DEQ	**Remediation and Redevelopment Division RESCISSION OF POLICY AND PROCEDURE**		DEPARTMENT OF ENVIRONMENTAL QUALITY
Rescinded Date: March 10, 2016	Subject: RRD Operational Memorandum No. 2 Sampling and Analysis		Category: ☐ Internal/Administrative ☐ External/Non-Interpretive ☒ External/Interpretive Type: ☐ Policy ☐ Procedure ☒ Policy and Procedure
	Program Name: Part 201, Environmental Remediation Part 213, Leaking Underground Storage Tanks		
	Number: Operational Memorandum RRD-2	Page: 1 of 1	

The Remediation and Redevelopment Division (RRD) Operational Memorandum No 2: Sampling and Analysis, dated October 22, 2004, in its entirety is rescinded.

The target detection limits (TDLs) and analytical methods designated to meet the TDLs formerly contained within Operational Memorandum No. 2 have been replaced by the Michigan Department of Environmental Quality's published list of Target Detection Limits and Designate Analytical Methods.

General information contained in former Operational Memorandum No. 2 has been reformatted as Application of Target Detection Limits and Designated Analytical Methods Resource Materials.

The following RRD Policies and Procedures have been developed to replace direction for RRD staff and their contractors to address:

- Methanol Preservation in the Field, RRD-25-02-01
- Sample Preservation, Sampling Handling, and Holding Times, RRD-25-02-02
- Low Level Mercury Sample Collection, RRD-25-02-03

These materials are available to staff and to assist any party in implementing response activities or corrective action proposals regulated by Part 201, Environmental Remediation, and Part 213, Leaking Underground Storage Tanks, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended.

DIVISION CHIEF APPROVAL:

Robert Wagner, Chief
Remediation and Redevelopment Division

CHIEF DEPUTY DIRECTOR APPROVAL:

Jim Sygo, Chief Deputy Director

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: SAMPLING AND ANALYSIS

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
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
Response Action:	Includes "response activities" as defined by Part 201 and "corrective action" as defined by Part 213

PURPOSE

This operational memorandum has been prepared to facilitate implementation of Part 201, Part 211, and Part 213. This operational memorandum supercedes all previous MDEQ Part 201, Part 211, and Part 213 sampling and analysis guidance.

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 representative concentrations of the hazardous substances in a given environmental medium. To facilitate gathering the information necessary for the department to determine compliance with the applicable provisions of Part 201, Part 211, or Part 213, this operational memorandum designates consistent sampling and analysis protocols and consolidates, as attachments, specific sampling and analysis related specifications for the following:

Attachment 1. Target Detection Limits and Designated Analytical Methods

This attachment provides direction for analytical target detection limits for site assessment, site investigation, and response activities under Part 201, Part 211, and Part 213. This attachment constitutes the department's published list of target detection limits and available analytical methods pursuant to R 299.5103(l).

Attachment 2. Soil Leaching Methods

This attachment provides specifications for soil leaching methods acceptable to the department to establish the concentration of a hazardous substance leaching from soil. Alternate methods are provided pursuant to R299.5722(3)(b).

Attachment 3. Indoor Air Designated Methods and Target Detection Limits

This attachment provides direction for acceptable methods and analytical target detection limits for acceptable indoor air concentrations for response activities under Part 201, and Part 213.

Attachment 4. Sample Preservation, Sample Handling, and Holding Time Specifications

This attachment provides specifications applicable for the collection, preservation, holding times, and handling of groundwater and soil samples applicable to site assessment, site investigation, and response activities under Part 201, Part 211, and Part 213.

Attachment 5. Collection of Samples for Comparison to Generic Criteria

This attachment provides direction for collection of groundwater and soils samples. Additional guidance regarding sampling strategies is available in RRD Operational Memorandum No. 4.

Attachment 6. Sampling Methods for Volatile Organic Compounds

This attachment provides specifications for the collection and preservation of samples collected to determine concentrations of volatile organic compounds, and is applicable for site assessments, site investigations, and response activities under Part 201, Part 211, and Part 213.

Attachment 7. Low Level Mercury Sampling Specifications

This attachment provides specifications for the collection of groundwater samples from monitoring wells to determine mercury concentrations for the evaluation of groundwater that vents to surface water, and is applicable to site assessments, site investigation, and response activities under Part 201, Part 211, and Part 213.

This document is intended to provide direction and guidance for sampling and analysis conducted for facilities regulated under Part 201, Part 211, and Part 213. State programs administered under other parts of NREPA or Federal programs may have requirements in addition to this guidance. Questions about sampling and analysis requirements should be directed to appropriate program staff.

original signed by Andrew W. Hogarth on October 22, 2004 Dated:_____

Andrew W. Hogarth, Chief

Remediation and Redevelopment Division

ATTACHMENTS

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.

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: **SAMPLING AND ANALYSIS - ATTACHMENT 1**
TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

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 R299.5706a(4).
Facility:	Includes "facility" as defined by Part 201 and "site" as defined by Part 213
Response Actions:	Includes "response activities" as defined in Part 201 and "corrective action" as defined in Part 213

PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides direction for analytical target detection limits (TDLs) for response actions under Part 201 and Part 213 and site assessments under Part 211. This attachment constitutes the department's published list of analytical target detection limits for hazardous substances and available analytical methods that are capable of achieving the target detection limits pursuant to R 299.5103(l).

The TDLs and designated analytical methods identified in this attachment shall apply to all sampling and analysis conducted more than 30 days after the date of issuance of Operational Memorandum No. 2.

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 the data reliably establish a representative concentration of the hazardous substance in a given environmental medium. This attachment establishes analytical target detection limits for hazardous substances and designates available analytical methods that are capable of achieving the target detection limits to facilitate gathering the information necessary for the department to determine compliance with the applicable provisions of Part 201, Part 211, or Part 213.

TARGET DETECTION LIMITS

Analytical TDLs have been established by the MDEQ for hazardous substances with generic cleanup criteria. In establishing TDLs the MDEQ considered the need to be able to measure the hazardous substances at concentrations at or below cleanup criteria. The TDLs were

derived by reviewing the low-level capabilities of state laboratories and methods published by government agencies and referenced in this document.

If the established TDL is greater than the risk-based cleanup criteria for a hazardous substance in a given environmental medium, the TDL shall be used in place of the risk-based value as the cleanup criterion.

For soil matrices, laboratory reporting limits should be equal to, or less than, the listed TDLs on a dry weight basis. For groundwater matrices, laboratory reporting limits should be equal to, or less than, the listed TDLs. Achieving the TDL is critical for site assessment and site investigation activities where the objective is the characterization of the nature and extent of contamination. For response activities under Part 201 or Part 213, where the goal is to determine compliance with applicable cleanup criteria alternate TDLs may be used if the pathways with the most restrictive cleanup criteria are appropriately determined to be "not relevant" and are therefore not applicable. Alternate TDLs are footnoted with the relevant pathway's applicable criteria.

DESIGNATED METHODS

Table 1 identifies the TDLs and the analytical methods judged capable of achieving the TDLs. The source documents for the analytical methods are listed in Table 2. The designated analytical methods include multiple methods in those cases where more than one method has been judged capable of achieving the TDL.

Alternate Acceptable Analytical Methods: The methods listed in Table 1 are primarily from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Edition 3, (SW-846) Office of Solid Waste & Emergency Response, U.S. EPA. Alternate methods, and revisions of the listed methods, may be used with prior written approval of the RRD. Except when specifically indicated in this document, prior written approval is not needed for the following specific cases:

- Revisions of methods in Table 1 from subsequent revisions published in SW-846.
- Methods approved by the U.S. EPA for use in the Contract Laboratory Program (CLP).
- Methods promulgated for use under the Federal Safe Drinking Water Act that are acceptable for raw source and finished drinking waters.
- Methods promulgated for use under the Federal Clean Water Act that are acceptable for wastewater, groundwater and surface water analysis.

Confirmations: Gas chromatography methods with mass spectrometry (GC/MS) confirmations of the contaminants' identity are preferred when the TDL can be met. When other GC methods are used, confirmation techniques should be used whenever possible such as measurements on dual columns and confirmation of a select number of samples with high levels of the contaminants that can be detected and confirmed by GC/MS.

CONTAMINANTS WITH TDLS HIGHER THAN THE MOST RESTRICTIVE CRITERIA

Table 6 lists contaminants that have TDLs greater than the most restrictive risk-based criteria. These TDLs are also identified in Table 1 through the use of bold font and by enclosing the TDLs with brackets. For these contaminants, laboratories should always report results below the TDL down to the laboratory's limits of detection. Appropriate codes must be used to indicate that the results are below the laboratory's reporting limits and are estimated. The results will be interpreted as provided in R299.5742.

CONTAMINANTS WITHOUT TDLS OR DESIGNATED ANALYTICAL METHODS

Table 7 lists contaminants with established risk-based criteria that do not have TDLs or designated analytical methods. For these contaminants, or for contaminants with no established criteria, proposed appropriate TDLs and analytical methods should be submitted to the MDEQ for review and approval. Analytical methods proposed must be supported by submission of detailed descriptions of the methods and method performance validations. When methods used are listed in Table 1 and applied to contaminants not listed in the published method, method performance validations for those contaminants must be provided to the MDEQ.

ELEVATION OF REPORTING LIMITS

Reporting limits may be elevated above the TDLs because of matrix effects, including interferences resulting from non-target or high levels of target compounds, interferences from species native to the sample matrices under investigation, and when results from the analysis of soils are adjusted for the moisture content. The use of elevated reporting limits must be approved by the MDEQ. For response actions under Part 201 or Part 213, elevated reporting limits may be acceptable if the most restrictive cleanup criterion is not exceeded. For contaminants where the TDLs are greater than the most restrictive risk-based criteria (Table 7) elevated reporting limits may be unacceptable. When reporting limits are increased for these contaminants, or when increased beyond the cleanup criteria, it is necessary to further evaluate the elevated reporting limits. This may include reviews of laboratory procedures to determine their appropriateness, re-analysis at other laboratories, further sample cleanups, modifications to methods, or other actions.

USE OF ALTERNATE REPORTING LIMITS

Alternate reporting limits may be acceptable:

- When site-specific background levels or statewide default background levels for certain metals are substituted as the cleanup criteria, it may not be necessary to report data below the background levels.
- For response actions under Part 201 or Part 213, when the most restrictive criteria has been appropriately documented to not be applicable, reporting limits may be specified, based on the most restrictive applicable criteria.
- When concentrations are determined for off-site waste disposal requirements.
- When sample concentrations lower than the TDL can be quantified; i.e., the lower sample concentrations are within the analytical range of the method.
- When monitoring levels of contaminants lower than the TDLs is necessary, particularly when risk-based criteria are lower than the TDL.

APPLICATION OF REPORTING LIMITS

The TDLs are applicable to site assessments, environmental investigations, and response activities performed pursuant to Part 201, Part 211, and Part 213. They may not be applicable to other environmental statutes. Facilities subject to regulation under other environmental statutes should consult the appropriate MDEQ division.

Questions about this memorandum attachment should be directed as follows:

- Site investigation and response activities under Part 201 and Part 213:
  A. Ralph Curtis, Laboratory Specialist
  Remediation and Redevelopment Division; Toxicology Unit
  Phone: 517-373-8389, FAX: 517-241-9581, Email: curtisar@michigan.gov
- Site assessments under Part 211:
  Marcia Jo Poxson
  Waste and Hazardous Materials Division; Storage Tank Unit
  Phone: 517-373-3290, FAX: 517-335-2245; Email: poxsonm@michigan.gov

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

- Environmental Response Division Operational Memorandum 6 , Revision 6, Analytical Method Detection Level Guidance for Environmental Contamination Response Activities under Part 201 of NREPA dated January 12, 2001, and addendum dated May 5, 2003.
- Storage Tank Division Operational Memorandum 4, Attachment 13, Analytical Detection Level Guidance under Part 211, and Part 213, of NREPA dated February 15, 2001, and addendum dated May 5, 2003.

Major changes from the direction in the rescinded documents are summarized as follows:

GENERAL CHANGES FROM PREVIOUS GUIDANCE

- The use of CFR 40 Part 136, Appendix B, to confirm TDLs was removed.
- Emphasis was placed on preferring GC/MS methods.
- Table 6 was added that listed contaminants with TDLs higher than the most restrictive criteria.
- Notations were added to contaminants in Table 1 to indicate: pathways that are relevant for the associated TDL; contaminants present in light petroleum products and oxygenates; and contaminants which are solvents commonly used in laboratories.
- Contaminant groupings in Table 1 were altered to increase compatibility with RRD Operational Memorandum No. 2, Attachment 4, Sample Preservation, Sample Handling, and Holding Time Specifications.

CHANGES IN METHODS

- Methods were removed from Table 1 that were never used. Language was added to allow methods from other programs.
- Additional methods approved in SW-846 were added to improve flexibility in choices.
- The notation SIM was added to specific methods, where appropriate, to indicate the use of the selected ion monitoring (SIM) technique for GC/MS methods.
- Methods for the analysis for 1,4-Dioxane that were laboratory specific were replaced with the source methods used.
- The method to determine the fraction of organic matter changed due to method revision.
- The method to determine Dacthal was changed to 8081B.
- Specific extraction methods for soil nitrate, nitrite, fluoride, and chloride were added.

- Language was added to specify distillation of ammonia from soils as the recommended method.
- The extraction method for chlorides was specified as “water extracts,” as each laboratory had their own extraction procedure.
- Methods for the analysis for explosives were added.

TDL REVISIONS MADE WITH THIS DOCUMENT

- Table 3 “Contaminants Added to TDL and Designated Analytical Methods Lists” lists contaminants added to the MDEQ TDL and Designated Analytical Methods List .
- Table 4 “Contaminants Removed from TDL and Designated Analytical Methods Lists”, lists contaminants removed from the MDEQ TDL and Designated Analytical Methods List .
- Table 5 “Rationale for Reducing TDLs from the Previous Operational Memoranda”, lists those TDLs which have been reduced to allow measurement at or nearer to the most restrictive criteria, and rationale for the reduction.

APPENDAGES TO THIS ATTACHMENT:

TABLE 1. Target Detection Limits And Designated Analytical Methods
TABLE 2. Source Documents For Designated Analytical Methods
TABLE 3. New Contaminants Added to TDLs and Designated Analytical Methods List
TABLE 4. Contaminants Removed From TDLs and Designated Analytical Methods List
TABLE 5. Rationale For Reducing TDLs From Previous Operational Memoranda
TABLE 6. TDLS Greater Than The Most Restrictive Risk-based Criteria
TABLE 7. Contaminants With Established Risk-based Criteria And Without TDLs And Designated Analytical Methods

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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. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Specific Contaminants				
Acetic Acid	64197	**[1,000]**	20,000	Analysis for acetate is used
Acetate	ACETATE	1,000	20,000	Ion Chromatography [1]
Chloride	16887006	10,000	200,000	300.1 9056 9212 9250 9251 9253 [325 methods] Use water extracts for soils
Dissolved Oxygen	DO	80	-----	360.1 360.2
Fluoride	7782414	1000	5000	9214 300.1 9056 340.1 Soils [2]
Formic Acid	64186	1,000	20,000	Analysis for formate is used
Formate [3]	FORMATE	1,000	20,000	Ion Chromatography [1]
Hardness[4]	HARDCALC	-----	NA	Calculate from separate Ca and Mg results using SM 2340B
Perchlorate	14797730	3	-----	314.0 9058
pH	PH	-----	-----	9040C (waters) 9045D (soils)
Phosphorus (White)	12185103	0.005	1	7580
Phosphorus (total)	7723140	10	200	365.4 (waters) 6010 6020 200.7 200.8 Soils [5]
Petroleum Hydrocarbon Material	PET_HYD	See Method	See Method	1664 9071B 8440
Sulfate	14808798	1000	50,000	300.1 9056 9035 9036 375.1 375.2 Soils [6]
Sulfide, Dissolved .and Acid Solution.	18496258	200	1000	[9030 with 9034 or 9215] 376.1 376.2
Total Dissolved Solids	TDS	10,000	----	160.1
Cyanide [7]	57125			
Cyanide, Available	CN_AVAIL	5	100	OIA 1677 Soils: Extract with 9013. 335.1 Modified for soils.
Cyanide, Amenable	CN_AMEN	5	----	9019B 9012A
Cyanide, Total	CN_TOTAL	----	100	9010B 9012A Kelada-01 335.2
Nitrogen Forms [8]				
Ammonia-N	7664417	25	1000	350.1/2/3 (Waters) For soils see [9]
Nitrate-N	14797558	100	1000	300.1 9056 353.2 For soils see [10]
Nitrite-N	14797650	100	1000	300.1 9056 353.2 For soils see [10]
Kjeldahl-N	TKN	100	1000	351.1 351.2 351.3 351.4
Urea	57136	400	20,000	983.01
Nitrogen, Total (elemental)	7727379	100	1000	See footnote 8

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Metals [11]	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg
Aluminum	7429905	50	1000
Antimony	7440360	2	**[300]**
Arsenic	7440382	5	100
Barium [12]	7440393	100	1000
Beryllium [12]	7440417	**[1]**	500
Boron	7440428	300	8000
Cadmium [12]	7440439	1	200
Chromium III	16065831	10	2000
Chromium (total)	7440473	10	2000
Cobalt	7440484	20	500
Copper [12]	7440508	4	1000
Iron	7439896	200	5000
Lithium	7439932	10	400

Metals [11]	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg
Magnesium	7439954	1000	4000
Manganese [12]	7439965	50	1000
Molybdenum	7439987	50	1000
Nickel [12]	7440020	20	1000
Selenium	7782492	5	200
Silver	7440224	**[0.2]**	**[100]**
Sodium	7440235	1000	10000
Strontium	7440246	1000	5000
Thallium	7440280	2	500
Thorium	7440611	10	1000
Vanadium	7440622	4	1000
Zinc [12]	7440666	50	1000

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods for Lead[11] See MDEQ Laboratory SOP #213
Lead, Total [12]	7439921	3	1000	Report as Lead, Total
Lead, Fine Fraction [13]	PB_FINE	-----	1000	Report as Lead, Fine Fraction
Lead, Coarse Fraction [13]	PB_COARSE	-----	1000	Report as Lead, Coarse Fraction
Contaminants				**Designated Methods**
Chromium VI	18540299	10	2000	7199 (waters) 3060A/7199 (soils)
Mercury, Total [14,15]	7439976	0.001	**[50]**	1669/1631 [16] 6000 & 7000 245.7 200.8
Metals by XRF				
Instrument Specific	Various	-----	Varies	6200[17]

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
DRO and GRO [18]				
Diesel Range Organics (DRO)	DRO	100	4000	Wisconsin Modified DRO
Gasoline Range Organics (GRO)	GRO	200	4000	Wisconsin Modified GRO
Carbonyls				
Acetaldehyde	75070	100	2500	8315A
Formaldehyde	50000	100	2000	8315A

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Glycols				Use water extracts for soils
Triethylene Glycol	112276	4,000	50,000	8015C
Ethylene Glycol	107211	10,000	10,000	8015C 8430
Propylene Glycol	57556	10,000	50,000	8015C 8430
Dissolved Gases In Waters[19]				
Methane [19]	74828	500	-----	Methods: RSKSOP-175 and Isotec Method
Ethane	76017			
Ethylene	75218			
Nitrous oxide	10024972			
Soil Gases [19]			**Soil Gas TDL %**	
Methane[19]	74828	-----	0.005 (50 ppm)	Modified EPA Method 8015B, EPA Method 8015B, EPA Method TO-3, or ASTM 3416M (EPA 3C), Field methods discussed in Operational Memorandum No. 6.
Soil Gases (except methane)	Various	-----	Varies	Laboratory Methods: TO Air Methods Field Sampling and Analysis: D5314 – 92

Polynuclear Aromatics (PNAs) [20]	CAS/ID	Water TDL GC/MS ug/L	Soil TDL GC/MS ug/Kg	Designated Methods
Acenaphthene	83329	5	330	8270C (SIM) 8310
Acenaphthylene	208968	5	330	8270C (SIM) 8310
Anthracene	120127	5	330	8270C (SIM) 8310
Benzo(a)anthracene	56553	1	330	8270C (SIM) 8310
Benzo(b)fluoranthene	205992	1	330	8270C (SIM) 8310
Benzo(k)fluoranthene	207089	**[1]**	330	8270C (SIM) 8310
Benzo(ghi)perylene	191242	**[1]**	330	8270C (SIM) 8310
Benzo(a)pyrene	50328	**[1]**	330	8270C (SIM) 8310
2-Chloronaphthalene	91587	5	330	8270C (SIM) 8310 8260B
Chrysene	218019	1	330	8270C (SIM) 8310
Dibenzo(ah)anthracene	53703	**[2]**	330	8270C (SIM) 8310
Fluoranthene	206440	1	330	8270C (SIM) 8310
Fluorene	86737	5	330	8270C (SIM) 8310
Indeno(1,2,3-cd)pyrene	193395	**[2]**	330	8270C (SIM) 8310
2-Methylnaphthalene	91576	5	330	8270C (SIM) 8310 8260B 8261
Phenanthrene	85018	2	330	8270C (SIM) 8310
Pyrene	129000	5	330	8270C (SIM) 8310

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Nitrosoamines				
N-Nitrosodi-n-propylamine	621647	**[5]**	**[330]**	8270C 8261 8070
N-Nitrosodimethylamine	62759	5	330	8270C 8261 8070
N-Nitrosodiphenylamine	86306	5	330	8270C 8261 8070
Benzidines				
Benzidine[21]	92875	**[0.3]**	**[1000]**	605 (Waters) 8270C (Ion Trap) (SIM)
3,3'-Dichlorobenzidine[21]	91941	**[0.3]**	**[2000]**	605 (Waters) 8270C (Ion Trap) (SIM)

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Acid Extractables (Phenols)				
2-Chlorophenol	95578	10	330	8270C 8041A
3-Chlorophenol	108430	10	330	8270C 8041A
4-Chloro-3-methylphenol	59507	5	280	8270C 8041A
2,4-Dichlorophenol	120832	10	330	8270C 8041A
2,6-Dichlorophenol	87650	5	330	8270C 8041A
2,3-Dimethylphenol	526750	5	330	8270C 8041A
2,4-Dimethylphenol	105679	5	330	8270C 8041A
2,6-Dimethylphenol	576261	4	**[330]**	8270C 8041A
3,4-Dimethylphenol	95658	5	**[330]**	8270C 8041A
3,5-Dimethylphenol	108689	5	330	8270C 8041A
2,4-Dinitrophenol	51285	25	830	8270C 8041A
2-Methyl-4,6-dinitrophenol	534521	**[20]**	**[830]**	8270C
Methylphenols [22]	1319773	30	1000	8270C
2-Methylphenol [22]	95487	10	330	8270C
3-Methylphenol [22]	108394	10	330	8270C
4-Methylphenol [22]	106445	10	330	8270C
2-Nitrophenol	88755	5	330	8270C 8041A
3-Nitrophenol	554847	20	830	8270C 8041A
4-Nitrophenol	100027	25	830	8270C 8041A
Pentachlorophenol [21, 23]	87865	1	20	8151A 515.1 515.2 8041A 8270C (SIM)
Phenol	108952	5	330	8270C 8041A
2,4,5-Trichlorophenol	95954	5	330	8270C 8041A
2,4,6-Trichlorophenol	88062	4	330	8270C 8041A

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Semivolatiles				
Acetophenone	98862	5	330	8270C
Aniline[21]	62533	4	**[330]**	8270C 8131 8270C (SIM) 8261
Azobenzene	103333	2	200	8270C
Benzal Chloride	98873	10	330	8270C
Benzoic acid	65850	50	3300	8270C
Benzotrichloride	98077	0.1	20	8121
Benzyl Alcohol	100516	50	3300	8270C
Bis(2-chloroethoxy)ethane	112265	5	330	8270C
Bis(2-chloroethoxy)methane	111911	5	330	8270C
Bis(2-chloroethyl)ether	111444	1	100	8270C 8430
Bis(2-chloroisopropyl) ether	108601	5	330	8270C
Bis(2-ethylhexyl)phthalate	117817	5	330	8270C 8061A
4-Bromophenyl phenylether	101553	5	330	8270C
Butyl benzyl phthalate	85687	5	330	8270C 8061A
Caprolactam	105602	10	330	8270C
Carbazole	86748	**[10]**	330	8270C
4-Chloroaniline	106478	10	330	8270C 8131
2-Chloronaphthalene	91587	5	330	8270C 8121 8310
4-Chlorophenyl phenylether	7005723	5	330	8270C
Dibenzofuran	132649	4	330	8270C
Dicyclohexyl phthalate	84617	5	330	8270C 8061A
Di(2-ethylhexyl)adipate	103231	5	330	8270C 8061A
Diethyl phthalate	84662	5	330	8270C 8061A
Dimethyl phthalate	131113	5	330	8270C 8061A
Di-n-butyl phthalate	84742	5	330	8270C 8061A
Di-n-octyl phthalate	117840	5	330	8270C 8061A
1,3-Dinitrobenzene	99650	5	330	8270C 8095
2,4-Dinitrotoluene	121142	5	330	8270C 8330A 8095
2,6-Dinitrotoluene	606202	5	330	8270C 8330A 8095
1,2-Diphenylhydrazine	122667	5	330	8270C
Hexachlorobenzene (C-66)[21]	118741	0.2	330	8121 8270C – Ion Trap - (SIM)

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Semivolatiles				
Hexachlorobutadiene (C-46) [21, 24]	87683	0.05	50	8121 8081B 8270C (SIM) 8261
Hexachloroethane	67721	5	300	8270C 8121
Hexachlorocyclopentadiene (C-56)	77474	5	330	8270C 8121
Isophorone	78591	5	330	8270C
4,4'-Methylene-bis-2-chloroaniline	101144	1	500	8270C
2-Methylnaphthalene	91576	5	330	8270C 8260B 8310
2-Nitroaniline	88744	25	830	8270C 8131
3-Nitroaniline	9909	25	830	8270C 8131
4-Nitroaniline	100016	25	830	8270C 8131
Nitrobenzene	98953	3	330 [25]	8270C 8330A 8095
Octachlorocyclopentene	706785	5	330	8270C
Pentachlorobenzene	608935	**[5]**	330	8270C 8121
Pentachloronitrobenzene	82688	20	330	8270C 8081B
Pyridine	110861	**[20]**	330	8270C 8261 8015C
1,2,3,4-Tetrachlorobenzene	634662	5	330	8270C 8121
1,2,3,5-Tetrachlorobenzene	634902	5	330	8270C 8121
1,2,4,5-Tetrachlorobenzene	95943	2	330	8270C 8121
p-Toluidine	106490	10	**[660]**	8270C

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods See Op Memo 2, Attachment 6 [26]
Volatiles				
Acetone [27]	67641	50	1000	8260B 8261
Acetonitrile [27]	75058	50	2500	8260B 8261 8033
Acrylamide	79061	0.5	-----	8032A 8316
Acrylonitrile	107131	2	**[{100}]**	524.2 8260B 8261 8031 8316
Acrolein	107028	20	{250}	8260B 8261 8316
Benzyl Chloride	100447	5	{150}	8260B 8121
Benzene	71432	1	50	8260B 8261 8021B
Bromobenzene	108861	1	100	8260B 8021B
Bromochloromethane	74975	1	100	8260B 8261 8021B
Bromomethane (Methyl bromide)	74839	5	{200}	8260B 8261 8021B

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Volatiles				
2-Butanone (MEK)	78933	25	750	8260B 8261 8021B
n-Butyl Acetate	123864	10	250	8260B
n-Butyl Alcohol	71363	800	4400	8260B [28] 8015C
n-Butylbenzene	104518	1	50	8260B 8261 8021B
s-Butylbenzene	135988	1	50	8260B 8261 8021B
t-Butylbenzene	98066	1	50	8260B 8261 8021B
Carbon Disulfide	75150	5	250	8260B 8261
Carbon Tetrachloride	56235	1	50	8260B 8261 8021B
Chlorobenzene	108907	1	50	8260B 8261 8021B
Chloroethane	75003	5	250	8260B 8261 8021B
2-Chloroethylvinyl ether [29]	110758	10	5000	8260B
Chloromethane	74873	5	250	8260B 8261 8021B
2-Chlorotoluene	95498	5	50	8260B 8261 8021B
4-Chlorotoluene	106434	5	50	8260B 8261 8021B
Cyclohexanone	108941	50	2500	8260B 8261 8315A
1,2-Dibromo-3-chloropropane[21]	96128	0.2	**[{10}]**	8011 504.1 8260B 8081B (SIM)
Dibromomethane	74953	5	250	8260B 8261 8021B
1,2-Dichlorobenzene	95501	1	100	8260B 8261 8021B 8121
1,3-Dichlorobenzene	541731	1	100	8260B 8261 8021B 8121
1,4-Dichlorobenzene	106467	1	100	8260B 8261 8021B 8121
1,4-dichloro-2-butene, trans	764410	1	50	8260B 8261 8021B
Dichlorodifluoromethane	75718	5	250	8260B 8261 8021B
1,1-Dichloroethane	75343	1	50	8260B 8261 8021B
1,2-Dichloroethane	107062	1	50	8260B 8261 8021B
1,1-Dichloroethylene	75354	1	50	8260B 8261 8021B
1,2-Dichloroethylene, cis	156592	1	50	8260B 8261 8021B
1,2-Dichloroethylene, trans	156605	1	50	8260B 8261 8021B
1,2-Dichloropropane	78875	1	50	8260B 8261 8021B
2,2-Dichloropropane	594207	1	50	8260B 8261 8021B
1,3-Dichloropropane	142289	1	50	8260B 8261 8021B
1,1-Dichloropropene	563586	1	50	8260B 8261 8021B

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Volatiles				
1,3-Dichloropropene [30]	542756	1	100	8260B 8261 8021B
1,3-Dichloropropene, cis	10061015	1	50	8260B 8261 8021B
1,3-Dichloropropene, trans	10061026	1	50	8260B 8261 8021B
1,3-Diethylbenzene	141935	1	150	8260B
Diethyl ether [27]	60297	10	200	8260B 8015C
Diethoxymethane	462953	10	500	8260B
1,4-Dioxane[21]	123911	1	500	8260B [28] 8261 1624 (SIM)
Epichlorohydrin	106898	**[5]**	{100}	8260B
Ethylbenzene	100414	1	50	8260B 8261 8021B
Ethylene Dibromide[29]	106934	0.05	**[{20}]**	8011 504.1 8260B 8261
Ethylene Oxide	75218	200	10000	8260B 8015B
2-Hexanone	591786	50	2500	8260B 8261 8021B
Isobutyl Alcohol	78831	1000	4400	8260B 8261 8015C
Isopropyl Alcohol	67630	400	4400	8260B [28] 8015C
Isopropylbenzene	98828	5	250	8260B 8261 8021B
p-Isopropyl toluene (p-Cymene)	99876	5	100	8260B 8261 8021B
Methyl Alcohol [31]	67561	400	4400	8260B [28] 8015C
4-Methyl-2-pentanone (MIBK) [27]	108101	50	2500	8260B 8261 8021B
Methylene Chloride [27]	75092	5	{100}	8260B 8261 8021B
Methyl iodide	74884	1	100	8260B
Methylcyclopentane	96377	50	2500	8260B
Naphthalene[21]	91203	5	330	8260B 8261 8270C (SIM) 8310
Pentane	109660	100	5000	8260B
n-Propyl benzene	103651	1	100	8260B 8261 8021B
Styrene [29]	100425	1	50	8260B 8261 8021B
1,1,1,2-Tetrachloroethane	630206	1	100	8260B 8021B
1,1,2,2-Tetrachloroethane	79345	1	50	8260B 8261 8021B
Tetrachloroethylene	127184	1	50	8260B 8261 8021B
Tetrahydrofuran	109999	90	1000	8260B 8261
Tetranitromethane	509148	100	**[500]**	8260B
Toluene	108883	1	100	8260B 8261 8021B

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Volatiles				
1,2,4-Trichlorobenzene	120821	5	330	8260B 8261 8021B
1,1,1-Trichloroethane	71556	1	50	8260B 8261 8021B
1,1,2-Trichloroethane	79005	1	50	8260B 8261 8021B
Trichloroethylene	79016	1	50	8260B 8261 8021B
Trichlorofluoromethane	75694	1	100	8260B 8261 8021B
1,1,2-Trichloro-1,2,2-trifluoroethane	76131	1	250	8260B
1,2,3-Trichloropropane	96184	1	100	8260B 8261 8021B
Trihalomethanes [32]		100	-----	8260B 8261
Dibromochloromethane	124481	5	100	8260B 8261 8021B
Chloroform	67663	1	50	8260B 8261 8021B
Bromodichloromethane	75274	1	100	8260B 8261 8021B
Bromoform	75252	1	100	8260B 8261 8021B
1,2,4-Trimethylbenzene	95636	1	100	8260B 8261 8021B
1,3,5-Trimethylbenzene	108678	1	100	8260B 8261 8021B
2,2,4-Trimethylpentane	540841	50	2500	8260B
Vinyl Acetate	108054	100	5000	8260B
Vinyl Chloride	75014	1	{40}	8260B 8261 8021B
Xylenes [33]	1330207	3	150	8260B 8261 8021B
m-Xylene	108383	1	50	8260B 8261 8021B
p-Xylene	106423	1	50	8260B 8261 8021B
o-Xylene	95476	1	50	8260B 8261 8021B
Oxygenates [31]				**Designated Methods** [28]
t-Butyl alcohol (TBA)	75650	50	2,500	8260B
Di-isopropyl ether (DIPE)	108203	5	250	8260B
Ethyl(tert)butylether (ETBE)	637923	5	250	8260B
Ethyl alcohol	64175	1,000	2,500	8260B 8015C
Methanol	67561	400	4400	8260B 8015C
Methyl(tert)butylether (MTBE)	1634044	5	250	8260B
Tertiaryamylmethylether (TAME)	994058	5	250	8260B
Carbamates				
Aldicarb	116063	2	50	531.1 8318A
Aldicarb Sulfone [34]	1646884	2	**[200]**	531.1 8318A
Aldicarb Sulfoxide [34]	1646873	2	**[200]**	531.1 8318A

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Carbamates				
Carbaryl	63252	20	200	531.1 8318A 8270C
Carbofuran	1563662	40	200	531.1 8318A
Diuron	300541	1	500	632 8321B 8325
Linuron	330552	0.1	-----	632
Oxamyl	23135220	100	1000	531.1 8318A
Acid Herbicides				
Dacthal metabolites [35]	DACMET	1	-------	8151A 515.1 515.2 515.4
Dalapon	75990	10	500	8151A
2,4-Dichlorophenoxyacetic acid	94757	10	200	8151A
Dicamba	1918009	1	50	8151A
Dinoseb	88857	**[1]**	**[200]**	8151A 8041A
2-Methyl-4-chlorophenoxyacetic acid (MCPA)	94746	5	300	8151A
MCPP	93652	5	300	8151A
Silvex (2,4,5-TP)	93721	30	300	8151A
Picloram	1918021	40	500	8151A
2,4,5-T	93765	10	500	8151A
Chlorinated Pesticides				
Alachlor	15972608	1	20	8081B 8270C 525.2 507
Aldrin	309002	**[0.01]**	20	8081B
Chlordane [36]	57749	2	30	8081B
Chlorpyrifos, ethyl	2921882	**[2]**	**[100]**	8081B 8141B
4,4'-DDD [37]	72548	0.1	20	8081B
4,4'-DDE [37]	72559	0.1	20	8081B
4,4'-DDT	50293	**[0.02]**	20	8081B
Dacthal	1861321	5	100	8081B 1656 608.2
Dichloran (2,6-Dichloro-4-nitroaniline)	99309	0.01	0.1	608.2
Dieldrin	60571	**[0.02]**	20	8081B
Endosulfan [38]	115297	0.03	20	8081B
Endosulfan I	959988	0.03	20	8081B
Endosulfan II	33213659	0.03	20	8081B
Endosulfan Sulfate	1031078	0.05	20	8081B

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Chlorinated Pesticides				
Endrin	72208	0.02	20	8081B
Endrin Aldehyde	7421934	0.02	20	8081B
Endrin Ketone	53494705	0.02	20	8081B
Heptachlor	76448	**[0.01]**	20	8081B
Heptachlor epoxide	1024573	0.01	20	8081B
Hexabromobenzene	87821	0.02	100	8081B
alpha-Hexachlorocyclohexane (BHC)	319846	0.05	10	8121 8081B
beta-Hexachlorocyclohexane (BHC)	319857	0.02	20	8081B 8121
delta-Hexachlorocyclohexane (BHC)	319868	0.05	20	8081B 8121
Lindane (gamma-BHC)	58899	0.03	**[20]**	8081B 8121
Methoxychlor	72435	0.5	50	8081B
Mirex	2385855	**[0.02]**	50	8081B
Propachlor	1918167	50	200	8081B
Toxaphene	8001352	**[1]**	170	8081B
3-Trifluoromethyl-4-nitrophenol	88302	50	1000	8081B
tris(2,3-Dibromopropyl) phosphate	126727	**[10]**	330	8081B
Organophosphorus				
Atrazine	1912249	3	50	8141B 8270C 619 507
Cyanazine	21725462	2	200	8141B 629
Diazinon	333415	1	50	8141B 507
Dichlorvos	62737	1	**[50]**	8141B 507
Disulfoton	298044	1	50	8141B 507
EPTC	759944	3	100	8141B 507
Fonofos	944229	5	100	8141B 622.1
Molinate	2212671	2	100	8141B 507
Methyl parathion	2980000	1	40	8141B
Metolachlor	51218452	10	200	507 551.1
Metribuzin	21087649	0.1	10	507 551.1 1656
Prometon	1610180	50	200	507 619
Propazine	139402	100	2000	507 619
Simazine	122349	4	80	8141B 507 525.2 619 1656
Terbacil	5902512	20	-----	8141B 507
Triphenylphosphate	115866	10	500	8141B
Terbufos	13071799	5	-----	8141B 507

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Specific Pesticides				
Clopyralid	1702176	1	20	PAM II ACR 75.6 ACR 86.1 547 8151A
Diallate	2303164	0.5	20	1618 1656 8081B
Diquat	85007	20	-----	549
Endothall	145733	100	-----	548
Glyphosate	1071836	100	1000	547 SM6651
Aminomethylphosphoric acid (AMPA-Glyphosate metabolite)	AMPA	100	10,000	547 SM6651
Pendimethalin	40487421	10	200	1656
Tebuthiuron	34014181	100	2000	8321B
Triallate	2303175	50	2000	8270C
Trifluralin	1582098	30	200	8270C 8081B

PCB AND PBB Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Polybrominated biphenyls (FireMaster)[39]	67774327	0.01	50	8081B 8082A
Polychlorinated biphenyls (PCBs) [40]	1336363	**[0.2]**	330	8082A 8270C
Aroclor (unspecified) [41]	1267792	-----	-----	8082A 8270C
Aroclor 1016	12674112	-----	-----	8082A 8270C
Aroclor 1221	11104282	-----	-----	8082A 8270C
Aroclor 1232	11141165	-----	-----	8082A 8270C
Aroclor 1242	53469219	-----	-----	8082A 8270C
Aroclor 1248	12672296	-----	-----	8082A 8270C
Aroclor 1254	11097691	-----	-----	8082A 8270C
Aroclor 1260	11096825	-----	-----	8082A 8270C
Aroclor 1262	37324235	-----	-----	8082A 8270C
Aroclor 1268	11100144	-----	-----	8082A 8270C
Polychlorinated biphenyls congeners	Various	-----	-----	1668

Dioxins & Furans [42] Contaminants	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746016	**[0.00001]**	0.001	8290A 1613
2,3,7,8-Tetrabromodibenzo-p-dioxin	50585416	0.0001	0.01	8290A 1613 (Lab specific procedures)

TABLE 1. TARGET DETECTION LIMITS AND DESIGNATED ANALYTICAL METHODS

Polybrochlorinated and polybrominated diphenyl ethers	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Methods
Decabromodiphenyl ether	1163195	10	330	8270C1614
Polybrominated diphenyl ethers	Various		----	1614

Explosives	CAS/ID	Water TDL ug/L	Soil TDL ug/Kg	Designated Method
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	35572782	1	50	8095
4-Amino-2,6-dinitrotoluene (4-AM-DNT)	1946510	1	50	8095
3,5-Dinitroaniline (3,5-DNA)	618871	1	50	8095
1,3-Dinitrobenzene (1,3-DNB)	99650	1	50	8095
2,4-Dinitrotoluene (2,4-DNT)	121142	1	50	8095
2,6-Dinitrotoluene (2,6-DNT)	606202	1	50	8095
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121824	1	50	8095
Nitrobenzene (NB)	98953	5	50	8095
Nitroglycerine (NG)	55630	5	50	8095
2-Nitrotoluene (2-NT)	88722	5	50	8095
3-Nitrotoluene (3-NT)	99081	5	50	8095
4-Nitrotoluene (4-NT)	99990	5	50	8095
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2691410	10	50	8095
Pentaerythritoltetranitrate (PETN)	78115	5	50	8095
1,3,5-Trinitrobenzene (1,3,5-TNB)	99354	1	50	8095
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	479458	1	50	8095
2,4,6-Trinitrotoluene (2,4,6-TNT)	118967	1	50	8095

Parameter	CAS/ID	Water TDL MFL	Soil TDL %	Designated Method
Asbestos	1332214	7	**[1]**	100.1 [43]

Parameter	CAS/ID	Designated Methods
Acute Toxicity	ACUTE	EPA-821-R-02-012
Chronic Toxicity	CHRONIC	EPA-821-R-02-013
Organic Carbon [44]	OC	Waters: 415.3 [45] Soils: Walkley-Black. [46] Total Organic Carbon [47]
Soil Bulk Density	SBD	ASTM Methods. [48] D2937-94
Soil Vapor Permeability	SVP	ASTM 1990 Methods D5126-90 and D5084-90

Abbreviations used in Table 1:

GC/MS: Gas chromatography with mass spectrum confirmation.
ICP/ES: Inductive coupled plasma emission spectroscopy.
SIM: Selected/single ion monitoring.
ICP/MS: Inductive coupled plasma with mass spectrometry detection.
MFL: Million fibers per liter (MFL) greater than 10 micrometer.
pH: Acidity as measured with pH meter.
GSI: Groundwater surface water interface.

Notations in Table 1:

- The TDLs in bold type and enclosed with **[ ]** brackets indicate that the contaminant's TDL is higher than the most restrictive criteria.
- For volatile organics, TDLs enclosed with **{ }** brackets indicate that the low level soil method may be required to reach a risk-based criteria. Check with the laboratory to determine if risk-based criteria can be reached for methanol-preserved samples, to determine if the low level method must be used.
- Contaminants listed in italicized format indicate that analysis is not available from the MDEQ laboratory.
- Underlined TDLs indicate the TDL was lowered from the previous operational memorandum.

Table 1 Footnotes:

1. The analysis using ion chromatography is not performed routinely by environmental laboratories. Arrangements for laboratories to perform this analysis must be made well in advance of sampling.
2. The bottle shake procedures, using reagent water, can be used for extraction of soil fluoride. If interferences are encountered, distillation procedures must be used. Colorimetric methods for the measurement of fluoride cannot be used.
3. Analysis of formate is used to determine compliance with formic acid cleanup criteria.
4. Hardness results must be calculated using separate determinations of calcium and magnesium and appropriate procedures for determining metals in SW-846. Hardness results determined by titration methods or other means than from calcium and magnesium results cannot be used for purposes of Part 201 or Part 213. No TDLs are needed because the methods available for metals can determine calcium and magnesium at any levels expected in surface and groundwaters.
5. Soil samples for total phosphorus must be digested using Kjeldahl or similar digestion techniques. See Association of Official Analytical Chemists 957.18
6. Soil sulfate analysis: Add to 5 g soil, 20 ml of extracting solution, 0.5N Ammonium Acetate/0.25N Acetic Acid in water mixture, extract for one hour on a mechanical shaker, filter on 42 Whatman ™ filter.
7. R 299.5750 footnote (P) requires, amenable cyanide or OIA 1677 methods to quantify cyanide concentrations for compliance with all groundwater criteria, and total cyanide or OIA 1677 methods to quantify cyanide concentrations for compliance with soil criteria. Method OIA 1677 is the preferred method for both waters and soils. (See Cyanide Information Sheet) The standard TDL for total cyanide in soils, in the methods provided, is 200 ug/Kg. The 100 ug/Kg TDL is applicable for site assessment and site investigation, and the total cyanide method is used with appropriate leaching procedures (See RRD Operational

TABLE 1. ABBREVIATIONS AND FOOTNOTES

Memorandum No. 2, Attachment 2). A TDL of 200 ug/Kg for cyanide may be used for response activities under Part 201 or Part 213 when the GSI pathway is appropriately documented to be not relevant.

8. The concentrations of all potential sources of nitrogen in groundwater and soils must be added together and compared to the nitrate drinking water criteria and soils protective of drinking water criteria. (See R299.5750 footnote(N)). All potential sources of nitrogen may be determined as elemental nitrogen in waters and soils provided the TDLs for nitrate are met. Several instruments and methods are available. Prior approval must be obtained from the MDEQ for use of specific methods to measure elemental nitrogen. Approval will be based on a review of the quality control and site-specific factors. For an example of the quality control required, see Method 440.0, Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis, Carl F. Zimmermann, Carolyn W. Keefe, University of Maryland System Center for Environmental Estuarine Studies, Chesapeake Biological Laboratory Solomns, MD 20688-0038 and Jerry Bashe, Technology Applications, Inc., 26 W. Martin Luther King Drive, Cincinnati, OH 45219, Revision 1.4, September 1997, National Exposure Research Laboratory, Office of Research and Development, U.S.EPA, Cincinnati, Ohio 45268. Other methods may be proposed.
9. Soil Ammonia: Air dry soil; do not heat. Soil ammonia must be distilled from soils. Standard Methods 4500 and EPA Methods 350.2 or 350.3, modified for soils can be used. Soil ammonia cannot be determined using extraction procedures.
10. Nitrate/nitrite, Reference: Methods of Soil Analysis, Part 2, Number 9 in the Agronomy Series, 1982. Extraction of soils for exchangeable nitrate/nitrite. Extraction can be accomplished by extraction of 3 g soil with 30 ml of 2M KCl for 30 minutes. Filter on 42 Whatman ™ filter.
11. The methods designated for analyses of metals include the methods in SW-846 (Methods 6000 & 7000 series), and Methods 200.7, 200.8 approved by the U.S. EPA for waters. ICP/MS procedures 6020 and 200.8 are preferred for waters analyses. Metals digestion procedures that allow recoverable metals to be determined must be used. The U.S. EPA Method 200.2, Sample Preparation Procedure for Spectrochemical Determinations of Total Recoverable Elements, Rev 2.8, is preferred for soils.
12. Criteria for the GSI pathway are based upon the hardness and pH of the receiving waters. See R 299.5750 footnote (G) for additional information.
13. Laboratories must determine lead concentrations in both the fine and coarse soil fractions when possible, and calculate total lead based on the lead concentrations in each fraction taking into consideration the relative weights of each fraction. When it is not possible to separate out any fraction, total lead must be determined and the appropriate project manager immediately informed of the affected samples. If upon sieving, the weights of any of the fractions are too small for sampling, lead analysis must be conducted on that fraction with sufficient sample and total lead should be conducted on a separate aliquot of the sample. The appropriate project manager must be immediately informed of the situation, and advised on any options that can be exercised, such as determining the lead in the sample available and qualifying the results. The MDEQ Laboratory SOP #213 provides appropriate procedures for sample preparation by the laboratory. The concentration of lead in each soil fraction should be compared to the lead direct contact criteria. The concentration of lead in the fine fraction should be compared to the lead particulate inhalation criteria. The total lead concentration should be compared to the remaining lead

TABLE 1. ABBREVIATIONS AND FOOTNOTES

soil criteria. Additional guidance is available in RRD Operational Memorandum No. 2, Attachment 5.

14. R 299.5750 footnote (Z) notes that generic cleanup criteria are based upon the toxicity of different species of mercury for different exposure pathways. The footnote allows comparison of generic criteria to species specific analytical data only if sufficient facility characterization has been conducted to rule out the presence of other species of mercury. Species specific analytical methods are not included in this document. Any proposal to use species specific methods requires MDEQ approval.
15. For response activities under Part 201 and Part 213, if the GSI pathway has been appropriately documented to be not relevant, a water TDL of 0.2 ug/L may be used.
16. The GSI criterion is a total mercury value and must be compared to total mercury analytical data. Low level mercury analysis (method 1631) must be used for waters. Low level mercury sampling specifications are provided in RRD Operational Memorandum No. 2, Attachment 7.
17. The reliability of XRF measurements are highly dependent upon the soil characteristics, mode of operation, training of personnel operating the instrument, and other factors. Results must be considered as screening measurements and cannot be used to establish compliance, unless coupled with adequate laboratory analysis to establish the validity of the results as quantitative.
18. Evaluation of Aesthetic Impacts – See RRD Operational Memorandum No. 2, Attachment 8 regarding application of these methods. GC/MS methods may be employed if it can be demonstrated that data is equivalent to the Wisconsin Modified Methods.
19. Dissolved Gases in Waters: Samples should be drawn from the wells using bladder pumps and collected in Tedlar bags. The use of bailers is not an acceptable method for sampling dissolved gases from wells. Care must be taken to keep gases dissolved until transferred to a suitable container. For the arrangement of a good sampling mechanism used to retain the pressure and keep gases dissolved, see the field sampling method “Collection of Ground Water Samples for Dissolved Gas Analysis” developed by Isotech Laboratories, Incl, 1308 Parkland Court, Champaign, IL 61821-1826, (217-398-3490). TDLs for gases other than methane are not provided. Consult the laboratories regarding reporting limits.
    Methane in Soils: See Operational Memorandum No. 6, Methane, for guidance on sampling and measuring methane in the field. Laboratory methods to analyze for light hydrocarbons include Method 3C designed for landfill gases, and various other methods using various types of detectors such as flame ionization. Since some labs may have separate canisters and instruments for trace and high levels of gases, the laboratory should be advised of the source of the methane and the expected levels in the samples in order to plan their analyses and provide suitable containers. Landfills are expected to contain percentage levels of methane, while ambient and indoor air may be expected to contain low parts per million or parts per billion.
    Soil Gases other than methane: Soil gas concentrations should be measured as a percent by volume in the soil gas, or converted to percent by volume (50 ppm = .005% by volume). Appropriate field sampling procedures in the ASTM Standard Method D 5314-92 should be used for sampling and analysis of soil gases other than methane. Other methods may be used if approved by the MDEQ. TDLs are only provided for methane. Consult with laboratories regarding reporting limits and other requirements for other gases. TO Air methods refer to various methods in Compendium of Methods for the Determination of Toxic

TABLE 1. ABBREVIATIONS AND FOOTNOTES

Organic Compounds in Ambient Air, U.S. EPA. Consult the laboratory regarding appropriate sampling procedures for specific methods.

20. GC/MS may be used anytime the laboratory's reporting limits for the method can measure the applicable criteria, including Ion Trap and single/selected ion monitoring (SIM). SIM can be used to lower the reporting limits for the PNAs about twenty times less than obtainable using full scan on the GC/MS.
21. When analyses of these are requested using GC/MS, SIM analyses must be conducted on all samples with no detects found in the full scan mode. Positive detects in the SIM mode should then be appropriately coded to indicate SIM analyses was conducted.
22. Isomer specific concentrations of 2-, 3-, and 4-, methylphenols must be added together for comparison to methylphenols criteria for pathways other than the GSI pathway. For the GSI pathway isomer specific concentrations should be compared to the following values: 2-methylphenol 82 ug/l; 3-methylphenol 71 ug/l; 4-methylphenol 25 ug/l.
23. For response activities under Part 201 and Part 213, if the GSI and the drinking water pathways have been appropriately documented to be "not relevant", then a water TDL of 20 ug/L and soil TDL of 800 ug/Kg may be used.
24. For response activities under Part 201 and Part 213, if the GSI pathway has been appropriately documented to be "not relevant", then a water TDL of 10 ug/L and soil TDL of 330 ug/Kg may be used.
25. This TDL applies only for response activities under Part 201 and Part 213, if the drinking water pathway has been appropriately documented to be not relevant. See the parameter group "Explosives" for the appropriate method for this compound for site assessment and site investigation. Aniline is a product of nitrobenzene degradation in waters and soils and should be included in the analytical scheme when possible.
26. Soil sampling collection and preservation specifications for volatiles including protocol for methanol preservation are contained in RRD Operational Memorandum No. 2, Attachment 6.
27. This is a common laboratory solvent. Cautious review is required of analytical results for laboratory blanks to assess compliance.
28. High temperature purging and/or isotope dilution procedures may be required.
29. This contaminant is a reactive compound which requires special sampling and holding time requirements.
30. The concentrations of the cis and trans isomers must be added and reported as 1,3-Dichloropropene.
31. These contaminants are oxygenates and may be found at sites where gasoline products were used.
32. Trihalomethanes refers to chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The concentrations of all trihalomethanes must be added and compared to the criteria. (See R 299.5750 footnote (W)).
33. The concentrations of the m-, p-, and o- xylene isomers must be added and the total compared to the total xylenes criteria.
34. Aldicarb Sulfone and Aldicarb Sulfoxide are metabolites of Aldicarb.
35. The monoacid (CAS 887547) and diacid (CAS 2136790) metabolites of Dacthal are measured as one compound and compared to the criteria for Dactal (CAS 1861321).
36. For comparison to the criteria, isomer specific concentrations for trans-Chlordane, (CAS RN 5103719), and cis-Chlordane, (CAS RN 510374) must be reported separately and the sum of their concentrations reported as Chlordane, (CAS RN 57749). If compounds other than

TABLE 1. ABBREVIATIONS AND FOOTNOTES

cis and trans-Chlordane are used to calculate the chlordane concentration, report the concentrations of each separately and report Chlordane, (CAS RN 57749) using the guidance in Method 8081B for calculation. Some components of the mixture may have specific criteria, which must also be met.

37. 4,4'-DDD and 4,4'DDE are metabolites of DDT.
38. Isomer specific concentrations of Endosulfan I, (CAS 959988), and Endosulfan II, (CAS 33213659) must be added for comparison to Endosulfan criteria.
39. The term "Polybrominated biphenyls" listed in the rules and in this table (CAS 67774327) refers to a product used in Michigan, called Firemaster FF1. Firemaster FF1 consisted of several polybrominated biphenyls, the most prevalent being hexabrominated biphenyl (56%). Subsequently, cleanup criteria was established for waters and soils which applied to that product, and designated methods for the product were based on the concentrations of hexabrominated biphenyl. Recently the group of contaminants known as brominated biphenyl congeners have become a concern and it is necessary to distinguish between the product Firemaster FF1 and the individual brominated biphenyl congeners. Calibration and quantitation of FireMaster in samples should be accomplished by using technical brand FireMaster as the calibrant and quantitating using the procedures in method 8082 for calibrating Aroclor products. If the FireMaster technical product is not available, use the most dominant hexabromobiphenyl peak present in the FireMaster product as the calibrant, and report the concentrations found for that isomer as FireMaster.
40. Commercial products with specific mixtures of polychlorinated congeners were sold in the United States under product names beginning with Aroclor. The term in the table, Polychlorinated biphenyls (PCBs) refers to the total concentration of all Aroclor products found at a facility. The concentrations of the Aroclors found at a facility must be added together to obtain a total concentration, and the total concentration used for comparison to the criteria. (R 299.5750 footnotes (J) and (T)). Laboratories should report data below the reporting limits and above the method detection limits when possible, coded to indicate estimates.
41. When attempts are not successful to match the patterns of the Aroclor products with the pattern found in a sample, laboratories should report Aroclor (unspecified), (CAS 1267792), and its concentration determined using the Aroclor 1260 calibration.

TABLE 1. ABBREVIATIONS AND FOOTNOTES

42. The concentrations of polychlorinated and polybrominated dibenzodioxin and dibenzofuran isomers present at a facility, expressed as an equivalent concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin based on their relative potency must be added together Those isomers with non-zero TEF are provided in the table below. The toxicity equivalency of a specific dioxin, furan or PCB in a sample is calculated by multiplying its concentration by its respective TEF. The toxicity equivalencies must be added together to obtain a total toxic equivalency (TEQ) and the TEQ compared to the criteria for 2,3,7,8-tetrachlorodibenzo-p-dioxin. (R 299.5750 footnote (O)).

TOXICITY EQUIVALENT FACTORS FOR CHLORINATED DIBENZODIOXINS AND DIBENZOFURANS

COMPOUND	TEF
2,3,7,8-TCDD	1.0
1,2,3,7,8-PeCDD	1.0 (0.5)*
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
1,2,3,4,6,7,8,9-OCDD	0.0001 (0.001)*
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.05

COMPOUND	TEF
2,3,4,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HxCDF	0.01
1,2,3,4,7,8,9-HxCDF	0.01
1,2,3,4,6,7,8,9-OCDD	0.0001 (0.001)*

* For comparing groundwater samples to GSI criteria, use the TEF in parentheses. (R 323.1209).

43. Bulk sampling requirements as designated by the laboratory chosen for the analysis must be used. Laboratories certified by various state and federal agencies for asbestos analysis should be used. MDEQ approved methods must be used. One procedure approved is: Method Number ID-191 Matrix: Bulk, 29 CFR, Part 1915, Occupational Safety and Health Standards for Shipyard Employment, Subpart Z, Toxic and Hazardous Substances, 1915.1001 App K, Polarized light microscopy of Asbestos – Non Mandatory, U.S. Department of Labor, Occupational Safety and Health Administration. For samples with more than 1 percent asbestos content in soils, or above 7 MFL in waters, additional information of the asbestos types may be confirmed using Transmission Electron Microscopy. One method approved for use is: CFR, Part 763, Subpart E, Appendix A, Interim Transmission Electron Microscopy Analytical Methods-Mandatory and Non Mandatory-and Mandatory Section to Determine Completion of Response Actions. For preparation of soils, see U.S. EPA, Region 1 – Office of Environmental Evaluation and Measurement, The Protocol for Screening Soil and Sediment Samples for Asbestos Content used by the U.S. EPA, Region 1 Laboratory.

TABLE 1. ABBREVIATIONS AND FOOTNOTES

44. Organic carbon and total organic carbon are different descriptions for the same parameter being determined, organic carbon. The following are requirements in the sampling and analysis for organic carbon.

    a) Results for organic carbon may not be used to calculate organic matter concentrations without prior approval from the MDEQ.
    b) Results for organic matter may not be used to calculate organic carbon concentrations without prior approval from the MDEQ.
    c) Soil samples must be representative of the soils at sites, from about six inches below the surface down to the mean annual depth of the water table, and representative of the soils based on heterogeneity.
    d) Soil vegetation should not be included with the soil samples as organic carbon results must represent that in the natural soil.
    e) Soil samples should not be taken from areas significantly impacted by contamination.

45. Method 415.3, "Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water", Revision 1.0, June 2003, U.S. EPA, Office of Research and Development, U.S. EPA, Cincinnati, OH 45268, or an equivalent method, is recommended. Other methods can be used upon approval by the MDEQ and equivalency to the analysis and quality control as provided in method 415.3 will be the basis by which other methods are evaluated.
46. Walkley-Black methods measure the organic carbon in soils that is easily oxidized after removal of inorganic forms of carbon by acidification and heating. These methods are most appropriate for soils with less than 2 percent organic matter, and should not be used for soils with more than 6 percent organic matter.
47. Total organic carbon (TOC) methods generally refer to those methods that measure the organic carbon by ignition at high temperatures. See method 415.3 for guidance for waters. For soils, the following are minimum sampling and analysis requirements for these methods. Prior approval must be obtained from the MDEQ to use specific methods. Approval to use proposed methods will be based on a review for adequate quality control and application based on site specific factors.

    a) Instrument systems must be used that are capable of quantitatively determining organic carbon in the presence of inorganic forms of carbon, such as carbonate and bicarbonate.
    b) Methods must demonstrate capability to remove inorganic forms prior to measurements for organic carbon.
    c) Strong acids must be used to remove inorganic forms of carbon. Persulfate and hydrochloric acids are recommended.
    d) Methods that use a mixture of water and soil, and/or use methods designed for waters and/or wastes, are unacceptable.
    e) Methods that determine organic carbon by subtracting inorganic carbon measurements from total carbon measurements are unacceptable.
    f) Organic carbon must be reported as a percentage of the dry weight of the unacidified samples to the nearest 0.1% unit.
    g) TOC methods are most appropriate for soils with greater the 6 percent organic matter.

TABLE 1. ABBREVIATIONS AND FOOTNOTES

48. Soil bulk density is defined as the ratio of the mass of dry solids to the bulk volume of the soil occupied by those dry solids. The bulk volume includes the volume occupied by the soil solids and the pore spaces. The dry solids must be determined by drying the soil to constant mass in an oven at 105 ± 5 degrees centigrade. ASTM 1994, Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method, D2937-94, is the designated method for analysis of soil bulk density. Other ASTM methods may be acceptable when approved by the MDEQ and applied to the appropriate soils types, as provided in the individual methods.

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency – Office of Solid Waste & Emergency Response, Edition 3 (SW-846) (http://www.epa.gov/epaoswer/hazwaste/test/8_series.htm)

Method	Title
3060A	Alkaline Digestion for Hexavalent Chromium
3550	Ultrasonic Extraction
5021A	Volatile Organic Compounds in Various Sample Matrices using Equilibrium Headspace Analysis
5035A	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
6000	SW-846 Manual, Chapter 3 and 6000 Series Methods
6200	Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
7000	SW-846 Manual, Chapter 3 and 7000 Series methods
7196A	Chromium, Hexavalent (Colorimetric)
7199	Chromium, Hexavalent by Ion Chromatography
7473	Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
7474	Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry
7580	White Phosphorus by Solvent Extraction and Gas Chromatography
8011	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
8015C	Non-halogenated Organics Using GC/FID
8021B	Halogenated and Aromatic Volatiles by Gas Chromatography using Electrolytic Conductivity and Photoionization Detectors in Series: Capillary Column Technique
8031	Acrylonitrile by Gas Chromatography
8032A	Acrylamide by Gas Chromatography
8033	Method 8033, Acetonitrile by Gas Chromatography with Nitrogen-Phosphorus Detection
8041A	Phenols by Gas Chromatography
8061A	Phthalate Esters by Capillary Gas Chromatography With Electron Capture Detector (GC/ECD)
8081B	Organochlorine Pesticides and PCBs as Aroclors by GC Capillary Column Technique
8082A	Polychlorinated Biphenyls (PCBs) by Gas Chromatography
8121	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
8131	Aniline and Selected Derivatives by Gas Chromatography
8141B	Organophosphorus Pesticides by Gas Chromatography: Capillary Column Technique
8151A	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation, Derivation: Capillary Column Technique
8260B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique
8261	Volatile Organic Compounds by Vacuum Distillation in Combination with Gas Chromatography/Mass Spectrometry (VD/GC/MS)

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency – Office of Solid Waste & Emergency Response, Edition 3 (SW-846)

Method	Title
8270C	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, (GC/MS): Capillary Column Technique
8270C Ion Trap	This reference is simply to point out that the Method 8270C above allows the use of the ion trap technology and may be needed to reach low detection limits.
8270C SIM	This reference is simply to point out that the selective ion procedure can be used in Method 8270C above and may be needed to reach low detection limits.
8290A	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans, (PCDFs) by High-Resolution Gas Chromatograph/ High-Resolution Mass Spectrometry (HRGC/HRMS)
8310	Polynuclear Aromatic Hydrocarbons (GC/HPLC and UV or fluorescence detectors)
8315A	Determination of Carbonyl Compounds by HPLC
8316	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)
8318A	N-Methylcarbamates by HPLC
8321B	Solvent Extractable Nonvolatile Compounds by HPLC/MS or UV Detection
8325	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS)
8330A	Nitroaromatics and Nitramines by HPLC
8430	Analysis of Bis(2-chloroethyl) Ether and Hydrolysis Products by Direct Aqueous Injection GC/FT-IR (Gas Chromatography/Fourier Transform Infrared Spectrometer)
9010B	Total and Amenable Cyanide
9012	Total and Amenable Cyanide (Colorimetric, Automated UV)
9013	Cyanide Extraction Procedure for Solids and Oils
9014	Titrimetric and Manual Spectrometric Determinative Methods for Cyanide
9030	Acid-Soluble and Acid-Insoluble Sulfides
9034	Titrimetric Procedure for Acid-Soluble and Acid Insoluble Sulfides
9035	Sulfate (Colorimetric, Automated, Chloraniliate)
9036	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)
9040C	pH Electrometric Measurement
9045C	Soil and Waste Ph
9056	Determination of Inorganic Anions by Ion Chromatography
9058	Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection
9070A	See Method 1664, Publication No.EPA-821-R-98-002
9071B	n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples
9212	Potentiometric Determination of Chloride in Aqueous Samples with Ion-Selective Electrode
9213	Potentiometric Determination of Cyanide in Aqueous Samples and Distillates with Ion-Selective Electrode
9214	Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency – Office of Solid Waste & Emergency Response, Edition 3 (SW-846)

Method	Title
9215	Potentiometric Determination of Sulfide in Aqueous Samples and Distillates with Ion-Selective Electrode
9250	Chloride (Colorimetric, Automated Ferricyanide AAI)
9251	Chloride (Colorimetric, Automated Ferricyanide AAII)
9253	Chloride (Titrimetric, Silver Nitrate)

Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia 30613

Method	Title
100.1	Analytical Method for Determination of Asbestos Fibers in Water

Guidelines Establishing Test Procedures for the Analysis of Pollutants, 40 CFR Part 136, Appendix A, Revised: July 1990

Method	Title
605	Benzidines

Methods for the Determination of Organic Compounds in Drinking Water & Supplement I, III, U.S. EPA, EMSL, Cincinnati, OH 45268, Edition: December 1988 and July 1990

Method	Title
502.2	Method 502.2, Volatile Organic Compounds In Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors In Series
504.1	1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-chloropropane (DBCP) in Water by Microextraction and Gas Chromatography
507	Determination of Nitrogen and Phosphorous-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorous Detector
515.1	Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector
515.2	Determination of Chlorinated Acids in Water using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector
515.3	Determination of Chlorinated Acids in Water using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector (Stand alone Method)
515.4	Method 515.4, Determination of Chlorinated Acids in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Fast Gas Chromatography with Electron Capture Detection, Revision 1.0, April 2000
524.2	Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry
525.2	Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capilliary Column Gas Chromatography/Mass Spectrometry

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Methods for the Determination of Organic Compounds in Drinking Water & Supplement I, III, U.S. EPA, EMSL, Cincinnati, OH 45268, Edition: December 1988 and July 1990

Method	Title
531.1	Measurement of N-Methylcarbomoylzimes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post Column Derivatization, Revision 3.1
547	Determination of Glyphosate in Drinking Water by Direct-Aqueous-Injection HPLC, Post-Column Derivatization, and Fluorescence Detection
548	Determination of Endothall in Drinking Water by Aqueous Derivatization, Liquid Solid Extraction, and Gas Chromatography with Electron-Capture Detection
549	Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and HPLC with Ultraviolet Detection
551.1	Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection

EPA:USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis and Classical Chemistry Parameters, Multi-Media, Multi-Concentration, ILM05.1, June 2001

Method	Title
CLP-CN	Exhibit D – Part D, Analytical Methods for Total Cyanide Analysis

U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), 401 M Street SW, Washington, D.C.20460

Method	Title
Kelada-01	Kelada Automated Test Methods For Total Cyanide, Acid Dissociable Cyanide, And Thiocyanate, Revision 1.2
OIA-1677	Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, August 1999, EPA-821-R-99-013
200.2	Revision 2.8: Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, October 1999, EPA-821-R-99-018
218.6	Revision 3.4, Determination Of Dissolved Hexavalent, Chromium In Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography, October 1999, EPA-821-R-99-016
245.7	Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Draft, January 2001, EPA-821-R-01-008
1636	Determination of Hexavalent Chromium by Ion Chromatography, January 1996

EPA:Volatile/Semivolatile Organic Compounds by Isotope Dilution GC/MS, USEPA Office of Water Regulations and Standards, Ind. Tech. Div., Edition: June 1989

Method	Title
1624	Volatile Organic Compounds by Isotope Dilution GC/MS

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), 401 M Street SW, Washington, D.C.20460

Method	Title
1630	Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, August 1998
1631E	Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
1631E (mod)	EPA-821-R-01-013, January 2001, Appendix to Method 1631 Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation
1669	Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, July 1996

U.S. Environmental Protection Agency, Office of Water(4304T), 1200 Pennsylvania Avenue, NW, Washington, D.C. 20460

Method	Title
EPA-821-R-00-002	Method 1668, Revision A, Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS
EPA-821-R-02-012	Short Term Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition, October 2002
EPA-821-R-02-013	Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, Fourth Edition, October 2002.

Analytical Methods For the National Sludge Survey, US Environmental Protection Agency, Officer of Water (WH-585), Edition: September 1990

Method	Title
1613	Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Rev B
1618	Organo-Halide Pesticides, Organo-Phosphorus Pesticides, and Phenoxy Acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors

Methods for Chemical Analysis of Water and Wastes, USEPA, EMSL, Cincinnati.OH 45268

Method	Title
160.1	Residue, Filterable (Gravimetric, Dried at 180°C)
200.7	ICP-AES Method for Trace Element Analysis of Water and Wastes
200.8	Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry
300.1	The Determination of Inorganic Anions in Water by Ion Chromatography -
314	Method 314.0, Determination of Perchlorate in Drinking Water Using Ion Chromatography
325.1	Chloride (Colorimetric, Automated Ferricyanide, AAI)
325.2	Chloride (Colorimetric, Automated Ferricyanide, AAII)
340.1	Fluoride, Total
350.1	Nitrogen, Ammonia (Colorimetric, Automated Phenate)

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Methods for Chemical Analysis of Water and Wastes, USEPA, EMSL, Cincinnati.OH 45268

Method	Title
350.2	Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)
350.3	Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode)
351.x	Kjeldahl Nitrogen
353.2	Nitrogen, Nitrate-Nitrite, Colorimetric, Automated, Cadmium Reduction
360.1	Oxygen, Dissolved, Membrane Electrode
360.2	Oxygen, Dissolved, Modified Winkler Full Bottle Technique
365.4	Phosphorous, Total (Colorimetric, Automated, Block Digester AA II)
375.1	Sulfate (Colorimetric, Automated, Chloranilate)
376.2	Sulfide (Colorimetric, Methylene Blue)
375.2	Sulfate (Colorimetric, Automated, Methylthymol Blue, AAII)
376.1	Sulfide, Titrimetric, Iodine

Standard Methods for the Examination of Water and Wastewater

Method	Title
SM6651	Glyphosate Herbicide
SM2340 B	Hardness by Calculation

Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater, USEPA Office of Water, Engineering and Analysis Division, WH-552, Edition: April 1992

Method	Title
1656	The Determination of Organo-Halide Pesticides in Municipal and Industrial Wastewater
608.1	The Determination of Organochlorine Pesticides in Municipal and Industrial Wastewater
608.2	The Determination of Certain Organochlorine Pesticides in Municipal and Industrial Wastewater
619	The Determination of Triazine Pesticides in Municipal and Industrial Wastewater
629	The Determination of Cyanazine in Municipal and Industrial Wastewater

Official Methods of Analysis, Association of Official Analytical Chemists, Edition: 15, 1990

Method	Title
983.01	Urea and Methyleneureas
957.18	Microdetermination of Phosphorus, Kjeldahl Digestion Method

Pharmaceutical Industry Pollutants, USEPA, Engineering and Analysis Division, EPA 821 B-94-001

Method	Title
1671	Volatile Organic Compounds Specific to the Pharmaceutical Manufacturing Industry By GC/FID

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Method

Walkley-Black Method

Instruments are available that utilize a form of the Walkley-Black digestion procedure. The following documents provide the original method and some modifications.

Walkley, A., and Black., 1934. An examination of the Degtijareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci.37:29-38

Walkley, A., 1947. A critical examination of a rapid method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. Soil Sci.63:251-257

Jackson, M.L.1958.Soil Chemical Analysis.214-221.

Schollenberger, C.J.1927. A Rapid Approximate Method for Determining Soil Organic Matter. Soil Sci.24:65-68

USEPA Office of Research and Development, USEPA, Cincinnati, OH 45268

Method	Title
415.3	Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water, Revision 1.0, June 2003

Methods of Soil Analysis

Keeney, D. R. and D. W. Nelson. 1987.
Nitrogen--Inorganic Forms, sec. 33-3, extraction of exchangeable ammonium, nitrate, and nitrite. pp.648-9. In A. L. Page et al., eds., **Methods of Soil Analysis: Part 2, Chemical and Microbiological Properties.** *Agronomy, A Series of Monographs*, no.9 pt.2, Soil Science Society of America, Madison, Wisconsin USA.

Modified Wisconsin Methods

Method	Title
Wisconsin Modified GRO	Method for Determining Gasoline Range Organics, Wisconsin DNR, September 1995, WDNR PUBL-SW-140
Wisconsin Modified DRO	Method for Determining Diesel Range Organics, Wisconsin DNR, September 1995, WDNR PUBL-SW-141

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency – Office of Solid Waste and Emergency Response, Edition 3

Method	Title
4030	Soil Screening for Petroleum Hydrocarbons by Immunoassay
4035	Soil Screening for Polynuclear Aromatic Hydrocarbons by Immunoassay

ASTM Standards, Americal Society of Testing Materials

Method	Title
D 5314-92	Standard Guide for Soil Gas Monitoring in the Vadose Zone

TABLE 2. SOURCE DOCUMENTS FOR DESIGNATED ANALYTICAL METHODS

Methane Procedures

Method	Title
RSKSOP-175	Standard Operating Procedure, Sample Preparation and Calculation for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, R.S. Kerr Environmental Research Laboratory, USEPA,1994.
IsoTech Laboratories Method	Collection of Ground Water Samples for Dissolved Gas Analysis, Isotech Laboratories, Inc., 1308 Parkland Court, Champaign, IL 61821-1826, (217-398-3490)
Method 3C	40 Code of Federal Regulations, Part 60, Appendix A, Method 3C – Determination of carbon dioxide, methane, nitrogen, and oxygen from stationary sources

Pesticide Analytical Methods (PAM), I and II

Method	Title
ACR 75.6	Pesticide Analytical Manual, U.S. Department of Health and Human Services, Public Health Service, Food and Drug Administration, Third Edition, Revised 1999.
ACR 86.1	Pesticide Analytical Manual, U.S. Department of Health and Human Services, Public Health Service, Food and Drug Administration, Third Edition, Revised 1999.

TABLE 3. CONTAMINANTS ADDED TO TDLs AND DESIGNATED ANALYTICAL METHODS LIST

Note: Some parameters in this group may be in Table 1 also. They are included in the table below to indicate an addition as a group.

Contaminant Group	Contaminant	CAS/ID	WATER TDL ug/L	SOIL TDL ug/Kg
Specific Contaminants	*Acetate*	ACETATE	1,000	20,000
	Asbestos	1332214	7 MFL	1 %
	Dissolved Oxygen	DO	80	-----
	Formate	FORMATE	1,000	20,000
	Perchlorate	14797730	3	-----
	Petroleum Hydrocarbon Material	PET_HYD	5,000	250,000
	pH	pH	-----	-----
	Total Dissolved Solids	TDS	10,000	----
Nitrogen Forms	Kjeldahl-N	TKN	50	1,000
	Nitrogen, Total (elemental)	7727379	100	1,000
Metals	Chromium III	16065831	10	2,000
	Lead, Coarse Fraction	7439921	3	1,000
	Lead, Fine Fraction	7439921	3	1,000
Glycols	Triethylene Glycol	112276	4,000	50,000
Volatiles	Trihalomethanes (group)	THM	100	-----
	Tetranitromethane	509148	100	500
Oxygenates	*Di-isopropyl ether (DIPE)*	108203	5	250
	Ethyl(tert)butylether (ETBE)	637923	5	250
	Tertiaryamylmethylether (TAME)	994058	5	250
Carbamates	Linuron	330552	0.1	-----
	Oxamyl	23135220	10	100
Acid Herbicides	*Dacthal metabolites*	DACMET	1	-----
Chlorinated Pest.	Endosulfan (group)	115297	0.03	20
Organophosphorus	Disulfoton	198044	1	50
	EPTC (s-ethyl-diproplythiocarbamate)	759944	3	100
	Molinate	2212671	2	100
	Terbacil	5902512	20	-----
	Triphenylphosphate	115866	10	500
	Turbofos	13071799	20	-----
Specific Pesticides	Aminomethylphosphoric acid (AMPA-Glyphosate metabolite)	AMPA	100	10,000
	Clopyralid	1702176	1	20
	Fonofos	944229	10	-----
	Metribuzin	21087649	0.1	10
PCB AND PBB	Aroclor (unspecified)	1267792	0.2	330
Soil Bulk Density	Soil Bulk Density	SBD	-----	-----

TABLE 3. CONTAMINANTS ADDED TO TDLs AND DESIGNATED ANALYTICAL METHODS LIST

Note: Some parameters in this group may be in Table 1 also. They are included in the table below to indicate an addition as a group.

Contaminant Group	Contaminant	CAS/ID	WATER TDL ug/L	SOIL TDL ug/Kg
Explosives	2-Amino-4,6-dinitrotoluene (2-Am-DNT)	35572782	1	50
	4-Amino-2,6-dinitrotoluene (4-AM-DNT)	1946510	1	50
	3,5-Dinitroaniline (3,5-DNA)	618871	1	50
	1,3-Dinitrobenzene (1,3-DNB)	99650	1	50
	2,4-Dinitrotoluene (2,4-DNT)	121142	1	50
	2,6-Dinitrotoluene (2,6-DNT)	606202	1	50
	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121824	1	50
	Nitrobenzene (NB)	98953	5	50
	Nitroglycerine (NG)	55630	5	50
	2-Nitrotoluene (2-NT)	88722	5	50
	3-Nitrotoluene (3-NT)	99081	5	50
	4-Nitrotoluene (4-NT)	99990	5	50
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2691410	10	50
	Pentaerythritoltetranitrate (PETN)	78115	5	50
	1,3,5-Trinitrobenzene (1,3,5-TNB)	99354	1	50
	2,4,6-Trinitrophenylmethylnitramine (Tetryl)	479458	1	50
	2,4,6-Trinitrotoluene (2,4,6-TNT)	118967	1	50

TABLE 4. CONTAMINANTS REMOVED FROM TDLs AND DESIGNATED METHODS LIST

Contaminant	CAS/ID
Epifluorohydrin	503093
Epibromohydrin	3132647

Contaminant	CAS/ID
Methane (soils-soil gas))	74828
1,2,3-Trichlorobenzene	87616

TABLE 5. RATIONALE FOR REDUCING TDLs FROM PREVIOUS OPERATIONAL MEMORANDA

WATER				
CONTAMINANT	CAS/ID	New TDL ug/L	Previous TDL ug/L	RATIONALE
Specific Contaminants				
Acetic Acid	64197	**[1,000]**	18,000	GSI = 360
Formic Acid	64186	1,000	18,000	Formate TDL
Nitrogen Forms				
Ammonia-N	7664417	25	50	CALC GSI = 29
Metals				
Antimony	7440360	2	5	GSI DW = 2
Arsenic	7440382	5	20	DW PROPOSED = 10
Copper	7440508	4	5	CALC GSI = 4.1
Nickel	7440020	20	25	CALC GSI = 24
Vanadium	7440622	4	10	DWC = 4.5
DRO and GRO				
Diesel Range Organics	DRO	100	400	Consistency with
Gasoline Range Organics	GRO	200	400	previous guidelines for STD
Organics, Carbonyls				
Acetaldehyde	75070	100	500	GSI = 130
Dissolved Gases				
Methane	74828	500	500,000	Explosive Criteria = 520
Polynuclear Aromatics				
Benzo(ghi)perylene	191242	**[1]**	5	WS = 0.26
Benzo(b)fluoranthene	205992	1	2	WS = 1.5
Benzo(k)fluoranthene	207089	**[1]**	5	WS = 0.8
Benzo(a)pyrene	50328	**[1]**	2	GCC = 0.64
Chrysene	218019	1	5	WS = 1.6
Fluoranthene	206440	1	5	GSI = 1.6
Phenanthrene	85018	2	5	GSI =2.4
Semivolatiles				
Aniline	62533	4	20	GSI = 4
4-Chloroaniline	106478	10	20	Superfund QL = 10
Dibenzofuran	132649	4	5	GSI = 4
Hexachlorobutadiene (C-46)	87683	0.05	5	GSI = 0.053
1,2,4,5-Tetrachlorobenzene	95943	2	5	GSI = 2.9
Volatiles				
Tetrahydrofuran	109999	90	100	DWC = 95

TABLE 5. RATIONALE FOR REDUCING TDLs FROM PREVIOUS OPERATIONAL MEMORANDA

WATER				
		New TDL	Previous TDL	
CONTAMINANT	**CAS/ID**	**ug/L**	**ug/L**	**RATIONALE**
Oxygenates				
t-butyl Alcohol	75650	50	800	Monitoring of oxygenates
Acid Herbicides				
Dinoseb	88857	**[1]**	5	GSI = 0.48
Chlorinated Pesticides				
Endosulfan I	959988	0.03	0.05	GSI = 0.03
Endosulfan II	33213659	0.03	0.05	GSI = 0.03
Polychlorinated biphenyls				
Aroclor 1232	11141165	0.2	0.4	Default to total PCB TDL

TABLE 5. RATIONALE FOR REDUCING TDLs FROM PREVIOUS OPERATIONAL MEMORANDA

SOILS				
		New TDL	Previous TDL	
CONTAMINANT	**CAS/ID**	**ug/kG**	**ug/kG**	**RATIONALE**
Specific Contaminants				
Acetic Acid	64197	20,000	900,000	DW PC = 41,000
Formic Acid	64186	20,000	900,000	Acetate TDL
Cyanides				
Cyanide, Total	CN_TOTAL	100	200	GSI PC = 104
Cyanide, Available	CN_AVAIL	100	500	GSI PC = 104
Metals				
Antimony	7440360	**[300]**	500	GSI DW = 300
Mercury, Total	7439876	**[50]**	100	GSI = 0.026
Silver	7440224	**[100]**	500	GSI PC = 67
Acid Extractables (Phenols)				
2,4-Dinitrophenol	51285	830	1700	Superfund QL = 830
4-Chloro-3-methylphenol	59507	280	330	DW = 280
2-Methyl-4,6-dinitrophenol	534521	**[830]**	1700	DW PC = 400
3-Nitrophenol	554847	830	1700	Consistency
4-Nitrophenol	100027	830	1700	Superfund QL = 830
Semivolatiles				
Aniline	62533	330	1700	DW PC = 420
4-Chloroaniline	106478	330	1700	Superfund QL = 330
Hexachlorobutadiene (C-46)	87683	50	330	GSI PC = 91
2-Nitroaniline	88744	830	1700	Superfund QL = 830
3-Nitroaniline	9909	830	1700	Superfund QL = 830
4-Nitroaniline	100016	830	1700	Superfund QL = 830
Volatiles				
Benzyl Chloride	100447	150	200	DW PC = 154
1,4-Dioxane	123911	500	1000	DW PC = 680
Oxygenates				
t-butyl Alcohol	75650	2500	4400	Monitoring of oxygenates
Ethyl Alcohol	64175	2500	4400	Monitoring of oxygenates
Chlorinated Pesticides				
alpha-Hexachlorocyclohexane (BHC)	319846	10	20	DW PC = 18
Organophosphorus				
Atrazine	1912249	50	150	DW PC = 60
Cyanazine	21725462	200	500	DW PC = 200

Abbreviations Used in Table 5:

CALC GSI: Groundwater to surface water interface criterion that is based on a calculation.
Consistency: TDL was set at a level consistent with other contaminants of this type.
DW: Drinking water.
DWC: Drinking water criteria.
DW PC: Soil protective of drinking water criteria.
GCC: Groundwater direct contact criteria.
GSI: Groundwater to surface water interface.
PC: Protection criteria.
STD: Storage Tank Division.
Superfund QL: Quantitation limit established in the U.S. EPA Contract Laboratory Program.
WS: Water solubility criteria.

TABLE 6. TDLS GREATER THAN THE MOST RESTRICTIVE CRITERIA

CONTAMINANT	CAS/ID	WATER		SOIL	
		TDL	LOWEST HEALTH BASED CRITERIA	TDL	LOWEST HEALTH BASED CRITERIA
		ug/L	ug/L	ug/Kg	ug/Kg
Specific Contaminants					
Acetic Acid	64197	1,000	360		
Metals					
Beryllium	7440417	1 [1]	0.24		
Mercury, Total	7439976			50	1.2
Silver	7440224	0.2 [1]	0.06	100	27
Polynuclear Aromatics					
Benzo(k)fluoranthene	207089	1	0.8		
Benzo(ghi)perylene	191242	1	0.26		
Benzo(a)pyrene	50328	1	0.64		
Dibenzo(ah)anthracene	53703	2	0.21		
Indeno(1,2,3-cd)pyrene	193395	2	0.022		
Nitrosoamines					
N-Nitrosodi-n-propylamine	621647	5	0.19	330	100
Benzidines					
Benzidine	92875	0.3	0.0037	1000	6
3,3'-Dichlorobenzidine	91941	0.3	0.14	2000	28
Acid Extractables (Phenols)					
4-Chloro-3-methylphenol	59507			330	280
2,6-Dimethylphenol	576261			330	88
3,4-Dimethylphenol	95658			330	200
2-Methyl-4,6-dinitrophenol	534521	20	2.6	830	400
Semivolatiles					
Aniline	62533			330	80
Carbazole	86748	10	3.9		
Hexabromobenzene	87821	10	0.17		
Pentachlorobenzene	608935	5	0.019		
Pyridine	110861	20	7.3		
p-Toluidine	106490			660	300
Volatiles					
Acrylonitrile	107131			100	52
1,2-Dibromo-3-chloropropane	96128			10	4
Epichlorohydrin	106898	5	2		
Ethylene Dibromide	106934			20	1
Tetranitromethane	509148			500	51

TABLE 6. TDLS GREATER THAN THE MOST RESTRICTIVE CRITERIA

CONTAMINANT	CAS/ID	WATER		SOIL	
		TDL	LOWEST HEALTH BASED CRITERIA	TDL	LOWEST HEALTH BASED CRITERIA
		ug/L	ug/L	ug/Kg	ug/Kg
Carbamates					
Aldicarb Sulfone	1646884			200	40
Aldicarb Sulfoxide	1646873			200	80
Acid Herbicides					
Dinoseb	88857	1	0.48	200	43
Chlorinated Pesticides					
Aldrin	309002	0.01	8.7E-6		
Chlordane	57749	0.05	0.0025		
Chlorpyrifos, ethyl	2921882	0.2	0.002	10	1.5
4,4'-DDT	50293	0.02	0.00001		
Dieldrin	60571	0.02	6.5E-6		
Heptachlor	76448	0.01	0.0018		
Lindane (gamma BHC)	58899			20	0.99
Mirex	2385855	0.02	6.8E-6		
Toxaphene	8001352	1	0.000068		
tris(2,3-Dibromopropyl) phosphate	126727	10	0.71		
Organophosphorus					
Dichlorvos	62737			50	32
Polychlorinated Biphenyls					
Polychlorinated Biphenyls	1336363	0.2	0.000026		
Dioxins & Furans					
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746016	1E-5	3.0E-9		
Asbestos					
Asbestos	1332214			1%	68,000

1. The calculated GSI may be below the TDL in Table 1.

TABLE 7. CONTAMINANTS WITH ESTABLISHED RISK-BASED CRITERIA WITHOUT TDLS AND DESIGNATED ANALYTICAL METHODS

CONTAMINANT	CAS NO
Acrylic acid	79107
Camphene	79925
1-Chloro-1,1-difluoroethane	75683
Diacetone alcohol	123422
Diethylene glycol monobutyl ether	112345
Diisopropylamine	108189
N,N-Dimethylacetamide	127195
N,N-Dimethylaniline	121697
Dimethylformamide	68122
Dimethylsulfoxide	67685
Diquat (soils)	85007
Endothall (soils)	145733
Ethyl Acetate	141786
Ethylene glycol monobutyl ether	111762
1-Formylpiperidine	2591868

CONTAMINANT	CAS NO
Gentian violet	548629
n-Heptane	142825
n-Hexane	110543
2-Methoxyethanol	109864
N-Methyl-morpholine	109024
Oxo-hexyl acetate	88230357
2-Pentene	109682
Phthalic Acid	88993
Phthalic Anhydride	85449
Piperidine	110894
Propionic Acid	79094
Propyl alcohol	71238
Tributylamine	102829
Triethanolamine	102716
2,2,4-Trimethyl-2-pentene	107404

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: **SAMPLING AND ANALYSIS – ATTACHMENT 2**
SOIL LEACHING METHODS

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
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
Leachate:	Specific aqueous solutions are used to evaluate the risks due to hazardous substances in soils as a result of the leaching of the substances into surface waters, groundwater, and drinking waters. The term "leachate", as used in this guidance, refers to those solutions after the leaching process is completed.

PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides specifications for designated methods to evaluate the capability of the soil to leach hazardous substances, for site assessment, site investigation and response activities under Part 201, Part 211, and Part 213. Designated methods include those specified in R 299.5722(3)(a) and alternate leaching methods identified in this document.

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 heath, safety, or welfare and the environment. To assure that soils do not pose a threat of aquifer contamination, the concentration of a hazardous substance in soil must be below that which produces a concentration in soil leachate that is equal to the most restrictive applicable groundwater criteria. Leach testing is not required to demonstrate compliance with applicable criteria if soil concentrations do not exceed the applicable generic criteria (see RRD Operational Memorandum No. 1, Residential and Commercial I Soil and Industrial and Commercial II, III, and IV Soil tables, Groundwater protection columns). If the leachate concentration generated by background soils, or the background groundwater concentration is greater than the generic criteria, the background concentration shall be used in place of the risk-based value as the cleanup criterion. Background soils and background groundwater concentrations must represent background conditions not impacted by a release at, or regionally proximate to, the facility. RRD Operational Memorandum No. 4 provides guidance on establishing background concentrations.

If concentrations exceed applicable generic criteria additional leach testing may be conducted to demonstrate compliance for soils. Leachable concentrations must be determined by a method that best represents in-situ conditions. Methods the MDEQ has designated as acceptable soil

leachate methods are identified in R 299.5722(3)(a) as the toxicity characteristic leaching procedure (TCLP), and the synthetic precipitation leaching procedure (SPLP). Further details concerning these procedures are provided in Table 1.

Alternative methods accepted by the MDEQ to simulate conditions at the facility are also provided in Table 1. Proposals for use of other standard methods may be made to the MDEQ for consideration. If contaminants in the soils have the potential to be characteristically hazardous (based on the 20X rule), then TCLP testing must be conducted to determine the applicability of Part 111, Hazardous Waste Management, of NREPA (Part 111) and the associated administrative rules.

When soil leachate analysis methods are relied upon, analysis of samples of those soils must also be conducted, following an appropriate available method, to determine concentrations of contaminants in the soils prior to leaching. Soil sample analysis results must be provided with the leachate data. Soil sample collection and preservation specifications for volatiles analysis may require that different collection methods be used to obtain samples appropriate for both leachate and soil analyses. Additional guidance on sample collection and preservation specifications for volatiles is available in RRD Operational Memorandum No. 2, Attachment 6.

Soils which exceed the TCLP regulatory levels must be managed according to Part 111.

Questions regarding this document should be directed to Mr. A. Ralph Curtis at 517-373-8389, curtisar@michigan.gov.

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

- Environmental Response Division, Operational Memorandum 12, Alternate Soil Leaching Procedures, dated January 5, 1995.

- Storage Tank Division Operational Memorandum 14, Analytical Parameters and Methods, Sample Handling, and Preservation for Petroleum Releases, Table 3 Acceptable Soil Leaching Procedures for Evaluating the Mobility of Specific Contaminants in Soil, dated June 12, 1998.

APPENDAGE

Designated Soil Leaching Methods

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.

DESIGNATED SOIL LEACHING METHODS

1. Toxicity Characteristic Leaching Procedure (TCLP) EPA Method 1311. Use buffered acetic acid solutions at pH 2.88 or 4.93 for leaching soils to determine the concentrations of metals, semi volatiles, pesticides, PCBs, and volatiles that can be leached. This method is not acceptable for leaching soils to determine the concentrations of cyanides, sulfides, and hexavalent chromium that can be leached.
2. Synthetic Precipitation Leaching Procedure (SPLP) EPA Method 1312. Use Extraction Fluid #1, H_2SO_4 & HNO_3 solutions at pH 4.20, for leaching soils to determine the concentrations of metals, semi volatiles, pesticides, and PCBs that can be leached. Use Extraction Fluid #3, reagent water, for leaching soils to determine the concentrations of cyanides, sulfides, volatiles, and hexavalent chromium that can be leached.
3. ASTM Neutral Leach Procedure, ASTM D3987-85. Use reagent water for leaching soils to determine the concentrations of semi volatiles, pesticides, PCBs, cyanide, sulfides, and hexavalent chromium that can be leached. This method is not acceptable for leaching soils to determine the concentrations of metals and volatiles that can be leached. This procedure provides for reporting the leachable contaminant levels in terms of the weight of the soil (mg/Kg). However, in order to use this soil leaching procedure for the purpose of evaluating contaminant mobility and potential impact on groundwater, leachable contaminant levels must be reported in terms of the volume of the leaching fluid, in ug/L units. This requirement must be conveyed to the lab prior to sample analysis.
4. ASTM D5233-92 ASTM Single Batch. Use buffered acetic acid solutions at pH 2.88 or 4.93, to leach soils and determine the concentrations of metals, semi volatiles, pesticides, and PCBs that can be leached. The method is not acceptable for leaching soils to determine the concentrations of volatiles, cyanides, sulfides, and hexavalent chromium that can be leached. The method is useful for large particle-sized materials. Any monolith subject to this method must also be evaluated with ASTM D4842-89 to evaluate freeze-thaw effects.

<u>Soil Collection for Determining Volatiles Leachable to Groundwater.</u>

To evaluate leaching of volatiles from soils, using the appropriate methods above, the MDEQ requires a specific sample collection and preservation procedure. A syringe-type coring device, documented to be effective for retaining the volatiles that are to be analyzed, is used to collect a 25 gm (±3 gm) soil sample. The sample must be weighed in the field by subtracting the device weight from the weight of the device with the soil. Exposing the soil to the environment to obtain the weight either in the field or in the laboratory to is not acceptable. The sample must be frozen immediately whenever feasible, otherwise the sample must be cooled to 4º C (± 2º), and transferred to the laboratory. The soil must be extruded from the syringe-type coring device directly into the leaching fluid within 48-hours of collection. After completion of the leaching procedure, an aliquot of leachate must be immediately collected and preserved as a volatile organic water sample. If large sample sizes are required, multiple coring devices should be used.

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: SAMPLING AND ANALYSIS – ATTACHMENT 3
INDOOR AIR DESIGNATED METHODS AND TARGET DETECTION LIMITS

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 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
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 guidance for Target Detection Limits (TDLs) and designated methods judged capable of achieving the TDLs for acceptable indoor air concentrations. Acceptable indoor air concentrations were generated as part of the calculation used to establish groundwater and soil volatilization to indoor air cleanup criteria. Representative indoor air sampling may be used to evaluate whether there is a current unacceptable exposure that requires mitigation for due care or interim response activities at a facility. Indoor air sampling is not appropriate for evaluating compliance with soil or groundwater cleanup criteria. This document must be used in coordination with the guidance on indoor air sampling provided in RRD Operational Memorandum No. 4.

This attachment establishes analytical target detection limits for hazardous substances and designates available analytical methods that are capable of achieving the target detection limits to facilitate gathering the information necessary for the department to determine compliance with the applicable provisions of Part 201, or Part 213.

TARGET DETECTION LIMITS AND AVAILABLE METHODS

Table 1 provides TDLs for hazardous substances with established acceptable indoor air concentrations. These TDLs were derived by reviewing the low-level capabilities of state laboratories and methods published by government agencies and referenced in this document. Laboratory reporting limits should be equal to or less than these reporting limits to evaluate indoor air exposure risks.

Analytical methods judged capable of achieving the TDLs are specified in Table 1. Other validated and published methods from nationally recognized organizations can also be used, provided the TDLs in Table 1 are met. Organizations that publish such methods include the American Society for Testing and Materials (ASTM), National Institute for Occupational Safety and Health, (NIOSH) and the U.S. EPA. Modifications of methods are acceptable if method

performance documentation that demonstrates adequate performance is available and provided to the MDEQ.

The methods specified in this document were published in the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition (EPA/625/R-96/010b), by the Office of Research and Development of the U.S. EPA. The method titles are included with the source documentation listed in Table 1.

INDOOR AIR CONTAMINANT LIST

Indoor air sampling should not be evaluated without adequate site characterization to evaluate the soil and groundwater contaminants that exceed volatilization to indoor air cleanup criteria. All contaminants identified in the site characterization which exceed generic residential cleanup criteria are contaminants of concern. Table 1 does not include all contaminants that can be measured by the designated methods. When reporting analyses for indoor air, the laboratory should report the identified contaminants of concern and any additional contaminants that are routinely analyzed and reported to clients. Contaminants of concern and the capabilities of candidate laboratories must be reviewed when selecting a laboratory as a laboratory may or may not routinely analyze for all contaminants specified in Table 1.

RESULT REPORTING

The TDLs need to be achieved to evaluate whether there is a current unacceptable exposure that requires mitigation for due care or interim response activities at a facility. Levels below the TDL may be required to evaluate ambient air conditions within the immediate vicinity of the building. The laboratory's reporting levels for specific samples will be dependent upon the air volume collected. Careful planning is required during the sampling phase to ensure valid data is obtained for evaluation of both the indoor as well as ambient air if required.

Concentrations of contaminants in air are reported in units such as micrograms of contaminant per cubic meter of air and micrograms of contaminant per liter of air: Units of micrograms of contaminant per liter of air are equivalent to parts per billion of contaminant in the air on a volume basis, and are abbreviated as PPBV.

- Results must be appropriately coded to indicate the confidence of the data. Results with no codes are meant to be quantitative and within the accuracy and precision routinely achieved for the method.
- Results must be reported with the actual calculated reporting limit determined from the capabilities of the method and the volume of air used.
- Results for compounds detected below the laboratory reporting limits must be reported and coded to indicate estimated data.

Questions about this memorandum attachment should be directed to: A. Ralph Curtis, Laboratory Specialist, Remediation and Redevelopment Division, Toxicology Unit, Phone: 517-373-8389, FAX: 517-241-9581, Email: curtisar@michigan.gov.

APPENDAGE:

Table 1 – Target Detection Limits, Designated Analytical Methods, and Source Documents

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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. Target Detection Limits, Designated Analytical Methods, and Source Documents

Polychlorinated Biphenyls	CAS	TDL (PPBV)	Designated Methods
Polychlorinated biphenyls (PCBs) [1]	1336363	0.02	TO-10A
Aroclor 1016	12674112	------	TO-10A
Aroclor 1221	11104282	------	TO-10A
Aroclor 1232	11141165	------	TO-10A
Aroclor 1242	53469219	------	TO-10A
Aroclor 1248	12672296	------	TO-10A
Aroclor 1254	11097691	------	TO-10A
Aroclor 1260	11096825	------	TO-10A
Aroclor 1262	37324235	------	TO-10A
Aroclor 1268	11100144	------	TO-10A
Pesticides			
Aldrin	309002	0.002	TO-10A
Chlordane [2]	57749	0.1	TO-10A
Chlordane, trans	5103719	0.04	TO-10A
Chlordane, cis	5103742	0.04	TO-10A
Chlorpyrifos, ethyl	2921882	1	TO-10A
Dieldrin	60571	0.003	TO-10A
Heptachlor	76448	0.01	TO-10A
Hexachlorobenzene	118741	0.03	TO-10A
Hexachlorocyclopentadiene	77474	0.01	TO-10A
alpha-Hexachlorocyclohexane	319846	0.007	TO-10A
Tris(2,3-dibromopropyl) phosphate	126727	0.02	TO-10A
Polycyclic Aromatic Hydrocarbons			
Acenaphthene	83329	100	TO-13
Acenaphthylene	208968	20	TO-13
Anthracene	120127	500	TO-13
Fluoranthene	206440	80	TO-13
Fluorene	86737	80	TO-13
Naphthalene	91203	2	TO-13
Phenanthrene	85018	0.05	TO-13
Pyrene	129000	50	TO-13
Mercury Vapor and Particulates			
Mercury, Total	7439976	0.2	Various [3]

Table 1. Target Detection Limits, Designated Analytical Methods, and Source Documents

Polar/Non-Polar Organic Compounds	CAS	TDL(PPBV)	Designated Methods
Acetone	67641	3000	TO-11A TO-17 TO-15A
Acetonitrile	75058	30	TO-15A TO-17
Acetophenone	98862	300	TO-15A
Acetaldehyde	75070	5	TO-11A TO-15A
Acrolein	107028	0.01	TO-15A TO-17
Acrylonitrile	107131	0.2	TO-15A TO-17
Azobenzene	103333	0.4	TO-13
Benzene	71432	1	TO-15A TO-17
Benzyl Chloride	100447	0.2	TO-15A TO-17
Bis(2-chloroethyl)ether	111444	0.04	TO-13 TO-15A TO-17
Bromobenzene	108861	4	TO-1
Bromodichloromethane	75274	0.3	TO-15A TO-17
Bromoform	75252	10	TO-15A TO-17
Bromomethane	74839	3	TO-15A TO-17
2-Butanone	78933	500	TO-15A TO-17
n-Butyl acetate	123864	4000	TO-17
t-Butyl alcohol	75650	1000	TO-17
Carbon disulfide	75150	400	TO-15A TO-17
Carbon tetrachloride	56235	0.5	TO-15A TO-17
Chlorobenzene	108907	40	TO-15A TO-17
Chloroethane	75003	5000	TO-15A TO-17
Chloroform	67663	5	TO-15A TO-17
Chloromethane	74873	20	TO-15A TO-17
2-Chlorotoluene	95498	40	TO-15A TO-17
Cyclohexanone	108941	500	TO-17
Decabromodiphenyl ether	1163195	20	TO-17
Dibromochloromethane	124481	0.5	TO-15A TO-17
1,2-Dibromo-3-chloropropane	96128	0.1	TO-15A TO-17
1,2-Dichlorobenzene	95501	800	TO-13 TO-15 TO-17
1,4-Dichlorobenzene	106467	2	TO-13 TO-15 TO-17
Dichlorodifluoromethane	75718	20,000	TO-15A TO-17
1,1-Dichloroethane	75343	300	TO-15A TO-17
1,2-Dichloroethane	107062	0.5	TO-15A TO-17
1,1-Dichloroethylene	75354	0.3	TO-15A TO-17
1,2-Dichloroethylene, cis	156592	20	TO-15A TO-17
1,2-Dichloroethylene, trans	156605	40	TO-15A TO-17

Table 1. Target Detection Limits, Designated Analytical Methods, and Source Documents

Polar/Non-Polar Organic Compounds	CAS	TDL(PPBV)	Designated Methods
1,2-Dichloropropane	78875	2	TO-15A TO-17
1,3-Dichloropropene	542756	3	TO-15A TO-17
Diethyl ether	60297	7000	TO-15A
Di-isopropyl ether	108203	200	TO-15A TO-17
Epichlorohydrin	106898	0.5	TO-15A TO-17
Ethylbenzene	100414	40	TO-15A TO-17
Ethylene dibromide	106934	0.06	TO-15A TO-17
Ethyl(tert)butylether	637923	200	TO-15A TO-17
Formaldehyde	50000	0.5	TO-11A TO-15A
Hexachloroethane	67721	2	TO-13 TO-15A TO-17
Hexachlorobutadiene	87683	0.5	TO-13 TO-15A TO-17
2-Hexanone	591786	20	TO-15A TO-17
Isobutyl alcohol	78831	800	TO-15A TO-17
Isopropylbenzene	98828	50	TO-15A TO-17
Methyl(tert)butylether	1634044	2000	TO-15A TO-17
Methyl alcohol	67561	2000	TO-15A TO-17
Methylene chloride	75092	30	TO-15A TO-17
4-Methyl-2-pentanone	108101	1000	TO-15A TO-17
Naphthalene	91203	2	TO-13 TO-17
Nitrobenzene	98953	0.4	TO-13 TO-15A TO-17
Pentane	109660	9000	TO-17
Pentachloronitrobenzene	82688	3	TO-17
Pyridine	110861	2	TO-17
Styrene	100425	20	TO-15A TO-17
Tertiaryamylmethylether	994058	30	TO-15A TO-17
1,1,2,2-Tetrachloroethane	79345	0.2	TO-15A TO-17
1,1,1,2-Tetrachloroethane	630206	2	TO-15A TO-17
Tetrachloroethylene	127184	20	TO-15A TO-17
Tetrahydrofuran	109999	3000	TO-1
1,1,2-Trichloro-1,2,2-trifluoroethane	76131	40,000	TO-15A TO-17
1,2,4-Trichlorobenzene	120821	200	TO-13 TO-15A TO-17
1,1,1-Trichloroethane	71556	500	TO-15A TO-17
1,1,2-Trichloroethane	79005	0.8	TO-15A TO-17
Trichloroethylene	79016	7	TO-15A TO-17
Trichlorofluoromethane	75694	30,000	TO-15A TO-17

Table 1. Target Detection Limits, Designated Analytical Methods, and Source Documents

Polar/Non-Polar Organic Compounds	CAS	TDL(PPBV)	Designated Methods
1,2,4-Trimethylbenzene	95636	700	TO-15
1,3,5-Trimethylbenzene	108678	700	TO-15
Toluene	108883	200	TO-15A TO-17
Vinyl acetate	108054	100	TO-15A TO-17
Vinyl chloride	75014	3	TO-15A TO-17
Xylenes	1330207	2000	TO-15A TO-17

Footnotes:

1. The term Polychlorinated bipenyls (PCBs) refers to the total concentration of Aroclors found at the site. The Aroclors must be summed and reported as total PCBs. The Aroclors analyzed are listed without TDLs. The individual TDLs for these Aroclors must be sufficiently low that the reporting limit for PCBs can be met.
2. The concentrations of the trans and cis isomers must be summed and reported as Chlordane. Other procedures for summing concentrations of appropriate compounds may be used.
3. There are many instruments available to measure mercury vapor and particulates. Each instrument has instructions provided by the manufacturer. The appropriate method, or instructions for the use of the instrument, is dependent upon the specific instrument used.

Source Documents for Indoor Air Measurements

All of the following methods are from the Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Center for Environmental Research Information, Office of Research and Development, U.S. EPA, Cincinnati, OH 45268, January 1999 (http://www.epa.gov/ttn/amtic/files/ambient/airtox/tocomp99.pdf):

Method TO-10A: Determination of Pesticides and Polychlorinated Biphenyls in Ambient Using Low Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD).

Method TO-11A: Determination of Formaldehyde in Ambient Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC).

Method TO-13A: Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS).

Method TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by GC/MS.

Method TO-17: Determination of VOCs in Ambient Air Using Active Sampling on to Sorbent Tubes.

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	1,2-Dibromoethane (EDB)
Acrolein	Nitrosamines
Acrylonitrile	Organophosphorus Pesticides
Acrylamide	Phenolics
Benzidines	Polychlorinated biphenyls
Chlorinated Acids/Herbicides	1,2,3-Trichloropropane
Chlorinated Pesticides	Semivolatiles
1,2-Dibromo-3-Chloropropane	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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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 HNO3 , 4° C	28	Days		
Mercury, Low Level	1669/1631	MS	L	10 ml 1:1 Hg-free HNO3 per L, 4° C	28	Days		
Hexavalent Chromium								
Chromium VI (waters)	7199	----	HDP	Use buffer solution [16] to adjust pH 9-9.5 (check with pH paper or pH meter) 4° C	24	Hours		
	7196	----	MN	4° C	24	Hours		
					Collection To Preparation		**Preparation To Analysis**	
Chromium VI (soils)	3060A [17]	MS	----	4° C, Store field-moist.				
				Dry Soils:	2	Days	7	Days
				High moisture soils and sediments:	30	Days	7	Days
Low Molecular Weight Acids	5560 C	GS	GN	None Required		NA		NA
Glycols	8015C	GS	GN	None Required		NA		NA
Phosphorus, White [18]	7580	OX	VOA	Limit contact with air. No headspace, 4° C, store in dark. Tightly seal extracts and refrigerate.	5	Days		
				Extracts:				
				Ether Extract		----→	8	Hours
				Iso-Octane Extract		-----→	30	Days

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

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

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

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

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

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

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

Hazardous Waste Characterization Using Method 1312

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

Radiochemistry Contaminants

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

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

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

Wisconsin GRO/DRO Guidelines

Contaminants 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 4ºC.
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.

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: SAMPLING AND ANALYSIS - ATTACHMENT 5
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

General Considerations

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://www2.epa.gov/quality/low-stress-low-flow-purging-and-sampling-procedure-collection-groundwater-samples-monitoring). 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.

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 Cº. Care must be taken to not freeze the vials below -20 Cº 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 mailto:mcurtisar@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

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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.

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.

October 22, 2004

RRD OPERATIONAL MEMORANDUM NO. 2

SUBJECT: SAMPLING AND ANALYSIS - ATTACHMENT 7
LOW LEVEL MERCURY SAMPLING 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 guidance for the collection of groundwater samples from monitoring wells for analysis using U.S. EPA Method 1631, Revision B; Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, Office of Water, EPA-821-R-99-005, May 1999, to evaluate mercury concentrations in groundwater venting to surface water and determine compliance with the groundwater to surface water interface (GSI) criterion. The GSI criterion is based on "total" mercury, i.e., all forms of mercury existing in the groundwater. This includes both inorganic and organic types, dissolved or attached to particulate present in the groundwater.

This attachment is applicable to site investigation and response activities under Part 201, and Part 213 of NREPA.

SUMMARY

The U.S. EPA Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Criteria Levels, July 1996, U.S. EPA, Office of Water, Engineering and Analysis Division, Washington D.C., was used as a reference to develop this attachment. The two-person team approach, as described in Method 1669, "Dirty Hands," and "Clean Hands" sampling was adopted, and quality assurance and control requirements of that method have been incorporated.

Modifications of this method, and other methods, may be proposed and used if found adequate by the MDEQ to produce reliable results for sampling groundwaters for low level mercury. The presentations of information that validate the use of other methods or modifications of this method are the responsibility of the parties proposing their use. This attachment is not intended to be used in place of Method 1669 when the use of that method is required.

CONTACTS

Information regarding this operational memorandum attachment may be directed to:

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Sandra Gregg: Lab Analysis: 517-335-9800; greggs@michigan.gov.

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

- Environmental Response Division Procedure, "Groundwater Sampling from Monitoring Wells for Low Level Analysis of Mercury" dated April 13, 2001.

APPENDAGE:

Low Level Mercury Sampling and Analysis Specification

This memorandum and its attachment 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.

LOW LEVEL MERCURY SAMPLING AND ANALYSIS SPECIFICATIONS

Summary

Sampling equipment, materials, and containers are cleaned using high purity chemicals and double bagged for protection from contamination during storage and transportation. Highly purified reagent water is provided to the field personnel for the decontamination of the equipment and collection of field blanks. High purity, diluted, hydrochloric acid (HCl) is also provided to field staff for preservation of the sample.

A two-person team, as described in Method 1669, is used for sample collection. One member of the two-person sampling team is designated as "Dirty Hands," and the second member is designated as "Clean Hands." The individual designated as "Clean Hands" will handle all operations involving contact with the sample bottle and transfer of the samples from the sample collection device to the sample bottle. "Dirty Hands" is responsible for the preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample. Sampling teams wear clean non-talc gloves as well as clean, lint-free, outer clothing to protect samples from contamination by lint and dust.

Special precautions are incorporated to minimize contamination. When possible the facility history and results showing previous results of mercury levels at specific locations are used to design the collection process, in order to minimize the chances of cross contamination. Where decontamination of the equipment is required, equipment blanks are taken before each sample. Sample collection is performed by a strict protocol designed to minimize contamination.

Because of the likelihood of positive blanks and the affect they have upon the results, staff should carefully evaluate blank levels before making regulatory decisions. For application to regulatory requirements, it is recommended that blank mercury levels be less than one-fifth of the mercury in the associated sample. This is the guideline recommended in Method 1631.

Definitions

1. Trace Metal Grade Reagents – Reagents that make no significant contribution of mercury to the sample.
2. Dirty and Clean Hands: All operations involving contact with the sample bottle, and transfer of the samples from the sample collection device to the sample bottle, are handled by the individual designated as "Clean Hands." An individual designated as "Dirty Hands" is responsible for the preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.

Contamination and Interferences

The need to avoid contamination when collecting samples for extremely low level measurements cannot be over emphasized. Field collection personnel should be familiar with the potential sources of mercury contamination, and implement those steps necessary for adequate control. Field and equipment blanks are used to discover contamination problems during the collection steps.

1. Potential Sources of Mercury Contamination: These include metallic and metal-containing equipment, containers, lab ware, reagents, and de-ionized water, improperly cleaned, and stored equipment, as well as atmospheric sources such as dirt and dust, automobile

exhaust, laboratory workers, and cigarette smoke. Well construction materials, e.g., the gravel pack and well screen, may also be a source of contamination.

2. Potential Contamination from Well Construction Materials: Levels of mercury in groundwater samples can be a result of natural background, well construction material, or environmental contamination. To reliably distinguish the mercury contribution of both natural background and well construction materials from environmental contamination, measurements from up-gradient background wells, constructed in the same manner as down-gradient wells, are necessary. RRD Operational Memorandum No. 4 provides guidance on establishing background.
3. Use of Peristaltic Pumps: Peristaltic pumps have distinct advantages in controlling contamination, and should be used when possible. Most other pumps have metal parts that may come in contact with the sample; hence, pumps must be decontaminated. For peristaltic pumps, only the tubing is in contact with the sample: consequently, clean tubing is all that is necessary to minimize contamination.
4. Control: The best way to control contamination is to minimize exposure of the sample and sampling equipment to possible sources of contamination. When possible, prior knowledge of mercury levels at sampling locations is used for planning collection activities to minimize chances of contamination from high sources, cross contamination resulting from sequentially sampling locations of high and low levels, and cross contamination during storage and transportation. Appropriate equipment and field blanks are used to discover contamination.
5. Filtering: If filtering is determined necessary (see RRD Operational Memorandum No. 2, Attachment 5 for direction on filtering) it must be performed at the laboratory to prevent contamination.
6. Preservation: Preservation at the laboratory is optional for samples not requiring filtering. Unpreserved samples should be sent to the laboratory overnight.

Apparatus and Materials

1. Disposable Materials: Disposable materials such as gloves, storage bags, and plastic wrap, may be used new without additional cleaning unless the equipment blank results identify any of these materials as a source of contamination. If new disposable materials are found to be a source of contamination, then a different supplier must be obtained or the materials must be cleaned.
2. Sample Bottles: Fluoropolymer (FEP, PTFE) or borosilicate glass, 125 ml to 1 L, depending upon laboratory specifications with fluoropolymer or fluoropolymer lined caps, cleaned according to Method 1669/1631 procedures, with air tight cap. Containers are filled with 0.1 percent HCl (v/v), tightly capped, double bagged in new polyethylene zip-type bags until needed, and stored in cardboard boxes until use. Sample bottles are transferred to the facility with 0.1 percent HCI, or emptied and filled with reagent water for transportation.
3. Tubing for use with low-flow sampling pump: Use fluoropolymer tubing in lengths as required to reach the sampling point. Tubing must be cleaned by soaking in a 5-10 percent HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. Tubing must be double-bagged in clear polyethylene bags, serialized with a unique number to identify it in case of contamination problems, and stored until use.
4. Peristaltic Pump: 115V A.C., 12V D.C. internal battery, variable-speed, single head, Cole-Palmer or equivalent, portable, “Masterflex L/S,” Catalog No. H-07570-10 drive with Quick Load Pump head, Catalog No. H-07021-24, or equivalent.
   a. Tubing for use with peristaltic pump. Styrene/ethylene/butylene/silicone (SEBS) resin, approximately 3/8 in. internal diameter (i.d.) by approximately 3 ft., Cole-Palmer size 18,

Cat. No. G-06464-18, or approximately ¼ in. i.d., Cole-Palmer size 17, Catalog No. G06464-17, or equivalent. Tubing is cleaned and stored as provided above.

b. Tubing for connection to peristaltic pump as provided above. Fluoropolymer, 3/8 or ¼ in. outside diameter (o.d.), in lengths required to reach the point of sampling. Tubing is cleaned and stored as provided above. If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.

5. Bladder Pump: QED[1] model MP-SP-4P.
   a. Water Level Meter – Provided as part of the QED bladder pump equipment, QED part number MP30-150.
   b. Controller – Provided as part of the QED bladder pump equipment, QED part number MP-15.
   c. Bladders – QED Bladder Kit, part number 38360. Unless it is known, the bladders do not contribute to contamination, the bladders must be cleaned and stored as provided above.
   d. Spare CO2 Tank – QED part number 38304.
6. Water Quality Instruments: Use instruments capable of measuring temperature, hydrogen ion activity (pH), specific conductance, redox, dissolved oxygen, and turbidity to determine when formation water is entering the pump. With the equipment provided to staff, a separate meter is necessary for turbidity measurements.
7. Gloves: Clean, non-talc polyethylene, latex, vinyl, or polyvinylchloride (PVC): various lengths.
8. Gloves: PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.
9. Wind Suit: Suitable to protect samples from contamination from lint and dust. Unlined, long sleeve wind suit consisting of pants and jacket constructed of nylon or synthetic fiber are suitable. Tyvek® suits are used in this procedure.
10. Storage bags: Clean, zip-type, non-vented, colorless polyethylene (various sizes). Large size bags are needed for storage of the pump during transportation between sampling locations.
11. Plastic Wrap: Clean, colorless polyethylene.
12. Cooler: Clean, nonmetallic, with white interior for shipping samples.
13. Ice: Use ice to keep samples chilled during shipment. Chemical packs are less effective.
14. Carboys: Dedicate one specific carboy for “Reagent Water.”
15. Plastic Decontamination Tubs: Containers of various sizes to immerse the submersible pump, sampling tubing, and the wetted parts of the water level meter and multi-parameter monitor. Four tubs are needed, one for a soap solution, one for tap water rinse solution, one for reagent water rinse, and one to hold the reagent water for obtaining field blanks.
16. Pipette: Automatic pipette, capable of dispensing 10.0 ml and automatic tip ejector.
17. Pipette Tips: Colorless, 10 ml, for use with automatic pipette. Pipette tips must be cleaned and stored as described under tubing above.

Reagents

1. Reagent Water: Ultra pure deionized water, starting from a pre-purified (distilled, reverse osmosis, etc.) source, 18 Megaohms minimum, provided in a carboy suitable to prevent mercury contamination. The water should be tested at the laboratory for suitability for sampling. The quantity needed depends on the amount of water needed for each decontamination cycle and the number of wells sampled. The laboratory should provide this water.
2. Preservative: Hydrochloric acid (HCl), 6 N (normal) made from Trace Metal Grade acid and reagent water, and tested to contain less than 0.5 ng/L of mercury. The laboratory should provide this reagent.

3. Soap: Alconox [2] CITRANOX®, suitable for cleaning instruments for low level mercury sampling. Prepare a 2 percent solution as per the manufacturer's instructions.

Site Sampling Plans and Sample Delivery Strategies to Minimize Contamination

1. Sample Collection Strategy: Sample collection activities should be designed that will minimize the potential for cross contamination.
   a. If possible, use previous facility data showing mercury levels at the locations to be sampled. If mercury data is not available, use other information to make a judgement whether the mercury level is suspected to be high or low. For example, if data is available for other metal levels, the relative levels of these metals may be a good indicator of whether high or low mercury levels are suspected.
   b. Arrange the sampling sequence in order of their known or expected levels of mercury. Collect samples starting from locations known to have the lowest and approximate same levels of mercury, and proceed to those of higher levels. In this manner, if decontamination procedures fail to remove all residual mercury, the effect on samples will be minimized.
   c. Group samples so that samples of high and low levels are separately grouped in storage and transportation. For purposes of separating samples based on expected concentration levels, samples believed to have concentrations more than 200 ng/L of mercury should be identified as high level samples, and low level samples less than or equal to 200 ng/L.
2. Sample Information Provided to the Laboratory: Laboratory areas and instrumentation used for low level analysis of mercury are extremely clean and designed to prevent mercury contamination from outside sources. Processing a sample with an extremely high level of mercury in these areas can result in contamination of the area and instrumentation, resulting in delays and additional expense. Using the evaluation described above, provide information to the laboratory regarding the known or expected levels of mercury for each location sampled. Information useful to the laboratory and recommended to be provided is as follows:

Mercury (Hg) Level	**Provide to Laboratory**
Hg levels not known and high levels expected.	Expected > 200 ng/L
Hg levels not known and low levels expected.	Expected < 200 ng/L
Hg levels previously found	Provide Data
Hg levels and expectations not known	Not Known

Sample Collection, and Handling Considerations

Sampling precautions should be taken as follows:
1. Use low-flow rates (0.5 L/min.) during both purging and sampling to maintain minimal draw-down in the well.[3]
2. Place the sampling pump intake at the proper sampling point.
3. Minimize disturbance of the stagnant water column above the screened interval during water level measurement and sampling device insertion.
4. Make proper adjustments to stabilize the flow rate as soon as possible.
5. Monitor water quality indicators during purging.
6. Collect unfiltered samples to represent contaminant loading and transport potential in the subsurface system.

7. Filtering (if necessary): If it is not feasible to collect samples representative of the water flowing in the aquifer, and filtering is determined necessary, (see RRD Operational Memorandum No 2 – Attachment 5 for direction on filtering), collect duplicate samples and identify one of these to be filtered and preserved upon receipt at the laboratory. Appropriate arrangements must be made with the laboratory to ensure the filtering and subsequent preservation is accomplished for identified samples immediately upon receipt. Arrangements with the laboratory to utilize appropriate filters should be made well in advance of sample collection, so that immediate filtering and preservation at the laboratory can be accomplished upon receipt of samples.
8. Water samples should not be taken immediately following well development. Sufficient time should be allowed for the groundwater flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on facility conditions and methods of installation but often exceeds one week.
9. Well purging is nearly always necessary to obtain samples of water flowing through the formation associated with the screened interval. The required purging procedure relies on the stabilization of several water quality parameters to determine when formation water is being pumped. The pH, specific conductance, redox, dissolved oxygen, and turbidity are monitored for this purpose. Temperature is also measured and recorded during this process but is not used as an indicator for formation water. Data on pumping rate draw-down, not to exceed 0.1 meter, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.
10. Water Level Measurements and Monitoring: Well depth should be obtained from the well logs. Since measuring to the bottom of the well casing will cause re-suspension of the settled solids and require longer purging times for turbidity equilibration, measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point, which is surveyed relative to ground elevation.

Sample Collection using Bladder Pumps

1. Upon arrival at the sample location, one member of the two-person sampling team is designated as “Dirty Hands,” and the other as “Clean Hands.”
2. An area, expected or known to be free of high levels of mercury, is selected.
3. The team removes the bags containing the pump, monitoring instruments, tubing, carbon dioxide (CO2) cartridges, gloves, plastic wrap, and wind suits, from the coolers or storage containers in which they are packed.
4. The team puts on Wind Suits and PVC gloves.
5. The team generates the Initial Equipment Blank, following the steps listed under Decontamination and Initial Equipment Blank.
6. The team proceeds to the sampling location.
7. The team opens the well.
8. The team changes gloves.
9. Keeping both bags together, Dirty Hands opens the outer bag containing the pump.
10. Clean Hands opens the inner bag and removes the pump.
11. Clean Hands lowers the submersible sampling pump into the monitoring well. Lower the pump slowly and carefully to the middle of the screened interval or slightly above the middle. This should minimize excessive mixing of the stagnant water above the screen with water in the screened interval and minimize suspension of solids from the bottom of the well.
12. Dirty Hands opens bag containing static water level meter. Clean Hands removes water level meter. Clean Hands sets up the water level meter.

13. Clean Hands connects the multi-meter flow through cell to the pump outlet.
14. Dirty Hands turns on the submersible pump, sets the pump for the allowable water level draw-down (not to exceed 0.1 meters), and slowly pumps the water while monitoring the water level to assure that that the pumping rate does not result in draw-down of the water level. With the QED bladder pump in this standard operating procedure (SOP), the pump will turn off automatically if this level is exceeded. As the well is pumped, water quality parameters are monitored to determine when formation water is flowing through the pump. Formation water is considered to be flowing, if three consecutive measurements of the water quality parameters, conducted at 3-5 minute intervals, meet the following requirements:
    a. Turbidity, within $\pm$ 10 percent.
    b. pH, within $\pm$ 0.1 pH units.
    c. Specific conductance, within 3 percent.
    d. Redox, within $\pm$ 10 millivolts
    e. Dissolved oxygen, within $\pm$ 10 percent. If dissolved oxygen is used for comparison to criteria or a mixing zone calculation, the dissolved oxygen calibration must be corrected for local barometric pressure and elevation. The equipment in this procedure (YSI multi-parameter meter) automatically corrects the dissolved oxygen for these conditions.
15. After stabilization, Clean Hands disconnects the meter.
16. The team changes gloves.
17. Dirty Hands retrieves the sample containers required, and unzips their outer bags. Retrieve two sample containers if filtering is required, for duplicate samples, or for field blanks. If split samples are to be generated a larger size container is required, at least twice the size of normal samples.
18. Dirty Hands prepares the label(s).
19. Clean Hands opens the inner bag, removes the sample container, and reseals the inner bag.
20. Clean Hands removes the cap for the sample being collected, and while holding the cap upside down, discards the diluted acid into a waste carboy, or empties the reagent water onto the ground.
21. If a field blank is being generated, proceed as follows:
    a. Clean Hands opens the inner bag and places the emptied sample bottle and its cap in its inner bag. This bottle is to be identified as the field blank.
    b. Clean Hands obtains another sample bottle from its inner bag, removes and, discards its cap.
    c. Clean Hands retrieves the field blank bottle, and pours the contents of the sample bottle into the field blank bottle.
    d. Skip to step 27 below.
22. Clean Hands rinses the sample bottle and cap three times with the formation water flowing from the pump, and collects the sample from the flowing tube.
23. Clean Hands caps the sample, opens the inner bag, and places the sample in its inner bag.
24. If filtering is required or a duplicate sample is to be taken, Steps 18 through 23 are repeated to immediately take another sample.
25. For samples required to be filtered or preserved at the laboratory, skip to step 27 below.
26. Preserve each sample taken as follows:
    a. Dirty Hands opens the outer bag containing the preservative, pipette, and tips.
    b. Clean Hands opens the inner bag, opens the preservative, retrieves the pipette, and prepares it for dispensing.

c. Use the information included in Sample Preservation and Holding Time for the correct amount of preservative. Clean Hands pipettes the required amount of preservative into the sample container(s), ejects the pipette tip into the waste container, places the pipette back into its inner bag, recaps the preservative, and seals the inner bag.
d. Dirty Hands seals the outer bag for the preservative.

27. Clean Hands caps the sample(s), opens the inner bag(s) for the sample(s), places the sample bottle(s) into the inner bag(s), and seals the inner bag(s).
28. Dirty Hands seals the outer bag(s), writes sample identification information in permanent ink on the outside of the plastic bag, places the sample(s) in the cooler (on ice), and closes the cooler.
29. Dirty Hands measures and records the depth to the bottom of the well.
30. Dirty Hands records the sample number(s) in the sampling log, water quality parameters, and notes any unusual observations.
31. Clean Hands removes the equipment from the well, removes the water level meter, and places them into bags for transportation.
32. Both Dirty and Clean Hands move to the decontamination area with the equipment.
33. Decontamination Between Sampling Locations steps are used to decontaminate the equipment.
34. Generating the Equipment Blank steps are used to collect an equipment blank.
35. If other samples are to be taken at the facility, the team proceeds to the next sampling location, and collects another sample beginning with step 6 above.
36. If samples are to split, proceed as follows:
    a. The team selects a suitable place for splitting samples.
    b. The team changes gloves.
    c. Dirty Hands opens the cooler, removes the bag containing the sample to be split. The volume of this sample must be at least twice the volume of normal samples.
    d. Dirty Hands removes two bags with sample containers, and unzips their outer bags. These containers will hold the split samples.
    e. Dirty Hands prepares the label(s).
    f. Clean Hands opens the inner bags holding all containers, removes the containers, removes the caps of all containers and places them in their respective inner bags.
    g. Clean Hands discards the diluted acid from the two sample containers, into a waste carboy, or empties the reagent water onto the ground.
    h. Clean Hands pours from the container holding the sample to be split, into each of the sample containers.
    i. Clean Hands discards the container that held the sample to be split.
    j. Clean Hands retrieves the caps, seals the samples with their respective caps, places the samples into their inner bags, and seals the inner bags.
    k. Dirty Hands seals the outer bag(s), writes sample identification information in permanent ink on the outside of the plastic bag, places the sample(s) in the cooler (on ice), and closes the cooler.
    l. Equipment blanks associated with the respective samples must be provided to both parties receiving split samples.
    m. Repeat steps for each additional split sample.
    n. Information specific for splitting samples must be documented. If others request split samples, use the MDEQ Laboratory's chain of custody sheet. If the MDEQ is requesting the split sample, and a chain of custody is not forthcoming from the sampler, use the MDEQ chain of custody, fill out information, sign it, and request this be signed by the provider of the samples.

Sample Collection using Peristaltic Pumps

1. Upon arrival at the sample location, one member of the two-person sampling team is designated as "Dirty Hands," and the other as "Clean Hands."
2. The team opens the well to be sampled.
3. An area, expected or known to be free of high levels of mercury, is selected. Sampling should proceed from lowest to highest expected level of contamination.
4. The team removes the bags containing the pump, batteries, monitoring instruments, SEBS resin tubing, gloves, plastic wrap, and wind suits, from the coolers or storage containers in which they are packed.
5. The team puts on Wind Suits and PVC gloves.
6. Dirty Hands removes the pump from its storage bag and opens the bag containing SEBS resin tubing.
7. Clean Hands installs the tubing in the well. Lower the tubing slowly and carefully to the middle of the screened interval or slightly above the middle, to minimize excessive mixing of the stagnant water above the screen with water in the screened interval, and to minimize resuspension of solids from the bottom of the well.
8. Clean Hands installs tubing on the pump.
9. Dirty Hands opens bag with water level meter.
10. Clean Hands removes water level meter and lowers it into the well.
11. Clean Hands connects the multi-parameter meter flow through the cell to the pump outlet.
12. Dirty Hands turns on the peristaltic pump and slowly pumps the water while monitoring the water level to assure that that the pumping rate does not result in excessive draw-down of the water level (not to exceed 0.1 meters). As the well is pumped, water quality parameters are monitored to determine when formation water is flowing through the pump. Formation water is considered to be flowing if three consecutive measurements of the water quality parameters, conducted at 3-5 minute intervals, meet the following requirements:
    a. Turbidity, within $\pm$ 10 percent.
    b. pH, within $\pm$ 0.1 pH units.
    c. Specific conductance, within 3 percent.
    d. Redox, within $\pm$ 10 mv.
    e. Dissolved oxygen, within $\pm$ 10 percent. If dissolved oxygen is used for comparison to criteria or a mixing zone calculation, the dissolved oxygen calibration must be corrected for local barometric pressure reading and elevation. The equipment in this procedure (YSI multi-parameter meter) automatically corrects the dissolved oxygen for these conditions.
13. After stabilization, Clean Hands disconnects the meter.
14. The team changes gloves.
15. Dirty Hands opens the cooler containing the sample bottle, and unzips the outer bag containing the sample container. If the sample is to be split, a larger size container is required at least twice the size of normal samples. If filtering is necessary, a field blank is being generated, or a duplicate sample is to be taken, Dirty Hands unzips the outer bag of another sample container.
16. Dirty Hands prepares the sample label(s).
17. Clean Hands opens the inner bag, removes the sample container, and reseals the inner bag.
18. Clean Hands unscrews the cap, and while holding the cap upside down, discards the diluted acid into a waste carboy, or empties the reagent water onto the ground.
19. If a field blank is being generated, proceed as follows:

a. Clean Hands places the sample bottle and its cap in its bag. This is to be identified as the field blank.
b. Clean Hands obtains another sample bottle from its bag, unscrews and discards the cap.
c. Clean Hands retrieves the field blank bottle, and pours the contents of the other bottle into the field blank bottle, discards this other bottle, retrieves the cap of the field blank and caps the field blank.
d. Skip to step 22 below.

20. Clean Hands rinses the sample bottle and cap three times with the formation water, and collects the sample from the flowing tube.
21. Clean Hands caps the sample.
22. Clean Hands places a label on the sample container, and places it in its inner bag.
23. If filtering is required, or a duplicate sample is to be taken, steps 17 through 22 are repeated to immediately take another sample.
24. For samples required to be filtered, and samples requiring preservation at the laboratory, skip to step 26 below.
25. Preserve sample as follows:
    a. Dirty Hands opens the outer bag containing the preservative, pipette, and tips.
    b. Clean Hands opens the inner bag, opens the preservative, retrieves the pipette, prepares it for dispensing, and pipettes the required amount of preservative into the sample container(s). Use the information included in Sample Preservation and Holding Time for the correct amount of preservative.
    c. Clean Hands ejects the pipette tip into the waste container, places the pipette back into its inner bag, and seals the inner bag.
    d. Clean Hand caps the preservative, places it in its inner bag, and seals the inner bag.
    e. Dirty Hands seals the outer bags for the pipette and preservative.
26. Clean Hands caps the sample(s), opens the inner bag(s) for the sample(s), places the sample bottle(s) into the inner bag(s), and seals the inner bag(s).
27. Dirty Hands seals the outer bag(s), writes sample identification information on the outer bag, places the sample(s) in the cooler (on ice), and closes the cooler.
28. Dirty Hands measures and records the depth to the bottom of the well.
29. Dirty Hands records the sample number(s) in the sampling log, water quality parameters, and notes any unusual observations.
30. Clean Hands removes the equipment from the well, removes the water level meter, and places them into bags for transportation.
31. Both Dirty and Clean Hands move to the decontamination area with the equipment.
32. Decontamination Between Sampling Locations steps are used to decontaminate the water level meter and multi-parameter meter. The SEBS resin tubing is replaced prior to sampling each new monitoring well.
33. If other samples are to be collected, the team proceeds to the next sampling location, and collects another sample beginning with the step 1.
34. If samples are to be split, follow the steps in Sample Collection Using Bladder Pumps, starting with step 36.

Decontamination and Initial Equipment Blank

1. Dirty Hands prepares the decontamination solutions.
2. Dirty Hands opens outer bag containing tubing and pump bladder.
3. Dirty Hands opens bags containing pump and water level meter.
4. Dirty Hands removes the pump.

5. Dirty Hands holds the pump while Clean Hands removes the bladder from the inner bag and places the bladder on the pump. Clean Hands removes tubing from the inner bag and installs tubing on pump and controller.
6. Dirty Hands lowers pump into tub 1 containing the soap solution.
7. Dirty Hands turns on controller and pumps three volumes of soap solution through the pump and tubing.
8. Clean Hands moves the pump to tub 2 containing tap water.
9. Dirty Hands turns on controller to pump three volumes of tap water through the pump.
10. Clean Hands moves the pump to tub 3 and pumps three volumes of reagent water.
11. Clean Hands places the pump in tub 4 containing reagent water.
12. An equipment blank is taken following steps in Generating the Equipment Blank.
13. Clean Hands removes the water level meter from its storage bag, decontaminates the water level meter by successively cleaning with solutions from tub 1, 2, and 3, and places the meter into a clean storage bag.

Decontamination Between Sampling Locations

1. The team changes gloves.
2. Dirty Hands prepares the decontamination solutions.
3. Dirty Hands lowers pump into tub 1 containing the 2 percent Alconox/tap water solution.
4. Dirty Hands turns on controller and pumps three volumes of Alconox solution through the pump.
5. Clean Hands moves the pump to tub 2 containing tap water (fresh tap water should be used between each sampling location.)
6. Dirty Hands turns on controller to pump three volumes of tap water through the pump.
7. Clean Hands moves the pump to tub 3 and pumps three volumes of reagent water (fresh reagent water should be used between each sampling location.)
8. Clean Hands changes gloves.
9. Dirty Hands opens outer bag containing tubing and pump bladder.
10. Dirty Hands changes gloves.
11. Dirty Hands removes the pump from tub 3.
12. With Dirty Hands holding the pump, Clean Hands removes the bladder from the inner bag and places the bladder on the pump. Clean Hands removes tubing from the inner bag and installs tubing on pump and controller.
13. Clean hands places pump in reagent water in tub 4.
14. The team changes gloves.
15. An equipment blank is taken following steps in Generating the Equipment Blank.
16. Clean Hands places the pump in the storage bag or proceeds to place pump in monitoring well.
17. Clean Hands removes the water level meter from its storage bag, decontaminates the water level meter by successively cleaning with solutions from tub 1, 2, and 3, and places the meter back into a clean storage bag or into the monitoring well.
18. Clean Hands changes gloves.

Generating the Equipment Blank

1. One equipment blank is generated for each location sampled.
2. With the submersible pump in tub 4 holding the fresh reagent water, Dirty Hands turns on the pump and allows several volumes of reagent water to be pumped.
3. The team changes gloves.

4. Dirty Hands opens the box or cooler containing the sample bottles, and unzips the bag containing a sample container. If a split sample is scheduled to be taken, Dirty Hands unzips another bag containing a sample container.
5. Clean Hands opens the inner bag, removes the sample container, and reseals the inner bag.
6. Dirty Hands reseals the outer bag.
7. Clean Hands unscrews the cap, and while holding the cap upside down, discards the diluted acid into a waste carboy, or empties the reagent water on the ground.
8. As reagent water is flowing through the pump, Clean Hands collects the sample by emptying the solution from the sample bottle, rinsing the sample bottle and cap three times with the flowing reagent water, and collecting the sample from the flowing tube.
9. If preservation is performed at the laboratory, skip to step 11.
10. Preserve sample(s) as follows:
    a. Dirty Hands opens the outer bag holding the automatic pipette and preservative.
    b. Clean Hands opens the inner bag containing the preservative and automatic pipette, opens the preservative bottle, and pipettes 10 ml of the preservative into the sample bottle.
    c. Clean Hands recaps the preservative bottle, removes the pipette tip, and places the preservative and pipette back into its bag.
    d. Clean Hands seals the inner bag holding the preservative and pipette.
    e. Dirty Hands seals the outer bag.
    f. Clean Hands opens the inner bag for the sample, places the sample bottle into the inner bag, and seals the inner bag.
11. Dirty Hands seals the outer bag, opens the sample cooler, places the equipment or field blank in the cooler (on ice), and closes the cooler.
12. Dirty Hands records the sample in the sampling log as the “Equipment Blank”.
13. If the scheduled sample to be taken is a split sample, follow the steps in Sample Collection Using Bladder Pumps, starting with step 36.
14. Clean Hands removes the pump from the tub, places it in a clean protective bag, and seals the bag.

Sample Preservation and Holding Time

1. Preservation: Samples are transported on ice during shipment to the laboratory. Samples are preserved in the field using 10 ml/L 6N HCl per liter of sample. If filtering and preservation is required at the laboratory, equivalent amounts of HCl per liter of sample can be used.
2. Laboratory Processing of Filtered/Preserved Samples: If filtering and preservation is to be performed at the laboratory, make arrangements with the laboratory for receipt of samples well in advance. If special filters are necessary, these must be provided to the laboratory prior to sample collection activities or arrangements made with the laboratory to ensure they are available upon sample receipt. It is not advisable to plan sampling immediately proceeding non-working days for the laboratory. Upon shipment of samples to a laboratory, it is good practice to immediately contact the laboratory. If the laboratory is not advised of these arrangements, extra effort and expense must be incurred to ensure necessary filtering and preservation.
3. Sample analysis must be performed within 28 days of sample collection.

Quality Assurance/Quality Control

Equipment Blank: The equipment blanks are used to verify the equipment is free from contamination prior to the collection of the sample. (See Decontamination and Initial Equipment Blank and Generating the Equipment Blank)

1. Frequency of Collection: Collect one initial equipment blank, and an equipment blank per monitoring well sampled.
2. Evaluation Criteria: If the mercury concentration in the blank is greater or equal to 0.5 ng/L, or greater than one-fifth of sample concentration, whichever is higher, the associated sample result is an estimate and may be unusable for regulatory application.
3. Corrections: If the initial equipment blank indicates contamination, above 0.5 ng/L, review the process used for cleaning, and have reagents replaced as appropriate.

Field Blanks: The purpose of field blanks is to assess the suitability of the container, preservative, and sample handling. The field blank is generated by simply pouring the solution provided in one of the sample containers into another sample container whose contents have been emptied at the facility. (See Sample Collection Using Bladder Pumps step 21 and Sample Collection using Peristaltic Pumps step 19)

1. Frequency of Collection: One per facility, per day, or one per sampling event, whichever is greater.
2. Evaluation: If the mercury concentration in the blank is greater or equal to 0.5 ng/L, or greater than one-fifth of sample concentration, whichever is higher, the associated sample result is an estimate and may be unusable for regulatory application.

Field Duplicates: The purpose of field duplicates is to assess the precision for the field sampling and analytical process. A field duplicate is collected by filling a second sample container, in rapid succession after the first sample, from the outlet of the sampling stream.

1. Frequency of Collection: Collect duplicates minimally for every 10 samples collected, or at the frequency specified in the project objectives. If possible, select a location with detectable amounts of mercury.

Split Samples: Split samples are used to independently confirm results of the laboratory performing the analysis. Typically a laboratory known to produce valid, unbiased results, is selected as the laboratory to which the split samples are sent.

1. Collection: Split samples are created by dividing one sample collected in the field into two aliquots. This requires the collection of at least twice the volume of sample normally collected, properly preserved if field preservation is performed. Because of the influence that equipment blanks may have upon the use of the data, an equipment blank associated with the sample should be provided along with the split sample. This will require the generation of two equipment blanks prior to the collection of the sample to be split.

Footnotes

1. QED, P.O. Box 3726, Ann Arbor, MI 48160.
2. Alconox, Inc., 30 Glenn Street, Suite 309, White Plains, NY, 10603.
3. Puls, R. W. and Barcelona, M. J. 1996 Low-Flow (Minimal Draw Down) Ground-Water Sampling Procedures, EPA Ground Water Issues, U.S. EPA Office of Research and Development, EPA/540/S-95/504.

Disclaimer

Mention of specific manufacturers and associated instruments does not constitute endorsement by the MDEQ RRD of that manufacturer and equipment.

This SOP is intended to be a performance-based method. Acceptance of results using modifications of this procedure, and using other procedures, will depend upon the demonstration of equivalent performance.