any unauthorized tampering with samples from the time of sample collection to the time of analysis.

A record should be kept of data-collecting activities performed. A field logbook is a useful tool for keeping such records. Entries into the logbook may contain a variety of information such as site contacts, phone numbers, assigned laboratories, addresses, etc. Documentation of on site weather conditions and activities that take place during sampling events should be described in as much detail as possible so that persons going to the site can re-construct a particular situation without reliance on memory. The record for each sampling event should include the date, start time, names of all persons present, level of personal protection being used, and the signature of the person recording the information. Measurements made and samples collected should be recorded. All entries in field logbooks should be made in ink and no erasures made. If an incorrect entry is made, the information should be crossed out with a single strike mark. When a sample is collected, or a measurement is made, a detailed description of the location of sample collection (such as a map point which includes compass and distance measurements or Global Positioning System location information) should be recorded. Equipment used to make measurements should be identified, along with the date of calibration.

A chain of custody record should be filled out and should accompany every sample container shipped or delivered to the laboratory. This record becomes especially important if the sample data could be introduced as evidence in litigation. For each sample in the container, the chain of custody record should include the sample number, signature of the collector, date and time of collection, place and address of collection, sample matrix, and signature and inclusive dates of possession for each person involved in the chain of possession from the point of sample collection through sample analysis.

The following document is rescinded with the issuance of this attachment:

- Storage Tank Division Informational Memorandum 16, Policy regarding the appropriate use of saturated soil sampling results under the Leaking Underground Storage Tank (LUST) Program, dated October 21, 1998.

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.