Revised Long-Term Monitoring and Maintenance Implementation Plan

Keith Middle School Property
225 Hathaway Boulevard
New Bedford, Massachusetts

August 2012
Revision 5.5

Prepared for:

City of New Bedford
New Bedford Public Schools
133 William Street
New Bedford, MA 02740

Revised by:

TRC Environmental Corporation
Wannalancit Mills
650 Suffolk Street
Lowell, Massachusetts 01854

TABLE OF CONTENTS

1.0 INTRODUCTION 1-1

1.1 Background 1-1
1.2 Summary of Changes to the LTMMIP 1-1
1.2.1 LTMMIP Section 2 – Indoor Air Monitoring 1-2
1.2.2 LTMMIP Section 3 – Groundwater Monitoring 1-2
1.2.3 LTMMIP Section 4 – Foundation Vent Stack Air Monitoring 1-2
1.2.4 LTMMIP Section 7 – Long-Term Cap Monitoring Plan 1-3

2.0 INDOOR AIR MONITORING 2-1

2.1 Air Sampling Procedures 2-1
2.2 Sample Locations 2-2
2.3 Analytical Parameters 2-2
2.4 Quality Assurance/Quality Control 2-2
2.5 Action Levels 2-3
2.5.1 PCBs in Indoor Air 2-3
2.5.1.1 Results Exceeding PCB Action Level 2-4
2.6 Reporting 2-4

3.0 GROUNDWATER MONITORING 3-1

3.1 Groundwater Sampling Procedures 3-1
3.2 Sample Locations 3-1
3.3 Analytical Parameters 3-2
3.4 Quality Assurance/Quality Control 3-2
3.5 Action Levels 3-3
3.6 Reporting 3-3

4.0 FOUNDATION VENT STACK AIR MONITORING 4-1

4.1 Air Sampling Procedures 4-1
4.2 Sample Locations 4-1
4.3 Analytical Parameters 4-2
4.4 Quality Assurance/Quality Control 4-2
4.5 Trend Analysis 4-2
4.6 Reporting 4-2

5.0 WETLAND SEDIMENT INSPECTION AND MONITORING 5-1

5.1 Wetland Sediment Inspection 5-1
5.2 Sediment Sampling Procedures 5-1
5.3 Sample Locations 5-2
5.4 Analytical Parameters 5-2
5.5 Quality Assurance/Quality Control 5-2
5.6 Action Levels 5-2
5.6.1 PCBs in Sediment 5-2
5.6.1.1 PCB Results Exceeding Action Levels 5-3
5.7 Reporting 5-3

6.0 LABORATORY QC & DATA USABILITY 6-1

6.1 Laboratory Quality Control Requirements 6-1
6.2 Laboratory Data Management and Documentation 6-1
6.3 Assessment and Response Actions 6-2
6.4 Data Validation and Usability 6-2

7.0 LONG-TERM CAP MONITORING PLAN 7-1

7.1 Background 7-1
7.2 Cap Maintenance 7-2
7.3 Cap Inspections 7-3
7.4 Deed Restriction 7-4
7.5 Soil Management Plan 7-5
7.6 Health and Safety Plan 7-5
7.7 Record Keeping 7-5
7.8 Reporting 7-5

8.0 COMMUNICATION PLAN 8-1

9.0 TRAINING 9-1

10.0 AMENDMENTS TO LTMMIP 10-1

11.0 REFERENCES 11-1

Table

Table 1: Laboratory Quality Control Requirements for PCB Homologue Analyses Using EPA Methods TO-4A and TO-10A 6-1

Figures

Figure 1: Site Location Map
Figure 2: Indoor Air Sampling Locations
Figure 3: Groundwater Monitoring Well Locations
Figure 4: Foundation Vent Stack Identification Plan
Figure 5: Site Topographic Plan

Appendices

Appendix A: Approval for Risk-Based PCB Cleanup and Disposal under 40 CFR §761.61(c)

Appendix B: Supporting Information for Sampling and Analysis

B1 – Air Sampling Protocol

B2 – EPA TO-4A and TO-10A Air Sampling Methods

B3 – Laboratory Reporting Limits: Air, Sediment, and Groundwater

B4 – Laboratory Standard Operating Procedures

Appendix C: Risk-based Air Concentration Calculations

Appendix D: Groundwater Sampling Procedure

D1 - EPA Region I Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells

D2 – TRC SOP 001, Groundwater Sampling, Revision 0, September 2004

Appendix E: Field Instrument Calibration Procedures

E1 - Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction potential [ORP], and turbidity)

E2 – TRC SOP 024, Calibration of Field Instruments for Water Quality Parameter, Revision 0, December 2003

Appendix F: MCP Groundwater Standards

Appendix G: Inspection Forms

Appendix H: Sediment Sampling Protocol

Appendix I: Letter to EPA Recommending Changes to the LTMMIP

1.0 INTRODUCTION

This Long-term Monitoring and Maintenance Implementation Plan (LTMMIP) is utilized by the City of New Bedford (the City) to provide long term monitoring and maintenance of the exposure management barrier, groundwater, wetland sediment, vent stack air, and indoor air quality of the Keith Middle School (KMS) located at 225 Hathaway Boulevard in New Bedford, Massachusetts (see Figure 1). The LTMMIP also describes the maintenance activities to be performed at the Site to prevent exposure to the impacted fill layer located beneath an exposure management barrier. This LTMMIP was prepared per the August 31, 2005 "Approval for Risk-Based PCB Cleanup and Disposal under 40 CFR §761.61 (c)" letter issued by the U.S. Environmental Protection Agency (EPA) to the City of New Bedford (provided in Appendix A).

1.1 Background

Based on prior work conducted by the BETA Group, Incorporated (BETA) (BETA, 2006), the Site impacts were identified as polychlorinated biphenyls (PCBs) and metals (e.g., lead and barium) in soil/fill. BETA also noted the potential presence of volatile organic compounds (VOCs) based on soil gas sampling conducted prior to the construction of the KMS building (BETA, 2005a). In general, BETA concluded that the Site impacts have low migration potential and that installation of an exposure management barrier was an appropriate response action for the Site (BETA, 2006).

The results of a soil gas sampling event performed in 2002 under the location of the new KMS building were evaluated by BETA assuming that no vapor barrier was installed. The conclusion was that no significant risk to human health was posed by the measured soil gas concentrations (BETA, 2006). Nevertheless, the City and the City of New Bedford School Department decided to install a vapor barrier as added protection against vapor intrusion. Passive ventilation was also added with vent stacks installed through the school building up to the roof.

BETA further noted that fate and transport characteristics indicate that it is not likely that indoor air or groundwater will be impacted at the Site.

The collection of the groundwater, indoor air, vent stack air, and sediment samples described in this LTMMIP will be performed by knowledgeable and experienced environmental scientist(s) or engineer(s) and under the direction of a Massachusetts Licensed Site Professional (LSP) or other appropriately qualified environmental professional.

1.2 Summary of Changes to the LTMMIP

The ongoing evaluation of the Site over time has resulted in a conclusion by the City that revision to the LTMMIP is warranted. These revisions include: modification in the frequency of sample collection, modification of the number or types of analyses performed, changes in the locations of sample collection, and changes in the comparison criteria and associated comparison methods. A copy of the complete letter requesting the changes to the LTMMIP can be found in Appendix I. The City will not implement this revised LTMMIP without written authorization by EPA.

1.2.1 LTMMIP Section 2 – Indoor Air Monitoring

- **Indoor air sampling frequency for Volatile Organic Compounds (VOCs) –** Eliminate sampling of VOCs in indoor air at KMS from the monitoring protocol. VOCs are not the principal contaminants of the soil/fill underlying the cap and the cost associated with monitoring VOCs is not warranted.

- **Indoor air sampling frequency for PCBs –** Reduce the frequency of sampling of PCBs to two events per year. Based on the twenty eight rounds of indoor air monitoring conducted by the city, the remedy implemented for the KMS site has been shown to be protective of potential airborne PCB exposures associated with the capped PCB contamination. Reducing PCB indoor air sampling to two rounds per year will reduce the level of effort of the monitoring program and still achieve the associated goals.

- **Analytical parameters –** Specify PCB air analysis by the homologue method (EPA Method 680) rather than congeners and Aroclors since it provides reliable total PCB quantification (upon which the site-specific risk-based comparison criteria are based) and the data are comparable to the air data gathered at New Bedford High School (NBHS), facilitating public communication. In addition, the Aroclor approach to the analysis of PCBs in air is not a suitable characterization methodology since PCBs do not vaporize as pure technical mixtures, whereas the homologue measurement approach is not impacted by this potentially significant source of measurement error. This change in PCB sampling for indoor air eliminates an unnecessary laboratory expense (based on the sampling currently specified in the LTMMIP).

- **PCB sample media analysis –** Extract the quartz pre-filter and adsorbent (PUF) together per Method TO-4A, rather than separately as currently required by the LTMMIP. A separate analysis of the filter and PUF does not yield useful information about the physical state of the PCBs at the time of sampling due to evaporative losses of the analyte from the filter on to the PUF during sampling (as stated in the method). The associated cost of the separate filter analyses is not warranted.

1.2.2 LTMMIP Section 3 – Groundwater Monitoring

- **Groundwater monitoring analytes –** Eliminate the requirement for VOC sampling and analysis for KMS groundwater, which is not a contaminant of concern and maintain monitoring with PCBs and metals. Removing the VOC analysis from the groundwater monitoring program eliminates an unnecessary laboratory expense.

1.2.3 LTMMIP Section 4 – Foundation Vent Stack Air Monitoring

- **Vent stack air sampling frequency for VOCs and PCBs –** Reduce the frequency of sampling of PCBs to two events per year and eliminate VOC sampling. Based on the twenty seven rounds of vent stack air monitoring, the sub slab venting system installed for the KMS building has been shown to effectively mitigate the migration of subsurface VOCs and PCBs

into indoor air. Reducing PCB indoor air sampling to two rounds per year will reduce the level of effort of the monitoring program and still achieve the associated goals.

- **Background sampling –** Using the indoor air background sample (flag pole location) as a background sample for both indoor air and vent stack air sampling (VOCs and PCBs) to reduce laboratory expenses and achieve equivalent goals.

- **Analytical parameters –** Specify PCB air analysis by the homologue method (EPA Method 680) rather than congeners and Aroclors since it provides reliable total PCB quantification (upon which the site-specific risk-based comparison criteria are based) and the data are comparable to the air data gathered at New Bedford High School (NBHS), facilitating public communication. In addition, the Aroclor approach to the analysis of PCBs in air is not a suitable characterization methodology since PCBs do not vaporize as pure technical mixtures, whereas the homologue measurement approach is not impacted by this potentially significant source of measurement error. This change in PCB sampling for indoor air eliminates an unnecessary laboratory expense (based on the sampling currently specified in the LTMMIP).

1.2.4 LTMMIP Section 7 – Long-Term Cap Monitoring Plan

- **Cap inspections** – Schedule cap inspections for twice per year (spring and early fall). The change in inspection frequency reduces the level of effort and achieves equivalent goals.

2.0 INDOOR AIR MONITORING

2.1 Air Sampling Procedures

The following section describes the indoor air monitoring procedures at KMS for PCBs.

Indoor air sampling for PCBs will be conducted twice per year. High volume air sampling pumps will be used to draw air through a quartz prefilter and polyurethane foam (PUF) cartridges to collect 24-hour composite PCB air samples. The air sampling pumps will be set up and calibrated to collect approximately 250 liters per minute (lpm) resulting in a sample volume of approximately 360 cubic meters (m^3). Refer to Appendix B1 for the sampling protocol, Appendix B2 for copies of the EPA air sampling methods, Appendix B3 for a list of analytes and laboratory reporting limits, and Appendix B4 for copies of the laboratory's standard operating procedures (SOPs).

Indoor air samples will be collected in July/August (during summer vacation) and December (during the school's winter break).

- **July /August Sampling Event –** Air samples will be collected in July or early August during the school summer vacation with the goal of collecting the samples, performing laboratory analyses, evaluating the data, and providing the results to the City and school officials in a written report so that the results can be evaluated and explained in the context of the detailed risk evaluation. The goal of this sampling event is to assess indoor air conditions during the warmer weather, when the potential for volatilization is greatest. Also, at that time, the school will likely experience lower than normal air exchanges, since the doors and windows of the school building will be mostly closed and air handling equipment will be largely inactive or running in an efficiency mode. Collection of samples during this school vacation will allow the sampling to occur without interfering with normal school activities.

- **December Sampling Event –** The second sampling event will occur during the December school vacation. The goal of this sampling event is to obtain a potential "worst-case" air sample (per Section 5.0 of MassDEP 2002). During the winter vacation, the doors and windows will be mostly closed and the heating equipment will be in operation. Frozen ground surrounding the school may create conditions conducive to buildup of vapors and increase potential for vapor migration into the building. Collection of samples during the December school break will allow the sampling to occur without interfering with normal school activities.

2.2 Sample Locations

One indoor air sample will be collected from the ground floor of each of the three school building sections (Sections A, B, and C), as outlined below and illustrated in Figure 2.

- Section A – Classroom Section
- Section B – Auditorium/Cafeteria Area
- Section C – Gymnasium, Library, Public Meeting Room Section

Each location will be selected to be representative of portions of the school building normally occupied by students and teachers. In addition, one PCB sample will be collected using the same methods from immediately outside of the building near the flag pole to provide comparative ambient air results. Sample locations may be changed to facilitate evaluation and data collection. Samples will typically be collected from a height of four to six feet (the height of the normal breathing zone).

2.3 Analytical Parameters

During each sampling event, air samples will be collected, extracted, and analyzed for PCB homologues by EPA Method TO-4A in conjunction with EPA Method 680. The samples will be analyzed for homologue groups (mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and decachlorobiphenyl).

Prior to the sampling program, the air concentration associated with acceptable risk levels (e.g., an excess lifetime cancer risk of $1x10^{-6}$ and a hazard index of 0.2 or less under continuous exposure conditions) will be calculated for all analytes covered in the analytical method. Adjustments to sampling volumes will be made, if needed and if consistent with the method, to attain the needed reporting limit.

Refer to Appendix B2 for a copy of the EPA TO-4A method and Appendix B4 for copies of the laboratory's preparation and analysis SOPs.

2.4 Quality Assurance/Quality Control

At one random location during each sampling event, a co-located duplicate PCB sample will be collected to verify precision. The duplicates will be evaluated by measuring the relative percent difference (RPD) of detected analytes. The RPDs should be $\leq$ 40 when positive results for both samples are $\geq$ 5-times the reporting limit. If RPD is > 40, results may be qualified during validation.

One unused PUF cartridge and pre-filter will be transported from the laboratory to the field and back to the laboratory without being used; this sample will represent a trip blank. PCBs must not be detected in the trip blanks; otherwise data may be qualified during validation.

2.5 Action Levels

2.5.1 PCBs in Indoor Air

Two risk-based air concentrations (RBACs) for PCBs in the gaseous phase within the school have been calculated. Both RBACs are based on an occupational exposure within the school (8 hours per day, 250 days per year, for 25 years, since this represents the longest likely exposure in the school), and are based on non-carcinogenic health effects in addition to carcinogenic health effects of PCBs [using U.S. EPA's unit risk value of 0.1 $(mg/m^3)^{-1}$].

For both maximum acceptable levels (excess lifetime cancer risk = $1x10^{-5}$ and hazard index = 1) and action levels (excess lifetime cancer risk = $1x10^{-6}$ and hazard index = 0.2), the non-cancer endpoint results in the greater risk (or lower acceptable/action levels) and is the endpoint that is applied. The action limits are calculated from the "middle tier" slope factor developed by EPA and recommended for assessing inhalation exposure to volatilized PCBs. This middle tier slope factor was developed from oral test data on a variety of Aroclor mixtures (-1016, -1242, -1254, and -1260) and is to be applied to exposure estimates of total PCBs. These actions levels are, therefore, to be applied to total PCBs, the sum of all detected homologs.

- **Action Level –** The first RBAC is an Action Level set at a target non-cancer hazard index of 0.2. This Action Level is intended to be used as an initial indicator that PCB concentrations above background levels have been detected and that investigation of the source of PCBs is warranted (BETA, 2006).

- **Acceptable Long-Term Average Exposure Concentration –** The second RBAC is the Acceptable Long-Term Average Exposure Concentration (ALTAEC), which represents a long-term average concentration that corresponds to risk benchmarks established by MassDEP, assuming 25 years of daily work place exposure. Short-term exposures at this concentration do not represent an immediate threat to health. Since long-term, rather than short-term, exposure is of concern, the maximum acceptable air concentration could be exceeded over the short-term and still result in acceptable risk levels. Use of the ALTAEC value is considered conservative.

The calculations of the two values are included in Appendix C and are summarized below:

RBAC for PCBs in Air	RBAC ($\mu g/m^3$)
Action Level (hazard index = 0.2)	0.05
ALTAEC (hazard index = 1)	0.3

In September 2009, EPA published Public Health Levels (PHLs) for PCBs, which are calculated indoor air concentrations that maintain PCB exposures below a level that EPA does not believe will cause harm. PHLs were calculated for all ages of children from toddlers in day care to adolescents in high school as well as for adult school employees. For adult school employees and children 12 to 15 years old, representative of the middle school age range, EPA calculated a PHL of 0.45 $\mu g/m^3$. This PHL is also used as a RBAC for PCBs in the gaseous phase. In calculating the PHL, EPA considered average PCB exposures from both school environments.

For middle school age children, a 6.5-hour school day was assumed as well as a 180-day school year. As noted above, the KMS is monitored at a more conservative 0.3 $\mu g/m^3$ level for total PCBs.

2.5.1.1 Results Exceeding PCB Action Level

Any indoor air PCB result with a concentration exceeding the Action Level of 0.05 $\mu g/m^3$ will initiate a follow-up assessment. At a minimum, such assessment will consist of consultation with the analytical laboratory to confirm the validity of the result, a visual inspection of the sample location area, resampling of the subject location prior to the next round of regularly scheduled sampling and providing the results to the City and school officials in a supplemental written report so that the results can be evaluated and explained in the context of the risk evaluation. The follow up assessment will also include interviews with Site personnel to help identify Site activities or changes to the building that may have occurred during sample collection.

If the follow-up assessment determines that the previously detected elevated level(s) persists, the City will develop a supplemental assessment plan for submittal to EPA. If the follow up assessment determines that the previously detected elevated level(s) are either no longer present above 0.05 $\mu g/m^3$ or were anomalous or incorrect results, no further assessment will be required and the sampling program will return to its regular schedule. If warranted, additional monitoring and/or corrective actions will be developed and implemented on a case-by-case basis.

2.6 Reporting

Except as specified elsewhere in this LTMMIP, the results of the validated data will be provided to the City in a written report so that the results can be evaluated and explained in the context of the detailed risk evaluation. The report will present sampling methods, analytical methods (including description and justification for any changes to the above methods), analytical results, deviations from the standard sampling or analytical methods, and a discussion of the implications of the analytical results. Reports will be prepared, finalized, and distributed within 10 weeks of the sampling event. The reports will be provided by the consultant to EPA and the School Department, and will be posted on the City's website.

Upon review of the initial data reports received from the laboratory from each sampling event, if the City determines that there is a potential observation of an exceedance, the City will provide a copy of the draft (unvalidated) laboratory data to EPA for review via e-mail within two business days of receipt, assuming the normal two-week turn-around from the laboratory, and assuming no extenuating circumstances. If the data received show no potential or actual exceedance, then the City will report the results to EPA in the formal sampling report.

3.0 GROUNDWATER MONITORING

3.1 Groundwater Sampling Procedures

Groundwater monitoring will be performed as part of this LTMMIP for the KMS.

Groundwater samples will be collected from three (3) groundwater monitoring wells in the spring and fall. Samples will be collected using low stress (low flow) sampling protocols as per the EPA Region I "Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells," dated January 19, 2010, and SOP No. 001 (Groundwater Sampling), which are included in Appendices D1 and D2, respectively.

Prior to sampling, the monitoring instruments will be calibrated per the EPA Region I SOP for the "Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction potential [ORP], and turbidity)" dated January 19, 2010, and SOP No. 024 (Calibration of Field Instruments for Water Quality Parameters), which are included in Appendices E1 and E2 respectively. Water quality parameters (i.e., pH, temperature, specific conductance, dissolved oxygen, ORP, and turbidity) will be monitored during well purging. Per the EPA SOP, stabilization of these parameters is considered to be achieved when three consecutive readings are within the following limits:

Parameter	Stabilization Goal
Temperature	3%
pH	±0.1 standard unit
Dissolved Oxygen	10% [1]
Specific Conductance	3%
Oxidation/Reduction Potential	±10 millivolts
Turbidity	10% [2]

Notes:
[1] Stabilization goal for values greater than 0.5 milligrams per liter (mg/L). If three dissolved oxygen values are less than 0.5 mg/L the values will be considered stable
[2] Stabilization goal for values greater than 5 nephelometric turbidity units (NTU). If three turbidity values are less than 5 NTU the values will be considered stable.

3.2 Sample Locations

Three (3) monitoring wells will be sampled during implementation of the LTMMIP, including two groundwater monitoring wells installed along the western edge (MW-2 and MW-3) and one groundwater monitoring well installed along the northern edge (MW-1) of the KMS campus (see Figure 3). The monitoring wells were constructed of two-inch diameter polyvinyl chloride (PVC) riser pipe and screen. The monitoring wells were installed with 10 feet of screen intersecting the approximate average annual elevation of the water table and in accordance with the MassDEP's *Standard References for Monitoring Wells* (WSC # 310-91) (BETA, 2006).

3.3 Analytical Parameters

During each monitoring well sampling event, groundwater samples will be collected, prepared, and analyzed for the following parameters:

- PCB Aroclors by SW-846 Methods 3510C or 3520C/3665A/8082; and
- Dissolved Resource Conservation and Recovery Act (RCRA 8) metals by EPA SW-846 Methods 3005A/6020A/7470A.

Refer to Appendix B3 for a list of analytes. Laboratory SOPs for each method, including preparation and cleanup methods, are included in Appendix B4. All analyses will be performed per the Massachusetts Compendium of Analytical Methods (CAM).

Groundwater samples will be run for PCB Aroclors using routine SW-846 method 8082A (gas chromatography [GC] using an electron capture detector [ECD]) with a reporting limit of 0.05 ug/L. Analyses will be performed using dual columns. There is the potential for a sample to contain what appears to be PCBs but still be reported as non-detect for the PCB Aroclors due to weathering, degradation, etc. of the PCBs causing an unclear match or "fingerprint" of the PCB Aroclor. Therefore, chromatograms from samples which yield non-detect results in the PCB Aroclor analysis will be qualitatively evaluated for the presence of PCB peaks.

If the results for the groundwater samples are non-detect but the chromatograms from both columns show the presence of peaks that are not attributable to typical baseline noise, then the laboratory will include these chromatograms in the laboratory report and provide notification to the LSP of the possible presence of PCBs. If peaks are evident on both chromatograms that are not attributable to typical baseline noise, the laboratory will be authorized to analyze the associated sample extract from the Aroclor analysis using EPA method 680 (PCB homologue analysis using gas chromatography/mass spectrometry [GC/MS] with selective ion monitoring) in order to provide a definitive identification of the potential PCB peaks and an accurate quantitation of total PCBs, if these peaks are indeed determined to be PCBs. The laboratory will be instructed to retain extracts as a contingency for these potential additional analyses.

3.4 Quality Assurance/Quality Control

During each sampling event, a field duplicate sample will be collected at one groundwater monitoring well and submitted for laboratory analysis to verify precision of the dissolved metals and PCB results. Field duplicates will be evaluated in accordance with EPA Region I data validation criteria (USEPA, 2004). If outside that criteria, results may be qualified during validation. In addition, triple volume of each parameter will be collected during each groundwater sampling event for matrix spike/matrix spike duplicate analyses to verify the effect of the matrix on the accuracy and precision of the methods.

3.5 Action Levels

The results of each groundwater sample will be evaluated by comparison to the Massachusetts Contingency Plan (MCP; 310 CMR 40.0000) Method 1 GW-1, GW-2 and GW-3 standards, applicable to monitoring wells MW-2 and MW-3, and GW-3 standards applicable to monitoring well MW-1. A copy of MCP section 310 CMR 40.0974 containing the GW-1, GW-2 and GW-3 standards is included in Appendix F.

A groundwater result with an analyte concentration exceeding an applicable MCP Method 1 GW-1, GW-2 or GW-3 groundwater standard will be cause to initiate a follow-up assessment by the LSP. EPA will also be informed of the results. For the follow-up assessment for the discovery of a groundwater result in excess of MCP groundwater standards for PCBs, the condition will be evaluated by the LSP in consultation with EPA. At a minimum, such assessment will consist of consultation with the analytical laboratory to confirm the validity of the result, and potentially re-sampling of the subject location prior to the next round of regularly scheduled sampling and providing the results to the City and school officials in a supplemental written report so that the results can be evaluated and explained in context. If the follow-up assessment determines that the result is no longer present above applicable GW-1, GW-2 and GW-3 standards, or the result was anomalous or incorrect, no further assessment will be required and the sampling program will return to its regular schedule.

3.6 Reporting

Except as specified elsewhere in this LTMMIP, the results will be provided to the City in a letter so that the results can be evaluated and explained in context. Results will have undergone data validation (in the case of PCBs) and will have been subjected to a data usability evaluation (all parameters) prior to providing results to the City and school officials. The report will present sampling methods, analytical methods (including description and justification for any changes to the above methods), analytical results, any deviations from the standard sampling or analytical methods, and a discussion of the implications of the analytical results. The reports will be issued within 10 weeks of the sampling event. The reports will be provided by the City to EPA and MassDEP and will be posted on the City's website.

Upon review of the initial data reports received from the laboratory from each sampling event, if the City determines that there is a potential observation of an exceedance, the City will provide a copy of the draft (unvalidated) laboratory data to EPA for review via e-mail within two business days of receipt, assuming the normal two-week turn-around from the laboratory, and assuming no extenuating circumstances. If the data received show no potential or actual exceedance, then the City will report the results to EPA in the formal sampling report.

4.0 FOUNDATION VENT STACK AIR MONITORING

4.1 Air Sampling Procedures

Foundation vent stack air monitoring will be performed as a qualitative assessment two times per year at KMS for PCBs.

The passive venting system is comprised of six sub-slab vapor collection zones, each vented by two or four vent stacks located on the roof of the KMS building. The day prior to the collection of the vent stack air samples, all vent stacks will be sealed with temporary covers. The following day air samples will be collected from vent stacks through a sample port in the vent stack cover. During sampling, all other vent stack covers will be removed to allow for the inflow of air as the sample is collected. The purpose of this method will be to collect a sample representative of all air within the venting system.

Stack samples will be collected over a four-hour period that is concurrent with the indoor air sampling described in Section 2.0. Personal low volume air sampling pumps will be used to draw air through PUF cartridges to collect the 4-hour composite PCB samples. The air sampling pumps will be set up and calibrated to collect approximately 5 lpm resulting in a sample volume of about 1.2 m^3.

Refer to Appendix B1 for the air sampling protocols, Appendix B2 for a copy of the EPA air sampling method, Appendix B3 for a list of analytes and laboratory reporting limits, and Appendix B4 for copies of laboratory SOPs.

4.2 Sample Locations

An illustration of vent stack locations is provided in Figure 4. Sampling will be conducted at four vent stacks, two at Section A and two at either Sections B or C. Section A vent stacks VS-1 and VS-4 will be sampled during every sampling event in order to evaluate trending of PCB concentrations. A rotation of monitoring has been established to include two random vent stacks as well as the Section A vent stacks, VS-1 and VS-4. The example sampling sequence is set forth in the table below:

Sampling Event	Building A	Building B	Building C
A	VS-1, VS-4	VS-9, VS-16	--
B	VS-1, VS-4	VS-7	VS-14
C	VS-1, VS-4	VS-10	VS-12

The indoor air background (ambient) sample described in Section 2.2 will serve as the background (ambient) sample for the vent stack samples as well. Sampling locations are subject to change based on weather related conditions (e.g., ice on the pitched roof may cause an in-field case-specific adjustment for safety concerns).

4.3 Analytical Parameters

During each sampling event, vent stack air samples will be collected, extracted, and analyzed for PCB Homologues by EPA Method TO-l0A in conjunction with EPA Method 680. The samples will be analyzed for homologue groups (mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and decachlorobiphenyl).

Laboratory reporting limits will be set low enough to achieve the risk-based reporting limits for the indoor air sampling program, even though there will be no risk evaluation of the data. Consistent with the indoor air sampling program for KMS, the air concentrations associated with acceptable risk levels (e.g., an excess lifetime cancer risk of $1x10^{-6}$ and a hazard index of 0.2 or less under continuous exposure conditions) will be calculated for all analytes covered in the analytical method. Adjustments to sampling volumes will be made, if needed and if consistent with the method, to attain the needed reporting limit.

Refer to Appendix B2 for a copy of the EPA TO-l0A method and Appendix B4 for copies of the laboratory's preparation and analysis SOPs.

4.4 Quality Assurance/Quality Control

At one vent stack location during each sampling event, a co-located duplicate PCB sample will be collected and analyzed to verify precision. The duplicates will be evaluated by measuring the RPD of detected analytes. The RPDs should be $\leq$ 40 when positive results for both samples are $\geq$ 5-times the reporting limit. If RPD is > 40, results may be qualified during validation.

One unused PUF cartridge will be transported from the laboratory to the field and back to the laboratory without being used; this sample will represent a trip blank. PCBs must not be detected in the trip blanks; otherwise data may be qualified during validation.

4.5 Trend Analysis

PCB concentrations will not be quantitatively compared to the two RBACs calculated for PCBs that are applied to indoor air within the school. Laboratory results will be examined qualitatively to determine whether the system is functioning as designed through trend analysis. Recently collected vent stack air sampling results will be graphically compared to vent stack air sampling results collected during previous sampling rounds. This comparison will demonstrate the continued functionality of the system and obvious trends toward reduced off-gassing of subsurface PCBs.

4.6 Reporting

Except as specified elsewhere in this LTMMIP, the results will be provided to the City in a letter so that the results can be evaluated and explained in context. Results will have undergone data validation and will have been subjected to a data usability evaluation (all parameters) prior to providing results to the City and school officials. The report will present sampling methods, analytical methods (including description and justification for any changes to the above

methods), analytical results, any deviations from the standard sampling or analytical methods, and a discussion of the implications of the analytical results. The reports will be issued within 10 weeks of the sampling event. The reports will be provided by the City to EPA and MassDEP and will be posted on the City's website.

Upon review of the initial data reports received from the laboratory from each sampling event, if the City determines that there is a potential observation of an exceedance, the City will provide a copy of the draft (unvalidated) laboratory data to EPA for review via e-mail within two business days of receipt, assuming the normal two-week turn-around from the laboratory, and assuming no extenuating circumstances. If the data received show no potential or actual exceedance, then the City will report the results to EPA in the formal sampling report.

5.0 WETLAND SEDIMENT INSPECTION AND MONITORING

5.1 Wetland Sediment Inspection

An inspection of the wetlands to the west of the KMS building will be performed during May of each year. The purpose of the inspection is to visually observe the wetlands and vicinity for unacceptable conditions including indications of excessive sedimentation occurring within the wetlands. Indications of excessive sedimentation or conditions that could lead to future excessive sedimentation include: dumping of debris, exposed side slopes, erosion from spring rains, stressed or dead vegetation, etc.

The inspection will consist of a walking traverse of the entire length of the top and the toe of the slope leading down from the school facility to the abutting wetland. Any area(s) of the wetland or the slope leading down to the wetland that are determined during the inspection to be unacceptable will be noted on an inspection form and photographically documented. Upon completion of the cleanup or repair of the unacceptable area, a follow up confirmatory inspection will be made and documented on the inspection form with accompanying photographs of the area. Refer to Appendix G for a copy of the Wetland Sediment Inspection Form.

Examples of general guidelines for conditions that the inspector will record and photograph as unacceptable include:

- Dumping of debris
- Stained soil
- Erosion of soil on slope leading down to wetland
- Animal burrows in slope
- Visible accumulation of mineral sediment in wetland
- Subsidence of greater than two inches or slumping of soil on slope leading down to wetland
- Dead vegetation, if such vegetation is required for erosion control and/or
- Evidence of unauthorized excavation.

In addition to the list above, the inspector will use good judgment in the evaluation of the acceptability of the condition of the slope and the wetland, and the need to identify these or other problem conditions requiring additional cleanup, maintenance, or repair.

5.2 Sediment Sampling Procedures

Sediment sampling will be performed as part of this LTMMIP for the KMS. The sediment sampling will be conducted in conformance with current industry standards and engineering practices, and per SOP No. 003 (Surface Water and Sediment Sampling) provided in Appendix H.

Site wetland sediment monitoring will be conducted on an annual basis. Sediment samples will be connected from a depth of 0-6 inches with a dredge, coring device, or other appropriate manual sediment sampling implement.

5.3 Sample Locations

For each sampling event, four sediment samples will be collected from the portion of the wetland that abuts the slope leading down from the school. The sample locations will be determined randomly based on the wetland flag locations (see Figure 5). Four sampling locations will be randomly selected each year (using a random number generator or equivalent method to select sampling coordinates). No more than two samples will be chosen from a given section (north side vs. south side) without prior approval from the EPA. The sediment sample will be collected from the wetland within 10 feet of the randomly selected point. Additional samples may be collected at the discretion of the City.

5.4 Analytical Parameters

At each sampling event, sediment samples will be collected, extracted, and analyzed for PCB Aroclors by SW-846 Methods 3540C or 3541/3665A/8082.

Laboratory SOPs for this method, including extraction and cleanup methods, are included in Appendix B4. Refer to Appendix B3 for a list of analytes and reporting limits. All analyses must be performed consistent with the Massachusetts CAM.

Changes based on technical justification may be made in the specific sample collection intervals and/or substitutions may be made by equal or improved sampling and/or analytical methods upon review and approval of the LSP-of-Record. Any such changes and its/their justification will be described in the subsequent summary report.

5.5 Quality Assurance/Quality Control

At one sediment sampling location during each sampling event, a duplicate PCB sample will be collected and analyzed to verify precision. Field duplicates will be evaluated in accordance with EPA Region I data validation criteria (USEPA, 2004). If outside that criteria, results may be qualified during validation.

5.6 Action Levels

5.6.1 PCBs in Sediment

PCB results will be compared to the 1.0 mg/kg cleanup level described in the “Wetland Risk-Based Cleanup Request” dated June 17, 2005, prepared by BETA and previously submitted to the EPA (BETA, 2005b).

5.6.1.1 PCB Results Exceeding Action Levels

Any sediment result with an analyte concentration exceeding 1.0 mg/kg will be cause to initiate a follow-up assessment. At a minimum, such assessment will consist of:

- Consultation with the analytical laboratory to confirm the validity of the result;
- Collection of a follow up sediment sample from as close as possible to the location of the sample containing the greater than 1.0 mg/kg result; and
- Collection of a minimum of four samples surrounding the greater than 1.0 mg/kg PCB sample to provide initial information on the extent of the elevated PCB concentrations.

If the follow-up assessment confirms the previously detected elevated PCB concentration and/or that concentrations in sediment greater than 1.0 mg/kg PCB are present in any of the four second round samples, the City will develop a supplemental assessment plan for submittal to EPA (and MassDEP if an MCP reporting obligation is triggered). If the follow-up assessment finds that laboratory analysis of the second round of sediment samples does not detect concentrations greater than 1.0 mg/Kg, or that the initial result(s) were anomalous or incorrect, no further assessment will be required and the sampling program will return to its regular schedule. Corrective actions will be evaluated on a case-by-case basis.

5.7 Reporting

A copy of each completed Wetland Inspection Form will be submitted to the EPA by the City within one month of each inspection.

Upon review of the laboratory data reports from each sampling event, if the City determines that the PCB in sediment action level of 1.0 mg/kg was potentially exceeded, the City will contact EPA and MassDEP within 24 hours.

Except as specified elsewhere in this LTMMIP, the results of the validated data will be provided to the City and school officials in a written report so that the results can be evaluated and explained in context. The report will present sampling methods, analytical methods (including description and justification for any changes to the above methods), analytical results, any deviations from the standard sampling or analytical methods, and a discussion of the implications of the analytical results. The reports will be issued within 10 weeks of the sampling event. The reports will be provided by the City to EPA and MassDEP and will be posted on the City's website.

Upon review of the initial data reports received from the laboratory from each sampling event, if the City determines that there is a potential observation of an exceedance, the City will provide a copy of the draft (unvalidated) laboratory data to EPA for review via e-mail within two business days of receipt, assuming the normal two-week turn-around from the laboratory, and assuming no extenuating circumstances. If the data received show no potential or actual exceedance, then the City will report the results to EPA in the formal sampling report.

6.0 LABORATORY QC & DATA USABILITY

6.1 Laboratory Quality Control Requirements

Along with the field quality control requirements, the laboratories being utilized for this project maintain quality control/quality assurance programs.

Precision is a measure of the reproducibility of the results. This quality control indicator is evaluated by examining the variability of results from field duplicates and laboratory duplicates. Accuracy is a measure of the closeness of the analytical result to the true concentration. The percent recovery of spiked samples reflects whether the analytical result has a high or low bias. Accuracy is measured using percent recoveries. Precision is measured using the RPD.

Laboratory precision and accuracy requirements for groundwater and sediment are summarized in the MassDEP CAM protocols for PCB Aroclors by SW-846 8082A (WSC-CAM-VA) and dissolved metals by SW-846 6020/7470A (WSC-CAM-III B and D). Laboratory precision and accuracy requirements for the analysis of PCB homologues in air samples using EPA Methods TO-4A and TO-10A are summarized in Table 1.

Table 1: Laboratory Quality Control Requirements for PCB Homologue Analyses Using EPA Methods TO-4A and TO-10A

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Extraction Blank	One/20 samples/matrix/day of extraction	PCB Homologues reporting limits	Reanalyze blank, Depending on concentration, results may be qualified.
Surrogates[1]	All samples, standards and associated QC	TCMX: 40-140% DCB: 40-140%	Reanalyze if both surrogates outside limits or one >10%, and/or qualify data.
Laboratory Control Sample[1] (LCS)	One/20 samples/matrix/day of extraction	Monochlorobiphenyl 29-79% Dichlorobiphenyl 31-83% Trichlorobiphenyl 34-87% Tetrachlorobiphenyl 35-87% Pentachlorobiphenyl 37-92% Hexachlorobiphenyl 41-95% Heptachlorobiphenyl 42-98% Octachlorobiphenyl 43-102% Decachlorobiphenyl 46-102%	Determine cause of problem, reanalyze, and/or qualify data.
LCS Duplicate[1]	One/20 samples/matrix/day of extraction	Same as LCS; RPD $\leq$ 40	Determine cause of problem, reanalyze, and/or qualify data

[1]Acceptance criteria (control limits) are periodically updated by the laboratory. The latest control limits will be utilized at the time of sample analysis.

6.2 Laboratory Data Management and Documentation

All laboratory results will be delivered both electronically and in hard copy. Following the receipt of all laboratory reports, the results will be tabulated in a spreadsheet format using the electronically delivered data. The electronic deliverable prevents the introduction of errors

during data tabulation. The results of all data produced by the laboratory are automatically transferred to an electronic file; no manual data entry of the results is required, thereby eliminating the introduction of errors. All raw data including chromatograms and copies of internal chains of custody will be maintained by the laboratory.

All field data will be recorded in the form of field notes to maintain a permanent record of all field activities per SOP No. 021 (Field Activity Documentation). Information will include date, weather, individuals on site, field screening results, sampling observations and techniques, and any additional relevant information. All field notes and photographs will be maintained and stored in dedicated project files.

6.3 Assessment and Response Actions

Throughout the course of the project, the following procedures will be implemented to detect and correct any problems that may occur:

- Project management meetings;
- Peer reviews of all reports, documents, and correspondence;
- Periodic field meetings during *all* site investigations; and
- Ongoing communication between the LSP-of-record, regulatory agencies, the City of New Bedford, and all Subcontractors.

As warranted, problems that occur will be communicated through the issuance of project memoranda and e-mail correspondence. All correspondence will detail the problem encountered and any corrective actions taken. Correspondence will be maintained in dedicated project files.

All field sampling will be overseen by a LSP to ensure that the LTMMIP and sampling SOPs are followed. Any sampling problems will be immediately communicated to the LSP and documented in the field notes.

6.4 Data Validation and Usability

<u>Data Validation</u>

Tier II data validation will be performed on all PCB data in accordance with EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses, revised December 1996 and February 2004 (USEPA, 2004).

The following items are included in a Tier II data validation review, as applicable to the air, sediment, and groundwater matrices.

- Chain-of-Custody
- Case narrative
- Presence of field and sample identifications (IDs)
- Holding times
- Preservation and cooler receipt

- Initial and continuing calibrations
- Surrogate recoveries
- Laboratory blanks
- Trip blanks
- Matrix spike/matrix spike duplicates
- Laboratory Control Samples (LCS)
- Field duplicates
- Reporting limits
- Dual column RPDs

Data review will also be performed by the laboratory analyst prior to reporting results, in accordance with the laboratories, documented QA protocols. The laboratory will review data against pre-existing criteria before proceeding with subsequent analytical processes and/or data. The LSP-of-Record will review reported results and ensure that any required corrective action is taken. Criteria used for accepting or rejecting data are based on laboratory quality control and specific EPA methodology standard operating procedures, as well as Appendix IV of the MassDEP Policy # WSC-07-350, MCP Representativeness Evaluations and Data Usability Assessments (MassDEP, 2007).

Data Usability

Deviations from any SOPs will be reviewed to identify potential limitations in the data. If a substantial deviation to SOP is identified, consideration may be given to either re-sampling or disregarding the sample result.

A review of sample representativeness from field notes will be performed. A non-representative or non-homogeneous sample increases the potential for false negatives or false positives. Adherence to applicable field sample collection protocols, field QC measures, and transport and storage of sample to the laboratory will decrease the possibility of having a sample result that is not representative of true site conditions.

Poor data quality or lost samples will decrease confidence in the data set. To ensure completeness, adherence to all field protocols, sample tracking procedures and laboratory procedures shall be maintained. Completeness will be described in terms of the total number of samples that meet data validation requirements compared to the total number of samples that do not satisfy such requirements.

All data will undergo a usability assessment. During the data usability evaluation, the effect of any field or laboratory QC nonconformance on the achievement of the project objectives (i.e., meeting the regulatory cleanup criteria) will be assessed. The QA Officer (or designee) will perform the data usability assessment. In general, the following procedure will be used:

- All analytical results will be tabulated in comparison to the applicable regulatory criteria and all exceedance will be highlighted. This table will be used when assessing the effects of the QC nonconformance, as discussed below.

- A written report of the data usability assessment will be generated. This report will have one section per matrix (i.e., soil, sediment, groundwater, surface water). For each matrix, there will be four subsections, low-biased data, high-biased data, data with potential uncertainty, and sensitivity of the data.

- The subsection on low-biased data will discuss any nonconformances that may cause the data to be biased low. Common causes of low biased data are summarized below:
  - Holding time exceedances
  - Low surrogate recoveries
  - Low recoveries in LCS/LCS Duplicates
  - Low recoveries in MS/MSDs
  - Elevated cooler temperatures
  - Improper field preservation

- The subsection on high-biased data will discuss any nonconformances that may cause the data to be biased high. Common causes of high biased data are summarized below:
  - Blank contamination
  - High surrogate recoveries
  - High recoveries in LCS/LCS Duplicates
  - High recoveries in MS/MSDs
  - High turbidity in low-flow groundwater samples

- The subsection on data with potential uncertainty will discuss any nonconformances that may cause the data to be uncertain. Common causes of data with potential uncertainty are summarized below:
  - Field duplicate variability
  - LCS/LCS duplicate variability
  - MS/MSD variability
  - High moisture content

- The subsection on sensitivity will evaluate whether there are any nondetect results with reporting limits above the regulatory criteria either due to dilutions or analytical limitations. The effect of these elevated reporting limits on the decision-making process will be assessed and will be dependent on the amount of data available for the analyte of interest with acceptable reporting limits, whether the analyte is a constituent of concern based on site history, etc.

- Within each subsection, the effect of the low bias, high bias, or uncertainty on the achievement of project objectives is assessed. This will be dependent on the specific analyte affected. In general, the following guidelines are used:

  - If the data are biased low and the associated result is slightly below the regulatory criteria, the data usability assessment would alert the data user to the potential limitation of this result.
  - If the data are biased high and the associated result is just slightly above the regulatory criteria, the data usability assessment would alert the data user to the potential limitation of this result.
  - If the data exhibit potential uncertainty and the associated result is either slightly above or below the regulatory criteria, the data usability assessment would alert the data user to the potential limitation of this result.
  - In all of the above cases, the data user may have to consider potential resampling, analytical method modifications, etc. depending on whether the analyte is a constituent of concern, how much other data exists on this analyte in the specific matrix, etc.
  - In addition to the above guidelines, if the data exhibit low bias, high bias, or potential uncertainty and the results are significantly above or below regulatory criteria, the data usability assessment notes that this does not affect the usability of the data or the decision-making process in achieving the project objectives.

- Within each subsection, data which are definitively not usable (i.e., rejected) will be discussed. In general, causes for rejecting data are provided in Appendix IV of MassDEP 2007 or the EPA Region 1 data validation guidelines (USEPA, 2004).

The data user (or Project Manager) will use the results of the data usability evaluation in conjunction with tabulated data and site figures to determine if there has been any effect on the conceptual site model and whether the overall project objectives have been met. The Recommendations section of the final project report would indicate any potential re-sampling needed as a result of this evaluation.

7.0 LONG-TERM CAP MONITORING PLAN

7.1 Background

The fate and transport characteristics of the site impacts have been evaluated and the following apply per BETA, 2006:

- All site impacts are relatively insoluble in water;
- All site impacts are either non-volatile or only minimally volatile; and
- Direct contact, adsorption and/or ingestion are the only significant pathways for human exposure.

Therefore, by installing exposure control barriers and eliminating direct exposure to impacted media, the risk to human health and the environment has been substantially eliminated.

The exposure control barriers must be maintained in accordance with the following monitoring plan, to keep the impacted fill layer isolated from human and environmental receptors:

- The KMS has been constructed on steel H-piles, with the base of the concrete floor of the school at or near grade. Within the building footprint, a minimum of one foot of clean, imported sand and gravel has been placed on top of the impacted fill. The ground floor of the school consists of a minimum of six inches of poured-in-place reinforced concrete. Prior to placement of the concrete floor, an impermeable elastomeric gas membrane (Liquid Boot®) was applied beneath the floor, as an added precaution to prevent migration of any volatile gases into the building. In addition, a passive vent system has been installed to vent any accumulated gases that may accumulate beneath the Liquid Boot® membrane to the atmosphere.

- Portions of exterior areas of the school facility are landscaped. All landscaped areas were constructed by removing Site soil to a minimum depth of three feet below final grade, placing a geotextile fabric to demarcate the limits of excavation and to separate residual PCB-impacted soil from clean fill, backfilling with a 6- to 12-inch base of imported clean crushed stone, placing an orange polyethylene mesh warning barrier, followed by 2 to 2 ½ feet of imported clean sandy gravel and topsoil to achieve finished grade.

- The remaining exterior Site areas are either asphalt or concrete paved. Asphalt has been placed at a minimum thickness of three inches on top of at least two feet of imported crushed stone sub-base underlain by a geotextile fabric. The concrete sidewalks have a minimum thickness of six inches also placed on top of two feet of imported clean crushed sub-base, gravel and geotextile fabric.

In combination, these three barriers (building floor, landscaping, and exterior asphalt and concrete pavement) represent the cap for the school facility, the purpose of which is to prevent human exposure in accordance with the requirements of 40 CFR 761.61 (a)(7).

7.2 Cap Maintenance

The City of New Bedford will be responsible for the performance of the cap maintenance and inspection activities as described herein. In the event that activities prohibited in this section must be undertaken, an LSP must be involved to direct and oversee the activities. The following activities are required to maintain the integrity of the cap.

- **Asphalt Pavement, Concrete Pavement, and Sidewalks**. Maintain all asphalt pavement, concrete pavement, and sidewalks such that the integrity of each is not compromised. This will include:
  - If replacement of asphalt surfaces, concrete pavement and/or sidewalks is required, it will be limited to the material to be replaced such that the underlying soil is not significantly disturbed (soil six inches deep or less below the bottom of surface being removed) and the surface material is repaired or replaced with a comparable barrier within 72 hours;
  - Prohibition against any excavation to a depth greater than two feet beneath paved areas;
  - Prohibition against any activities that result, or could result, in compromising the structural integrity of asphalt pavement, concrete pavement, or sidewalks; and
  - Any damage to pavement, whatever the cause, must be repaired to substantially restore the cap to its original design condition. Damages may consist of identifiable conditions listed in Section 7.3 (i.e., cracks greater than ¼-inch wide, etc.), or other deteriorated conditions noted to be unacceptable by the inspector. Repairs must be fully completed, if not scheduled for completion, prior to the next scheduled cap inspection.

- **Interior Building Floors**. Maintain all interior building floors such that the integrity of each is not compromised. This will include:
  - Prohibition against removal of building floor slab that would expose underlying impacted soil (Note that a minimum of one foot of clean compacted granular fill directly underlies the concrete slab);
  - Prohibition against any penetration or breaching of the vapor barrier beneath the building floor;
  - Prohibition against any excavation beneath building floors;
  - Prohibition against any activities that result, or could result, in compromising the structural integrity of building floors; and
  - Any damage to interior building floors, whatever the cause, must be repaired to substantially restore the cap to its original design condition. Damages may consist of identifiable conditions listed in Section 7.3 (i.e., cracks greater than ¼-inch wide, etc.), or other deteriorated conditions noted to be unacceptable by the

inspector. Repairs must be fully completed, if not scheduled for completion, prior to the next scheduled cap inspection.

- **Landscaped Areas**. Maintain all landscaped areas such that exposure to underlying impacted fill is prevented. This will include:
  - If vegetation is to be planted or removed, excavation for planting and/or removal of existing root systems shall not extend beyond one foot below existing grade;
  - Prohibition against any excavation to a depth greater than two feet in landscaped areas;
  - Prohibition against any activities that result, or could result, in the erosion of soil in any unpaved area;
  - Prohibition against planting any deep-rooted vegetation (i.e., with roots typically extending greater than two feet below grade); and
  - Prohibition against any permanent removal of overburden soil that reduces the depth of clean fill over the residual PCB-impacted soil to less than three feet.
- **Best Management Practices**. Particular attention is drawn to the following best management practices:
  - Performance of frequent and short watering of landscape vegetation to encourage shallow root growth is recommended.
  - Any deep-rooted species identified in the landscaped area during routine inspections shall be immediately removed.
  - Regular mowing of lawn areas and mowing the cap slope a minimum of two times per year to discourage deep rooted vegetation and minimize the establishment of habitat for burrowing animals.

7.3 Cap Inspections

The City of New Bedford will perform regular inspections and associated record keeping activities to confirm that the cap is being properly maintained to prevent exposure to the impacted fill beneath. Each year, the cap shall be inspected two times: one inspection in the spring and one inspection in late summer or early fall.

The EPA has requested that any person performing this inspection be pre-approved by the agency. This will be performed by submitting the City inspector's name, title, and qualifications to the agency prior to the inspection.

The inspection will consist of a walking traverse of the entire Site such that visual observation of the entire cap (concrete and asphalt pavement, building floors, and landscaping) is made. The inspection will be made by a competent person designated by the City of New Bedford. The City will provide the name, title, and phone number of this person to EPA. The City will also inform EPA when a new person is designated. Any area of the pavement, building floors, or

landscaping that are determined during the inspection to be unacceptable will be noted on an inspection form and photographically documented. Upon completion of the repair of the unacceptable area, a follow-up confirmatory inspection of the repaired area will be made and documented on the inspection form with accompanying photographs of the repaired area. Refer to Appendix G for a copy of the Cap Inspection Form.

Examples of general guidelines for conditions that the inspector will record and photograph as unacceptable include:

- Any breach or other significant damage or deterioration in pavement or building floors other than minor cracking typically associated with horizontal concrete surfaces;
- Cracks in concrete or asphalt paving greater than ¼-inch width;
- Localized subsidence or heaving of asphalt surface(s) with a vertical displacement of greater than one inch;
- Gap between edge of concrete or asphalt and building wall or other abutting stationary feature of greater than ½-inch;
- Spalling or other deterioration of concrete resulting in a loss of greater than ½-inch thickness;
- Any other general deterioration of or damage to asphalt or concrete pavement that is allowing, or if unrepaired could allow, contact with soil below;
- Erosion in landscaped area resulting in the loss of more than one inch of soil;
- Dead vegetation, if such vegetation is required for erosion control; and/or
- Evidence of unauthorized excavation.

In addition to the list above, the inspector will use good judgment in the evaluation of the acceptability of the condition of the cap, and the need to identify these or other problem conditions requiring additional maintenance or repair.

7.4 Deed Restriction

The above maintenance requirements have been previously recorded in a Notice of Activity and Use Limitation (AUL) on the property deed(s) at the Bristol County Registry of Deeds. The AUL was filed in accordance with the requirements of the MCP 310 CMR 40.0000 and within 60 days of the EPA's acceptance of the AUL. The AUL will be maintained, and the Cap Monitoring Plan will continue to be implemented, in perpetuity, or until such time as additional response actions allow the modification or removal of the AUL and Cap Monitoring Plan in accordance with all applicable laws and regulations in force at the time; or until such time that the EPA and the MassDEP determine, in writing, that such activities are no longer necessary.

7.5 Soil Management Plan

A Soil Management Plan must be prepared by an LSP and implemented prior to the commencement of any activity which is likely to disturb impacted soil, the top of which is located at one and a half to four feet below surface grade within the AUL area (BETA, 2006). The Soil Management Plan should describe appropriate soil excavation, handling, storage, transport, and disposal procedures and include a description of the engineering controls and air monitoring necessary to ensure that workers and receptors in the vicinity are not affected by fugitive dust or particles. On-Site workers must be informed of the requirements of the soil management plan, and the Plan must be available on-Site throughout the course of the project.

7.6 Health and Safety Plan

A Health and Safety Plan must be prepared by a Certified Industrial Hygienist (CIH) or other qualified individual sufficiently trained in worker health and safety requirements and implemented prior to the commencement of any activity which is likely to disturb impacted soil, the top of which is located at one and a half to four feet below surface grade within the AUL area. The Health and Safety Plan should specify the type of personal protection (i.e., clothing, respirators), engineering controls, and environmental monitoring (if any) necessary to prevent worker exposures to impacted soil through dermal contact, ingestion, and/or inhalation. Workers must be informed of the requirements of the Health and Safety Plan, and the plan must be available on-Site throughout the course of the project.

7.7 Record Keeping

The City of New Bedford will maintain all records pertaining to cap maintenance and inspection for a minimum of twenty years from the date of generation of each document.

7.8 Reporting

The City of New Bedford will communicate the results of the semi-annual cap inspections by submitting copies of each completed Cap Inspection Form to EPA within one month of each inspection. If any necessary repairs and the subsequent follow-up inspection are completed such that the initial Cap Inspection Form and the follow up Cap Inspection Form documenting the repair are completed within one-month, both forms will be submitted concurrently. If the repair and subsequent follow-up inspection are not completed within one month, the initial Cap Inspection Form describing the unacceptable condition (including photographs) will be submitted to EPA along with a cover letter providing the schedule for completion of the repair The follow up Cap Inspection Form will subsequently be submitted to EPA no later than one-month after completion of the repair.

8.0 COMMUNICATION PLAN

All activities described herein will result in written documentation submitted to EPA and MassDEP. The submittals received by these government agencies will be considered public information, and as such will be available for review by all interested parties. To increase the ease of access to site maintenance and monitoring information, all written submittals will be concurrently posted on the City of New Bedford's Parker Street Waste Site website. The City will also evaluate other methods for providing public notice and communication of LTMMIP activities and results to the public.

9.0 TRAINING

The City of New Bedford will provide worker training, the purpose of which will be to educate appropriate School employees (e.g., facilities, maintenance, landscaping personnel, etc.) on the background, contents, and requirements of the AUL and the LTMMIP. The specific topics to be covered will include

- The location of impacted soil at the Site;
- The purpose of the AUL;
- What work is allowed under the AUL;
- What work is not allowed under the AUL;
- When an LSP should be contacted;
- Conducting the inspections required under the LTMMIP; and
- Summary of air, groundwater, vent stack, and annual wetland sediment sampling.

Each employee will receive a Certification of Training upon completion of the training session. The School Department will provide each existing employee and all new employees with this worker training within 30 days of the employee beginning work at the KMS. All applicable employees will subsequently receive Refresher Training every even numbered year on or near the anniversary of the initial training. An update memo discussing any changes to the LTMMIP or work practices around KMS will be issued for the odd numbered year. Each employee will sign off that they have read and understand the update memo to document that they have read this memo. The City will maintain a copy of all training records, including training sessions, employee names, etc., for a minimum of five years from the time of generation.

10.0 AMENDMENTS TO LTMMIP

In consideration of analytical results compiled under this LTMMIP, modifications to future monitoring requirements may be proposed to the EPA by an LSP retained by the City. No modifications to the LTMMIP will be implemented until written approval of such modifications is received by the City and from the EPA.

11.0 REFERENCES

BETA, 2005a. *Risk-Based Cleanup Request – Revision 2, School Site at McCoy Field, New Bedford, Massachusetts, RTN 4-15685*. Prepared for: City of New Bedford. Prepared by: BETA Group Incorporated. May 18, 2005

BETA, 2005b. *Wetlands Risk-Based Cleanup Request, Wetlands Site at McCoy Field, New Bedford, Massachusetts, RTN 4-15685*. Prepared for: City of New Bedford. Prepared by: BETA Group Incorporated. June 17, 2005.

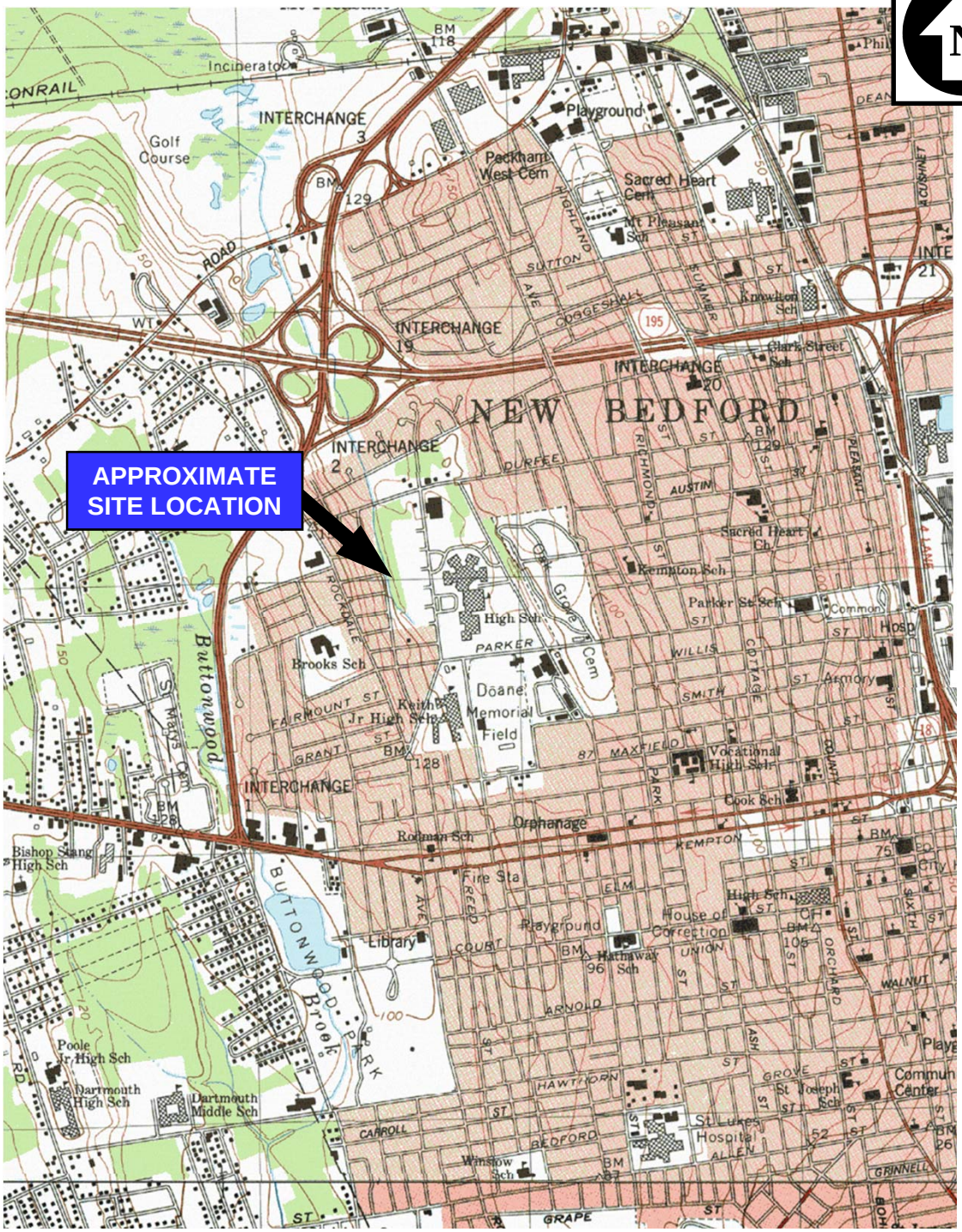
BETA, 2006. *Long-Term Monitoring and Maintenance and Implementation Plan. New Keith Middle School, 225 Hathaway Boulevard, New Bedford, MA 02740. Prepared for: City of New Bedford*. Prepared by: BETA Group, Incorporated, Revision 4.0, October 20, 2006.

MassDEP, 2007. MCP Representativeness Evaluations and Data Usability Assessments. MassDEP Policy # WSC-07-350. September 19, 2007.

United States Environmental Protection Agency (USEPA), 2004 EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses, Revised December 1996 and February 2004.

United States Environmental Protection Agency (USEPA), 2009. Public Health Levels for PCBs in Indoor School Air. http://www.epa.gov/pcbsincaulk/ September 2009.

FIGURES



BASE MAP IS A PORTION OF THE FOLLOWING 7.5' X 15' USGS TOPOGRAPHIC QUADRANGLES: NEW BEDFORD NORTH, MA, 1979; NEW BEDFORD SOUTH, MA 1977

0 1000 2000 3000

scale in feet

QUADRANGLE LOCATION

T:\E_CAD\115058\TOPO KEITH MIDDLE SCHOOL.ppt

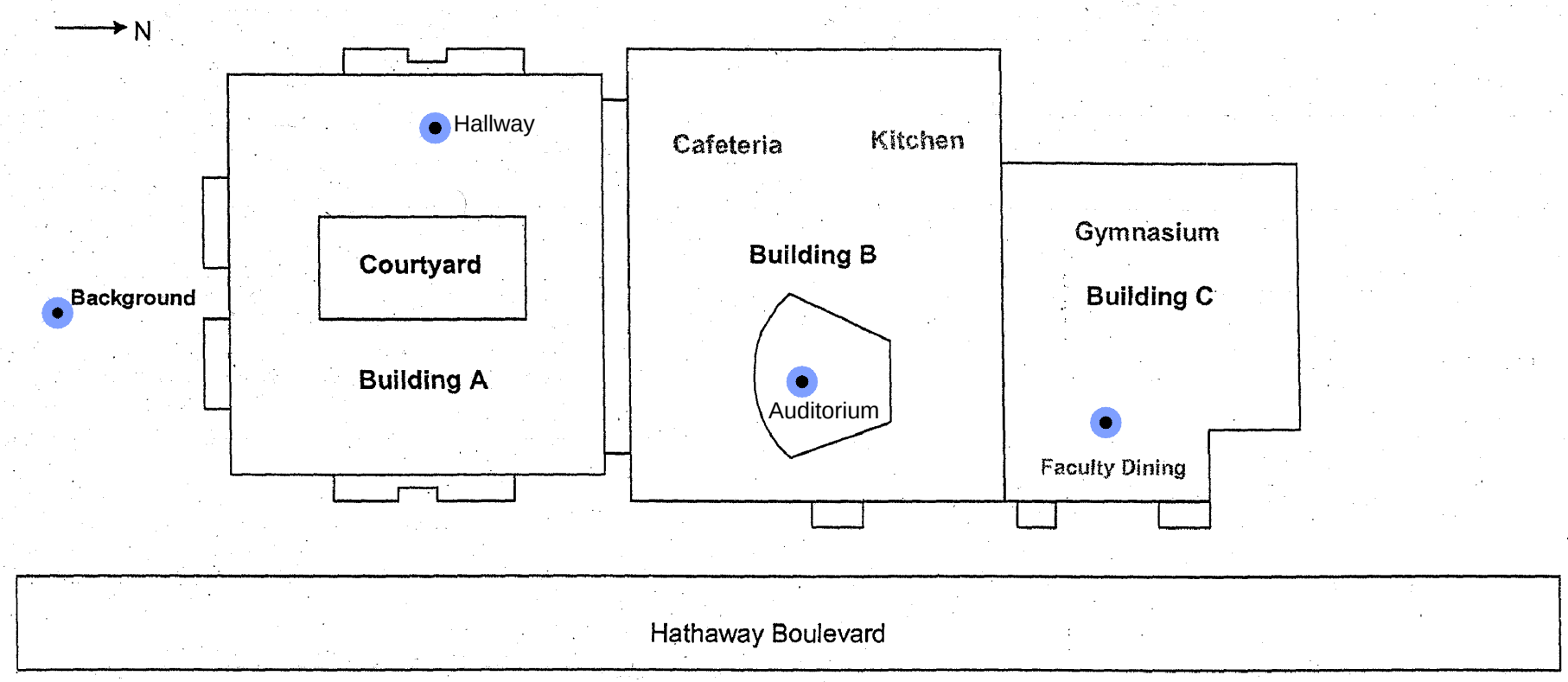
KEITH MIDDLE SCHOOL
NEW BEDFORD, MASSACHUSETTS

SITE LOCATION MAP

TRC
Wannalancit Mills
650 Suffolk Street
Lowell, MA 01854
978-970-5600

Drawn: HWB	SCALE: AS SHOWN	FIGURE 1
Checked: DS	Date: MARCH 2011	

Keith Middle School
Indoor Air Sampling Locations



● = Indoor Air Sampling Point

● = Sample Locations

KEITH MIDDLE SCHOOL
NEW BEDFORD, MASSACHUSETTS

INDOOR AIR SAMPLING LOCATIONS

TRC
Wannalancit Mills
650 Suffolk Street
Lowell, MA 01854
(978) 970-5600

FIGURE
2

DRAWN BY: ---
CHECKED BY: DMS
DATE:
MAY 2008

FILE: T:\E_CAD\115058\ARCHIVE PRE 2009\indoorventsys1.dwg

LEGEND:

82.5 GROUNDWATER CONTOUR, DASHED WHERE INFERRED

MW-5 (82.32) MONITORING WELL (GROUNDWATER ELEVATION JANUARY 20,2011)

PROPERTY LINE

NOTE:
ALL MONITORING WELL LOCATIONS ARE PRELIMINARY AND SUBJECT TO CHANGE AND ARE BASED ON SITE CONDITIONS AND BEST PROFESSIONAL JUDGEMENT.

APPROXIMATE GRAPHIC SCALE
0' 25' 50' 100'

KEITH MIDDLE SCHOOL

NEW BEDFORD, MASSACHUSETTS

KEITH MIDDLE SCHOOL
GROUNDWATER MONITORING WELL LOCATIONS

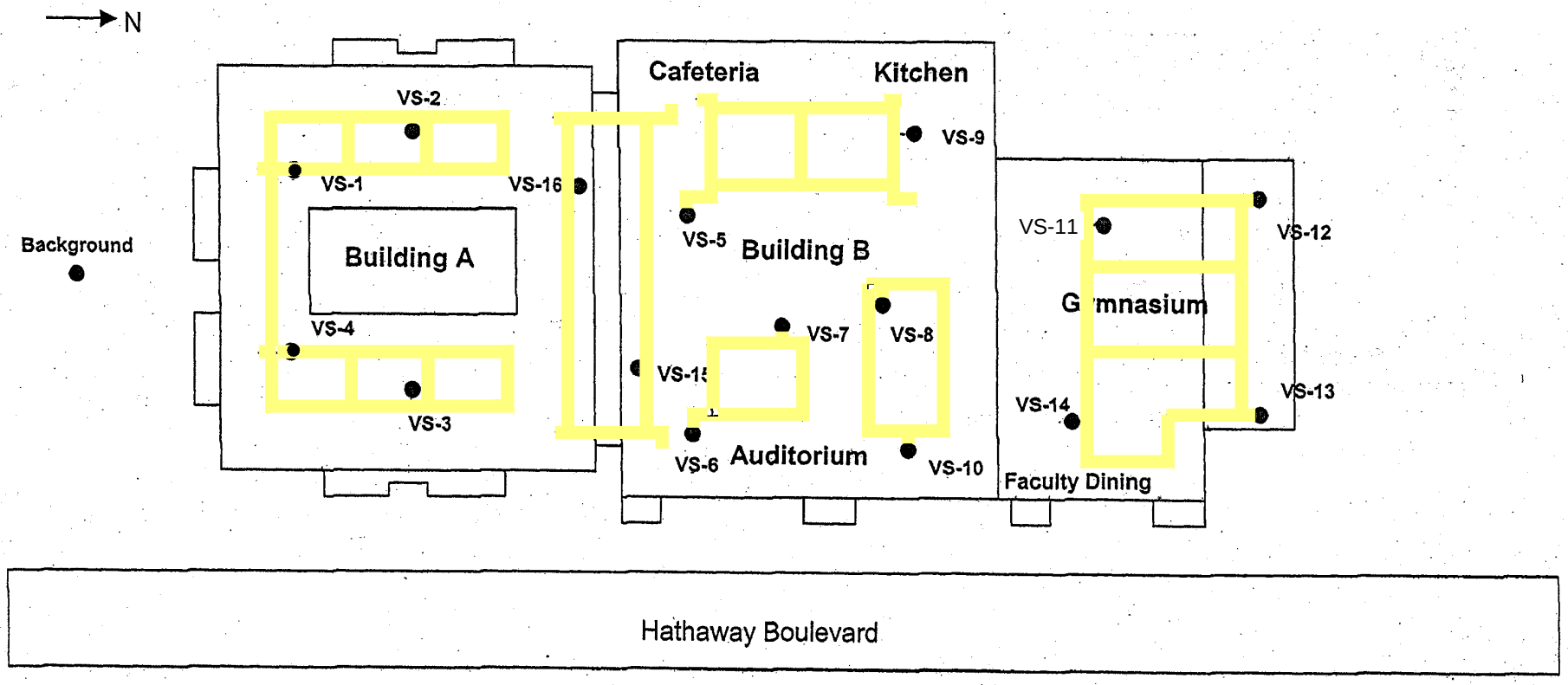
TRC
Wannalancit Mills
650 Suffolk Street
Lowell, MA 01854
(978) 970-5600

FIGURE
3

DRAWN BY: HWB
CHECKED BY: DMS
DATE: MARCH 2011

FILE: T:\E_CAD\115058\PROJECT GW MW 3-28-11.dwg

Keith Middle School
Foundation Venting System



● = Vent Riser / Vent Stack Sampling location

= Passive Venting and Collection System

KEITH MIDDLE SCHOOL
NEW BEDFORD, MASSACHUSETTS

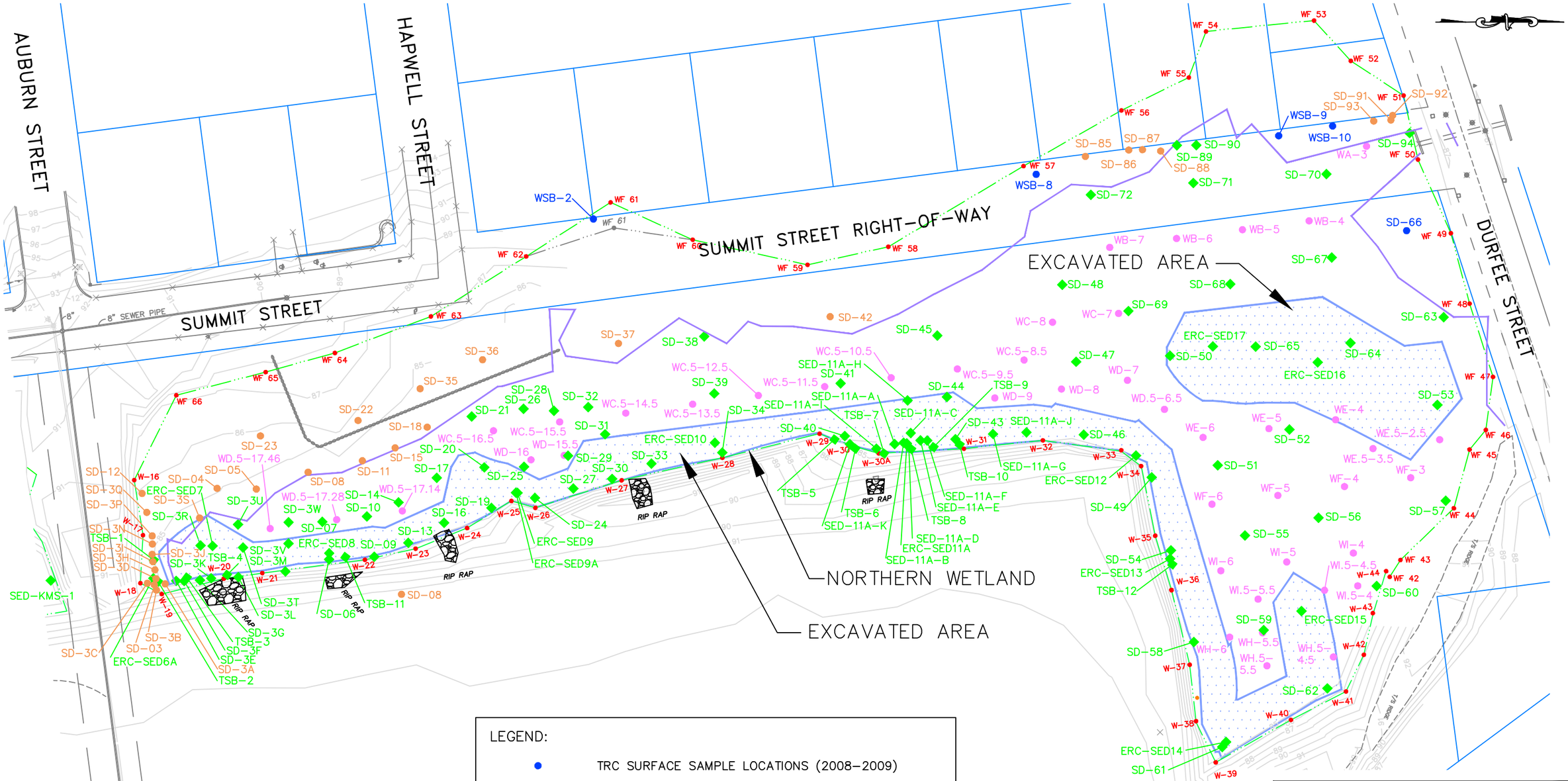
VENT STACK SAMPLE LOCATIONS

TRC
Wannalancit Mills
650 Suffolk Street
Lowell, MA 01854
(978) 970-5600

FIGURE 4

DRAWN BY: ---
CHECKED BY: DMS
DATE: MAY 2008

FILE: T:\E_CAD\115058\ARCHIVE PRE 2009\ventsys1A.dwg



LEGEND:

- TRC SURFACE SAMPLE LOCATIONS (2008–2009)
- TRC SURFACE SAMPLE LOCATIONS (2008–2009)
- TRC SEDIMENT SAMPLE LOCATIONS (2008–2010)
- BETA SURFACE SOIL SAMPLE LOCATIONS (2004, 2005)
- WETLAND BOUNDARY (WF 59)
- LIMIT OF PONDED WATER
- AREA OF BETA GROUP EXCAVATION

NOTE: DRAWING BASED ON "McCOY FIELD SITE PLAN" FROM BETA GROUP, NORWOOD, MA DATED 6–04 AND "NEW BEDFORD PROGRESS DRAWING" FROM BETA GROUP, NORWOOD, MA DATED 8–06.

APPROXIMATE GRAPHIC SCALE

0' 30' 60' 120'

KEITH MIDDLE SCHOOL
NEW BEDFORD, MASSACHUSETTS

NORTHERN WETLAND SURFACE - SEDIMENT SAMPLE LOCATIONS

TRC
Wannalancit Mills
650 Suffolk Street
Lowell, MA 01854
(978) 970–5600

DRAWN BY: HWB
CHECKED BY: REJ
DATE: MARCH 2011

FIGURE 5

FILE: T:\E_CAD\115058\KMS SURF - SED SAMP LOCS 3-11.dwg

APPENDIX A:

APPROVAL FOR RISK-BASED PCB CLEANUP AND DISPOSAL UNDER 40 CFR §761.61(C)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 1
1 Congress Street, Suite 1100
BOSTON, MA 02114-2023

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

AUG 31 2005

Scott Alfonse, Director
City of New Bedford
Department of Environmental Stewardship
133 William Street
New Bedford, Massachusetts 02740

Re: Approval for Risk-Based PCB Cleanup and Disposal under 40 CFR §761.61(c)

Dear Mr. Alfonse:

This is in response to the City of New Bedford (the City) application for approval of a risk-based plan to address PCB-contaminated materials at the property known as the McCoy Field, located on Hathaway Boulevard, New Bedford, Massachusetts (the Site).[1] The Site contains PCB-contaminated materials that exceed allowable PCB levels under the federal PCB regulations at 40 CFR §761.61.

The City has proposed to construct a school on the Site and has submitted a proposed cleanup plan that includes the following major activities:

- Removal and off-site disposal of PCB-contaminated soils with PCBs greater than or equal to 100 parts per million (≥ 100 ppm) in the excavation areas;
- Installation of at least two (2) feet of clean granular/soil cover in paved areas and at least three (3) feet of clean soil cover in landscaped areas;
- Installation of at least two (2) feet of clean material, a passive vapor ventilation system and solid vapor barrier in the building footprint;
- Establishment of institutional controls and deed restrictions, including recording an Activity and Use Limitation to restrict exposure to soil and disturbance of soil at the Site; and
- Establishment of a long-term monitoring plan for groundwater and indoor air quality, and a maintenance and monitoring plan for the surface covers (caps), including the building floor.

---

[1] Information was submitted on behalf of the City of New Bedford by BETA Group to support a risk-based cleanup and disposal approach for PCB remediation waste under 40 CFR §761.61(c). Attachment 2 provides a list of supporting information for this request. These submissions will be referred to as the "Application."

EPA published notice soliciting comment on the *draft* approval in the *New Bedford Standard Times* on June 14, 2005 and held an informational meeting on June 22, 2005. EPA received two sets of written comments on the technical remedial design and risk assessment methodology. These comments and EPA's responses are included as Attachment 3.

In the attached Approval Conditions, Attachment 1, EPA has added conditions for characterization and remediation of the New Bedford High School, potentially affected nearby private properties and athletic fields, and the existing Keith Middle School. (The wetlands adjacent to the Site will be cleaned up under a separate approval.) In consideration of the public comments received, EPA is requiring that sediments and vent gases be monitored under the long-term monitoring and maintenance implementation plan (MMIP).

As you are aware, the City commenced erection of the structural steel for the new school prior to the issuance of this Approval. In response to EPA concerns, the City wrote on June 14, 2005, to state that the construction work would not disturb PCB contaminated soils nor compromise the City's ability to comply with the conditions of the final Approval. At that time, EPA informed the City that any construction prior to issuance of an approval would be at the City's own risk. Note that Approval Condition 9 requires the City to notify EPA in writing of the scheduled date of commencement of on-site activities at least three business days before conducting any work under this Approval. As provided in Condition 10 of the Approval, the issuance of the Approval does not affect EPA's authority to take enforcement or regulatory action for any violations of the federal PCB regulations. Therefore, EPA continues to reserve its authority to take enforcement action for violating Condition 9 should we find that the City did not meet its commitments in the June 14, 2005 letter.

EPA has determined that the City's proposed plan is acceptable and that there will be no unreasonable risk to public health or the environment when the remediation and subsequent monitoring and maintenance are conducted in accordance with the Application and this Approval. Therefore, the City may proceed with this project, subject to the conditions of Attachment 1.

Should you have any questions on this matter, please contact Kimberly Tisa at (617) 918-1527.

Sincerely,

Robert W. Varney
Regional Administrator

Attachment 1, Approval Conditions
Attachment 2, Administrative Record
Attachment 3, EPA Response to Comments

cc: G. Martin, MADEP
A. Hanscom, BETA

ATTACHMENT 1: PCB CLEANUP AND DISPOSAL APPROVAL CONDITIONS MCCOY FIELD, HATHAWAY BOULEVARD NEW BEDFORD, MASSACHUSETTS

GENERAL CONDITIONS

1. This Approval is granted under the authority of Section 6(e) of the Toxic Substances Control Act (TSCA), 15 U.S.C. §2605(e), and the PCB regulations at 40 CFR Part 761, and applies solely to *PCB remediation waste* identified in the Application, specifically the PCB waste located at McCoy Field (the Site).

   a. This Approval does not address PCB contaminated sediments in the wetlands adjacent to the Site. A separate TSCA approval is required for the wetlands cleanup plan. The City of New Bedford (City) submitted a wetlands cleanup plan to EPA on June 21, 2005. This cleanup plan is currently under review by EPA.

   b. This Approval requires an assessment of potential PCB contamination at the New Bedford High School property. The City shall conduct an assessment of potential PCB contamination both indoors and outdoors and shall submit a cleanup plan for EPA review and approval. In the alternative, the City shall submit documentation that cleanup of this property is not required under TSCA and the federal PCB regulations at 40 CFR Part 761. The City shall submit the required documentation by June 2006. This does not preclude the applicability of regulatory requirements under the Massachusetts Contingency Plan.

   c. This Approval requires an assessment of potential PCB contamination on nearby private properties, at the existing Keith Middle School, and at the associated school athletic fields. The City shall conduct an assessment of the City-owned properties and the nearby privately-owned properties (if authorized by the private property owners.) If PCB contamination is identified, the City shall submit a cleanup plan for EPA review and approval. In the alternative, the City shall submit documentation that cleanup of these properties is not regulated under TSCA and the federal PCB regulations at 40 CFR Part 761. The City shall submit the required documentation by June 2006. This does not preclude the applicability of regulatory requirements under the Massachusetts Contingency Plan.

2. The City shall conduct on-site activities in accordance with the conditions of this Approval and the Application.

3. This Approval shall be revoked if the EPA does not receive written notification from the City of its acceptance of the conditions of this Approval within ten (10) business days of receipt.

4. In the event that the activities described in the Application differ from the conditions specified in this Approval, the conditions of this Approval shall govern.

5. The terms and abbreviations used herein shall have the meanings as defined in 40 CFR §761.3 unless otherwise defined within this Approval.

6. The City must comply with all applicable federal, state and local regulations in the storage, handling, and disposal of all PCB wastes, including PCBs, PCB Items and decontamination wastes generated under this Approval. In the event of a new spill during response actions, the City shall contact EPA within twenty-four (24) hours for direction on sampling and cleanup requirements.

7. The City is responsible for the actions of all officers, employees, agents, contractors, subcontractors, and others who are involved in activities conducted under this Approval. If at any time the City has or receives information indicating that the City or any other person has failed, or may have failed, to comply with any provision of this Approval, it must report the information to EPA in writing within twenty-four (24) hours of having or receiving the information.

8. This Approval does not constitute a determination by EPA that the transporters or disposal facilities selected by the City are authorized to conduct the activities set forth in the Application. The City is responsible for ensuring that the City's selected transporters and disposal facilities are authorized to conduct these activities in accordance with all applicable federal, state and local statutes and regulations.

9. The City shall notify EPA in writing of the scheduled date of commencement of on-site activities at least three (3) business days prior to conducting any work under this Approval.

10. This Approval does not waive or compromise EPA's enforcement and regulatory authority, nor release the City from any other applicable requirements of federal, state or local law, including those affecting any other contaminants.

USE CONDITIONS AND DEED RESTRICTION

11. Within the paved areas of the Site, the City shall not include the thickness of the final asphalt pavement coat as part of or to satisfy the minimum 2-foot clean cover requirement.

12. Within sixty (60) days of completing the activities described in the Application and in the Approval, the City shall submit for EPA's review and approval, an Activity and Use Limitation (AUL, i.e., a deed restriction) for the Site. The AUL shall include: a description of the extent and levels of contamination at the Site following remediation; a description of the actions taken at the Site; a description of the use restrictions for the

Site; and the long-term monitoring and maintenance requirements on the Site. Within sixty (60) days of EPA's acceptance of the AUL, the City shall record the AUL in the Registry of Deeds. A copy of this Approval shall be attached to the AUL. Within fifteen (15) business days of the recording, the City shall submit to EPA a copy of the AUL, with a certification(s) by an authorizing official that the City has recorded the AUL and Approval as required above.

13. Any modification(s) in the plan, specifications, or information submitted by the City, contained in the Application, and forming the basis upon which this Approval has been issued, must receive prior written approval from the EPA. The City shall inform the EPA of any modification, in writing, at least ten (10) days prior to such change. No action may be taken to implement any such modification unless the EPA has approved of the modification, in writing. The EPA may request additional information in order to determine whether to approve the modification.

    If such modification involves a change in the use of the Site which results in exposures not considered in the Application, the EPA may revoke, suspend, and/or modify this Approval upon finding that this risk-based cleanup and disposal action may pose an unreasonable risk of injury to health or the environment due to the change in use. EPA may take similar action if the EPA does not receive requested information from the City needed to make a determination regarding potential risk.

SALE, LEASE OR TRANSFER OF SITE

14. The City shall notify the EPA of the sale, lease or transfer of any portion of the Site, in writing, no later than thirty (30) days prior to such action. This notification shall include the name, address, and telephone number of the new owner(s). In the event that the City sells, leases or transfers any portion of the Site, the City shall continue to be bound by all the terms and conditions of this Approval, unless EPA allocates some or all of this Approval's responsibilities to the new owner through the issuance of a new approval. The procedures for the issuance of a new approval ("re-issued approval") are as follows:

    a. The new owner(s), lessee or transfer entity must request, in writing, that the EPA issue a new approval to the new owner(s), lessee or transfer entity which transfers some or all responsibilities to comply with the terms and conditions of this Approval to that entity or entities; and,

    b. The EPA reviews the request, and determines whether to issue a new approval; and,

c. The new owner(s), lessee or transfer entity provides written notification to the EPA of its acceptance of and intention to comply with the terms and conditions of the re-issued approval. The re-issued approval may be withdrawn if the EPA does not receive written notification from the new owner(s), lessee or transfer entity of its acceptance of, and intention to comply with, the terms and conditions of the re-issued approval within thirty (30) days of the date of the re-issued approval. Under such circumstances, all terms and conditions of this Approval will continue to be binding on the City.

d. In the event that the sale, lease or transfer of the Site will involve or result in a change in the use of the Site, EPA may revoke, suspend, and/or modify this Approval or the re-issued approval if it finds, due to the change in use, that this risk-based cleanup and disposal action will not be protective of health or the environment. The new owner shall record any amendment to the AUL, resulting from any approved modification(s), within sixty (60) days of such change(s).

15. In any sale, lease or transfer of the Site, the City shall retain sufficient access rights to enable it to continue to meet its obligations under this Approval for groundwater, vent gas, wetland sediment, and indoor air monitoring and for maintenance of the caps, except as provided above.

INSPECTION, MODIFICATION AND REVOCATION CONDITIONS

16. The City shall allow any authorized representative of the Administrator of the EPA to inspect the Site and to inspect records and take samples as may be necessary to determine compliance with the PCB regulations and this Approval. Any refusal by the City to allow such an inspection (as authorized by Section 11 of TSCA) shall be grounds for revocation of this Approval.

17. Within sixty (60) days of receipt of this Approval, the City shall submit for EPA's review and approval, a detailed long-term monitoring and maintenance implementation plan (MMIP) for the caps and for groundwater, wetland sediment, vent gas, and indoor air quality monitoring. At a minimum, this MMIP shall include: a description of the activities that will be conducted, including cap inspection criteria, frequency, and routine maintenance activities; groundwater, vent gas, wetland sediment, and indoor air quality monitoring locations; sampling protocols, sampling frequency, and analytical criteria; and reporting requirements.

The MMIP shall include a communications component which details how the maintenance and monitoring results will be communicated to the Site users, including teachers, parents, students, other on-site workers, and interested stakeholders. The MMIP also shall include a worker training component for maintenance or landscaping workers or for any person that will be conducting work that could impact the Site caps, including

pavement, landscaping areas, and building floors/foundations. The worker training plan must include a requirement for ongoing training and written certification of such training.

The City shall incorporate any changes to the MMIP required by EPA. Activities required under the MMIP shall be conducted until such time that EPA and the Massachusetts Department of Environmental Protection (MADEP) determine, in writing, that such activities are no longer necessary.

18. Any departure from the conditions of this Approval without prior, written authorization from the EPA may result in the revocation, suspension and/or modification of the Approval, in addition to any other legal or equitable relief or remedy the EPA may choose to pursue.

19. Any misrepresentation or omission of any material fact in the Application or in any future records or reports may result in the EPA's revocation, suspension and/or modification of the Approval, in addition to any other legal or equitable relief or remedy the EPA may choose to pursue.

20. Approval for these activities may be revoked, modified or otherwise altered: if EPA finds a violation of the conditions of this Approval or of 40 CFR Part 761, including EPA's PCB Spill Cleanup Policy, or other applicable rules and regulations; if EPA finds that these activities present an unreasonable risk to public health or the environment; if EPA finds that there is migration of PCBs from the Site; or if EPA finds that changes are necessary to comply with new rules, standards, or guidance for such approvals. The City may apply for appropriate modifications in the event new rules, standards, or guidance come into effect.

RECORDKEEPING AND REPORTING CONDITIONS

21. The City shall prepare and maintain all records and documents required by 40 CFR Part 761, including, but not limited to, the records required by Subparts J and K. The City shall maintain a written record of the cleanup and the analytical sampling for activities conducted under this Approval, at City Hall and at the Site. All records shall be made available for inspection by authorized representatives of the EPA, until such time as EPA approves in writing a request for an alternative disposition of such records.

22. The City shall submit a Final Completion and Inspection Report (Report) to the EPA within 120 days of completion of the activities described under this Approval. At a minimum, this Report shall include: a discussion of the project activities; characterization and confirmation sampling analytical results; copies of the accompanying analytical chains of custody; field and laboratory quality control/quality assurance checks; an estimate of the quantity of PCBs removed and disposed of off-site; copies of manifests; copies of certificates of disposal or similar certifications issued by the disposer, if applicable; and any additional report required under the Massachusetts Contingency Plan,

including the As-Built Construction Report. The Report shall also include a Completion Statement signed and sealed by a registered Licensed Site Professional or Professional Engineer in the Commonwealth of Massachusetts verifying that the activities have been implemented in accordance with this Approval and the Application.

23. As required under Condition 17 of this Approval, the City shall submit the results of the long-term monitoring and maintenance activities to EPA and MADEP as specified in the final MMIP to be approved by EPA and MADEP.

24. Required submittals shall be mailed to:

    Kimberly N. Tisa, PCB Coordinator
    United States Environmental Protection Agency
    1 Congress Street, Suite 1100 - CPT
    Boston, Massachusetts 02114-2023
    Telephone: (617) 918-1527
    Facsimile: (617) 918-0527

25. No record, report or communication required under this Approval shall qualify as a self-audit or voluntary disclosure under EPA audit, self disclosure or penalty policies.

****

End of Attachment 1

ATTACHMENT 2: ADMINISTRATIVE RECORD

A. APPLICATION DOCUMENTS

- *Alan Hanscom (BETA) to Kimberly Tisa (EPA) May 26, 2005 letter responding to VERSAR May 19, 2005 risk assessment comments*
- *William D. Sweet (ATSDR) to Kimberly Tisa (EPA), Health Consultation on McCoy Field Site, post remediation and after building construction. May 25, 2005.*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA) May 24, 2005 letter clarifying comments contained in May 18, 2005 letter*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA) letter responding to EPA Supplemental Comments on Risk-Based Application, May 18, 2005 and attached Risk-Based Cleanup Request, Rev. 2, May 18, 2005*
- *May 19, 2005 Versar Comments on Risk-Based Cleanup Request Risk Assessment Calculations*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA), Transmittal of Summary of Supplemental EPA Review Comments on Risk-Based Cleanup Application, via e-mail May 16, 2005*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA), Transmittal of Summary of EPA Review Comments on Risk-Based Cleanup Application, via e-mail May 12, 2005*
- *Letter from Scott Alfonse (City of New Bedford) to Kimberly Tisa (EPA), May 10, 2005*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA), Transmittal of Written Certification for Risk-Based Cleanup Request, Rev. 1, via e-mail May 9, 2005*
- *Memorandum from Cyndee Fuller (ESS) to Al Hanscom (BETA), Revision of Risk-based Air Concentrations for PCBs and comparison with MADEP air guidance, May 9, 2005*
- *Risk Based Cleanup Request, School Site at McCoy Field, New Bedford, Massachusetts, Revision 1, May 3, 2005, Volumes I and II*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA) letter dated April 29, 2005 responding to EPA April 5, 2005 memo on technical design of engineered cap*
- *Alan Hanscom (BETA) to Kimberly Tisa (EPA) letter dated May 2, 2005, responding to EPA April 19, 2005 comments on Risk-Based Cleanup Request, Rev. 0, March 21, 2005*

- *Alan Hanscom (BETA) to Kimberly Tisa (EPA) letter dated May 2, 2005, responding to Versar April 14, 2005 comments on Risk-Based Cleanup Request, Rev. 0, March 21, 2005*

- *Kimberly Tisa (EPA) to Scott Alfonse (City of New Bedford) letter dated April 19, 2005 transmitting comments on Risk-Based Cleanup Request, March 21, 2005*

- *Yoon-Jean Choi (EPA) to Kim Tisa (EPA), Comments on Proposed Engineered Cap, April 5, 2005*

- *Robert W. Varney (EPA) to Mayor Frederick M. Kalisz, Jr. (City of New Bedford) regarding cleanup application for the Keith Middle School Project, March 30, 2005*

- *Scott Alfonse (City of New Bedford) to Kimberly Tisa (EPA), Risk-Based Cleanup Request, Rev. 0, March 21, 2005*

B. ADDITIONAL DOCUMENTS

- *Technical Support Document – McCoy Field Risk-Based PCB Approval, August 24, 2005*

- *Matthew J. Thomas, Esq., (City of New Bedford) to Douglas Gutro (EPA), June 14, 2005, letter regarding erection of structural steel*

****
End of Attachment 2

ATTACHMENT 3. EPA RESPONSE TO COMMENTS

McCOY FIELD, HATHAWAY BOULEVARD
NEW BEDFORD, MASSACHUSETTS

I EPA's Revisions to the Draft Approval

In addition to minor editorial changes, the following revisions have been made to the *draft* risk-based PCB cleanup and disposal approval (*draft* approval):

1. The Risk-Based PCB Cleanup and Disposal Approval (Approval) under 40 CFR §761.61(c) requires submittal of a long term monitoring and maintenance implementation plan (MMIP) for the Site. The *draft* approval required that the MMIP include the surfaces caps, groundwater and indoor air. In the final Approval, EPA is requiring that vent gases and wetland sediments be included in the MMIP.

2. A requirement for development of a worker training component and a communications component in the MMIP has been added in the Approval conditions. The communications component shall detail how the maintenance and monitoring results will be communicated to the Site users, including teachers, parents, students, other on-site workers, and interested stakeholders. The worker training component shall apply to workers performing routine site activities such as landscapers, focusing on preventing accidental releases of contaminated soil as a result of improper disturbance of physical controls (e.g. caps). The worker training plan must include a requirement for ongoing training and written certification of such training.

3. A requirement for assessment of potential PCB contamination at the existing Keith Middle School and the nearby athletic fields has been incorporated in the Approval. If PCBs are found, the City shall submit a cleanup plan for EPA review and approval. In the alternative, the City shall submit documentation that cleanup of the properties is not required under TSCA and the federal PCB regulations at 40 CFR Part 761.

II Responsive Summary to Comments Received

The following summarizes EPA's response to written comments received on the *draft* approval. One set of written comments was received during the formal comment period on the *draft* approval from June 14 to July 15, 2005, which focused specifically on the technical aspects of the cleanup plan and the risk assessment methodology. Two written comments were received requesting an extension of the comment period. In order to provide additional public review time, the comment period was extended an additional two week period (until July 29, 2005). One set of written technical comments was received during this period.

In the following, EPA has organized the comments by subject matter and has provided a summary of relevant comments with our responses.

1. Adequacy of the Regulatory Process and Scope of Approval

COMMENT 1

The public review and comment period should be extended because the repository was incomplete and the public did not have full access to all the information.

EPA Response:

Since March 2005, McCoy Field documents submitted to EPA by the City have been placed in the McCoy Field repository at the New Bedford Free Public Library. EPA became aware that some of documents had been separated, and several citizens indicated during the Public Involvement Plan (PIP) meetings, and during the June 22, 2005 EPA Public Informational Meeting, that the PCB cleanup plan was unclear and incomplete.

EPA has always believed that the complete documents relevant to the PCB cleanup at the McCoy Field Site should be readily available for public review. Accordingly, in addition to the paper repository, EPA posted all relevant documents on its website on June 29, 2005 and notified all PIP members via US mail. EPA also extended the public review and comment period an additional two weeks until July 29, 2005 to allow the public a full 30 day review and comment period. In addition, the New Bedford Free Public Library implemented a formal process for tracking of all McCoy Field documents to ensure that the site file was complete at all times.

EPA has determined that an adequate public notice and comment process was provided, even though not required by the TSCA statute.

COMMENT 2

EPA departments identified deficiencies in the City's cleanup request, including lack of justification on transport, risk calculations and capping details.

EPA Response:

The commenter is correct that EPA staff, who reviewed the initial March 2005 PCB Risk-Based Cleanup Plan submitted by the City, identified deficiencies in the plan. All comments identified by the EPA reviewers were subsequently corrected and/or addressed in additional submittals and/or in the City's responses to EPA comments. These documents are part of the Administrative Record, are in the paper repository, and are on EPA's website.

COMMENT 3

The Notice of Activity and Use Limitation provided in the Risk-Based Cleanup Plan pertains to the entire property, including the wetlands. The wetlands are not addressed in the Risk-Based Cleanup Plan and should be.

EPA Response:

The Notice of Activity and Use Limitation (AUL) provided in the Risk-Based Application is draft only and has not been finalized. An executed AUL will be required upon completion of activities at the McCoy Field Site, including the wetlands. EPA has received the City's proposed risk-based cleanup plan to address PCB contaminated wetland sediments. This proposal includes excavation and off-site disposal of PCB-contaminated sediments with greater than 1 part per million PCBs, which is supported by an ecological risk assessment. While this plan is still under review, an AUL would not be required on the wetlands either under the federal PCB regulations or under the Massachusetts MCP, because the proposed cleanup will meet the standards. The wetlands remediation will be addressed through a separate TSCA approval as specified in the TSCA Approval for McCoy Field.

COMMENT 4

Submitted narratives are inconsistent with drawing and plans for depth of fill.

EPA Response:

The inconsistencies between the narrative and drawings/plans were addressed in the document *Alan Hanscom (BETA) to Kimberly Tisa (EPA) letter responding to EPA Supplemental Comments on Risk-Based Application, May 18, 2005 and attached Risk-Based Cleanup Request, Rev. 2, May 18, 2005.*

2. What Are the Appropriate Regulatory Standards

COMMENT 1

Incorrect cleanup standards are being applied to the Site and the S-1 cleanup standard of < 2 ppm should apply to this Site.

EPA Response:

The Risk-Based Cleanup Request for McCoy Field was submitted in accordance with the Toxic Substances Control Act (TSCA) and the federal PCB Regulations at 40 CFR §761.61(c). The comment refers to the requirements under the Massachusetts

Contingency Plan (MCP). Under the MCP, soils are categorized as S-1, S-2, or S-3 soils based on the human exposure potential. The McCoy Field Site surface soils (0-3 feet) are classified as S-1 category soils, since the S-1 category soils are associated with the highest potential for exposure. Under the MCP, the PCB cleanup standard for a S-1 category soil is 2 ppm. However, the MCP provides for an alternative to meeting prescribed cleanup standards if exposure is eliminated through establishment of an Activity and Use Limitation. The City's proposed cleanup for the Site will include the establishment of an AUL which is consistent with the allowances under the MCP. As a result, the S-1 category will apply to only the clean imported soil (fill) for the caps. The potential for any exposure to the deeper impacted soils (Category S-2 and S-3) will be eliminated by the clean soil cap, and/or pavement and AUL.

COMMENT 2

The 50 ppm limit for non-liquid PCB levels is not applicable and the 2 ppm limit for liquid PCB concentrations should be applied to this site.

EPA Response:

The commenter states that the 2 ppm limit for liquid PCB concentrations should apply to this site. The commenter provides no reference for this limit. EPA assumes that the 2 ppm limit refers to EPA's PCB decontamination standard for organic liquids and non-aqueous inorganic liquids at 40 CFR §761.79(b). This specific section is not applicable to the Site. As stated in the following applicability excerpt: "This section (i.e., §761.79) establishes decontamination standards and procedures for removing PCBs, which are regulated for disposal, from water, organic liquids, non-porous surfaces (including scrap metal from disassembled electrical equipment), concrete, and non-porous surfaces covered with a porous surface, such as paint or coating on metal..." Therefore, the 2 ppm decontamination standard cited is not applicable for cleanup of PCB-contaminated soils. The cleanup for McCoy Field is being addressed under the Risk-Based Cleanup and Disposal Option for PCB Remediation Waste at 40 CFR 761.61(c). Under this option, there are no specified cleanup standards. Rather, the cleanup is based on a risk assessment.

COMMENT 3

The proposed PCB remediation plan is inconsistent with the requirements under the MCP, and the capping plan fails to address S-1 standards for containment of contaminated soils.

EPA Response:

Given the contaminants identified at the McCoy Field Site, cleanup is regulated under both the federal PCB Regulations at 40 CFR Part 761 and the Massachusetts Contingency Plan. EPA has worked closely with the Massachusetts Department of Environmental

Protection (MADEP) on review of the cleanup proposed at the Site. The MCP and the regulations established therein provide for the establishment of Activity and Use Limitations (AULs) in lieu of meeting prescribed cleanup standards. As stated previously, the S-1 category soils will apply to only the clean imported soil (fill) for the caps. An AUL would prevent direct exposure to site contaminants, which is consistent with the proposal for McCoy Field. As such, EPA believes that the proposed cleanup is consistent with the MCP regulations.

COMMENT 4

Under TSCA, the EPA has in the past closed university buildings where PCB soil concentrations were greater than 10 ppm.

EPA Response:

The commenter states that under TSCA, EPA has closed university buildings in Massachusetts where soil concentrations exceeded 10 ppm PCBs. The commenter provides no reference material. EPA is unaware of any applicable precedents involving university buildings. Cleanup and disposal of PCBs at the McCoy Field Site are being conducted under the Risk-Based Cleanup and Disposal Option at 40 CFR §761.61(c). There are no prescribed cleanup standards under this option. Rather, cleanup requirements are determined based on Site contaminants and concentrations, exposure and resulting risk assessment.

COMMENT 5

Brownfield standards should not be applied to hazardous waste sites containing PCBs as per federal law. Brownfields standards are inadequate to protect the public health and safety of New Bedford neighborhoods from contamination at McCoy Field.

EPA Response:

The Brownfields regulations contain no prescribed PCB cleanup standards. PCBs are regulated for cleanup and disposal under the federal TSCA PCB regulations. Superfund is also mandated to address PCB contamination, but applies the requirements of the TSCA PCB Regulations in developing a cleanup plan for a PCB-contaminated Site.

COMMENT 6

S-1 standards for PCBs require active venting and EPA standards for school construction near PCB sites indicate active venting.

EPA Response:

EPA has determined that the PCB contamination at the McCoy Field Site has been adequately characterized.

The comment specifically refers to statements made by the City of New Bedford during Public Involvement Plan (PIP) meetings and activities conducted by the City. According to the City of New Bedford, the comment was taken out of context. Discussions at the subject PIP Meetings were related to further delineation of the nature and extent of contamination off the McCoy Field Site. All contamination at McCoy Field has been defined in accordance with MCP requirements and the EPA-approved Work Plan. Plans are underway for supplemental delineation of the off-site contamination, consistent with MCP and TSCA regulations.

COMMENT 2

PCB contamination on the entire site, including the wetlands should be addressed.

EPA Response:

The City of New Bedford has submitted a PCB cleanup plan for the wetlands adjacent to McCoy Field. The proposed plan and related documents are available on EPA's website at *www.epa.gov/ne/mccoyfield*. These documents are currently under review by EPA and EPA has made no final determination on the adequacy of the City's proposed plan. Any decisions related to the wetlands cleanup plan will be documented in a separate TSCA approval and posted on EPA's website.

COMMENT 3

The McCoy Field draft approval cannot be complete without remediation of areas adjacent to the Site, namely the wetlands and New Bedford High School.

EPA Response:

The City has submitted a wetlands remediation plan to EPA. This plan is currently under review. The Approval requires the City to submit a characterization and cleanup plan for New Bedford High School as well as for the other properties, including nearby privately-owned properties and athletic fields, and the existing Keith Middle School, unless the City can submit documentation to EPA confirming that the PCBs are not regulated under TSCA and the federal PCB regulations. Even if the PCB contamination at the High School is not regulated under TSCA, the assessment and cleanup is required by the MADEP under the MCP.

4. Adequacy of Risk Assessment

COMMENT 1

The use of averaging or eliminating high concentrations of PCBs (46,500 ppm) to determine the overall PCB concentration was inappropriate for this site and for protecting public health and safety.

EPA Response:

The City's risk evaluation followed acceptable EPA methodologies and guidelines. The 46,500 ppm PCB sample was not included in the risk analysis estimating exposure to PCBs that are volatilized from soil because that soil was excavated and removed from the Site, as was all soil in the excavated areas with PCBs concentrations of ≥ 100 ppm. Soils samples were not composited or averaged. The maximum PCB concentration from soil remaining at the site, 94.5 ppm, was used for calculating the volatilized PCB concentration in indoor air (see May 26, 2005, memorandum from BETA Group, Inc. to Ms. Kimberly Tisa, EPA). The use of the maximum concentration of 94.5 ppm is conservative, as the estimated average PCB concentration for the remaining soils is 10.5 ppm and the 97.5 percent upper confidence limit on the mean (based on the statistical evaluation that EPA guidance typically recommends using) is 13.4 ppm. Also, the risk analysis did not include or consider the protection provided by the vapor barrier or venting. Thus, it was concluded that the PCBs soil concentrations would not present a risk to human health at the McCoy Field site.

COMMENT 2

Numerous studies show exposure to PCBs cause elevated PCB blood levels and these studies advocate lowering the PCB cleanup level to < 1 ppm.

EPA Response:

The commenter provided no citations, specific results, nor validation of the studies. EPA assumes that the studies referenced by the commenter, are based on direct exposure to PCBs. The remedy proposed for McCoy Field includes isolation of PCB-contaminated soil using clean soil and pavement, and placement of passive ventilation and a solid vapor barrier beneath the building footprint. With these controls properly put in place, and properly maintained and monitored, there should be no potential for PCB exposure to persons at the Site.

Under the PCB Regulations at 40 CFR Part 761, EPA has established a PCB cleanup standard of < 1 ppm for soils without any physical controls or site use restrictions. As previously discussed, this is not the case with McCoy Field. The City is conducting

cleanup of PCBs under the Risk-Based Cleanup and Disposal Option which allows PCBs at > 1 ppm to remain in place if there is no unreasonable risk to public health.

COMMENT 3

PCB concentrations at up to 46,000 ppm have been found at the Site. A PCB concentration of 0.5 ppm versus 46,000 ppm represents a risk factor of 1 out of 100,000, which is greater than EPA's accepted risk factor of one in 10 million.

EPA Response:

The commenter has incorrectly identified ratios of PCB concentrations as risk factors. The 1 in 100,000 risk factor apparently is calculated by dividing 0.5 ppm by 46,000 ppm, then this value is compared to the EPA risk factor of 1 in 10 million or 1×10^{-7}. Risk factors are not determined by direct comparison to PCB concentrations. Rather, the risk factors are developed from the accepted hazards of PCBs as determined by the scientific community combined with an exposure assessment, which considers among other things, the PCB concentrations at the site, the exposure frequency, the amount of contamination intake, and the route of exposure (e.g. dermal, ingestion, inhalation). The risk assessment conducted and submitted by the City of New Bedford followed federally accepted guidelines and methodologies. As a point of clarification, EPA's acceptable risk level is 1 in 1 million or 1×10^{-6}. This acceptable risk is the de minimis standard for insignificant risk most often used in federal environmental statutes, regulations, and policies.

COMMENT 4

The PCB cleanup standard for the Site should be 0.5 ppm rather than 2 ppm since the daily dose is based on an adult's weight rather than a child's weight and since a 10% daily exposure rate is assumed.

EPA Response:

The commenter uses the terms daily dose and exposure limit interchangeably, and incorrectly, with PCB concentration. In the comment, the 2 ppm PCB soil limit is being equated, incorrectly, to a daily dose and a daily exposure rate. Thus, per the commenter, for 24 hours (i.e., 1 day), the daily limit is 2 ppm and 25% of this, 6 hours, would be equal to the 0.5 ppm concentration referenced in the comment. However, these values are incorrect for this risk assessment. The daily dose and daily exposure rate are factors that were considered as part of the overall human health risk assessment, submitted by the City and reviewed by EPA. Neither the MCP nor EPA's risk assessment guidance identifies the referenced 10% daily exposure rate, and therefore EPA does not consider the reference valid.

As a point of clarification, in the human health risk assessment conducted for the Site, an adult weight rather than child weight was used in the assessment since the adult and child inhalation rate to body weight ratios were similar. In order to confirm that this comparison was reasonable, EPA also calculated the exposure using a child weight rather than adult weight. The exposure calculation was based on conservative assumptions such as using the maximum PCB soil concentration of 94.5 ppm to determine the PCB indoor air concentration, and assuming that the students would be exposed for 8 hours a day for 250 days per year. Also, the risk assessment did not include or consider the protection provided by the vapor barrier or venting. The cancer risk estimated for students exposed to volatilized PCBs in indoor air was 7×10^{-10} (see May 19, 2005, memorandum from Diane Sinkowski, Versar, to Laura Casey, EPA), well below the 1×10^{-6} acceptable cancer risk level. Thus, it was concluded that the PCBs soil concentrations would not present a risk to human health at the McCoy Field site.

COMMENT 5

PCBs have been found in surface soils (6 out of 150 samples) at the New Bedford High School where 4 feet of clean fill was placed. A risk factor of 6/150 or 4% is too high for school children.

EPA Response:

With respect to the "risk factor" of 6/150 or 4%, the commenter uses this term incorrectly. The correct terminology would be "frequency of detection", not "risk factor". As previously stated, risk factors are determined based on exposure assessments, which would include but not be limited to, the concentration of site contaminants, the frequency of a person's exposure to PCBs, and how the person is exposed. The Approval requires the City to characterize PCB contamination at the High School and to submit a cleanup plan to EPA, if required under TSCA.

5. Adequacy of Remediation and Engineering Controls

COMMENT 1

The remedial design does not address stormwater runoff and erosion potential from the Site to the adjacent wetlands.

EPA Response:

A Storm Water Pollution Prevention Plan (SWPPP) dated September 2004 was submitted to EPA and the contractor is required to follow the procedures identified in the SWPPP during the project. EPA is unaware of any current erosion from the site into the wetlands. A July 13, 2005 Field Inspection Report by the City of New Bedford Conservation Commission did not identify any erosion issues and found that the erosion control measures were in place and functional, thus providing protection to the wetlands from contamination on McCoy Field.

COMMENT 2

The cleanup plan does not address horizontal transport factors, pollution movement into the wetlands, and exposure in landscaped areas.

EPA Response:

Based on the comment, EPA assumes that the commenter is specifically referencing the potential for migration into the wetlands from the McCoy Field Site. The City submitted a plan to address PCB contamination to the wetlands adjacent to McCoy Field in June 2005. EPA is currently reviewing the proposed plan and has made no determination on its adequacy. However, based on the data provided, the PCB contamination appears to be in surficial (less than one foot deep) sediments/soils located at the toe of the McCoy Field embankments. The data indicate that PCBs from the fill material located at the Site and in the embankments migrated to these low lying areas via wind erosion and storm water runoff. This is further supported by the groundwater sampling and native material sampling conducted at McCoy Field in which no PCB contamination was found. The capping plan for McCoy Field requires at least 2-feet of clean materials at the site surface. These capping materials must be maintained in accordance with the Activity and Use Limitation for the Site. Accordingly, surface runoff will not be a migration pathway for PCB-contaminated soils. Similarly, the capping materials will preclude the potential for entrainment of contaminated soil particulates to be released into the air and redeposited into the wetlands.

While it is not very likely that the wetlands will be impacted in the future from PCB contamination at McCoy Field, as an extra measure of precaution, EPA will require ongoing groundwater monitoring and wetland sediment monitoring. Should this monitoring indicate that there are new impacts resulting in unreasonable risk to the wetlands from McCoy Field, EPA will require the City to implement measures to mitigate the migration per the conditions of the Approval.

COMMENT 3

PCBs left in place continue to contribute to environmental contamination and public health dangers. There will be vertical and horizontal movement of PCBs due to groundwater and stormwater influences, soil settling, and subsurface drainage influences.

EPA Response:

EPA agrees that uncontrolled PCB contaminated sites have the potential for contributing to environmental contamination. However, given the chemical and physical properties of PCBs, the measures that will be employed at the McCoy Field site, including surface caps and activity and use limitations, will reduce to acceptable levels or eliminate the potential for release of PCB contamination from the Site.

EPA's analysis shows that the primary PCB of concern at the McCoy Field site is Aroclor 1254, a highly chlorinated PCB. In general, more highly chlorinated PCBs will have a lower tendency to leach and therefore are more likely to remain adsorbed to soil. These facts are supported by the high octanol to water coefficient (average K_{ow} is 1×10^6) and low water solubility (0.012 mg/L) consistent with accepted scientific literature, as well as the results of the soil/gas vapor and groundwater testing at the Site.

With respect to groundwater and stormwater infiltration, the majority of stormwater from the site will be collected through the on-site stormwater collection system. Stormwater from roof runoff will be collected through roof drains and discharged to the wetlands. While there will be areas of the site where water can freely infiltrate site soils (e.g. the landscaped areas), it is highly unlikely that this will be sufficient to completely saturate the clean fill at the site and create a water/air pathway for PCB evaporation. To date, PCB contamination has not been found in the native materials located beneath the PCB-contaminated material nor have PCBs been detected in the groundwater.

COMMENT 4

PCB-contaminated soils can migrate upwards as is evidenced by the PCBs which have been found in surface soils at New Bedford High School.

EPA Response:

The commenter provides no technical justification or reference to support that PCB-contaminated soils are upwardly mobile but refers to PCB concentrations found at New Bedford High School.

The New Bedford High School was constructed in the early 1970's and EPA is unaware of any controls or requirements which were put in place regarding landscaping, excavating, or maintenance. Based on information provided by BETA Group, the LSP of record for the High School, during the numerous soil borings conducted on the High

School property, the contaminated burn debris was not covered with 4 feet of clean material in any locations.

COMMENT 5

The proposed capping plan is one that is common for commercial structures with low-level contaminants. PCBs are not considered low-level by many state public health boards until under a 2 mg/l threshold and the capping plan uses a 50 mg/l limit instead. The capping plan, which is used for commercial development, should not be used for a public school.

EPA Response:

To address this comment, EPA assumes that the commenter has confused the concentration unit cited in the comment and meant to refer to threshold limits of 2 mg/Kg and 50 mg/Kg. The mg/Kg unit (which is equivalent to ppm) would be the correct unit for PCB concentrations in soil.

The commenter states that the capping plan uses the 50 mg/Kg limit rather than the 2 mg/Kg limit. With respect to the 2 mg/Kg, the PCB regulations under TSCA have no such soil standard, even though the MCP does reference this standard for its Category S-1 soils.

However, the commenter is incorrect in stating that the capping plan uses the 50 mg/Kg standard. The cleanup plan references the 50 mg/Kg PCB limit under the federal TSCA PCB regulations as one of the criteria which establish the applicability of TSCA for cleanup and disposal of PCB-contaminated soils at a Site. However, if the source of the PCB contamination was greater than or equal to 50 mg/Kg, and if the contamination occurred after 1979, materials that are contaminated at less than 50 mg/Kg are also regulated for cleanup and disposal. Given that PCBs at 50 mg/Kg or greater are present at the Site, and the fact that PCB-contaminated materials were spread across the Site in the 1990's, cleanup and disposal of the PCB-contaminated soils at McCoy Field are regulated under TSCA.

The PCB regulations provide 2 options for cleanup and disposal. The City of New Bedford opted to address the PCB contamination at the site under the Risk-Based Cleanup and Disposal option at 40 CFR 761.61(c). The 50 mg/Kg standard is not specified under the risk-based cleanup and disposal option. Rather, this option requires that the site owner (the City) provide justification to support its proposed plan by showing that there will be no unreasonable risk to site users. The City provided a human health risk assessment to support its proposed plan.

COMMENT 6

Geotextile provides no barrier to the upward movement of an average [PCB] molecule of 6 microns.

EPA Response:

The commenter states that the geotextile will not impede the movement of an average [PCB] molecule of 6 microns. While no reference was provided to support the 6 micron reference, the commenter is correct that the proposed geotextile is not a barrier to PCBs. Rather the geotextile serves to separate the contaminated soil from the clean soil. The use of the geotextile is reasonable given that PCBs adsorb to soil and therefore the issue is not with the size of the PCB molecule, but rather with the size of the soil particulates to which the PCBs are adsorbed. The fabric itself will restrict any significant upward migration of soil, and the overlying backfill material is largely granular (stone) and not subject to the capillary action that occurs in finer grained soil. Further, the weight of the clean soil above the contaminated soil further reduces the very unlikely upward migration of PCB-contaminated soil particulates.

COMMENT 7

Frost-heaving will facilitate upward migration of PCBs. The geotextile layer is prone to tears and stretching and will create more passage of contaminated soils toward the surface.

EPA Response:

As previously stated, the geotextile was not meant to act as a PCB barrier, but will serve to separate the contaminated soil from the clean soil. The geotextile is permeable allowing for the free passage of water. If the geotextile were impermeable, pockets of water could collect and intermittently freeze during the winter months, which would increase the potential for breakage to and/or stress on the geotextile and potentially compromise its effectiveness. Therefore, the overall cap design is less prone to breakage and frost due to the permeability and the relatively deep ground water table. Given that the geotextile will be placed across and atop a relatively even and homogeneous material, EPA does not anticipate any significant stress on the fabric, which will limit the potential for tearing or puncturing to the fabric.

COMMENT 8

The warning barrier and the geotextile separation material are not hazardous waste mitigation materials and therefore provide no additional protection to public health or safety.

EPA Response:

As previously discussed, the geotextile separation material was not intended to be a PCB barrier nor a hazardous waste mitigation system, but to physically separate the clean fill material from the PCB-contaminated materials. Likewise, the warning barrier was put in place as an additional visual aid for maintenance workers as a preventative measure to avoid breakage of the geotextile liner during landscaping or other maintenance activities. In the landscaped areas, clean material is beneath the warning barrier that overlays the geotextile. Therefore, in the event the warning barrier is breached, the material directly beneath is clean material.

COMMENT 9

The sample of the warning barrier presented at the informational meeting was fragile and it tore.

EPA Response:

EPA discussed this comment with the City and its consultant, BETA Group, who indicated that there was no breakage of the warning barrier at any time during the meeting. In fact, the warning barrier material is a plastic material, is not fragile, and is not readily prone to tearing.

COMMENT 10

No hazardous waste liners are proposed. The "sealed" geotextile liner cannot withstand temperature changes, frost action, penetration, or pollutant transport. The coated fabric is standard woven geotextile with a 10 micron thin coating of plastic to seal the material. The geotextile has a short life expectancy and cannot withstand a standard puncture test.

EPA Response:

The commenter appears to be referring to the coated separation fabric (Mirafi MCP-1212) which is being used temporarily to reduce the potential exposure to workers at the Site during construction activities. The cap design for the building footprint does not depend on the coated separation fabric. The actual cap in the building footprint consists of a geotextile barrier fabric installed over the contaminated material, then six to eight inches of clean granular material, then an adherence geotextile fabric, a gas vapor barrier, and the building foundation. This cap will be completed with a passive venting system.

COMMENT 11

PCB contaminated soils with concentrations up to 46,000 ppm were found at the Site. Three feet of fill does not stop a super concentration of PCBs.

EPA Response:

Sample # NSP-4 contained 46,500 ppm PCB, which was the highest concentration of PCBs found at the Site. This sample was collected from a stockpile located at the north end of the Site, which was approximately 1-foot high. Based on EPA's review of the analytical data, soils located in this stockpile and in piles in close proximity to this pile were not comparable in PCB concentration with soils collected from the remainder of the Site. The soils associated with these higher PCB concentrations were removed from the Site as were all soils in the excavation areas with PCBs at $\geq$ 100 ppm.

COMMENT 12

The pavement is inadequate and should not be counted as part of the clean fill layer.

EPA Response:

The final 1.5" asphalt coat will not be included as part of the 2-foot clean cover. This has been incorporated into the Approval language.

COMMENT 13

The pavement is not impermeable and will not last 40 to 50 years.

EPA Response:

With respect to the longevity of the pavement itself, EPA agrees that asphalt pavement will crack and will require periodic maintenance. Accordingly, the Long-Term Cap Monitoring and Maintenance Plan will require inspections and maintenance of all pavement and sidewalks to preserve the integrity of each barrier. EPA will require that inspections and any required corrective action be documented.

COMMENT 14

There is no historic justification to cap hazardous waste materials with asphalt pavement in the hazardous waste industry.

EPA Response:

In general, EPA agrees with the commenter's statement that asphalt is not used for capping hazardous waste [landfills]. However, hazardous waste landfills generally contain a variety of different types of contaminants at high concentrations. Capping of hazardous waste landfills requires a system which can address a large array of contaminants having different chemical properties. At McCoy Field, the contaminants of concern include PCBs, semi-volatile organics, and metals. These compounds do not readily leach, migrate, or volatilize. Thus, the capping measures proposed for McCoy Field are appropriate for these types of compounds.

COMMENT 15

The pavement will facilitate the upward migration of PCB-contaminated soils due to the affinity of PCBs to oil-based materials.

EPA Response:

With respect to the potential for the asphalt to facilitate upward transport of PCBs, the pavement will be underlain with a minimum of 2-feet of clean material. As there will be no direct contact of the asphalt with PCB-contaminated soil, EPA can find no evidence to support the claim that the pavement will in any way facilitate the transport of PCB-contaminated soils to the surface.

COMMENT 16

Proposed reduction of clean fill in parking areas from 24" to 15" is depending on paving to seal contaminants and is inadequate. Stones should not be considered part of the clean materials deterrent since the void space and porosity will aid moisture penetration which will result in increased "volubility" and vapor release potentials.

EPA Response:

As previously indicated, the Approval requires that the 1.5" final pavement coat not be counted toward meeting the 2-foot clean cover requirement. The granular material (stone) beneath the pavement is functional and will help support the integrity of the pavement. Additionally, granular materials (e.g. stones) help reduce capillary action.

COMMENT 17

Past events demonstrate that the City of New Bedford will not be able to carry out the requirements under the long-term monitoring and maintenance plan. PCB-contaminated

stockpiled soils have been left uncovered and uncontrolled, uncovered and contaminated trucks have left the site, and the site has been left unsecured. The City has demonstrated its unreliability in following acceptable hazardous material handling practices and mitigation.

EPA Response:

The long-term monitoring and maintenance activities include reporting requirements. EPA has the regulatory authority to oversee the City's compliance with the Approval, is committed to do so, and will take appropriate enforcement action against the City where necessary to protect public health and the environment. In addition, the Massachusetts Department of Environmental Protection has its own enforcement capabilities to ensure that the City carries out its responsibilities.

With respect to the purported events alluded to by the commenter, these were identified and discussed at several PIP meetings. The following explanation has been provided by the City of New Bedford:

> The only time stockpiled PCB-contaminated soils were left uncovered was when the piles were being accessed by trained workers. During this time, dust monitoring was conducted in accordance with applicable sections of the EPA approved Work Plan and the SOP included as Work Plan Attachment U. Appropriate dust suppression measures were implemented as necessary to keep the dust level below the risk-based threshold action level.
>
> All trucks transporting PCB-contaminated soils were properly covered and washed down prior to leaving the Site.
>
> All contaminated soil removed from the Site was disposed of at an appropriately licensed disposal facility in accordance with the EPA-approved Work Plan.
>
> The sources of all materials used as clean backfill were inspected and/or tested prior to transporting the materials to the Site.

COMMENT 18

Presence of other compounds such as barium and arsenic require a cover and capping plan akin to a hazardous waste landfill.

EPA Response:

The concentrations of barium and arsenic found at the site were similar to concentrations one would expect to find in urban fill, not in a hazardous waste landfill. However, given the chemical properties of these contaminants, specifically the low volatility and solubility, the capping that is proposed for the site, and the long-term monitoring/maintenance that is required under the Approval, will protect future site users from these site contaminants.

COMMENT 19

The capping plan does not address the lead contamination at the school.

EPA Response:

All site contaminants in the soil, including lead, have been addressed. Lead has similar chemical properties to barium and arsenic. As such, the capping that is proposed for the site, and the long-term monitoring/maintenance that is required under the Approval, will protect future site users from lead as well.

COMMENT 20

No documentation as to "cleanliness" of fill proposed was proposed.

EPA Response:

The specifications for the clean fill were provided in the City's cleanup request. These specifications require that all fill material brought to the site be tested to ensure that it meets regulatory definitions of "clean". In the PCB Regulations, EPA defines "clean" material to contain less than 1 ppm PCBs. Therefore, any fill materials brought to the Site must contain less than 1 ppm PCBs.

COMMENT 21

Only utility corridors have had complete removal of contaminated fill. Other areas, including travel paths, wetlands, play yards, etc. warrant complete removal of contaminants.

EPA Response:

For clarification, no play yards are proposed in the plan nor do any of the drawings or diagrams show such reuse activities. Further, the Activity and Use Limitation which will be placed on the site, will exclude this type of use. With respect to other areas on the site,

the exposure assessment concludes that there will be no unreasonable risk to site users following implementation of the caps, and provided there is long-term monitoring and maintenance of said caps. The Approval requires that the City submit monitoring and maintenance plans for caps, groundwater, sediment, vent gases, and the adjacent wetlands sediment to ensure the long-term integrity of these controls.

COMMENT 22

The venting system is passive and is not positioned to prevent gas venting from re-entering the building through HVAC intakes, windows, or roof access points. An active venting system should be standard for a site with elevated levels of pollutants.

EPA Response:

Given the chemical and physical properties of PCBs, EPA does not believe active venting is necessary. As discussed during the PIP meetings, PCBs have very low volatility and have not been detected in the soil/gas testing. Thus PCBs are not expected to be detected in any appreciable concentration in the venting system. Given this, it is very unlikely that PCBs beneath the school footprint would be detected in the indoor air even if the vapor barrier and venting system were not installed. However, the City proposed the installation of the vapor system as a conservative measure.

As a further safeguard, per *Alan Hanscom (BETA) to Kimberly Tisa (EPA) letter responding to EPA Supplemental Comments on Risk-Based Application, May 18, 2005,* the subslab vents will be located at least 20 feet away from the nearest HVAC unit, making entrance through the HVAC units as well as other access points most unlikely. However, should EPA find that the venting system is insufficient and/or creating indoor air concerns, EPA will require the City to conduct additional measures to correct the problem, such as adding carbon to the outlet of the vent stacks or requiring that the passive venting system be modified to an active venting system.

COMMENT 23

The plan indicates that PCBs are of low "volubility." However, EPA representatives have indicated that PCBs in the harbor are "voluble" under the right conditions and no information is provided on Keith to determine if the school site meets those conditions.

EPA Response:

EPA assumes that the commenter is referring to solubility and volatility. It is generally agreed in the scientific community that PCBs adsorb strongly to soil. Per the site characterization data, the primary PCB of concern at the McCoy Field Site is Aroclor 1254. In general, the more highly chlorinated PCBs, such as Aroclor 1254, will have a lower tendency to leach and therefore are more likely to remain adsorbed to soil. These

facts are supported by both the high octanol to water coefficient (average K_{ow} is 1×10^6) and low water solubility (0.012 mg/L) as well as the results of the soil/gas vapor testing at the site.

A recent publication "*Dioxin and Dioxin-Like Compounds in the Food Study: Strategies to Reduce Exposure,*" published by National Academies Press, 2003, presented a discussion of the environmental mobility of dioxin-like compounds (DLCs), including dioxin-like PCBs. The following are excerpts from this publication:

> "Once below the soil surface, soil-bound DLCs do not appear to move up or down via volatilization without a carrier; this is particularly true for the tetra- and higher chlorinated DLCs. The presence of a solvent such as oil may facilitate the diffusive movement of DLCs through soil."
>
> "In soils, DLCs bind strongly to organic matter with the result that degradation below the soil surface is virtually nonexistent."

Field conditions which would contribute to or facilitate transport of PCBs are not present at McCoy Field. These conditions would include factors such as the presence of other contaminants in which PCBs are soluble (e.g. oils and organic solvents); presence of colloidal particles; or where there is direct evaporation of water in contact with PCB-contaminated materials. The latter is the case with New Bedford Harbor where there are high concentrations of PCBs in the sediments. As the water evaporates it can facilitate partitioning of PCBs into the water column. In general, the partitioning tendency will be greatest with the least chlorinated congeners (mono to tri- chlorinated congeners). Arochlor 1254 has, on average, less than 1% of these congeners.

Given the chemical and physical properties of PCBs, the measures that will be employed at the McCoy Field site, including clean surface caps and activity and use limitations, should reduce to insignificant levels and/or eliminate the potential for release of PCB contamination from the Site. This will be confirmed by the monitoring of groundwater and indoor air.

COMMENT 24

The vapor issue, venting issue and "volubility" issue should be settled before reuse of the site as a school.

EPA Response:

EPA believes these issues have been satisfactorily addressed. As previously discussed, EPA's Approval will be amended to require additional measures should it be determined that an unreasonable risk develops in the future as shown by the environmental and indoor air monitoring.

COMMENT 25

The plan indicates that maintenance personnel need awareness training and information on use limitations created by the PCB contamination. Awareness training does not train maintenance workers to be LSPs and only LSPs should be in control of risk management and oversight.

EPA Response:

As part of the long-term monitoring and maintenance plan, EPA is requiring that a worker training plan be developed. The intent of this training is not to train workers on how to deal with or handle contaminated material nor to become LSPs. Any work occurring beneath any cap and into contaminated materials must be done by a trained professional and not by school personnel. This will also be required under the AUL. The training for everyday on-site workers, (e.g. maintenance staff, landscapers) will serve to acquaint workers with where the contamination is, what activities are allowed and not allowed, what to be aware of in performing their activities, etc., with the intent that the PCBs left on-site are not accidentally disturbed. The City will be required to certify that all workers have taken the training. EPA will require that new workers take the training and that "refreshers" are provided on an annual basis.

COMMENT 26

The McCoy Field draft approval cannot be complete without an effective, detailed monitoring and maintenance plan from the City of New Bedford.

EPA Response:

EPA agrees. The Approval requires that the City of New Bedford submit a detailed monitoring and maintenance plan for the Site, including the surface caps, indoor air, vent gases, groundwater, and wetland sediments. In addition, the Approval requires that the City submit a communication plan and a worker training plan for EPA review and approval.

APPENDIX B:

SUPPORTING INFORMATION FOR SAMPLING AND ANALYSIS

Appendix B1 –Air Sampling Protocol

Keith Middle School
New Bedford, MA

Collection of Polychlorinated Biphenyl (PCB) Samples by EPA Method TO-l0A

Refer to the copy of EPA Method TO-l0A in Appendix B2.

Equipment & Materials (for each foundation vent stack sample)

1. Thomas® Pump or similar
2. Bios Defender™ DryCal® Primary Calibrator or similar
3. 30 feet Teflon® tubing – 1/8-inch I.D.
4. Polyurethane foam (PUF) cartridge (supplied by laboratory)
5. Barometer
6. Thermometer

Sample Collection Method

1. Cover all vent stacks to be sampled with temporary air-tight caps the day before scheduled sampling.
2. Ensure all pumps are in proper working order. Locate nearest power supply to selected sampling locations and ensure power is reliable.
3. Calibrate Thomas Pump using Bios Defender™ DryCal® Primary Calibrator per manufacturer's instructions. Calibration will be conducted with the actual PUF cartridge in place by use of a specialized connector tube.
4. Insert upstream end of a PUF sampling cartridge into the end of the Teflon® sample collection tubing. Connect other end of Teflon® tubing into intake port of the Thomas® Pump.
5. Measure and record ambient barometric pressure and ambient temperature.
6. Lower sampling cartridge at end of Teflon® tubing into the vent stack.
7. Record sampling start time and sampling pump air flow rate.
8. Shield sampling pump from weather as necessary.
9. At end of sampling period, check the flow rate with the Bios Defender™ DryCal® and record on data sheet.
10. Shut off sampling pump, remove sampling cartridge from Teflon® tubing, and seal cartridges.
11. Label cartridge with sample location, sampling start date and time, sampling end date and time.
12. Record time that sampling pump was shut off and record ambient barometric pressure and ambient temperature.
13. Calculate sample volume using the duration of sampling and average flow rate.
14. Transport cartridge to laboratory under chain-of-custody at < 4°C. Include one trip blank (one opened but unused sample cartridge of each type) with each shipment of samples.
15. Secure Teflon® sampling tubing in vent stack for subsequent sampling events.

Collection of Polychlorinated Biphenyl (PCB) Samples by EPA Method TO-4A

Refer to the copy of EPA Method TO-4A in Appendix B2.

Equipment & Materials (for each indoor air sample location)

1. Tisch Environmental, Inc. TE-1000 PUF High Volume Air Sampler (city owned)
2. Tisch Environmental, Inc. TE-5040A Calibrator (city owned)
3. PUF cartridge (supplied by laboratory)
4. Quartz fiber prefilter (supplied by laboratory)
5. Barometer
6. Thermometer

Sample Collection Method

1. Set up sampler in desired location. Sampler should be placed at least 2 meters from any obstacle to air flow. Exhaust hose should be directed away from sampler.
2. Turn on sampler and allow warming up for approximately 10 minutes. Calibrate sampler using TE-5040A orifice per manufacturer's instructions. Turn off sampler.
3. Install prefilter and PUF cartridge in sampler per manufacturer's instructions.
4. Start high volume sampler. Sampling air flow rate should be approximately 250 liters per minute.
5. Record sampling start time and magnehelic gauge reading.
6. After approximately 24 hours, record magnehelic gauge reading and shut off high volume sampler.
7. Remove prefilter and sampling cartridge and package for analyses and for transport to laboratory.
8. Label each cartridge and prefilter with sample location, sampling start date and time, and sampling end date and time.
9. Perform final calculated sampler flow check using the calibration orifice. If calibration deviates by more than 10% from initial reading, mark flow data as suspect and inspect and/or remove sampler from service.
10. Transport cartridge to laboratory under chain-of-custody at < 4°C. Include one trip blank (one unused sample cartridge) with each shipment of samples.

TO-4A

Rental Equipment & Supplies List	**Quantity**
1. Tisch Environmental, Inc. TE-1000 PUF High Volume Air Sampler	5 (City owned)
2. Tisch Environmental, Inc. TE-5040A Calibrator	1 (City owned)
3. TO-4A PUF Cartridges and quartz fiber filters	6 (Supplied by Laboratory)
4. Laptop computer	
5. TE-1000 Calibration instructions/tables	
6. Thermometer	
7. Extension Cords	
8. Gloves	
9. Labels	
10. Aluminum Foil	
11. Cooler	
12. Floor Plan	
13. Field Book	
14. Camera	

TO-l0A

Rental Equipment & Supplies List	**Quantity**
1. Thomas® Pump	9 (Rental)
2. Bios Defender™ DryCal® Primary Calibrator	1 (Rental)
3. Vent Stack Caps	10
4. Barometer	1 (Rental)
5. Teflon® tubing - 1/8- inch ID	(Purchase)
6. TO-10A PUF Cartridges	6(Supplied by Laboratory)
7. Thermometer	
8. Duct Tape	
9. One-gallon zip lock bags	
10 Gloves	
11. Labels	
12. Cooler	
13. 100’ Tape	
14. Roof/Vent Stack Plan	
15. Field Book	
16. Camera	

Appendix B2 – EPA TO-4A and TO-10A Air Sampling Methods

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-4A

Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

Method TO-4A
Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), which was prepared under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, and Scott R. Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development (ORD), were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John O. Burckle, U.S. EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- Heidi Schultz, ERG, Lexington, MA
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

Method TO-4 was originally published in April of 1984 as one of a series of peer reviewed methods in *"Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"* EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-4 has been revised and updated as Method TO-4A in this Compendium to incorporate new or improved sampling and analytical technologies. In addition, this method incorporates ASTM Method D 4861-94, *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air*.

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

Author(s)

- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC
- Ralph Riggin, Battelle Laboratories, Columbus, OH
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC

Peer Reviewers

- Irene D. DeGraff, Supelco, Bellefonte, PA
- Ronald A. Hiles, Indiana University, Bloomington, IN
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled it's production.

DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

METHOD TO-4A

Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)

TABLE OF CONTENTS

Page

1. Scope 4A-1

2. Summary of Method 4A-1

3. Significance 4A-2

4. Applicable Documents 4A-2
   4.1 ASTM Standards 4A-2
   4.2 EPA Documents 4A-2
   4.3 Other Documents 4A-3

5. Definitions 4A-3

6. Interferences 4A-4

7. Safety 4A-4

8. Apparatus 4A-5
   8.1 Sampling 4A-5
   8.2 Sample Clean-up and Concentration 4A-6
   8.3 Sample Analysis 4A-7

9. Equipment and Materials 4A-7
   9.1 Materials for Sample Collection 4A-7
   9.2 Sample Extraction and Concentration 4A-8
   9.3 GC/MS Sample Analysis 4A-8

10. Preparation of PUF Sampling Cartridge 4A-9
   10.1 Summary of Method 4A-9
   10.2 Preparation of Sampling Cartridge 4A-9
   10.3 Procedure for Certification of PUF Cartridge Assembly 4A-10

11. Assembly, Calibration and Collection Using High-Volume Sampling System 4A-11
   11.1 Description of Sampling Apparatus 4A-11
   11.2 Calibration of Sampling System 4A-11
   11.3 Sample Collection 4A-18

TABLE OF CONTENTS (continued)

Page

12. Sample Extraction Procedure 4A-20
    12.1 Sample Extraction 4A-20
    12.2 Sample Cleanup 4A-21

13. Analytical Procedure 4A-22
    13.1 Analysis Organochlorine Pesticides by Capillary Gas Chromatography with Electron Capture Detector (GC/ECD) 4A-22
    13.2 Analysis of Organophosphorus Pesticides by Capillary Gas Chromatography with Flame Photometric or Nitrogen-Phosphorus Detectors (GC/FPD/NPD) 4A-23
    13.3 Analysis of Carbamate and Urea Pesticides by Capillary Gas Chromatography with Nitrogen-Phosphorus Detector 4A-23
    13.4 Analysis of Carbamate, Urea, Pyrethroid, and Phenolic Pesticides by High Performance Liquid Chromatography (HPLC) 4A-24
    13.5 Analysis of Pesticides and PCBs by Gas Chromatography with Mass Spectrometry Detection (GC/MS) 4A-24
    13.6 Sample Concentration 4A-25

14. Calculations 4A-25
    14.1 Determination of Concentration 4A-25
    14.2 Equations 4A-25

15. Performance Criteria and Quality Assurance 4A-27
    15.1 Standard Operating Procedures (SOPs) 4A-28
    15.2 Process, Field, and Solvent Blanks 4A-28
    15.3 Method Precision and Bias 4A-28
    15.4 Method Safety 4A-29

16. References 4A-29

METHOD TO-4A

Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)

1. Scope

1.1 This document describes a method for sampling and analysis of a variety of common pesticides and for polychlorinated biphenyls (PCBs) in ambient air. The procedure is based on the adsorption of chemicals from ambient air on polyurethane foam (PUF) using a high volume sampler.

1.2 The high volume PUF sampling procedure is applicable to multicomponent atmospheres containing common pesticide concentrations from 0.001 to 50 $\mu g/m^3$ over 4- to 24-hour sampling periods. The limits of detection will depend on the nature of the analyte and the length of the sampling period.

1.3 Specific compounds for which the method has been employed are listed in Table 1. The analytical methodology described in Compendium Method TO-4A is currently employed by laboratories throughout the U.S. The sampling methodology has been formulated to meet the needs of common pesticide and PCB sampling in ambient air.

1.4 Compendium Method TO-4 was originally published in 1989 (1). Further updates of the sampling protocol were published as part of Compendium Method TO-13 (2). The method was further modified for indoor air application in 1990 (3). In an effort to keep the method consistent with current technology, Compendium Method TO-4 has incorporated the sampling and analytical procedures in ASTM Method D4861-94 (4) and is published here as Compendium Method TO-4A.

2. Summary of Method

2.1 A high-volume (~8 cfm) sampler is used to collect common pesticides and PCBs on a sorbent cartridge containing PUF. Airborne particles may also be collected, but the sampling efficiency is not known (5). The sampler is operated for 24-hours, after which the sorbent is returned to the laboratory for analysis.

2.2 Pesticides and PCBs are extracted from the sorbent cartridge with 10 percent diethyl ether in hexane and determined by gas chromatography coupled with an electron capture detector (ECD), nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), Hall electrolytic conductivity detector (HECD), or a mass spectrometer (MS). For common pesticides, high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable.

2.3 Interferences resulting from analytes having similar retention times during GC analysis are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by column chromatography.

3. Significance

3.1 Pesticide usage and environmental distribution are common to rural and urban areas of the United States. The application of pesticides can cause adverse health effects to humans by contaminating soil, water, air, plants, and animal life. PCBs are less widely used, due to extensive restrictions placed on their manufacturer. However, human exposure to PCBs continues to be a problem because of their presence in various electrical products.

3.2 Many pesticides and PCBs exhibit bioaccumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance.

3.3 The relatively low levels of such compounds in the environment requires the use of high volume sampling techniques to acquire sufficient sample for analysis. However, the volatility of these compounds prevents efficient collection on filter media. Consequently, Compendium Method TO-4A utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most common pesticides, PCBs, and many other organics within the same volatility range.

3.4 Moreover, modifications to this method has been successfully applied to measurement of common pesticides and PCBs in outdoor air (6), indoor air (3) and for personal respiratory exposure monitoring (3).

4. Applicable Documents

4.1 ASTM Standards

- D1356 *Definition of Terms Relating to Atmospheric Sampling and Analysis*
- D4861-94 *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air*
- E260 *Recommended Practice for General Gas Chromatography Procedures*
- E355 *Practice for Gas Chromatography Terms and Relationships*
- D3686 *Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method*
- D3687 *Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption*
- D4185 *Practice for Measurement of Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry*

4.2 EPA Documents

- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-10, Second Supplement,* U. S. Environmental Protection Agency, EPA 600/4-89-018, March 1989.
- *Manual of Analytical Methods for Determination of Pesticides in Humans and Environmental Standards,* U. S. Environmental Protection Agency, EPA 600/8-80-038, June 1980.
- *Compendium of Methods for the Determination of Air Pollutants in Indoor Air: Method IP-8,* U. S. Environmental Protection Agency, EPA 600/4-90-010, May 1990.

4.3 Other Documents

- Code of Federal Regulations, Title 40, Part 136, Method 604

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard operating procedures (SOPs) should be consistent with ASTM D1356, E260, and E355. All abbreviations and symbols are defined within this document at point of use.]

5.1 Sampling efficiency (SE)-ability of the sampling medium to trap analytes of interest. The percentage of the analyte of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use is indicated by %SE.

5.2 Retention efficiency (RE)-ability of sampling medium to retain a compound added (spiked) to it in liquid solution.

5.3 Retention time (RT)-time to elute a specific chemical from a chromatographic column, for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.4 Relative retention time (RRT)-a rate of RTs for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

5.5 Method detection limit (MDL)-the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero.

5.6 Kuderna-Danish apparatus-the Kuderna-Danish (K-D) apparatus is a system for concentrating materials dissolved in volatile solvents.

5.7 MS-SIM-the GC is coupled to a mass spectrometer where the instrument is programmed to acquire data for only the target compounds and to disregard all others, thus operating in the select ion monitoring mode (SIM). This is performed using SIM coupled to retention time discriminators. The SIM analysis procedure provides quantitative results.

5.8 Sublimation-the direct passage of a substance from the solid state to the gaseous state and back into the solid form without any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly from the vapor phase to the solid state.

5.9 Surrogate standard-a chemically compound (not expected to occur in the environmental sample) which is added to each sample, blank and matrix spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

6. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelution of two or more compounds. The use of capillary or microbore columns with superior resolution or two or more columns of different polarity will frequently eliminate these problems. In addition, selectivity may be further enhanced by use of a MS operated in the selected ion monitoring (SIM) mode as the GC detector. In this mode, co-eluting compounds can often be determined.

6.2 The ECD responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC/ECD analysis. The NPD, FPD, and HECD detectors are element specific, but are still subject to interferences. UV detectors for HPLC are nearly universal, and the electrochemical detector may also respond to a variety of chemicals. Mass spectrometric analyses will generally provide positive identification of specific compounds.

6.3 PCBs and certain common pesticides (e.g., chlordane) are complex mixtures of individual compounds which can cause difficulty in accurately quantifying a particular formulation in a multiple component mixture. PCBs may interfere with the determination of pesticides.

6.4 Contamination of glassware and sampling apparatus with traces of pesticides or PCBs can be a major source of error, particularly at lower analyte concentrations. Careful attention to cleaning and handling procedures is required during all steps of sampling and analysis to minimize this source of error.

6.5 The general approaches listed below should be followed to minimize interferences.

6.5.1 Polar compounds, including certain pesticides (e.g., organophosphorus and carbamate classes) can be removed by column chromatography on alumina. Alumina clean-up will permit analysis of most common pesticides and PCBs (7).

6.5.2 PCBs may be separated from other common pesticides by column chromatography on silicic acid (8,9).

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil (9).

7. Safety

7.1 The toxicity or carcinogencity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for the analyst (10-12).

7.2 PCBs have been classified as a known or suspected, human or mammalian carcinogen. Many of the other common pesticides have been classified as carcinogens. Care must be exercised when working with these substances. This method does not purport to address all safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and

determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the chemical and physical properties of targeted substances.

7.3 Treat all target analytes as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.

7.4 The collection efficiency for common pesticides and PCBs has been demonstrated to be greater than 95 percent for the sampling configuration described in the method (filter and backup adsorbent). Therefore, no field recovery evaluation will occur as part of this procedure.

8. Apparatus

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

8.1 Sampling

8.1.1 High-volume sampler (see Figure 1). Capable of pulling ambient air through the filter/adsorbent cartridge at a flow rate of approximately 8 standard cubic feet per minute (scfm) (0.225 std m^3/min) to obtain a total sample volume of greater than 300 scm over a 24-hour period. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.1.2 Sampling module (see Figure 2). Metal filter holder (Part 2) capable of holding a 102-mm circular particle filter supported by a 16-mesh stainless-steel screen and attaching to a metal cylinder (Part 1) capable of holding a 65-mm O.D. (60-mm I.D.) x 125-mm borosilicate glass sorbent cartridge containing PUF. The filter holder is equipped with inert sealing gaskets (e.g., polytetrafluorethylene) placed on either side of the filter. Likewise, inert, pliable gaskets (e.g., silicone rubber) are used to provide an air-tight seal at each end of the glass sorbent cartridge. The glass sorbent cartridge is indented 20 mm from the lower end to provide a support for a 16-mesh stainless-steel screen that holds the sorbent. The glass sorbent cartridge fits into Part 1, which is screwed onto Part 2 until the sorbent cartridge is sealed between the silicone gaskets. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

A field portable unit has been developed by EPA (see Figure 3).

8.1.3 High-volume sampler calibrator. Capable of providing multipoint resistance for the high-volume sampler. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.1.4 Ice chest. To hold samples at <4°C or below during shipment to the laboratory after collection.

8.1.5 Data sheets. For each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.

8.2 Sample Clean-up and Concentration (see Figure 4).

8.2.1 Soxhlet apparatus extractor (see Figure 4a). Capable of extracting filter and adsorbent cartridges (2.3" x 5" length), 1,000 mL flask, and condenser, best source.

8.2.2 Pyrex glass tube furnace system. For activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually, best source.

8.2.3 Glass vial. 40 mL, best source.

8.2.4 Erlenmeyer flask. 50 mL, best source.

[Note: Reuse of glassware should be minimized to avoid the risk of cross contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400°C for 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8.2.5 White cotton gloves. For handling cartridges and filters, best source.

8.2.6 Minivials. 2 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon®-faced silicone disks, and a vial holder, best source.

8.2.7 Teflon®-coated stainless steel spatulas and spoons. Best source.

8.2.8 Kuderna-Danish (K-D) apparatus (see Figure 4b). 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Kontes K570050-1025 or equivalent) with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-570010500, K-50300-0121, and K-569001-219, or equivalent), best source.

8.2.9 Adsorption column for column chromatography (see Figure 4c). 1-cm x 10-cm with stands.

8.2.10 Glove box. For working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.

8.2.11 Vacuum oven. Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with nitrogen) overnight.

8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate. Best source.

8.2.13 Laboratory refrigerator. Best source.

8.2.14 Boiling chips. Solvent extracted, 10/40 mesh silicon carbide or equivalent, best source.

8.2.15 Water bath. Heated, with concentric ring cover, capable of ±5°C temperature control, best source.

8.2.16 Nitrogen evaporation apparatus. Best source.

8.2.17 Glass wool. High purity grade, best source.

8.3 Sample Analysis

8.3.1 Gas chromatograph (GC). The GC system should be equipped with appropriate detector(s) and either an isothermally controlled or temperature programmed heating oven. Improved detection limits may be obtained with a GC equipped with a cool on-column or splitless injector.

8.3.2 Gas chromatographic column. As an example, a 0.32-mm (I.D.) x 3-mm DB-5, DB-17, DB-608, DB-1701 are available. Other columns may also provide acceptable results.

8.3.3 HPLC column. As an example, a 4.6-mm x 25-cm Zorbax SIL or µBondpak C-18. Other columns may also provide acceptable results.

8.3.4 Microsyringes. 5 µL volume or other appropriate sizes.

8.3.5 Balance. Mettler balance or equivalent.

8.3.6 All required syringes, gases, and other pertinent supplies. To operate the GC/MS system.

8.3.7 Pipettes, micropipettes, syringes, burets, etc. To make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 µL and 100 µL.

9. Equipment and Materials

9.1 Materials for Sample Collection (see Figure 5)

9.1.1 Quartz fiber filter. 102-millimeter bindless quartz microfiber filter, Whatman Inc., 6 Just Road, Fairfield, NJ 07004, Filter Type QMA-4.

9.1.2 Polyurethane foam (PUF) plugs (see Figure 5a). 3-inch thick sheet stock polyurethane type (density .022 g/cm^3). The PUF should be of the polyether type used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; Supelco, Supelco Park, Bellefonte, PA; and SKC Inc., 334 Valley View Road, Eighty Four, PA.

9.1.3 Teflon® end caps (see Figure 5a). For sample cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH and University Research Glassware, Chapel Hill, NC.

9.1.4 Sample cartridge aluminum shipping containers (see Figure 5b). For sample cartridge shipping. Sources of equipment are Tisch Environmental, Village of Cleves, OH and University Research Glassware, Chapel Hill, NC.

9.1.5 Glass sample cartridge (see Figure 5a). For sample collection. Sources of equipment are Tisch Environmental, Village of Cleves, OH; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; and Supelco, Supelco Park, Bellefonte, PA.

9.1.6 Aluminum foil. Best source.

9.1.7 Hexane, reagent grade. Best source.

9.2 Sample Extraction and Concentration

9.2.1 Methylene chloride. Chromatographic grade, glass-distilled, best source.

9.2.2 Sodium sulfate-anhydrous (ACS). Granular (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

9.2.3 Boiling chips. Solvent extracted or heated in a muffle furnace at 450°C for 2 hours, approximately 10/40 mesh (silicon carbide or equivalent).

9.2.4 Nitrogen. High purity grade, best source.
9.2.5 Ether. Chromatographic grade, glass-distilled, best source.
9.2.6 Hexane. Chromatographic grade, glass-distilled, best source.
9.2.7 Dibromobiphenyl. Chromatographic grade, best source. Used for internal standard.
9.2.8 Decafluorobiphenyl. Chromatographic grade, best source. Used for internal standard.
9.2.9 Glass wool. Silanized, extracted with methylene chloride and hexane, and dried.
9.2.10 Diethyl ether. High purity, glass distilled.
9.2.11 Hexane. High purity, glass distilled.
9.2.12 Silica gel. High purity, type 60, 70-230 mesh.
9.2.13 Round bottom evaporative flask. 500 mL, T 24/40 joints, best source.
9.2.14 Capacity soxhlet extractors. 500 mL, with reflux condensers, best source.
9.2.15 Kuderna-Danish concentrator. 500 mL, with Snyder columns, best source.
9.2.16 Graduated concentrator tubes. 10 mL, with 19/22 stoppers, best source.
9.2.17 Graduated concentrator tubes. 1 mL, with 14/20 stoppers, best source.
9.2.18 TFE fluorocarbon tape. 1/2 in., best source.
9.2.19 Filter tubes. Size 40-mm (I.D.) x 80-mm.
9.2.20 Serum vials. 1 mL and 5 mL, fitted with caps lined with TFE fluorocarbon.
9.2.21 Pasteur pipetter. 9 in., best source.
9.2.22 Glass wool. Fired at 500°C, best source.
9.2.23 Alumina. Activity Grade IV, 100/200 mesh.
9.2.24 Glass chromatographic column. 2-mm I.D. x 15-cm long.
9.2.25 Vacuum oven. Connected to water aspirator, best source.
9.2.26 Die. Best source.
9.2.27 Ice chest. Best source.
9.2.28 Silicic Acid. Pesticide quality, best source.
9.2.29 Octachloronaphthalene (OCN). Research grade, best source.
9.2.30 Florisil. Pesticide quality, best source.

9.3 GC Sample Analysis

9.3.1 Gas cylinders of hydrogen, nitrogen, argon/methane, and helium. Ultra high purity, best source.
9.3.2 Combustion air. Ultra high purity, best source.
9.3.3 Zero air. Zero air may be obtained from a cylinder or zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup.
9.3.4 Chromatographic-grade stainless steel tubing and stainless steel fitting. For interconnections, Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL 60015, 312-948-8600, or equivalent.

[Note: All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.]

10. Preparation of PUF Sampling Cartridge

[Note: This method was developed using the PS-1 sample cartridge provider by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring

programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

10.1 Summary of Method

10.1.1 This part of Compendium Method TO-4A discusses pertinent information regarding the preparation and cleaning of the filter, adsorbent, and filter/adsorbent cartridge assembly. The separate batches of filters and adsorbents are extracted with the appropriate solvent.

10.1.2 At least one PUF cartridge assembly and one filter from each batch, or 10 percent of the batch, whichever is greater, should be tested and certified clean before the batch is considered for field use.

10.2 Preparation of Sampling Cartridge

10.2.1 Bake the Whatman QMA-4 quartz filters at 400°C for 5 hours before use.

10.2.2 Set aside the filters in a clean container for shipment to the field or prior to combining with the PUF glass cartridge assembly for certification prior to field deployment.

10.2.3 The PUF plugs are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 2). During cutting, rotate the die at high speed (e.g., in a drill press) and continuously lubricate with deionized or distilled water. Pre-cleaned PUF plugs can be obtained from many of the commercial sources identified in Section 9.1.2.

10.2.4 For initial cleanup, place the PUF plugs in a Soxhlet apparatus and extract with acetone for 16 hours at approximately 4 cycles per hour. When cartridges are reused, use diethyl ether/hexane (10 percent volume/volume [v/v]) as the cleanup solvent.

[Note: A modified PUF cleanup procedure can be used to remove unknown interference components of the PUF blank. This method consists of rinsing 50 times with toluene, acetone, and diethyl ether/hexane (5 to 10 percent v/v), followed by Soxhlet extraction. The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2 to 4 hours (until no solvent odor is detected). Alternatively, they may be dried at room temperature in an air-tight container with circulating nitrogen (zero grade). Place the clean PUF plug into a labeled glass sampling cartridge using gloves and forceps. Wrap the cartridge with hexane-rinsed aluminum foil and placed in a jar fitted with TFE fluorocarbon-lined caps. The foil wrapping may also be marked for identification using a blunt probe. The extract from the Soxhlet extraction procedure from each batch may be analyzed to determine initial cleanliness prior to certification.]

10.2.5 Fit a nickel or stainless steel screen (mesh size 200/200) to the bottom of a hexane-rinsed glass sampling cartridge to retain the PUF adsorbents, as illustrated in Figure 2. Place the Soxhlet-extracted, vacuum-dried PUF (2.5-cm thick by 6.5-cm diameter) on top of the screen in the glass sampling cartridge using polyester gloves.

10.2.6 Wrap the sampling cartridge with hexane-rinsed aluminum foil, cap with the Teflon® end caps, place in a cleaned labeled aluminum shipping container, and seal with Teflon® tape. Analyze at least 1 PUF plug from each batch of PUF plugs using the procedure described in Section 10.3, before the batch is considered acceptable for field use. A blank level of <10 ng/plug and filter for single component compounds is considered to be acceptable. For multiple component mixtures (e.g., PCBs), the blank level should be <100 ng/plug and filter. Cartridges are considered clean for up to 30 days from date of certification when stored in their sealed containers.

10.3 Procedure for Certification of PUF Cartridge Assembly

10.3.1 Extract 1 filter and PUF adsorbent cartridge by Soxhlet extraction and concentrate using a Kuderna-Danish (K-D) evaporator for each lot of filters and cartridges sent to the field.

10.3.2 Assemble the Soxhlet apparatus. Charge the Soxhlet apparatus (see Figure 4a) with 300 mL of the extraction solvent [10 percent (v/v) diethyl ether/hexane] and reflux for 2 hours. Let the apparatus cool, disassemble it, and discard the used extraction solvent. Transfer the filter and PUF glass cartridge to the Soxhlet apparatus (the use of an extraction thimble is optional).

[Note: The filter and adsorbent assembly are extracted together in order to reach detection limits, to minimize cost and to prevent misinterpretation of the data. Separate analyses of the filter and PUF would not yield useful information about the physical state of most of the common pesticides and PCBs at the time of sampling due to evaporative losses of the analyte from the filter during sampling.]

10.3.3 Add between 300 and 350 mL of diethyl ether/hexane (10 percent v/v) to the Soxhlet apparatus. Reflux the sample for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, then disassemble the apparatus.

10.3.4 Assemble a K-D concentrator (see Figure 4b) by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

10.3.5 Transfer the extract by pouring it through a drying column containing about 10 cm of anhydrous granular sodium sulfate (see Figure 4c) and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of 10 percent diethyl ether/hexane to complete the quantitative transfer.

10.3.6 Add 1 or 2 clean boiling chips and attach a 3-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL of the extraction solvent to the top of the column. Place the K-D apparatus on a hot water bath (50°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 5 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of hexane. A 5-mL syringe is recommended for this operation.

[Note: The solvent may have to be exchanged to another solvent to meet the requirements of the analytical procedure selected for the target analytes.]

10.3.7 Concentrate the extract to 1 mL and analyze according to Section 13.

10.3.8 Acceptable levels of common pesticides must be less than 10 ng for each pair of filter and adsorbent assembly analyzed. For multiple component mixtures (e.g., PCBs), the blank level should be less than 100 ng for each pair of filter and adsorbent. Once certified clean, the cartridges can be shipped to the field without being chilled.

11. Assembly, Calibration and Collection Using High-Volume Sampling System

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well.

However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

11.1 Description of Sampling Apparatus

The entire sampling system is diagrammed in Figure 1. This apparatus was developed to operate at a rate of 4 to 10 scfm (0.114 to 0.285 std m^3/min) and is used by EPA for high-volume sampling of ambient air. The method write-up presents the use of this device.

The sampling module (see Figure 2) consists of a filter and a glass sampling cartridge containing the PUF utilized to concentrate common pesticides and PCBs from the air. A field portable unit has been developed by EPA (see Figure 3).

11.2 Calibration of Sampling System

Each sampler should be calibrated (1) when new, (2) after major repairs or maintenance, (3) whenever any audit point deviates from the calibration curve by more than 7 percent, (4) before/after each sampling event, and (5) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling.

11.2.1 Calibration of Orifice Transfer Standard. Calibrate the modified high volume air sampler in the field using a calibrated orifice flow rate transfer standard. Certify the orifice transfer standard in the laboratory against a positive displacement rootsmeter (see Figure 6). Once certified, the recertification is performed rather infrequently if the orifice is protected from damage. Recertify the orifice transfer standard performed once per year utilizing a set of five multiple resistance plates.

[Note: The set of five multihole resistance plates are used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve. The following procedure outlines the steps to calibrate the orifice transfer standard in the laboratory.]

11.2.1.1 Record the room temperature (T_1 in °C) and barometric pressure (P_b in mm Hg) on the Orifice Calibration Data Sheet (see Figure 7). Calculate the room temperature in K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$T_1 \text{ in K} = 273° + T_1 \text{ in } °C$$

11.2.1.2 Set up laboratory orifice calibration equipment as illustrated in Figure 6. Check the oil level of the rootsmeter prior to starting. There are 3 oil level indicators, 1 at the clear plastic end and 2 site glasses, 1 at each end of the measuring chamber.

11.2.1.3 Check for leaks by clamping both manometer lines, blocking the orifice with cellophane tape, turning on the high volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, there is a leak in the system. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

11.2.1.4 Install the 5-hole resistance plate between the orifice and the filter adapter.

11.2.1.5 Turn manometer tubing connectors 1 turn counter-clockwise. Make sure all connectors are open.

11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water.)

11.2.1.7 Turn on the high volume motor and let it run for 5 minutes to set the motor brushes. Turn the motor off. Insure manometers are set to zero. Turn the high volume motor on.

11.2.1.8 Record the time, in minutes, required to pass a known volume of air (approximately 200 to 300 ft^3 of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

11.2.1.9 Record both manometer readings-orifice water manometer ($\triangle H$) and rootsmeter mercury manometer ($\triangle P$) on Orifice Calibration Data Sheet (see Figure 7).

[Note: $\triangle H$ is the sum of the difference from zero (0) of the two column heights.]

11.2.1.10 Turn off the high volume motor.

11.2.1.11 Replace the 5-hole resistance plate with the 7-hole resistance plate.

11.2.1.12 Repeat Sections 11.2.1.3 through 11.2.1.11.

11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 7). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks.

[Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]

11.2.1.14 Correct the measured volumes on the Orifice Calibration Data Sheet:

$$V_{std} = V_m \left(\frac{P_a - \triangle P}{P_{std}}\right)\left(\frac{T_{std}}{T_a}\right)$$

where:

V_{std} = standard volume, std m^3

V_m = actual volume measured by the rootsmeter, m^3

P_a = barometric pressure during calibration, mm Hg

$\triangle P$ = differential pressure at inlet to volume meter, mm Hg

P_{std} = 760 mm Hg

T_{std} = 273 + 25°C = 298 K

T_a = ambient temperature during calibration, K.

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{std} = \frac{V_{std}}{\theta}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min

θ = elapsed time, min

11.2.1.17 Record the standard flow rates to the nearest 0.01 std m^3/min.

11.2.1.18 Calculate and record $\sqrt{\triangle H\ (P_1/P_{std})(298/T_1)}$ value for each standard flow rate.

11.2.1.19 Plot each $\sqrt{\triangle H\ (P_1/P_{std})(298/T_1)}$ value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper and draw a line of best fit between the individual plotted points.

[Note: This graph will be used in the field to determine standard flow rate.]

11.2.2 Calibration of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

For this calibration procedure, the following conditions are assumed in the field:

- The sampler is equipped with a valve to control sample flow rate.
- The sample flow rate is determined by measuring the orifice pressure differential, using a Magnehelic gauge.
- The sampler is designed to operate at a standardized volumetric flow rate of 8 ft^3/min (0.225 m^3/min), with an acceptable flow rate range within 10 percent of this value.
- The transfer standard for the flow rate calibration is an orifice device. The flow rate through the orifice is determined by the pressure drop caused by the orifice and is measured using a "U" tube water manometer or equivalent.
- The sampler and the orifice transfer standard are calibrated to standard volumetric flow rate units (scfm or scmm).
- An orifice transfer standard with calibration traceable to NIST is used.
- A "U" tube water manometer or equivalent, with a 0- to 16-inch range and a maximum scale division of 0.1 inch, will be used to measure the pressure in the orifice transfer standard.
- A Magnehelic gauge or equivalent, with a 9- to 100-inch range and a minimum scale division of 2 inches for measurements of the differential pressure across the sampler's orifice is used.
- A thermometer capable of measuring temperature over the range of 32° to 122°F (0° to 50°C) to ±2°F (±1°C) and referenced annually to a calibrated mercury thermometer is used.
- A portable aneroid barometer (or equivalent) capable of measuring ambient barometric pressure between 500 and 800 mm Hg (19.5 and 31.5 in. Hg) to the nearest mm Hg and referenced annually to a barometer of known accuracy is used.
- Miscellaneous handtools, calibration data sheets or station log book, and wide duct tape are available.

11.2.2.1 Set up the calibration system as illustrated in Figure 8. Monitor the airflow through the sampling system with a venturi/Magnehelic assembly, as illustrated in Figure 8. Audit the field sampling system once per quarter using a flow rate transfer standard, as described in the EPA *High Volume-Sampling Method, 40 CVR 50, Appendix B.* Perform a single-point calibration before and after each sample collection, using the procedures described in Section 11.2.3.

11.2.2.2 Prior to initial multi-point calibration, place an empty glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.20 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desire flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Calibration Data Sheet (see Figure 9).

11.2.2.3 Place the orifice transfer standard on the sampling head and attach a manometer to the tap on the transfer standard, as illustrated in Figure 8. Properly align the retaining rings with the filter holder and secure

by tightening the three screw clamps. Connect the orifice transfer standard by way of the pressure tap to a manometer using a length of tubing. Set the zero level of the manometer or Magnehelic. Attach the Magnehelic gauge to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on face of the gauge.

11.2.2.4 To leak test, block the orifice with a rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler.

Caution: *Avoid running the sampler for too long a time with the orifice blocked. This precaution will reduce the chance that the motor will be overheated due to the lack of cooling air. Such overheating can shorten the life of the motor*.

11.2.2.5 Gently rock the orifice transfer standard and listen for a whistling sound that would indicate a leak in the system. A leak-free system will not produce an upscale response on the sampler's Magnehelic. Leaks are usually caused either by damaged or missing gaskets by cross-threading and/or not screwing sample cartridge together tightly. All leaks must be eliminated before proceeding with the calibration. When the sample is determined to be leak-free, turn off the sampler and unblock the orifice. Now remove the rubber stopper or plug from the calibrator orifice.

11.2.2.6 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a Magnehelic reading of approximately 70 in. is obtained. Allow the Magnehelic and manometer readings to stabilize and record these values on the orifice transfer Field Calibration Data Sheet (see Figure 9).

11.2.2.7 Record the manometer reading under Y1 and the Magnehelic reading under Y2 on the Field Calibration Data Sheet. For the first reading, the Magnehelic should still be at 70 inches as set above.

11.2.2.8 Set the Magnehelic to 60 inches by using the sampler's flow control valve. Record the manometer (Y1) and Magnehelic (Y2) readings on the Field Calibration Data Sheet (see Figure 9).

11.2.2.9 Repeat the above steps using Magnehelic settings of 50, 40, 30, 20, and 10 inches.

11.2.2.10 Turn the voltage variator to maximum power, open the flow control valve, and confirm that the Magnehelic reads at least 100 inches. Turn off the sampler and confirm that the Magnehelic reads zero.

11.2.2.11 Read and record the following parameters on the Field Calibration Data Sheet. Record the following on the calibration data sheet:

Data, job number, and operator's signature;

- Sampler serial number;
- Ambient barometric pressure; and
- Ambient temperature.

11.2.2.12 Remove the "dummy" cartridge and replace with a sample cartridge.

11.2.2.13 Obtain the Manufacturer High Volume Orifice Calibration Certificate.

11.2.2.14 If not performed by the manufacturer, calculate values for each calibrator orifice static pressure (Column 6, inches of water) on the manufacturer's calibration certificate using the following equation:

$$\sqrt{\triangle H(P_a/760)(298/[T_a + 273])}$$

where:

P_a = the barometric pressure (mm Hg) at time of manufacturer calibration, mm Hg

T_a = temperature at time of calibration, °C

11.2.2.15 Perform a linear regression analysis using the values in Column 7 of the manufacturer High Volume Orifice Calibration Certificate for flow rate (Q_{std}) as the "X" values and the calculated values as the Y

values. From this relationship, determine the correlation (CC1), intercept (B1), and slope (M1) for the Orifice Transfer Standard.

11.2.2.16 Record these values on the Field Calibration Data Sheet (see Figure 9).

11.2.2.17 Using the Field Calibration Data Sheet values (see Figure 9), calculate the Orifice Manometer Calculated Values (Y3) for each orifice manometer reading using the following equation:

Y3 Calculation

$$Y3 = [Y1(P_a/760)(298/\{T_a + 273\})]^{½}$$

11.2.2.18 Record the values obtained in Column Y3 on the Field Calibration Data Sheet (see Figure 9).

11.2.2.19 Calculate the Sampler Magnehelic Calculate Values (Y4) using the following equation:

Y4 Calculation

$$Y4 = [Y2(P_a/760)(298/\{T_a + 273\})]^{½}$$

11.2.2.20 Record the value obtained in Column Y4 on the Field Calibration Data Sheet (see Figure 9).

11.2.2.21 Calculate the Orifice Flow Rate (X1) in scm, using the following equation:

X1 Calculation

$$X1 = \frac{Y3 - B1}{M1}$$

11.2.2.22 Record the values obtained in Column X1, on the Field Calibration Data Sheet (see Figure 9).

11.2.2.23 Perform a linear regression of the values in Column X1 (as X) and the values in Column Y4 (as Y). Record the relationship for correlation (CC2), intercept (B2), and slope (M2) on the Field Calibration Data Sheet.

11.2.2.24 Using the following equation, calculate a set point (SP) for the manometer to represent a desired flow rate:

$$\text{Set point (SP)} = [(\text{Expected } P_a)/(\text{Expected } T_a)(T_{std}/P_{std})][M2\ (\text{Desired flow rate}) + B2]^2$$

where:

P_a = Expected atmospheric pressure (P_a), mm Hg
T_a = Expected atmospheric temperature (T_a), °C
M2 = Slope of developed relationship
B2 = Intercept of developed relationship
T_{std} = Temperature standard, 25°C
P_{std} = Pressure standard, 760 mm Hg

11.2.2.25 During monitoring, calculate a flow rate from the observed Magnehelic reading using the following equations:

$$Y5 = [\text{Average Magnehelic Reading } (\Delta H)\ (P_a/T_a)(T_{std}/P_{std})]^{1/2}$$

$$X2 = \frac{Y5 - B2}{M2}$$

where:

Y5 = Corrected Magnehelic reading
X2 = Instant calculated flow rate, scm

11.2.2.26 The relationship in calibration of a sampling system between Orifice Transfer Standard and flow rate through the sampler is illustrated in Figure 10.

11.2.3 Single-Point Audit of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

Single point calibration checks are required as follows:

- Prior to the start of each 24-hour test period.
- After each 24-hour test period. The post-test calibration check may serve as the pre-test calibration check for the next sampling period if the sampler is not moved.
- Prior to sampling after a sample is moved.

For samplers, perform a calibration check for the operational flow rate before each 24-hour sampling event and when required as outlined in the user quality assurance program. The purpose of this check is to track the sampler's calibration stability. Maintain a control chart presenting the percentage difference between a sampler's indicated and measured flow rates. This chart provides a quick reference of sampler flow-rate drift problems and is useful for tracking the performance of the sampler. Either the sampler log book or a data sheet will be used to document flowcheck information. This information includes, but is not limited to, sampler and orifice transfer standard serial number, ambient temperature, pressure conditions, and collected flow-check data.

In this subsection, the following is assumed:

- The flow rate through a sampler is indicated by the orifice differential pressure;
- Samplers are designed to operate at an actual flow rate of 8 scfm, with a maximum acceptable flow-rate fluctuation range of ±10 percent of this value;
- The transfer standard will be an orifice device equipped with a pressure tap. The pressure is measured using a manometer; and
- The orifice transfer standard's calibration relationship is in terms of standard volumetric flow rate (Q_{std}).

11.2.3.1 Perform a single point flow audit check before and after each sampling period utilizing the Calibrated Orifice Transfer Standard (see Section 11.2.1).

11.2.3.2 Prior to single point audit, place a "dummy" glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.19 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desired flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Test Data Sheet (see Figure 11).

11.2.3.3 Place the flow rate transfer standard on the sampling head.

11.2.3.4 Properly align the retaining rings with the filter holder and secure by tightening the 3 screw clamps. Connect the flow rate transfer standard to the manometer using a length of tubing.

11.2.3.5 Using tubing, attach 1 manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

11.2.3.7 Turn on high-volume motor and let run for 5 minutes.

11.2.3.8 Record the pressure differential indicated, ΔH, in inches of water, on the Field Test Data Sheet. Be sure stable ΔH has been established.

11.2.3.9 Record the observed Magnahelic gauge reading, in inches of water, on the Field Test Data Sheet. Be sure stable ΔM has been established.

11.2.3.10 Using previous established Orifice Transfer Standard curve, calculate Q_{xs} (see Section 11.2.2.23).

11.2.3.11 This flow should be within ±10 percent of the sampler set point, normally, 8 ft^3. If not, perform a new multipoint calibration of the sampler.

11.2.3.12 Remove flow rate transfer standard and dummy adsorbent cartridge.

11.3 Sample Collection

11.3.1 General Requirements

11.3.1.1 The sampler should be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

11.3.1.2 All cleaning and sample module loading and unloading should be conducted in a controlled environment, to minimize any chance of potential contamination.

11.3.1.3 When new or when using the sampler at a different location, all sample contact areas need to be cleared. Use triple rinses of reagent grade hexane contained in Teflon® rinse bottles. Allow the solvent to evaporate before loading the PUF modules.

11.3.2 Preparing Cartridge for Sampling

11.3.2.1 Detach the lower chamber of the cleaned sample head. While wearing disposable, clean, lint-free nylon, or powder-free surgical gloves, remove a clean glass adsorbent module from its shipping container. Remove the Teflon® end caps. Replace the end caps in the sample container to be reused after the sample has been collected.

11.3.2.2 Insert the glass module into the lower chamber and tightly reattach the lower chambers to the module.

11.3.2.3 Using clean rinsed (with hexane) Teflon-tipped forceps, carefully place a clean conditioned fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter. Place the aluminum protective cover on top of the cartridge head. Tighten the 3 screw clamps. Ensure that all module connections are tightly assembled. Place a small piece of aluminum foil on the ball-joint of the sample cartridge to protect from back-diffusion of semi-volatile into the cartridge during transporting to the site.

[Note: Failure to do so could result in air flow leaks at poorly sealed locations which could affect sample representativeness.]

11.3.2.4 Place in a carrying bag to take to the sampler.

11.3.3 Collection

11.3.3.1 After the sampling system has been assembled, perform a single point flow check as described in Sections 11.2.3.

11.3.3.2 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

11.3.3.3 With the sample cartridge removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

11.3.3.4 Attach a "dummy" sampling cartridge loaded with the exact same type of filter and PUF media to be used for sample collection.

11.3.3.5 Turn the sampler on and adjust the flow control valve to the desired flow as indicated by the Magnehelic gauge reading determined in Section 11.2.2.24. Once the flow is properly adjusted, take extreme care not to inadvertently alter its setting.

11.3.3.6 Turn the sampler off and remove the "dummy" module. The sampler is now ready for field use.

11.3.3.7 Check the zero reading of the sampler Magnehelic. Record the ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number on the Field Test Data Sheet (see Figure 11). Attach the loaded sampler cartridge to the sampler.

11.3.3.8 Place the voltage variator and flow control valve at the settings used in Section 11.3.2, and the power switch. Activate the elapsed time meter and record the start time. Adjust the flow (Magnehelic setting), if necessary, using the flow control valve.

11.3.3.9 Record the Magnehelic reading every 6 hours during the sampling period. Use the calibration factors (see Section 11.2.2.24) to calculate the desired flow rate. Record the ambient temperature, barometric pressure, and Magnehelic reading at the beginning and during sampling period.

11.3.4 Sample Recovery

11.3.4.1 At the end of the desired sampling period, turn the power off. Carefully remove the sampling head containing the filter and adsorbent cartridge. Place the protective "plate" over the filter to protect cartridge during transport to clean recovery area. Also, place a piece of aluminum foil around the bottom of adsorbent sampler head.

11.3.4.2 Perform a final calculated sampler flow check using the calibration orifice, as described in Section 11.3.2. If calibration deviates by more than 10 percent from initial reading, mark the flow data for that sample as suspect and inspect and/or remove from service, record results on Field Test Data Sheet, Figure 11.

11.3.4.3 Transport adsorbent sampler head to a clean recovery area.

11.3.4.4 While wearing disposable lint free nylon or powder-free surgical gloves, remove the PUF cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

11.3.4.5 Carefully remove the glass fiber filter from the upper chamber using clean Teflon®-tipped forceps.

11.3.4.6 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the PUF.

11.3.4.7 Wrap the combined samples in the original hexane rinsed aluminum foil, attached Teflon® end caps and place them in their *original* aluminum sample container. Complete a sample label and affix it to the aluminum shipping container.

11.3.4.8 Chain-of-custody should be maintained for all samples. Store the containers under dry ice and protect from UV light to prevent possibly photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample at 4°C.

11.3.4.9 Return at least 1 field filter/PUF blank to the laboratory with each group of samples. Treat a field blank exactly as the sample except that no air is drawn through the filter/adsorbent cartridge assembly.

11.3.4.10 Ship and store field samples chilled (<4°) (blue ice is acceptable) until receipt at the analytical laboratory, after which they should be refrigerated at less than or equal to 4°C. Extraction must be performed within 7 days of sampling and analysis within 40 days of extraction.

12. Sample Extraction Procedure

[Note: Sample extraction should be performed under a properly ventilated hood.]

12.1 Sample Extraction

12.1.1 All samples should be extracted within 1 week after collection. All samples should be stored at <4°C until extracted.

12.1.2 All glassware should be washed with a suitable detergent; rinsed with deionized water, acetone, and hexane; rinsed again with deionized water; and fired in an oven (500°C).

12.1.3 Prepare a spiking solution for determination of extraction efficiency. The spiking solution should contain one or more surrogate compounds that have chemical structures and properties similar to those of the analytes of interest. Octachloronaphthalene (OCN) and dibutylchlorendate have been used as surrogates for determination of organochlorine pesticides by GC with an ECD. Tetrachloro-m-xylene and decachlorobiphenyl can also be used together to insure recovery of early and late eluting compounds. For organophosphate pesticides, tributylphosphate or triphenylphosphate may be employed as surrogates. The surrogate solution should be prepared so that addition of 100 μL into the PUF plug results in an extract containing the surrogate compound at the high end of the instrument's calibration range. As an example, the spiking solution for OCN is prepared by dissolving 10 mg of OCN in 10 mL of 10% acetone in n-hexane, followed by serial dilution n-hexane to achieve a final spiking solution of OCN is 1 μg/mL.

[Note: Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sample processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits of 60-120 percent.]

12.1.4 The extracting solution (10% diethyl ether/hexane) is prepared by mixing 1800 mL of freshly opened hexane and 200 mL of freshly opened diethyl ether (preserved with ethanol) to a flask.

12.1.5 All clean glassware, forceps, and other equipment to be used should be rinsed with 10% diethyl ether/hexane and placed on rinsed (10% diethyl ether/hexane) aluminum foil until use. The condensing towers should also be rinsed with 10% diethyl ether/hexane. Then add 700 mL of 10% diethyl ether/hexane to the 1,000 mL round bottom flask and add up to three boiling granules.

12.1.6 Using precleaned (i.e., 10% diethyl ether/hexane Soxhlet extracted) cotton gloves, the filter/PUF cartridge is removed from the sealed container, the PUF removed from the glass cartridge, and the filter/PUF together are placed into the 300 mL Soxhlet extractor using prerinsed forceps.

12.1.7 Before extraction begins, add 100 µL of the OCN solution directly to the top of the PUF plug.

[Note: Incorporating a known concentration of the solution onto the sample provides a quality assurance check to determine recovery efficiency of the extraction and analytical processes.]

12.1.8 Connect the Soxhlet extractor to the 1,000 mL boiling flask and condenser. Wet the glass joints with 10% diethyl ether/hexane to ensure a tight seal between the fittings. If necessary, the PUF plug can be adjusted

using forceps to wedge it midway along the length of the siphon. The above procedure should be followed for all samples, with the inclusion of a blank control sample.

12.1.9 The water flow to the condenser towers of the Soxhlet extraction assembly should be checked and the heating unit turned on. As the samples boil, the Soxhlet extractors should be inspected to ensure that they are filling and siphoning properly (4 to 6 cycles/hour). Samples should cycle for a minimum of 16 hours.

12.1.10 At the end of the extracting process (minimum of 16 hours), the heating unit is turned off and the sample cooled to room temperature.

12.1.11 The extracts are then concentrated to 5 mL using a Kuderna-Danish (K-D) apparatus. The K-D is set up, assembled with concentrator tubes, and rinsed. The lower end of the filter tube is packed with glass wool and filled with sodium sulfate to a depth of 40 mm. The filter tube is then placed in the neck of the K-D. The Soxhlet extractors and boiling flasks are carefully removed from the condenser towers and the remaining solvent is drained into each boiling flask. Sample extract is carefully poured through the filter tube into the K-D. Each boiling flask is rinsed three times by swirling hexane along the sides. Once the sample has drained, the filter tube is rinsed down with hexane. Each Snyder column is attached to the K-D and rinsed to wet the joint for a tight seal. The complete K-D apparatus is placed on a steam bath and the sample is evaporated to approximately 5 mL.

[Note: Do not allow samples to evaporate to dryness.]

Remove sample from the steam bath, rinse the Snyder column with a minimum of hexane, and allow to cool. Adjust sample volume to 10 mL in a concentrator tube, close with a glass stopper, and seal with TFE fluorocarbon tape. Alternatively, the sample may be quantitatively transferred (with concentrator tube rinsing) to prescored vials and brought up to final volume. Concentrated extracts are stored at <4°C until analyzed. Analysis should occur no later than 40 days after sample extraction.

12.2 Sample Cleanup

12.2.1 If only polar compounds are sought, an alumina cleanup procedure is appropriate. Before cleanup, the sample extract is carefully reduced to 1 mL using a gentle stream of clean nitrogen.

12.2.2 A glass chromatographic column (2-mm I.D. x 15-cm long) is packed with alumina (7), activity grade IV, and rinsed with approximately 20 mL of n-hexane. The concentrated sample extract is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as per Section 13.

12.2.3 If both PCBs and common pesticides are sought, alternate cleanup procedures (8,9) may be required (i.e., silicic acid).

12.2.4 Finally, class separation and improved specificity can be achieved by column clean-up and separation on Florisil (9).

13. Analytical Procedure

13.1 Analysis of Organochlorine Pesticides by Capillary Gas Chromatography with Electron Capture Detector (GC/ECD)

[Note: Organochlorine pesticides, PCBs and many nonchlorinated pesticides are responsive to electron capture detection (see Table 1). Most of these compounds can be analyzed at concentration of 1 to 50 ng/mL by GC/ECD. The following procedure is appropriate. Sampling and analytical methods that have been used to determine pesticides and PCBs collected from air using a modification of this methodology have been published (14-22).]

13.1.1 Select GC column (e.g., 0.3-mm by 30-m DB-5 column) and appropriate GC conditions to separate the target analytes. Typical operating parameters for this column with splitless injection are: Carrier gas-chromatography grade helium at a flow rate of 1 to 2 mL/min and a column head pressure of 7 to 9 psi (48 to 60 kPa); injector temperature of 250°C; detector temperature of 350°C; initial oven temperature of 50°C held for 2.0 min., ramped at 15°C/min to 150°C for 8 min, ramped at 10°C/min to 295°C then held for 5 min; purge time of 1.0 min. A typical injection volume is 2 to 3 μL.

13.1.2 Remove sample extract from refrigerator and allow to warm to room temperature.

13.1.3 Prepare standard solution from reference materials of known purity. Analytically pure standards of organochlorine pesticides and PCBs are available from several commercial sources.

13.1.4 Use the standard solutions of the various compounds of interest to determine relative retention times (RRTs) to an internal standard such as p,p'-DDE, aldrin or octachloronaphthalene. Use 1 to 3-μL injections or other appropriate volumes.

13.1.5 Determine detector linearity by injecting standard solutions of three different concentrations (amounts) that bracket the range of analyses. The calibration is considered linear if the relative standard deviation (RSD) of the three response factors for the three standards is 20 percent or less.

13.1.6 Calibrate the system with a minimum of three levels of calibration standards in the linear range. The low standard should be near the analytical method detection limit. The calibration is considered linear if the relative standard deviation (RSD) of the three response factors for the three standards is 20 percent or less. The initial calibration should be verified by the analysis of a standard from an independent source. Recovery of 85 to 115 percent is acceptable. The initial calibration curve should be verified at the begining of each day and after every ten samples by the analysis of the midpoint standard; an RPD of 15% or less is acceptable for continuing use of the initial calibration curve.

13.1.7 Inject 1 to 3 μL of sample extract. Record volume injected to the nearest 0.05 μL.

13.1.8 A typical ECD response for a mixture of single component pesticides using a capillary column is illustrated in Figure 12. If the response (peak height or area) exceeds the calibration range, dilute the extract and reanalyze.

13.1.9 Quantify PCB mixtures by comparison of the total heights or areas of GC peaks (minimum of five) with the corresponding peaks in the best-matching standard. Use Aroclor 1242 for early-eluting PCBs and either Aroclor 1254 or Aroclor 1260 as appropriate for late-eluting PCBs.

13.1.10 If both PCBs and organochlorine pesticides are present in the same sample, use column chromatographic separation on silicic acid (8,9) prior to GC analysis.

13.1.11 If polar compounds are present that interfere with GC/ECD analysis, use column chromatographic cleanup or alumina (7), activity grade IV, in accordance with Section 12.2.

13.1.12 For confirmation use a second GC column such as DB-608. All GC procedures except GC/MS require second column confirmation.

13.1.13 For improved resolution use a capillary column such as an 0.25-mm I.D. x 30-m DB-5 with 0.25 μm film thickness. The following conditions are appropriate.

- Helium carrier gas at 1 mL/min.
- Column temperature program, 90°C (4 min)/16°C/min to 154°C/4°C/min to 270°C.
- Detector, ^{63}Ni ECD at 350°C.
- Make up gas, nitrogen, or 5% methane/95% argon at 60 mL/min.
- Splitless injection, 2 μL maximum.
- Injector temperature, 220°C.

13.1.14 Class separation and improved specificity can be achieved by column chromatographic separation on Florisil (9).

13.1.15 A Hall electrolytic conductivity detector (HECD) operated in the reductive mode may be substituted for the ECD for improved specificity. Sensitivity, however, will be reduced by at least an order of magnitude.

13.2 Analysis of Organophosphorus Pesticides by Capillary Gas Chromatography with Flame Photometric or Nitrogen-Phosphorus Detectors (GC/FPD/NPD)

[Note: Organophosphorus pesticides are responsive to flame photometric and nitrogen-phosphorus (alkali flame ionization) detection. Most of these compounds can be analyzed at concentrations of 50 to 500 ng/mL using either of these detectors.]

13.2.1 Procedures given in Section 13.1.1 through 13.1.9 and Section 13.1.13 through 13.1.14 apply, except for the selection of surrogates.

13.2.2 Use tributylphosphate, triphenylphosphate, or other suitable compound(s) as surrogates to verify extraction efficiency and to determine RRTs.

13.3 Analysis of Carbamate and Urea Pesticides by Capillary Gas Chromatography with Nitrogen-Phosphorus Detector

13.3.1 Trazine, carbamate, and urea pesticides may be determined by capillary GC (DB-5, DB-17, or DB-1701 stationary phase) using nitrogen-phosphorus detection or MS-SIM with detection limits in the 0.05 to 0.2 μL/mL range. Procedures given in Section 13.1.1 through 13.1.9 and Section 13.1.13 through 13.1.14 apply, except for the selection of surrogates, detector, and make up gas.

13.3.2 Thermal degradation may be minimized by reducing the injector temperature to 200°C. HPLC may also be used, but detection limits will be higher (1 to 5 μg/mL).

13.3.3 N-methyl carbamates may be determined using reverse-phase high performance liquid chromatography (HPLC) (C-18) (Section 13.4) and post-column derivization with o-phthaldehyde and fluorescence detection (EPA Method 531). Detection limits of 0.01 to 0.1 μg/mL can be achieved.

13.4 Analysis of Carbamate, Urea, Pyrethroid, and Phenolic Pesticides by High Performance Liquid Chromatography (HPLC)

[Note: Many carbamate pesticides, urea pesticides, pyrethrins, phenols, and other polar pesticides may be analyzed by high HPLC with fixed or variable wavelength UV detection. Either reversed-phase or normal phase chromatography may be used. Detection limits are 0.2 to 10 μg/mL of extract.]

13.4.1 Select HPLC column (i.e., Zorbax-SIL, 46-mm I.D. x 25-cm, or μ-Bondapak C18, 3.9-mm x 30-cm, or equivalent).

13.4.2 Select solvent system (i.e., mixtures of methanol or acetonitrile with water or mixtures of heptane or hexane with isopropanol).

13.4.3 Follow analytical procedures given in Sections 13.1.2 through 13.1.9.

13.4.4 If interferences are present, adjust the HPLC solvent system composition or use column chromatographic clean-up with silica gel, alumina, or Florisil (9).

13.4.5 An electrochemical detector may be used to improve sensitivity for some ureas, carbonates, and phenolics. Much more care is required in using this detector, particularly in removing dissolved oxygen from the mobile phase and sample extracts.

13.4.6 Chlorophenol (di- through penta-) may be analyzed by GC/ECD or GC/MS after derivatization with pentafluorobenzylbromide (EPA Method 604).

13.4.7 Chlorinated phenoxyacetic acid herbicides and pentachlorophenol can be analyzed by GC/ECD or GC/MS after derivatization with diazomethane (EPA Method 515). DB-5 and DBJ-1701 columns (0.25-mm I.D. x 30-m) at 60 to 300°C/4°C per min have been found to perform well.

13.5 Analysis of Pesticides and PCBs by Gas Chromatography with Mass Spectrometry Detection (GC/MS)

[Note: A mass spectrometer operating in the selected ion monitoring mode is useful for confirmation and identification of pesticides.]

13.5.1 A mass spectrometer operating in select ion monitoring (SIM) mode can be used as a sensitive detector for multi-residue determination of a wide variety of pesticides. Mass spectrometers are now available that provide detection limits comparable to nitrogen-phosphorus and electron capture detectors.

13.5.2 Most of the pesticides shown in Table 1 have been successfully determined by GC/MS-SIM. Typical GC operating parameters are as described in Section 13.1.1.

13.5.3 The mass spectrometer is typically operated using positive ion electron impact ionization (70 eV). Other instrumental parameters are instrument specific.

13.5.4 p-Terphenyl-d_{14} is commonly used as a surrogate for GC/MS analysis.

13.5.5 Quantification is typically performed using an internal standard method. 1,4-Dichlorobenzene, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} are commonly used as internal standards. Procedures given in Section 13.1.1 through 13.1.9 and Section 13.1.13 through 13.1.14 apply, except for the selection of surrogates, detector, and make up gas.

13.5.6 See ASTM Practice D 3687 for injection technique, determination of relative retention times, and other procedures pertinent to GC and HPLC analyses.

13.6 Sample Concentration

13.6.1 If concentrations are too low to detect by the analytical procedure of choice, the extract may be concentrated to 1 mL or 0.5 mL by carefully controlled evaporation under an inert atmosphere. The following procedure is appropriate.

13.6.2 Place K-D concentrator tube in a water bath and analytical evaporator (nitrogen blow-down) apparatus. The water bath temperature should be from 25°C to 50°C.

13.6.3 Adjust nitrogen flow through hypodermic needle to provide a gentle stream.

13.6.4 Carefully lower hypodermic needle into the concentrator tube to a distance of about 1 cm above the liquid level.

13.6.5 Continue to adjust needle placement as liquid level decreases.

13.6.6 Reduce volume to slightly below desired level.

13.6.7 Adjust to final volume by carefully rinsing needle tip and concentrator tube well with solvent (usually n-hexane).

14. Calculations

14.1 Determination of Concentration

14.1.1 The concentration of the analyte in the extract solution can be taken from a standard curve where peak height or area is plotted linearly against concentration in nanograms per milliliter (ng/mL). If the detector response is known to be linear, a single point is used as a calculation constant.

14.1.2 From the standard curve, determine the nanograms of analyte standard equivalent to the peak height or area for a particular compound.

14.1.3 Ascertain whether the field blank is contaminated. Blank levels should not exceed 10 ng/sample for organochlorine pesticides or 100 ng/sample for PCBs and other pesticides. If the blank has been contaminated, the sampling series must be held suspect.

14.2 Equations

14.2.1 Quantity of the compound in the sample (A) is calculated using the following equation:

$$A = 1000 \left(\frac{A_s \times V_e}{V_i} \right)$$

where:

A = total amount of analyte in the sample, ng.

A_s = calculated amount of material injected onto the chromatograph based on calibration curve for injected standards, ng.

V_e = final volume of extract, mL.

V_i = volume of extract injected, μL.

1000 = factor for converting microliters to milliliters.

14.2.2 The extraction efficiency (EE) is determined from the recovery of surrogate spike as follows:

$$EE(\%) = \left[\frac{S}{S_a}\right][100]$$

where:

EE = extraction efficiency, %

S = amount of spike recovered, ng.

S_a = amount of spike added to plug, ng.

The extraction efficiency (surrogate recovery) must fall between 60-120% to be acceptable.

14.2.3 The total volume of air sampled under ambient conditions is determined using the following equation:

$$V_a = \frac{\sum_{i=1}^{n} (T_i \times F_i)}{1000 \text{ L/m}^3}$$

where:

V_a = total volume of air sampled, m^3.

T_i = length of sampling segment between flow checks, min.

F_i = average flow during sampling segment, L/min.

14.2.4 The air volume is corrected to EPA standard temperature (25°C) and standard pressure (760 mm Hg) as follows:

$$V_s = V_a \left(\frac{P_b - P_w}{760 \text{ mm Hg}}\right)\left(\frac{298K}{t_A}\right)$$

where:

V_s = volume of air at standard conditions (25°C and 760 mm Hg), std. m^3.

V_a = total volume of air sampled, m^3.

P_b = average ambient barometric pressure, mm Hg.

P_w = vapor pressure of water at calibration temperature, mm Hg.

t_A = average ambient temperature, °C + 273.

14.2.5 If the proper criteria for a sample have been met, concentration of the compound in a standard cubic meter of air sampled is calculated as follows:

$$C_a(\text{ng/std. m}^3) = \left[\frac{(A)}{(V_s)}\right]$$

If it is desired to convert the air concentration value to parts per trillion (ppt) in dry air at standard temperature and pressure (STP), the following conversion is used:

$$ppt = 0.844\ (C_a)$$

The air concentration can be converted to parts per trillion (v/v) in air at STP as follows:

$$pptv = \left[\frac{(24.45)\ (C_a)}{(MW)}\right]$$

where:

MW = molecular weight of the compound of interest, g/g-mole.

14.2.6 If quantification is performed using an internal standard, a relative response factor (RRF) is calculated by the equation:

$$RRF = \left[\frac{(I_s)(C_{is})}{(I_{is})(C_s)}\right]$$

where:

I_s = integrated area of the target analyte peak, counts.

I_{is} = integrated area of the internal standard peak, counts.

C_{is} = concentration of the internal standard, ng/μL.

C_s = concentration of the analyte, ng/µL.

14.2.7 The concentration of the analyte (C_a) in the sample is then calculated as follows:

$$C_a = \frac{(I_s)(C_{is})}{(RRF)(I_{is})}$$

where:

I_s = integrated area of the target analyte peak, counts.

RRF = relative response factor (see Section 14.2.7).

15. Performance Criteria and Quality Assurance

[Note: This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.]

15.1 Standard Operating Procedures (SOPs)

15.1.1 Users should generate SOPs describing the following activities accomplished in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling cartridges, (3) assembly, calibration, and operation of the analytical system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

15.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

15.2 Process, Field, and Solvent Blanks

15.2.1 One filter/PUF cartridge from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.

15.2.2 During each sampling episode, at least one filter/PUF cartridge should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

15.2.3 Before each sampling episode, one PUF plug from each batch of approximately twenty should be spiked with a known amount of the standard solution. The spiked plug will remain in a sealed container and will not be used during the sampling period. The spiked plug is extracted and analyzed with the other samples. This field spike acts as a quality assurance check to determine matrix spike recoveries and to indicate sample degradation.

15.2.4 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no filter/PUF cartridge included) should be carried through the procedure and analyzed.

15.2.5 Levels for process, field and solvent blanks should not exceed 10 ng/sample for single components or 100 ng/sample for multiple component mixtures (i.e., for organochlorine pesticides and PCBs).

15.3 Method Precision and Bias

15.3.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each compound of concern, and the precision and bias of the sampling process.

15.3.2 Several different parameters involved in both the sampling and analysis steps of this method collectively determine the precision and bias with which each compound is detected. As the volume of air sampled is increased, the sensitivity of detection increases proportionately within limits set by: (a) the retention efficiency for each specific component trapped on the polyurethane foam plug, and (b) the background interference associated with the analysis of each specific component at a given site sampled. The sensitivity of detection of samples recovered by extraction depends on: (a) the inherent response of the particular GC detector used in the determinative step, and (b) the extent to which the sample is concentrated for analysis. It is the responsibility of the analyst(s) performing the sampling and analysis steps to adjust parameters so that the required detection limits can be obtained.

15.3.3 The reproducibility of this method for most compounds for which it has been evaluated has been determined to range from ±5 to ±30% (measured as the relative standard deviation) when replicate sampling cartridges are used (N>5). Sample recoveries for individual compounds generally fall within the range of 90 to 110%, but recoveries ranging from 65 to 125% are considered acceptable.

15.4 Method Safety

15.4.1 This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use.

15.4.2 It is the users responsibility to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the users SOP manual.

16. References

1. Riggin, R. M., *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, NC, EPA-600/4-84-041, April 1984.

2. Winberry, W. T. Jr., et al., "Determination of Benzo(a)Pyrene and Other Polynuclear Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatographic (GC) and High Performance Liquid Chromatographic (HPLC) Analysis: Method TO-13," in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Supplement*, U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, NC, EPA-600/4-89-018, March 1989.

3. Winberry, W. T. Jr., et al., "Determination of Organochlorine Pesticides in Indoor Air: Method IP-8," in *Compendium of Methods for the Determination of Air Pollutant in Indoor Air*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-90-010, May 1990.

4. "Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air," *Annual Book of ASTM Standards*, Method D4861-94, ASTM, Philadelphia, PA.

5. Lewis, R., and MacLeod, K., "Portable Sampler for Pesticides and Semi-Volatile Industrial Organic Chemicals in Air," *Anal. Chem.*, Vol. 54, 1982, pp. 310-315.

6. Winberry, W. T. Jr., et al., "Determination of Organochlorine Pesticides in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling with Gas Chromatography/Electron Capture Detector (GC/ECD): Method TO-10, in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Supplement*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-89-018, March 1989.

7. Lewis, R., and Brown, A., and Jackson, M., "Evaluation of Polyurethane Foam for Sampling of Pesticides, Polychlorinated Biphenyls and Polychlorinated Napththalenes in Ambient Air," *Anal. Chem.*, Vol. 49, 1977, pp. 1668-1672.

8. Armour, J., and Burke, J., "Method for Separating Polychlorinated Biphenyls from DDT and Its Analogs," *Journal of the Association of Official Analytical Chemists*, Vol. 53, No. 4, 1970, pp. 761-768.

9. *Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/8-80-038, June 1980 (NTIS No. PB82-208752).

10. *Carcinogens - Working with Carcinogens*, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

11. *OSHA Safety and Health Standards, General Industry*, (29CFR1910), Occupational Safety and Health Administration, OSHA, 2206, Revised, January 1976.

12. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

13. Kogan, V., Kuhlman, M., Coutant, R., and Lewis, R., "Aerosol Filtration in Sorbent Beds," *Journal of the Air and Waste Management Association*, Vol. 43, 1993, pp. 1367-1373.

14. Lewis, R., and Lee, R., "Air Pollution from Pesticide Sources, Occurrences and Dispersion," in: *Air Pollution from Pesticides and Agricultural Processes*, Lee, R., Editor, CRC Press, Boca Raton, FL, 1976, pp. 51-94.

15. Lewis, R., "Problem Associated with Sampling for Semi-Volatile Organic Chemicals in Air," in *Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants*, Air and Waste Management Association, Pittsburgh, PA, 1986, pp. 134-145.

16. Camann, D., Harding, J., and Lewis, R., "Trapping of Particle-Associated Pesticides in Indoor Air by Polyurethane Foam and Evaporation of Soil Track-In as a Pesticide Source," in: *Indoor Air* '90, Vol. 2, Walkinshaw, D., Editor, Canada Mortgage and Housing Corp., Ottawa, 1990, pp. 621-626.

17. Marple, V., Rubow, K., Turner, W., and Spengler, J., "Low Flow Rate Sharp Cut Impactors for Indoor Air Sampling Design and Calibration," *Journal of the Air Pollution Control Association*. Vol. 37, 1987, pp. 1303-1307.

18. Hsu, J., Wheeler, H., Camann, D., Shatterberg, H., Lewis, R., and Bond, A., "Analytical Methods for Detection of Non-Occupational Exposure to Pesticides," *Journal of Chromatographic Science*, Vol. 26, 1988, pp. 181-189.

19. Lewis, R. G., and Jackson, M. D., "Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Semi-Volatile Industrial Organic Chemicals," *Anal. Chem.*, 54, 592-594, 1982.

20. Lewis, R. G., Jackson, M. D., and MacLeod, K. E., "Protocol for Assessment of Human Exposure to Airborne Pesticides," U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/2-80-180, May 1980.

21. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/4-83-027, June 1983.

22. Longbottom, J. E., and Lichtenberg, J. J., "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," U. S. Environmental Protection Agency, Cincinnati, OH, EPA-600/4-82-057, May 1982.

TABLE 1. COMPOUNDS FOR WHICH PROCEDURE HAS BEEN TESTED[1]

Compound	Recommended Analysis[2]	Compound	Recommended Analysis
Alachlor	GC/ECD	Folpet	GC/ECD
Aldrin	GC/ECD	Heptachlor	GC/ECD
Allethrin	HPLC/UV	Heptachlor epoxide	GC/ECD
Aroclor 1242	GC/ECD	Hexachlorobenzene	GC/ECD
Aroclor 1254	GC/ECD	Lindane (γ-BHC)	GC/ECD
Aroclor 1260	GC/ECD	Linuron	HPLC/UV
Atrazine	GC/NPD	Malathion	GC/NPD or FPD
Bendiocarb	HPLC/UV	Methyl parathion	GC/NPD or FPD
BHC (α- and β-Hexachlorocyclohexanes)	GC/ECD	Methoxychlor	GC/FCD
Captan	GC/ECD	Metolachlor	GC/ECD
Carbaryl	HPLC/UV	Mexacarbate	GC/FCD
Carbofuran	HPLC/UV	Mirex	GC/ECD
Chlordane, technical	GC/ECD	Monuron	HPLC/UV
Chlorothalonil	GC/ECD	Trans-nonachlor	GC/ECD
Chlorotoluron	HPLC/UV	Oxychlordane	GC/ECD
Chlorpyritos	GC/ECD	Pentachlorobenzene	GC/ECD
2,4-D esters and salts	GC/ECD	Pentachlophenol	GC/ECD
Dacthal	GC/ECD	Permethrin (cis and trans)	HPLC/UV
ρ,ρ-'DDT	GC/ECD	o-Phenylphenol	HPLC/UV
ρ,ρ-'DDE	GC/ECD	Phorate	GC/NPD or FPD
Diazinon	GC/NPD or FPD	Propazine	GC/NPD
Dicloran	GC/ECD	Propoxur (Baygon)	HPLC/UV
Dieldrin	GC/ECD	Pyrethrin	HPLC/UV
Dicofol	GC/ECD	Resmethrin	HPLC/UV
Dicrotophos	HPLC/UV	Ronnel	GC/ECD
Diuron	HPLC/UV	Simazine	HPLC/UV
Ethyl parathion	GC/NPD or FPD	Terbuthiuron	HPLC/UV
Fenvalerate	HPLC/UV	Trifluralin	GC/ECD
Fluometuron	HPLC/UV		

[1] The following recommendations are specific for that analyte for maximum sensitivity.
[2] GC = gas chromatography; ECD = electron capture detector, FPD = flame photometric detector; HPLC = high performance liquid chromatography; NPD = nitrogen-phosphorus detector; UV = ultraviolet absorption detector; GC/MS = gas chromatography/mass spectrometry may also be used.

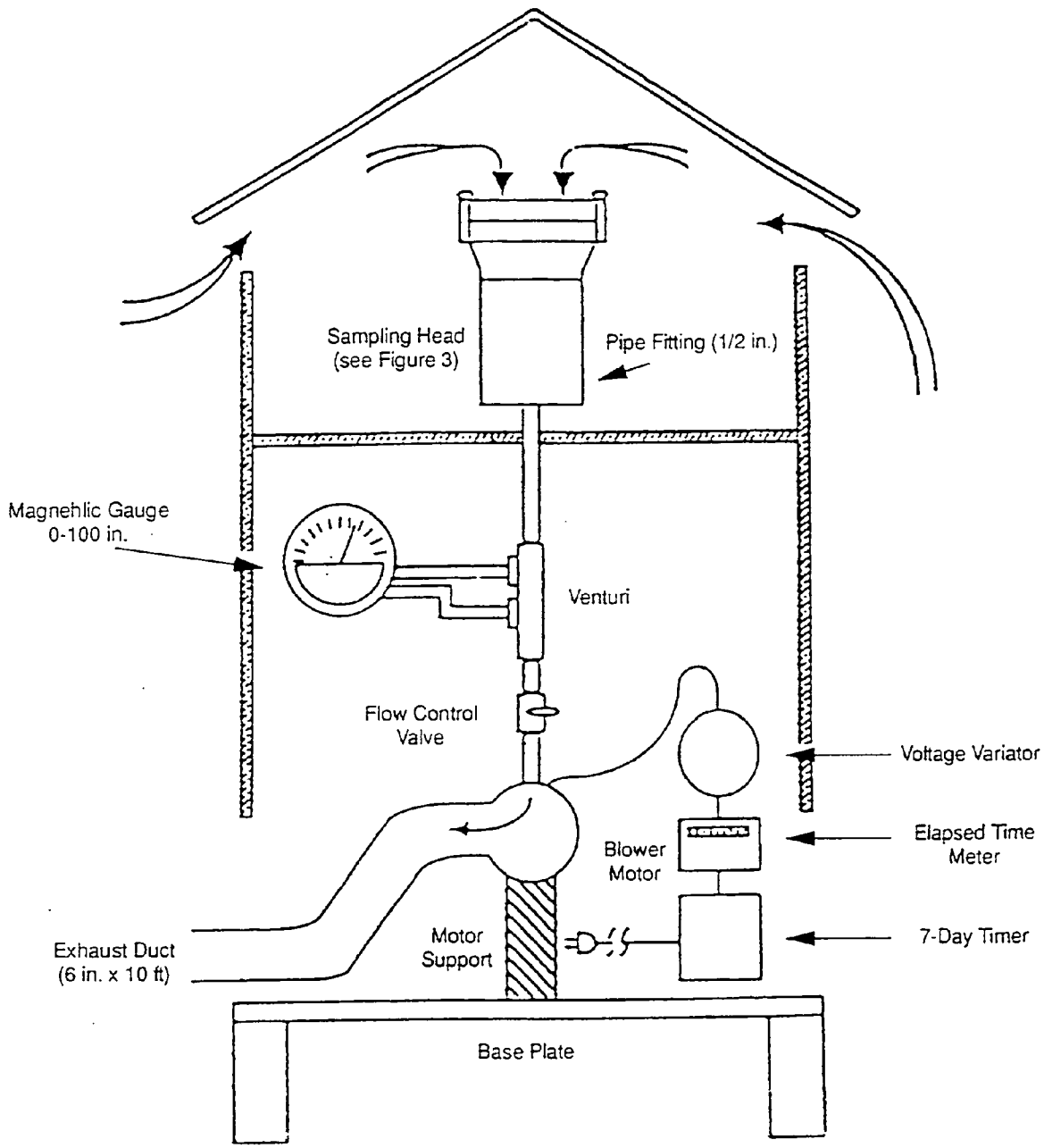


Figure 1. Typical high volume air sampler for monitoring common pesticides and PCBs.

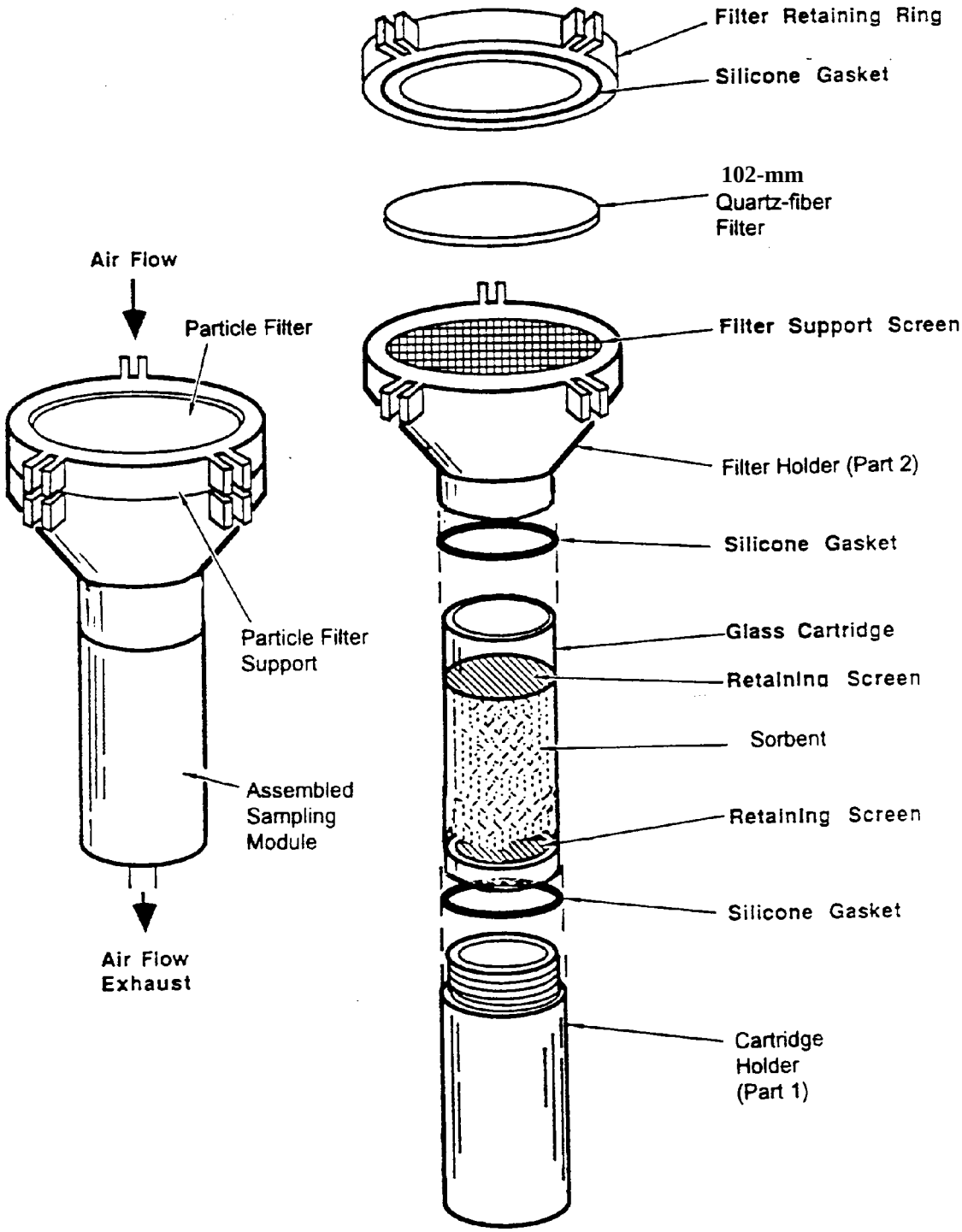


Figure 2. Typical absorbent cartridge assembly for sampling common pesticides and PCBs.

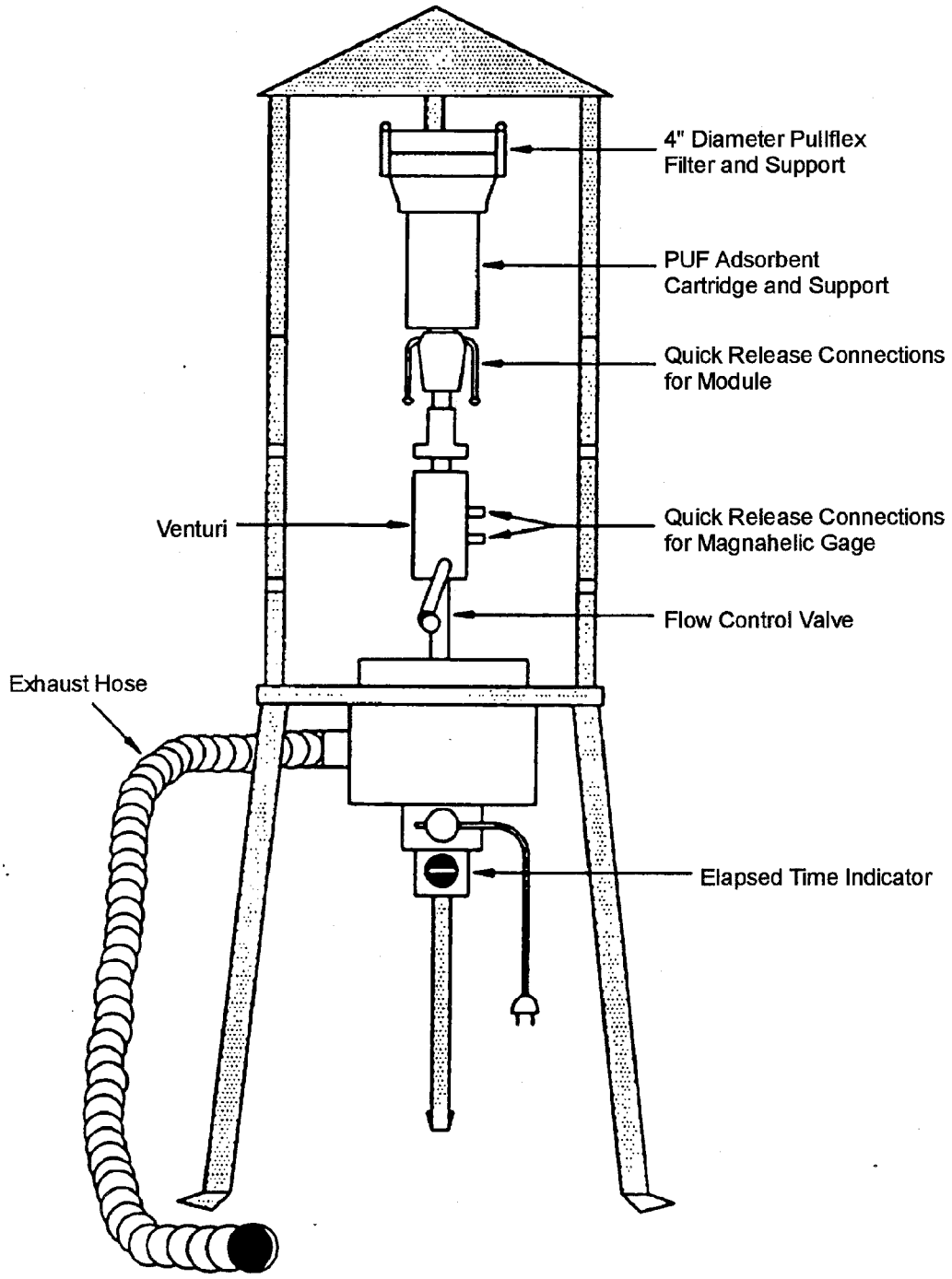


Figure 3. Portable high volume air sampler developed by EPA.

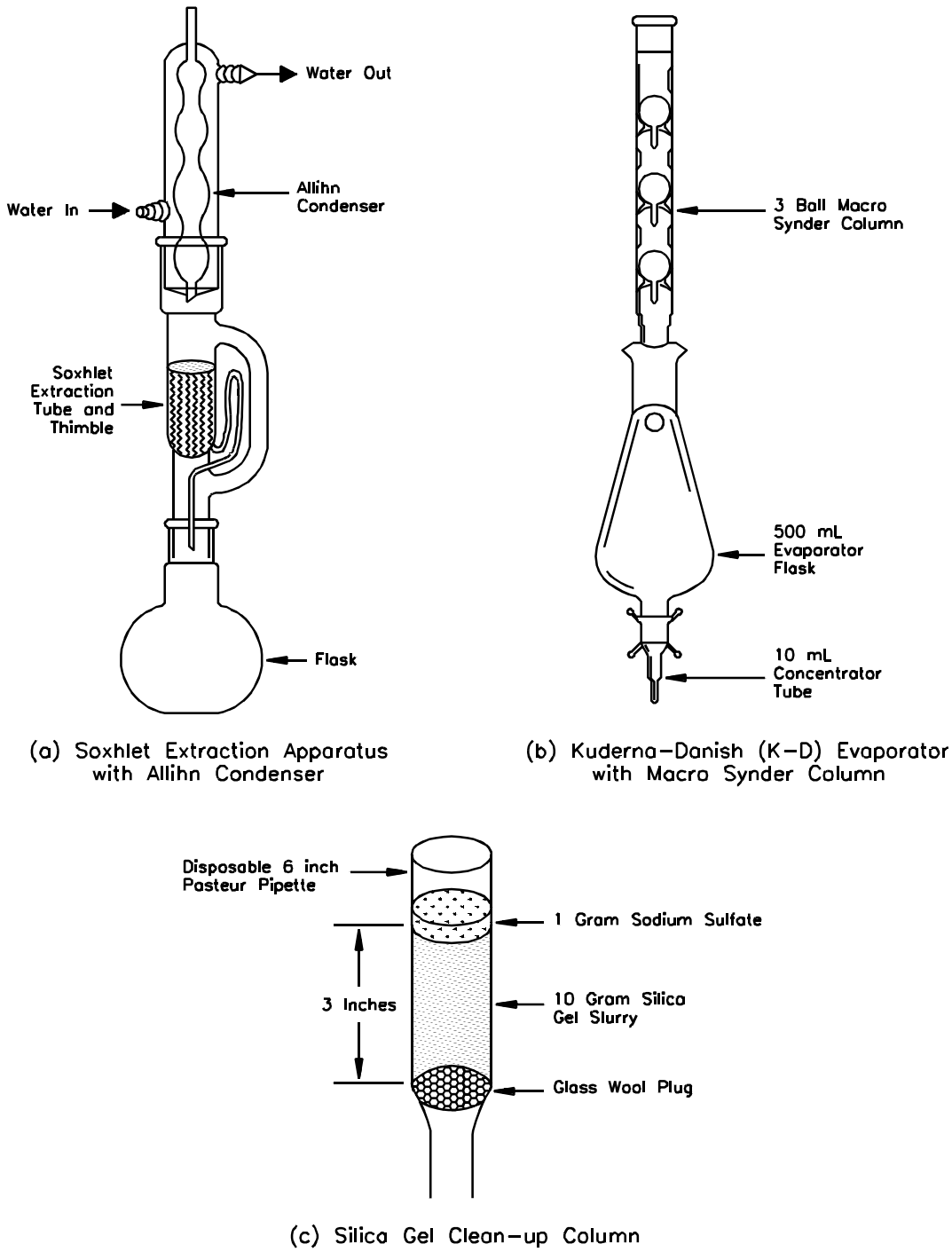
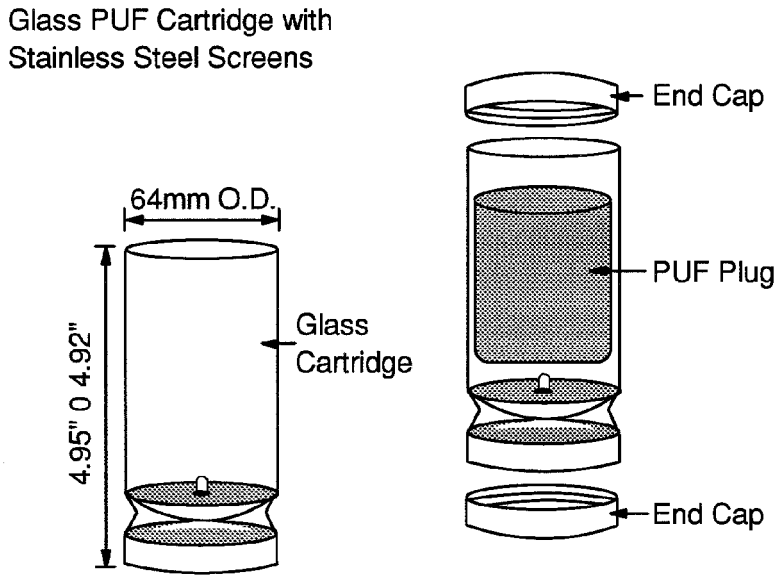
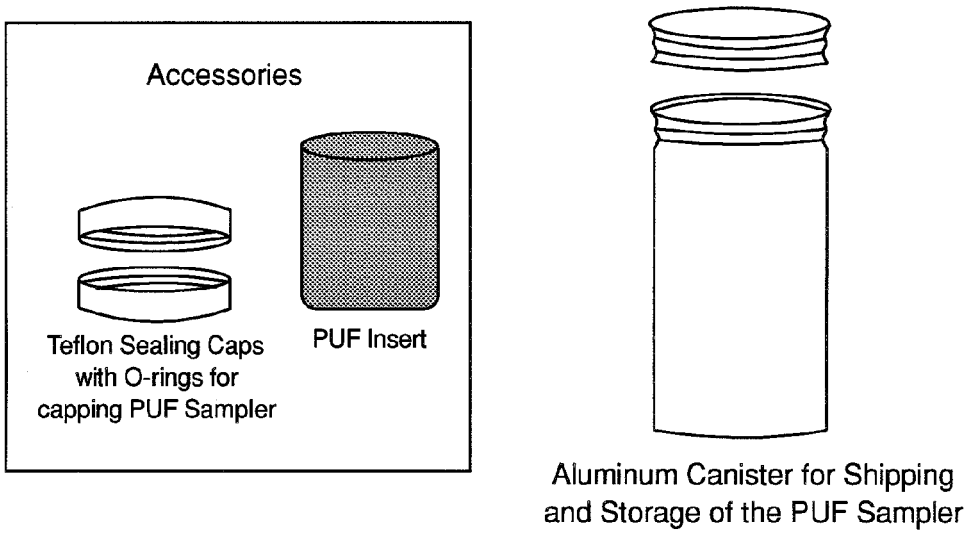


Figure 4. Apparatus used for sample clean-up and extraction.



5a. Glass PUF cartridge, plug, and end caps.



5b. PUF shipping container.

Figure 5. Glass PUF cartridge (5a) and shipping container (5b) for use with high-volume sampling systems.

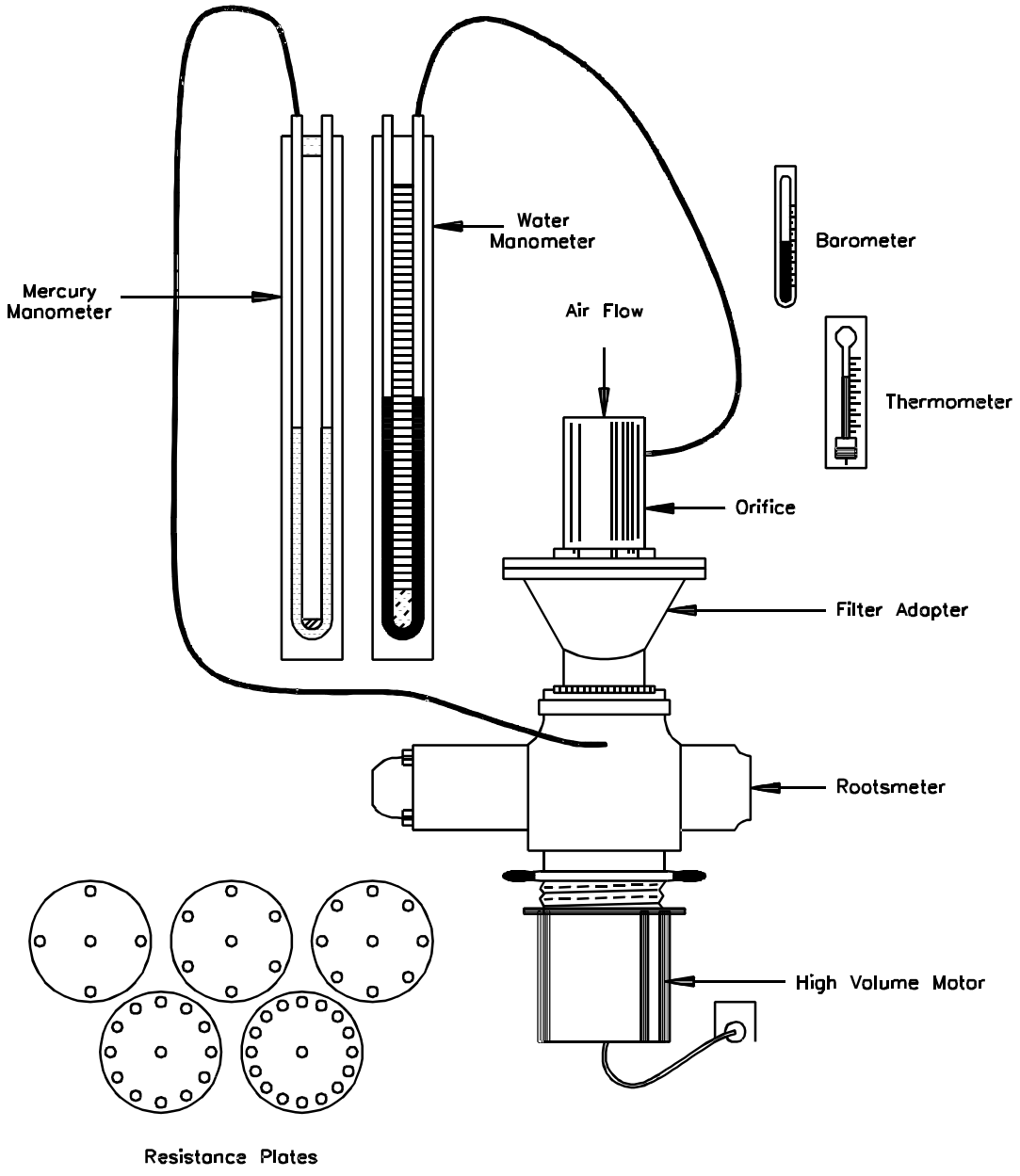


Figure 6. Positive displacement rootsmeter used to calibrate orifice transfer standard.

COMPENDIUM METHOD TO-4A
ORIFICE CALIBRATION DATA SHEET

T_1 _____ Name _____

P_1 _____ mmHg Date _____

Orifice No. _____

Rootsmeter No. _____

Resistance Plants (No. of holes)	Air Volume Measured by Rootsmeter V_m		Standard Volume, V_{std} (std m^3)	Time for Air Volume to Pass Through Rootsmeter, θ (min)	Rootsmeter Pressure Differential, ΔP (mm Hg)	Pressure Drop Across Orifice, ΔH (in. H_2O)	x-Axis Standard Flowrate, Q_{std} (std m^3/min)	Y - axis $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ value
	(R^3)	(m^3)						
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

Factors: $(R^3)(0.02832\ \frac{m^3}{R^3}) = m^3$ and (in. Hg) $25.4\ (\frac{\text{mm Hg}}{\text{in. Hg}})$ = mm Hg

Calculation Equations:

1. $V_{std} = V_m\ (\frac{P_1 - \Delta P}{P_{std}})(\frac{T_{std}}{T_1})$

where:

$T_{std} = 296°K$
$P_{std} = 760.0$ mm Hg

2. $Q_{std} = \frac{V_{std}}{\theta}$

Figure 7. Orifice calibration data sheet.

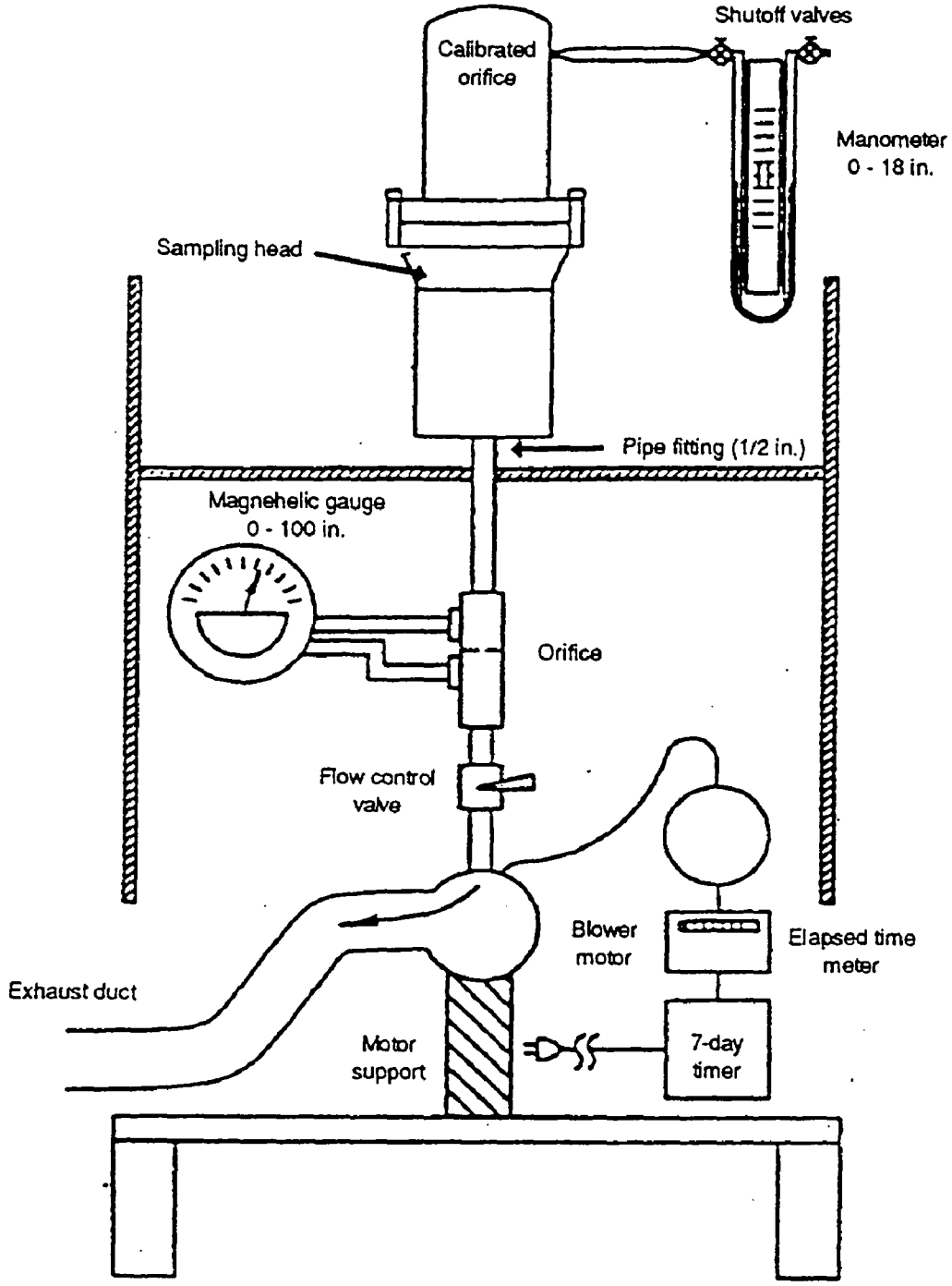


Figure 8. Field calibration configuration of the high-volume sampler for common pesticides and PCBs.

COMPENDIUM METHOD TO-4A
FIELD CALIBRATION DATA SHEET FOR SAMPLER CALIBRATION

Sampler ID: Calibration Orifice ID:

Sampler Location: Job No.:

High Volume Transfer Orifice Data:

Correlation Coefficient (CC1): Slope (M1):

(CC2): (M2):

Intercept (B1):

(B2):

Calibration Date: ____ Time:

Calibration Ambient Temperature: ____°F ____°C CALIBRATOR'S SIGNATURE

Calibration Ambient Barometric Pressure: ____ "Hg ____ mm Hg

Calibration set point (SP): _____

SAMPLER CALIBRATION

Actual values from calibration		Calibrated values		
Orifice manometer, inches (Y1)	Monitor Magnehelic, inches (Y2)	Orifice manometer (Y3)	Monitor Magnehelic (Y4)	Calculated value orifice flow, scm (X1)
	70			
	60			
	50			
	40			
	30			
	20			
	10			

Definitions

Y1 = Calibration orifice reading, in. H_2O

Y2 = Monitor Magnehelic reading, in. H_2O

P_a = Barometric pressure actual, mm Hg

B1 = Manfacturer's Calibration orifice Intercept

M1 = Manufacturer's Calibration orifice manometer slope

Y3 = Calculated value for orifice manometer

= $[Y1(Pa/760)(298/\{Ta + 273\})]^{½}$

Y4 = Calculated value for Magnehelic

= $[Y2(Pa/760)(298/\{Ta + 273\})]^{½}$

X1 = Calculated value orifice flow, scm

$= \frac{Y3 - B1}{M1}$

P_{std} = Barometric pressure standard, 760 mm Hg

T_a = Temperature actual, °C

T_{std} = Temperature standard, 25°C

Figure 9. Orifice transfer standard field calibration data sheet.

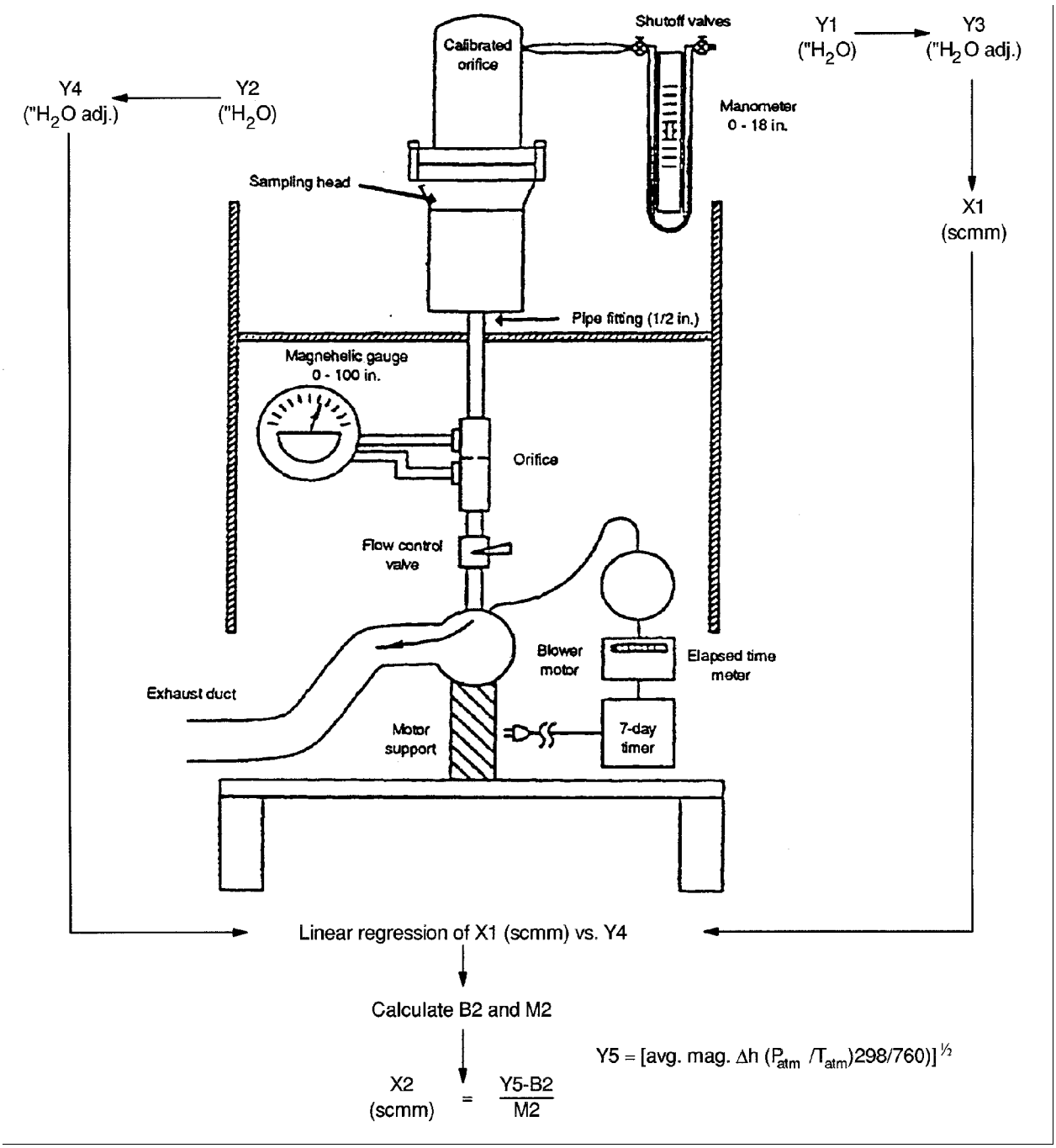


Figure 10. Relationship between orifice transfer standard and flow rate through sampler.

COMPENDIUM METHOD TO-4A
FIELD TEST DATA SHEET
GENERAL INFORMATION

Sampler I.D. No.: _____
Lab PUF Sample No.: _____
Sample location: _____
_____
_____

Operator: _____
Other: _____
_____
_____

PUF Cartridge Certification Date: _____
Date/Time PUF Cartridge Installed: _____
Elapsed Timer: _____
Start _____
Stop _____
Diff. _____
Sampling

M1 _____ **B1** _____
M2 _____ **B2** _____

	Start	Stop
Barometric pressure ("Hg)	_____	_____
Ambient Temperature (°F)	_____	_____
Rain	Yes _____ No _____	Yes _____ No _____

Sampling time
Start _____
Stop _____
Diff. _____

Audit flow check within ±10 of set point
_____ **Yes**
_____ **No**

TIME	TEMP	BAROMETRIC PRESSURE	MAGNEHELIC READING	CALCULATED FLOW RATE (scmm)	READ BY
Avg.					

Comments

_____
_____
_____

Figure 11. Field test data sheet.

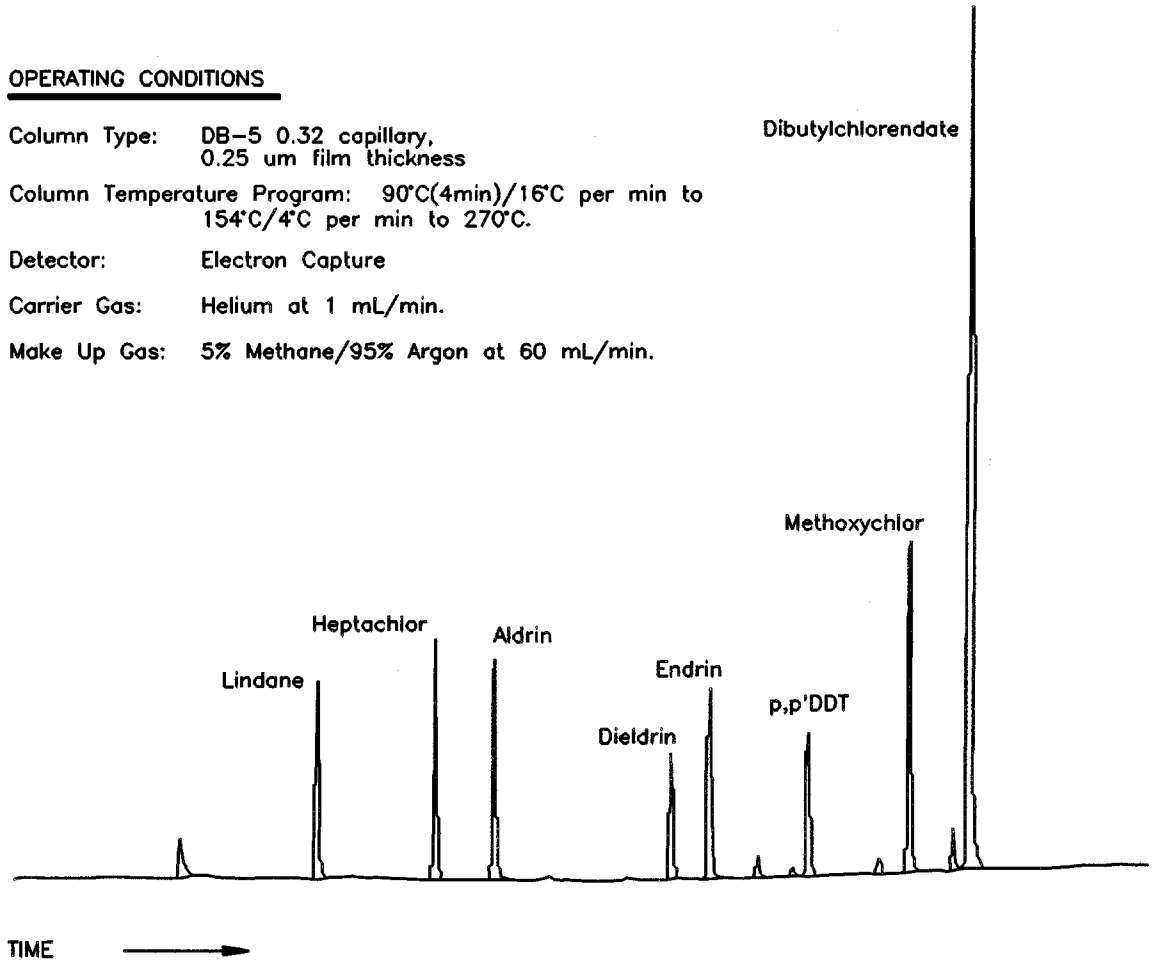


Figure 12. Chromatogram showing a mixture of single component pesticides determined by GC/ECD using a capillary column.

This Page Intentionally Left Blank

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-10A

Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

Method TO-10A
Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), which was prepared under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John Burckle, and Scott R. Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development (ORD), were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John Burckle, U.S. EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- Heidi Schultz, ERG, Lexington, MA
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

Method TO-10 was originally published in March of 1989 as one of a series of peer reviewed methods in the second supplement to *"Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"* EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-10 has been revised and updated as Method TO-10A in this Compendium to incorporate new or improved sampling and analytical technologies. In addition, this method incorporates ASTM Method D 4861-94, *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air*.

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

Author(s)
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC

Peer Reviewers
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC
- Irene D. DeGraff, Supelco, Bellefonte, PA
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled it's production.

DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

METHOD TO-10A

Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD)

TABLE OF CONTENTS

Page

1. Scope 10A-1

2. Summary of Method 10A-1

3. Significance 10A-2

4. Applicable Documents 10A-2
   4.1 ASTM Standards 10A-2
   4.2 EPA Documents 10A-2
   4.3 Other Documents 10A-3

5. Definitions 10A-3

6. Interferences 10A-3

7. Equipment and Materials 10A-4
   7.1 Materials for Sample Collection 10A-4
   7.2 Equipment for Analysis 10A-5
   7.3 Reagents and Other Materials 10A-5

8. Assembly and Calibration of Sampling System 10A-6
   8.1 Description of Sampling Apparatus 10A-6
   8.2 Calibration of Sampling System 10A-6

9. Preparation of PUF Sampling Cartridges 10A-6

10. Sampling 10A-7

11. Sample Extraction Procedure 10A-8
    11.1 Sample Extraction 10A-8
    11.2 Sample Cleanup 10A-9

TABLE OF CONTENTS (continued)

Page

12. Analytical Procedure 10A-10
    12.1 Analysis of Organochlorine Pesticides by Capillary Gas Chromatography with Electron Capture Detector (GC/ECD) 10A-10
    12.2 Analysis of Organophosphorus Pesticides by Capillary Gas Chromatography with Flame Photometric or Nitrogen-Phosphorus Detectors (GC/FPD/NPD) 10A-11
    12.3 Analysis of Carbamate and Urea Pesticides by Capillary Gas Chromatography with Nitrogen-Phosphorus Detector 10A-11
    12.4 Analysis of Carbamate, Urea, Pyrethroid, and Phenolic Pesticides by High Performance Liquid Chromatography (HPLC) 10A-11
    12.5 Analysis of Pesticides and PCBs by Gas Chromatography with Mass Spectrometry Detection (GC/MS) 10A-12
    12.6 Sample Concentration 10A-12

13. Calculations 10A-13
    13.1 Determination of Concentration 10A-13

14. Sampling and Retention Efficiencies 10A-15
    14.1 General 10A-15
    14.2 Determining SE 10A-15

15. Performance Criteria and Quality Assurance 10A-17
    15.1 Standard Operating Procedures (SOPs) 10A-17
    15.2 Process, Field, and Solvent Blanks 10A-17
    15.3 Sampling Efficiency and Spike Recovery 10A-17
    15.4 Method Precision and Bias 10A-18
    15.5 Method Safety 10A-18

16. References 10A-18

METHOD TO-10A

Determination Of Pesticides And Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector (GC/MD) Detection

1. Scope

1.1 This document describes a method for sampling and analysis of a variety of common pesticides and for polychlorinated biphenyls (PCBs) in ambient air. The procedure is based on the adsorption of chemicals from ambient air on polyurethane foam (PUF) or a combination of PUF and granular sorbent using a low volume sampler.

1.2 The low volume PUF sampling procedure is applicable to multicomponent atmospheres containing common pesticide concentrations from 0.001 to 50 $\mu g/m^3$ over 4- to 24-hour sampling periods. The limits of detection will depend on the nature of the analyte and the length of the sampling period.

1.3 Specific compounds for which the method has been employed are listed in Table 1. The analytical methodology described in Compendium Method TO-10A is currently employed by laboratories throughout the U.S. The sampling methodology has been formulated to meet the needs of common pesticide and PCB sampling in ambient air.

1.4 Compendium Method TO-10 was originally published in 1989. The method was further modified for indoor air application in 1990. In an effort to keep the method consistent with current technology, Compendium Method TO-10 has incorporated ASTM Method D4861-94 (1) and is published here as Compendium Method TO-10A.

2. Summary of Method

2.1 A low-volume (1 to 5 L/minute) sample is used to collect vapors on a sorbent cartridge containing PUF or PUF in combination with another solid sorbent. Airborne particles may also be collected, but the sampling efficiency is not known (2).

2.2 Pesticides and other chemicals are extracted from the sorbent cartridge with 5 percent diethyl ether in hexane and determined by gas chromatography coupled with an electron capture detector (ECD), nitrogen-phosphorus detector (NPD), flame photometric detector (FPD), Hall electrolytic conductivity detector (HECD), or a mass spectrometer (MS). For common pesticides, high performance liquid chromatography (HPLC) coupled with an ultraviolet (UV) detector or electrochemical detector may be preferable. This method describes the use of an electron capture detector.

2.3 Interferences resulting from analytes having similar retention times during GC analysis are resolved by improving the resolution or separation, such as by changing the chromatographic column or operating parameters, or by fractionating the sample by column chromatography.

3. Significance

3.1 Pesticide usage and environmental distribution are common to rural and urban areas of the United States. The application of pesticides can cause potential adverse health effects to humans by contaminating soil, water, air, plants, and animal life. However, human exposure to PCBs continues to be a problem because of their presence in the environment.

3.2 Many pesticides and PCBs exhibit bioaccumulative, chronic health effects; therefore, monitoring the presence of these compounds in ambient air is of great importance.

3.3 Use of a portable, low volume PUF sampling system allows the user flexibility in locating the apparatus. The user can place the apparatus in a stationary or mobile location. The portable sampling apparatus may be positioned in a vertical or horizontal stationary location (if necessary, accompanied with supporting structure). Mobile positioning of the system can be accomplished by attaching the apparatus to a person to test air in the individual's breathing zone.

3.4 Moreover, this method has been successfully applied to measurement of common pesticides in outdoor air, indoor air and for personal respiratory exposure monitoring (3).

4. Applicable Documents

4.1 ASTM Standards

- D1356 *Definition of Terms Relating to Atmospheric Sampling and Analysis*
- D4861-94 *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air*
- E260 *Recommended Practice for General Gas Chromatography Procedures*
- E355 *Practice for Gas Chromatography Terms and Relationships*
- D3686 *Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method*
- D3687 *Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption*
- D4185 *Practice for Measurement of Metals in Workplace Atmosphere by Atomic Absorption Spectrophotometry*

4.2 EPA Documents

- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-10, Second Supplement,* U. S. Environmental Protection Agency, EPA 600/4-89-018, March 1989.
- *Manual of Analytical Methods for Determination of Pesticides in Humans and Environmental Standards,* U. S. Environmental Protection Agency, EPA 600/8-80-038, June 1980.
- *Compendium of Methods for the Determination of Air Pollutants in Indoor Air: Method IP-8,* U. S. Environmental Protection Agency, EPA 600/4-90-010, May 1990.

4.3 Other Documents

- Code of Federal Regulations, Title 40, Part 136, Method 604

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard operating procedures (SOPs) should be consistent with ASTM D1356, E260, and E355. All abbreviations and symbols are defined within this document at point of use.]

5.1 Sampling efficiency (SE)-ability of the sampling medium to trap analytes of interest. The percentage of the analyte of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use is indicated by %SE.

5.2 Retention efficiency (RE)-ability of sampling medium to retain a compound added (spiked) to it in liquid solution.

5.3 Static retention efficiency-ability of the sampling medium to retain the solution spike when the sample cartridge is stored under clean, quiescent conditions for the duration of the test period.

5.4 Dynamic retention efficiency (RE_d)-ability of the sampling medium to retain the solution spike when air or nitrogen is drawn through the sampling cartridge under normal operating conditions for the duration of the test period. The dynamic RE is normally equal to or less than the SE.

5.5 Retention time (RT)-time to elute a specific chemical from a chromatographic column, for a specific carrier gas flow rate, measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.6 Relative retention time (RRT)-a rate of RTs for two chemicals for the same chromatographic column and carrier gas flow rate, where the denominator represents a reference chemical.

5.7 Surrogate standard-a chemically inert compound (not expected to occur in the environmental sample) that is added to each sample, blank, and matrix-spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

6. Interferences

6.1 Any gas or liquid chromatographic separation of complex mixtures of organic chemicals is subject to serious interference problems due to coelution of two or more compounds. The use of capillary or microbore columns with superior resolution or two or more columns of different polarity will frequently eliminate these problems. In addition, selectivity may be further enhanced by use of a MS operated in the selected ion monitoring (SIM) mode as the GC detector. In this mode, co-eluting compounds can often be determined.

6.2 The ECD responds to a wide variety of organic compounds. It is likely that such compounds will be encountered as interferences during GC/ECD analysis. The NPD, FPD, and HECD detectors are element specific, but are still subject to interferences. UV detectors for HPLC are nearly universal, and the electrochemical detector may also respond to a variety of chemicals. Mass spectrometric analyses will generally provide positive identification of specific compounds.

6.3 PCBs and certain organochlorine pesticides (e.g., chlordane) are complex mixtures of individual compounds which can cause difficulty in accurately quantifying a particular formulation in a multiple component mixture. PCBs may interfere with the determination of pesticides.

6.4 Contamination of glassware and sampling apparatus with traces of pesticides or PCBs can be a major source of error, particularly at lower analyte concentrations. Careful attention to cleaning and handling procedures is required during all steps of sampling and analysis to minimize this source of error.

6.5 The general approaches listed below should be followed to minimize interferences.

6.5.1 Polar compounds, including certain pesticides (e.g., organophosphorus and carbamate classes) can be removed by column chromatography on alumina. Alumina clean-up will permit analysis of most organochlorine pesticides and PCBs (4).

6.5.2 PCBs may be separated from other organochlorine pesticides by column chromatography on silicic acid (5,6).

6.5.3 Many pesticides can be fractionated into groups by column chromatography on Florisil (6).

7. Equipment and Materials

7.1 Materials for Sample Collection

7.1.1 Continuous-Flow Sampling Pump (see Figure 1). The pump should provide a constant air flow ($\leq\pm5\%$), be quiet and unobtrusive, with a flow rate of 1 to 5 L/min. Sources of equipment are Supelco, Supelco Park, Bellefonte, PA; SKC, 334 Valley View Road, Eighty Four, PA and other manufacturers.

7.1.2 Sampling Cartridge (see Figure 2). Constructed from a 20-mm (I.D.) x 10-cm borosilicate glass tube drawn down to a 7-mm (O.D.) open connection for attachment to the pump by way of flexible tubing (see Figure 1).

7.1.3 Sorbent, Polyurethane Foam (PUF). Cut into a cylinder, 22-mm I.D. and 7.6-cm long, fitted under slight compression inside the cartridge. The PUF should be of the polyether type, (density of 0.0225 g/cm^3). This is the type of foam used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. The PUF sorbent may be cut by one of the following means:

- With a high-speed cutting tool, such as a motorized cork borer. Distilled water should be used to lubricate the cutting tool.
- With a hot wire cutter. Care should be exercised to prevent thermal degradation of the foam.
- With scissors, while plugs are compressed between the 22-mm circular templates.

Alternatively, pre-extracted PUF plugs and glass cartridges may be obtained commercially.

7.1.4 Particle Filter. The collection efficiency of PUF for small-diameter (0.1 to 1 μm) airborne particles is only about 20% (7). However, most pesticides and PCBs exist in air under steady-state conditions primarily as vapors (8). Most particulate-associated pesticides or PCBs, if any, will also tend to be vaporized from filters after collection (9). Collocated sampling with and without a quartz-fiber pre-filter has yielded indistinguishable results for a broad spectrum of pesticides and PCBs found in indoor air (10).

7.1.4.1 An open-face filter may be attached to the sampling cartridge by means of a union for 1-in. (25.4-mm) tubing.

7.1.4.2 A 32-mm diameter quartz microfiber filter (e.g., Palifelex® type 2500 QAT-UP) is placed in the open end of the union and supported by means of a screen or perforated metal plate [e.g., a 304-stainless steel disk, 0.0312-in. (0.8-mm) thick with 1/16-in. (1.6-mm) diameter round perforations at 132 holes per in.^{2} (20 holes/cm^2), 41% open area.]. A 32-mm Viton® O-ring is placed between the filter and outer nut to effect a seal (see Figure 3). This filter holder is available from Supelco Park, Bellefonte, PA; SKC, 334 Forty Eight, PA; and other manufacturers.

7.1.5 Size-Selective Impactor Inlet. A size-selective impactor inlet with an average particle-size cut-point of 2.5 μm or 10 μm mean diameter at a sampling rate of 4 L/min may be used to exclude nonrespirable airborne particulate matter (11). This inlet, particle filter support, sampling cartridge holders are available commercially from Supelco, Supelco Park, Bellefonte, PA; SKC, 334 Forty Eight, PA and University Research Glassware (URG), Chapel Hill, NC.

7.1.6 Tenax-TA. 60/80 mesh, 2,6-diphenylphenylene oxide polymer. Commercially available from Supelco, Supelco Park, Bellefonte, PA and SKC, 334 Forty Eight, PA.

7.2 Equipment for Analysis

7.2.1 Gas Chromatograph (GC). The GC system should be equipped with appropriate detector(s) and either an isothermally controlled or temperature programmed heating oven. Improved detection limits may be obtained with a GC equipped with a cool on-column or splitless injector.

7.2.2 Gas Chromatographic Column. As an example, a 0.32 mm (I.D.) x 30 m DB-5, DB-17, DB-608, and DB-1701 are available. Other columns may also provide acceptable results.

7.2.3 HPLC Column. As an example, a 4.6-mm x 25-cm Zorbax SIL or μBondpak C-18. Other columns may also provide acceptable results.

7.2.4 Microsyringes. 5 μL volume or other appropriate sizes.

7.3 Reagents and Other Materials

7.3.1 Round Bottom Flasks. 500 mL, T 24/40 joints, best source.
7.3.2 Capacity Soxhlet Extractors. 300 mL, with reflux condensers, best source.
7.3.3 Kuderna-Danish Concentrator. 500 mL, with Snyder columns, best source.
7.3.4 Graduated Concentrator Tubes. 10 mL, with 19/22 stoppers, best source.
7.3.5 Graduated Concentrator Tubes. 1 mL, with 14/20 stoppers, best source.
7.3.6 TFE Fluorocarbon Tape. 1/2 in., best source.
7.3.7 Filter Tubes. Size 40 mm (I.D.) x 80 mm.
7.3.8 Serum Vials. 1 mL and 5 mL, fitted with caps lined with TFE fluorocarbon.
7.3.9 Pasteur Pipettes. 9 in., best source.
7.3.10 Glass Wool. Fired at 500°C, best source.
7.3.11 Boiling Chips. Fired at 500°C, best source..
7.3.12 Forceps. Stainless steel, 12 in., best source.
7.3.13 Gloves. Latex or precleaned (5% ether/hexane Soxhlet extracted) cotton.

7.3.14 Steam Bath.
7.3.15 Heating Mantles. 500 mL.
7.3.16 Analytical Evaporator. Nitrogen blow-down.
7.3.17 Acetone. Pesticide quality.
7.3.18 n-Hexane. Pesticide quality.
7.3.19 Diethyl Ether. Preserved with 2% ethanol.
7.3.20 Sodium Sulfate. Anhydrous analytical grade.
7.3.21 Alumina. Activity Grade IV, 100/200 mesh.
7.3.22 Glass Chromatographic Column. 2-mm I.D. x 15-cm long.
7.3.23 Soxhlet Extraction System. Including Soxhlet extractors (500 and 300 mL), variable voltage transformers, and cooling water source.
7.3.24 Vacuum Oven. Connected to water aspirator.
7.3.25 Die.
7.3.26 Ice Chest.
7.3.27 Silicic Acid. Pesticide grade.
7.3.28 Octachloronaphthalene (OCN). Research grade.
7.3.29 Florisil. Pesticide grade.

8. Assembly and Calibration of Sampling System

8.1 Description of Sampling Apparatus

8.1.1 A typical sampling arrangement utilizing a personal air pump is shown in Figure 1. This method is designed to use air sampling pumps capable of pulling air through the sampling cartridge at flow rates of 1 to 5 L/min. The method writeup presents the use of this device.

8.1.2 The sampling cartridge (see Figure 2) consists of a glass sampling cartridge in which the PUF plug or PUF/Tenax® TA "sandwich" is retained.

8.2 Calibration of Sampling System

8.2.1 Air flow through the sampling system is calibrated by the assembly shown in Figure 4. All air sampler must be calibrated in the laboratory before and after each sample collection period, using the procedure described below.

8.2.2 For accurate calibration, attach the sampling cartridge in-line during calibration. Vinyl bubble tubing or other means (e.g., rubber stopper or glass joint) may be used to connect the large end of the cartridge to the calibration system. Refer to ASTM Practice D3686 or D4185, for procedures to calibrate small volume air pumps.

9. Preparation of PUF Sampling Cartridges

9.1 The PUF adsorbent is white and yellows upon exposure to light. The "yellowing" of PUF will not affect its ability to collected pesticides or PCBs.

9.2 For initial cleanup and quality assurance purposes, the PUF plug is placed in a Soxhlet extractor and extracted with acetone for 14 to 24 hours at 4 to 6 cycles per hour.

[Note: If commercially pre-extracted PUF plugs are used, extraction with acetone is not required.]

Follow with a 16-hour Soxhlet extraction with 5% diethyl ether in n-hexane. When cartridges are reused, 5% diethyl ether in n-hexane can be used as the cleanup solvent.

9.3 Place the extracted PUF in a vacuum oven connected to a water aspirator and dry at room temperature for 2 to 4 hours (until no solvent odor is detected). Alternatively, they may be dried at room temperature in an air-tight container with circulating nitrogen (zero grade). Place the clean PUF plug into a labeled glass sampling cartridges using gloves and forceps. Wrap the cartridges with hexane-rinsed aluminum foil and placed in jars fitted with TFE fluorocarbon-lined caps. The foil wrapping may also be marked for identification using a blunt probe.

9.4 Granular sorbents may be combined with PUF to extend the range of use to compounds with saturation vapor pressures greater than 10^{-4} kPa (6). A useful combination trap can be assembled by "sandwiching" 0.6 g of Tenax-TA between two 22-mm I.D. x 3.8-cm pre-cleaned PUF plugs, as shown in Figure 2, Cartridge b. The Tenax-TA should be pre-extracted as described in Section 9.2. This trap may be extracted, vacuum dried, and removed without unloading it.

9.5 Analyze at least one assembled cartridge from each batch as a laboratory blank before the batch is acceptable. A blank level of <10 ng/plug for single component compounds is considered to be acceptable. For multiple component mixtures (e.g., PCBs), the blank level should be <100 ng/plug.

9.6 After cleaning, cartridges are considered clean up to 30 days when stored in sealed containers. Certified clean cartridges do not need to be chilled when shipping to the field.

10. Sampling

[Note: After the sampling system has been assembled and calibrated as per Section 8, it can be used to collect air samples as described below. The prepared sample cartridges should be used within 30 days of certification and should be handled only with latex or precleaned cotton gloves.]

10.1 Carefully remove the clean sample cartridge from the aluminum foil wrapping (the foil is returned to jars for later use) and attached to the pump with flexible tubing. The sampling assembly is positioned with the intake downward or in horizontal position. Locate the sampler in an unobstructed area at least 30 meters from any obstacle to air flow. The PUF or PUF/XAD-2 cartridge intake is positioned 1 to 2 m above ground level. Cartridge height above ground is recorded on the Compendium Method TO-10A field test data sheet (FTDS), as illustrated in Figure 5.

10.2 After the PUF cartridge is correctly inserted and positioned, the power switch is turned on and the sampling begins. The elapsed time meter is activated and the start time is recorded. The pumps are checked during the sampling process and any abnormal conditions discovered are recorded on the FTDS. Ambient temperatures and barometric pressures are measured and recorded periodically during the sampling procedure on the FTDS.

10.3 At the end of the desired sampling period, the power is turned off, the PUF cartridge removed from the sampler and wrapped with the original aluminum foil and placed in a sealed, labeled container for transport, under blue ice (<4°C), back to the laboratory. At least one field blank is returned to the laboratory with each group of

samples. A field blank is treated exactly like a sample except that no air is drawn through the cartridge. Samples are stored at <4°C or below until analyzed in the laboratory. Extraction must occur within 7 days of sampling and analysis within 40 days of extraction. Refer to ASTM D4861-94 (1), Appendix X3 for storage stability for various common pesticides and other compounds on PUF or PUF/Tenax TA sandwich.

11. Sample Extraction Procedure

[Note: Sample extraction should be performed under a properly ventilated hood.]

11.1 Sample Extraction

11.1.1 All samples should be extracted within 1 week after collection. All samples should be stored at <4°C until extracted.

11.1.2 All glassware should be washed with a suitable detergent; rinsed with deionized water, acetone, and hexane; rinsed again with deionized water; and fired in an oven (500°C).

11.1.3 Prepare a spiking solution for determination of extraction efficiency. The spiking solution should contain one or more surrogate compounds that have chemical structures and properties similar to those of the analytes of interest. Octachloronaphthalene (OCN) and dibutylchlorendate have been used as surrogates for determination of organochlorine pesticides by GC with an ECD. Tetrachloro-m-xylene and decachlorobiphenyl can also be used together to insure recovery of early and late eluting compounds. For organophosphate pesticides, tributylphosphate or triphenylphosphate may be employed as surrogates. The surrogate solution should be prepared so that addition of 100 μL into the PUF plug results in an extract containing the surrogate compound at the high end of the instrument's calibration range. As an example, the spiking solution for OCN is prepared by dissolving 10 mg of OCN in 10 mL of 10% acetone in n-hexane, followed by serial dilution n-hexane to achieve a final spiking solution of OCN of 1 μg/mL.

[Note: Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sample processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits of 60-120 percent.]

11.1.4 The extracting solution (5% diethyl ether/hexane) is prepared by mixing 1900 mL of freshly opened hexane and 100 mL of freshly opened diethyl ether (preserved with ethanol) to a flask.

11.1.5 All clean glassware, forceps, and other equipment to be used should be rinsed with 5% diethyl ether/ hexane and placed on rinsed (5% diethyl ether/hexane) aluminum foil until use. The condensing towers should also be rinsed with 5% diethyl ether/hexane. Then add 300 mL or 5% diethyl ether/hexane to the 500 mL round bottom boiling flask and add up to three boiling granules.

11.1.6 Using precleaned (i.e., 5% diethyl ether/hexane Soxhlet extracted) cotton gloves, the glass PUF cartridges are removed from the sealed container, the PUF removed from the glass container and is placed into the 300 mL Soxhlet extractor using prerinsed forceps.

[Note: If "sandwich" trap is used, carefully clean outside walls of cartridge with hexane-soaked cotton swabs or laboratory tissues (discard) and place cartridge into extractor with intake (large end) downward.]

11.1.7 Before extraction begins, add 100 µL of the OCN solution directly to the top of the PUF plug.

[Note: Incorporating a known concentration of the solution onto the sample provides a quality assurance check to determine recovery efficiency of the extraction and analytical processes.]

11.1.8 Connect the Soxhlet extractor to the 500 mL boiling flask and condenser. Wet the glass joints with 5% diethyl ether/hexane to ensure a tight seal between the fittings. If necessary, the PUF plug can be adjusted using forceps to wedge it midway along the length of the siphon. The above procedure should be followed for all samples, with the inclusion of a blank control sample.

11.1.9 The water flow to the condenser towers of the Soxhlet extraction assembly should be checked and the heating unit turned on. As the samples boil, the Soxhlet extractors should be inspected to ensure that they are filling and siphoning properly (4 to 6 cycles/hour). Samples should cycle for a minimum of 16 hours.

11.1.10 At the end of the extracting process (minimum of 16 hours), the heating unit is turned off and the sample cooled to room temperature.

11.1.11 The extracts are then concentrated to 5 mL using a Kuderna-Danish (K-D) apparatus. The K-D is set up, assembled with concentrator tubes, and rinsed. The lower end of the filter tube is packed with glass wool and filled with sodium sulfate to a depth of 40 mm. The filter tube is then placed in the neck of the K-D. The Soxhlet extractors and boiling flasks are carefully removed from the condenser towers and the remaining solvent is drained into each boiling flask. Sample extract is carefully poured through the filter tube into the K-D. Each boiling flask is rinsed three times by swirling hexane along the sides. Once the sample has drained, the filter tube is rinsed down with hexane. Each Synder column is attached to the K-D and rinsed to wet the joint for a tight seal. The complete K-D apparatus is placed on a steam bath and the sample is evaporated to approximately 5 mL.

[Note: Do not allow samples to evaporate to dryness.]

Remove sample from the steam bath, rinse Synder column with minimum of hexane, and allow to cool. Adjust sample volume to 10 mL in a concentrator tube, close with glass stopper and seal with TFE fluorocarbon tape. Alternatively, the sample may be quantitatively transferred (with concentrator tube rinsing) to prescored vials and brought up to final volume. Concentrated extracts are stored at <4°C until analyzed. Analysis should occur no later than 40 days after sample extraction.

11.2 Sample Cleanup

11.2.1 If polar compounds (from example, organophosphorus and carbamate classes) that interfere with GC/ECD analysis are present, use column chromatographic cleanup or alumina. The sample cleanup will permit the analysis of most organochlorine pesticides or PCBs.

11.2.2 Before cleanup, the sample extract is carefully reduced to 1 mL using a gentle stream of clean nitrogen.

11.2.3 A glass chromatographic column (2-mm I.D. x 15-cm long) is packed with alumina, activity grade IV, and rinsed with approximately 20 mL of n-hexane. The concentrated sample extract is placed on the column and eluted with 10 mL of n-hexane at a rate of 0.5 mL/minute. The eluate volume is adjusted to exactly 10 mL and analyzed as per Section 12.

11.2.4 If both PCBs and organochlorine pesticides are sought, alternate cleanup procedures (5,6) may be required (i.e., silicic acid).

11.2.5 Finally, class separation and improved specificity can be achieved by column clean-up and separation on Florisil (6).

12. Analytical Procedure

12.1 Analysis of Organochlorine Pesticides by Capillary Gas Chromatography with Electron Capture Detector (GC/ECD)

[Note: Organochlorine pesticides, PCBs and many nonchlorinated pesticides are responsive to electron capture detection (see Table 1). Most of these compounds can be analyzed at concentration of 1 to 50 ng/mL by GC/ECD. The following procedure is appropriate. Analytical methods that have been used to determine pesticides and PCBs collected from air by this procedure have been published (12).]

12.1.1 Select GC column (e.g., 0.3-mm by 30-m DB-5 column) and appropriate GC conditions to separate the target analytes. Typical operating parameters for this column with splitless injection are: Carrier gas-chromatography grade helium at a flow rate of 1 to 2 mL/min and a column head pressure of 7 to 9 psi (48 to 60 kPa); injector temperature of 250°C; detector temperature of 350°C; initial oven temperature of 50°C held for 2.0 min., ramped at 15°C/min to 150°C for 8 min, ramped at 10°C/min to 295°C then held for 5 min; purge time of 1.0 min. A typical injection volume is 2 to 3 μL.

12.1.2 Remove sample extract from the refrigerator and allow to warm to room temperature.

12.1.3 Prepare standard solution from reference materials of known purity. Analytically pure standards of organochlorine pesticides and PCBs are available from several commercial sources.

12.1.4 Use the standard solutions of the various compounds of interest to determine relative retention times (RRTs) to an internal standard such as p,p'-DDE, aldrin or octachloronaphthalene. Use 1 to 3-μL injections or other appropriate volumes.

12.1.5 Determine detector linearity by injecting standard solutions of three different concentrations (amounts) that bracket the range of analyses. The calibration is considered linear if the relative standard deviation (RSD) of the response factors for the three standards is 20 percent or less.

12.1.6 Calibrate the system with a minimum of three levels of calibration standards in the linear range. The low standard should be near the analytical method detection limit. The calibration is considered linear if the relative standard deviation (RSD) of the response factors for the three standards is 20 percent or less. The initial calibration should be verified by the analysis of a standard from an independent source. Recovery of 85 to 115 percent is acceptable. The initial calibration curve should be verified at the begining of each day and after every ten samples by the analysis of the mid point standard; an RPD of 15% or less is acceptable for continuing use of the initial calibration curve.

12.1.7 Inject 1 to 3 μL of the sample extract. Record volume injected to the nearest 0.05 μL.

12.1.8 A typical ECD response for a mixture of single component pesticides using a capillary column is illustrated in Figure 6. If the response (peak height or area) exceeds the calibration range, dilute the extract and reanalyze.

12.1.9 Quantify PCB mixtures by comparison of the total heights or areas of GC peaks (minimum of 5) with the corresponding peaks in the best-matching standard. Use Aroclor 1242 for early-eluting PCBs and either Aroclor 1254 or Aroclor 1260 as appropriate for late-eluting PCBs.

12.1.10 If both PCBs and organochlorine pesticides are present in the same sample, use column chromatographic separation on silicic acid (5,6) prior to GC analysis.

12.1.11 If polar compounds are present that interfere with GC/ECD analysis, use column chromatographic cleanup or alumina, activity grade IV, in accordance with Section 11.2.

12.1.12 For confirmation use a second GC column such as DB-608. All GC procedures except GC/MS require second column confirmation.

12.1.13 For improved resolution use a capillary column such as an 0.25-mm I.D. x 30-m DB-5 with 0.25 μm film thickness. The following conditions are appropriate.

- Helium carrier gas at 1 mL/min.
- Column temperature program, 90°C (4 min)/16°C/min to 154°C/4°C/min to 270°C.
- Detector, ^{63}Ni ECD at 350°C.
- Make up gas, nitrogen, or 5% methane/95% argon at 60 mL/min.
- Splitless injection, 2 μL maximum.
- Injector temperature, 220°C.

12.1.14 Class separation and improved specificity can be achieved by column chromatographic separation on Florisil (6).

12.2 Analysis of Organophosphorus Pesticides by Capillary Gas Chromatography with Flame Photometric or Nitrogen-Phosphorus Detectors (GC/FPD/NPD)

[Note: Organophosphorus pesticides are responsive to flame photometric and nitrogen-phosphorus (alkali flame ionization) detection. Most of these compounds can be analyzed at concentrations of 50 to 500 ng/mL using either of these detectors.]

12.2.1 Procedures given in Section 12.1.1 through 12.1.9 and Section 12.1.13 through 12.1.14 apply, except for the selection of surrogates.

12.2.2 Use tributylphosphate, triphenylphosphate, or other suitable compound(s) as surrogates to verify extraction efficiency and to determine RRTs.

12.3 Analysis of Carbamate and Urea Pesticides by Capillary Gas Chromatography with Nitrogen-Phosphorus Detector

12.3.1 Trazine, carbamate, and urea pesticides may be determined by capillary GC (DB-5, DB-17, or DB-1701 stationary phase) using nitrogen-phosphorus detection or MS-SIM with detection limits in the 0.05 to 0.2 μL/mL range. Procedures given in Section 12.1.1 through 12.1.9 and Section 12.1.13 through 12.1.14 apply, except for the selection of surrogates, detector, and make up gas.

12.3.2 Thermal degradation may be minimized by reducing the injector temperature to 200°C. HPLC may also be used, but detection limits will be higher (1 to 5 μg/mL).

12.3.3 N-methyl carbamates may be determined using reverse-phase high performance liquid chromatography (HPLC) (C-18) (Section 12.4) and post-column derivatization with o-phthaldehyde and fluorescence detection (EPA Method 531). Detection limits of 0.01 to 0.1 μg/mL can be achieved.

12.4 Analysis of Carbamate, Urea, Pyrethroid, and Phenolic Pesticides by High Performance Liquid Chromatography (HPLC)

[Note: Many carbamate pesticides, urea pesticides, pyrethrins, phenols, and other polar pesticides may be analyzed by high HPLC with fixed or variable wavelength UV detection. Either reversed-phase or normal phase chromatography may be used. Detection limits are 0.2 to 10 μg/mL of extract.]

12.4.1 Select HPLC column (i.e., Zorbax-SIL, 46-mm I.D. x 25-cm, or μ-Bondapak C18, 3.9-mm x 30-cm, or equivalent).

12.4.2 Select solvent system (i.e., mixtures of methanol or acetonitrile with water or mixtures of heptane or hexane with isopropanol).

12.4.3 Follow analytical procedures given in Sections 12.1.2 through 12.1.9.

12.4.4 If interferences are present, adjust the HPLC solvent system composition or use column chromatographic clean-up with silica gel, alumina, or Florisil (6).

12.4.5 An electrochemical detector may be used to improve sensitivity for some ureas, carbamates, and phenolics. Much more care is required in using this detector, particularly in removing dissolved oxygen from the mobile phase and sample extracts.

12.4.6 Chlorophenol (di- through penta-) may be analyzed by GC/ECD or GC/MS after derivatization with pentafluorobenzylbromide (EPA Method 604).

12.4.7 Chlorinated phenoxyacetic acid herbicides and pentachlorophenol can be analyzed by GC/ECD or GC/MS after derivatization with diazomethane (EPA Method 515). DB-5 and DB-1701 columns (0.25-mm I.D. x 30-m) at 60 to 300°C/4°C per min have been found to perform well.

12.5 Analysis of Pesticides and PCBs by Gas Chromatography with Mass Spectrometry Detection (GC/MS)

[Note: A mass spectrometer operating in the selected ion monitoring mode is useful for confirmation and identification of pesticides.]

12.5.1 A mass spectrometer operating in the select ion monitoring (SIM) mode can be used as a sensitive detector for multi-residue determination of a wide variety of pesticides. Mass spectrometers are now available that provide detection limits comparable to nitrogen-phosphorus and electron capture detectors.

12.5.2 Most of the pesticides shown in Table 1 have been successfully determined by GC/MS/SIM. Typical GC operating parameters are as described in Section 12.1.1.

12.5.3 The mass spectrometer is typically operated using positive ion electron impact ionization (70 eV). Other instrumental parameters are instrument specific.

12.5.4 p-Terphenyl-d_{14} is commonly used as a surrogate for GC/MS analysis.

12.5.5 Quantification is typically performed using an internal standard method. 1,4-Dichlorobenzene, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} are commonly used as internal standards. Procedures given in Section 12.1.1 through 12.1.9 and Section 12.1.13 through 12.1.14 apply, except for the selection of surrogates, detector, and make up gas.

12.5.6 See ASTM Practice D 3687 for injection technique, determination of relative retention times, and other procedures pertinent to GC and HPLC analyses.

12.6 Sample Concentration

12.6.1 If concentrations are too low to detect by the analytical procedure of choice, the extract may be concentrated to 1 mL or 0.5 mL by carefully controlled evaporation under an inert atmosphere. The following procedure is appropriate.

12.6.2 Place K-D concentrator tube in a water bath and analytical evaporator (nitrogen blow-down) apparatus. The water bath temperature should be from 25°C to 50°C.

12.6.3 Adjust nitrogen flow through hypodermic needle to provide a gentle stream.

12.6.4 Carefully lower hypodermic needle into the concentrator tube to a distance of about 1 cm above the liquid level.

12.6.5 Continue to adjust needle placement as liquid level decreases.

12.6.6 Reduce volume to slightly below desired level.

12.6.7 Adjust to final volume by carefully rinsing needle tip and concentrator tube well with solvent (usually n-hexane).

13. Calculations

13.1 Determination of Concentration

13.1.1 The concentration of the analyte in the extract solution can be taken from a standard curve where peak height or area is plotted linearly against concentration in nanograms per milliliter (ng/mL). If the detector response is known to be linear, a single point is used as a calculation constant.

13.1.2 From the standard curve, determine the nanograms of analyte standard equivalent to the peak height or area for a particular compound.

13.1.3 Ascertain whether the field blank is contaminated. Blank levels should not exceed 10 ng/sample for organochlorine pesticides or 100 ng/sample for PCBs and other pesticides. If the blank has been contaminated, the sampling series must be held suspect.

13.1.4 Quantity of the compound in the sample (A) is calculated using the following equation:

$$A = 1000 \left(\frac{A_s \times V_e}{V_i} \right)$$

where:

A = total amount of analyte in the sample, ng.

A_s = calculated amount of material injected onto the chromatograph based on calibration curve for injected standards, ng.

V_e = final volume of extract, mL.

V_i = volume of extract injected, μL.

1000 = factor for converting microliters to milliliters.

13.1.5 The extraction efficiency (EE) is determined from the recovery of surrogate spike as follows:

$$EE(\%) = \left| \frac{S}{S_a} \right| [100]$$

where:

EE = extraction efficiency, %.

S = amount of spike recovered, ng.

S_a = amount of spike added to plug, ng.

The extraction efficiency (surrogate recovery) must fall between 60-120% to be acceptable.

13.1.6 The total volume of air sampled under ambient conditions is determined using the following equation:

$$V_a = \frac{\sum_{i=1}^{n} (T_i \times F_i)}{1000 \text{ L/m}^3}$$

where:

V_a = total volume of air sampled, m^3.

T_i = length of sampling segment between flow checks, min.

F_i = average flow during sampling segment, L/min.

13.1.7 The air volume is corrected to EPA standard temperature (25°C) and standard pressure (760 mm Hg) as follows:

$$V_s = V_a \left(\frac{P_b - P_w}{760 \text{ mm Hg}} \right) \left(\frac{298K}{t_A} \right)$$

where:

V_s = volume of air at standard conditions (25°C and 760 mm Hg), std. m^3.

V_a = total volume of air sampled, m^3.

P_b = average ambient barometric pressure, mm Hg.

P_w = vapor pressure of water at calibration temperature, mm Hg.

t_A = average ambient temperature, °C + 273.

13.1.8 If the proper criteria for a sample have been met, concentration of the compound in a standard cubic meter of air sampled is calculated as follows:

$$C_a(\text{ng/std. m}^3) = \left[\frac{(A)}{(V_s)} \right] \left[\frac{(100)}{(SE(\%))} \right]$$

where:

SE = sampling efficiency as determined by the procedure outlined in Section 14.

If it is desired to convert the air concentration value to parts per trillion (ppt) in dry air at standard temperature and pressure (STP), the following conversion is used:

$$\text{ppt} = 0.844\ (C_a)$$

The air concentration can be converted to parts per trillion (v/v) in air at STP as follows:

$$\text{pptv} = \left[\frac{(24.45)\ (C_a)}{(MW)} \right]$$

where:

MW = molecular weight of the compound of interest, g/g-mole.

13.1.9 If quantification is performed using an internal standard, a relative response factor (RRF) is calculated by the equation:

$$RRF = \left[\frac{(I_s)(C_{is})}{(I_{is})(C_s)}\right]$$

where:

I_s = integrated area of the target analyte peak, counts.

I_{is} = integrated area of the internal standard peak, counts.

C_{is} = concentration of the internal standard, ng/μL.

C_s = concentration of the analyte, ng/µL.

13.1.10 The concentration of the analyte (C_a) in the sample is then calculated as follows:

$$C_a = \frac{(I_s)(C_{is})}{(RRF)(I_{is})}$$

where:

C_a = concentration of analyte, ng/m^3

I_s = integrated area of the target analyte peak, counts.

RRF = relative response factor (see Section 13.1.10).

14. Sampling and Retention Efficiencies

14.1 General

14.1.1 Before using Compendium Method TO-10A, the user should determine the sampling efficiency for the compound of interest. The sampling efficiencies shown in Tables 2, 3, 4, and 5 were determined for approximately 1 m^3 of air at about 25°C, sampled at 3.8 L/min. The SE values in these tables may be used for similar sampling conditions; for other compounds or conditions, SE values must be determined.

14.1.2 Sampling efficiencies for the pesticides shown in Table 6 are for a flowrate of 3.8 L/min and at 25°C. For compounds not listed, longer sampling times, different flow rates, or other air temperatures, the following procedure may be used to determine sampling efficiencies.

14.2 Determining SE

14.2.1 SE is determined by a modified impinger assembly attached to the sampler pump, as illustrated in Figure 7. A clean PUF is placed in the pre-filter location and the inlet is attached to a nitrogen line.

[Note: Nitrogen should be used instead of air to prevent oxidation of the compounds under test. The oxidation would not necessarily reflect what may be encountered during actual sampling and may give misleading sampling efficiencies.]

Two PUF plugs (22-mm x 7.6-cm) are placed in the primary and secondary traps and are attached to the pump.

14.2.2 A standard solution of the compound of interest is prepared in a volatile solvent (i.e., hexane, pentane, or benzene). A small, accurately measured volume (i.e., 1 mL) of the standard solution is placed into the modified midget impinger. The sampler pump is set at the rate to be used in field application and then activated. Nitrogen is drawn through the assembly for a period of time equal to or exceeding that intended for field application. After the desired sampling test period, the PUF plugs are removed and analyzed separately as per Section 12.

14.2.3 The impinger is rinsed with hexane or another suitable solvent and quantitatively transferred to a volumetric flask or concentrator tube for analysis.

14.2.4 The sampling efficiency (SE) is determined using the following equation:

$$\% \ SE = \frac{W_1}{W_0 - W_r} \times 100$$

where:

W_1 = amount of compound extracted from the primary trap, ng.

W_o = original amount of compound added to the impinger, ng.

W_r = residue left in the impinger at the end of the test, ng.

14.2.5 If material is found in the secondary trap, it is an indication that breakthrough has occurred. The addition of the amount found in the secondary trap, W_2, to W_1, will provide an indication for the overall sampling efficiency of a tandem-trap sampling system. The sum of W_1, W_2 (if any), and W_r must equal (approximately ±10%) W_o or the test is invalid.

14.2.6 If the compound of interest is not sufficiently volatile to vaporize at room temperature, the impinger may be heated in a water bath or other suitable heater to a maximum of 50°C to aid volatilization. If the compound of interest cannot be vaporized at 50°C without thermal degradation, dynamic retention efficiency (RE_d) may be used to estimate sampling efficiency. Dynamic retention efficiency is determined in the manner described in Section 14.2.7. Table 7 lists those organochlorine pesticides which dynamic retention efficiencies have been determined.

14.2.7 A pair of PUF plugs is spiked by slow, dropwise addition of the standard solution to one end of each plug. No more than 0.5 to 1 mL of solution should be used. Amounts added to each plug should be as nearly the same as possible. The plugs are allowed to dry for 2 hours in a clean, protected place (i.e., desiccator). One spiked plug is placed in the primary trap so that the spiked end is at the intake and one clean unspiked plug is placed in the secondary trap. The other spiked plug is wrapped in hexane-rinsed aluminum foil and stored in a clean place for the duration of the test (this is the static control plug, Section 14.2.8). Prefiltered nitrogen or ambient air is drawn through the assembly as per Section 14.2.2.
[Note: Impinger may be discarded.]

Each PUF plug (spiked and static control) is analyzed separately as per Section 12.

14.2.8 This dynamic retention efficiency (% RE_d) is calculated as follows:

$$\% \ RE_d = \frac{W_1}{W_o} \times 100$$

where:

W_1 = amount of compound recovered from primary plug, ng.

W_o = amount of compound added to primary plug, ng.

If a residue, W_2, is found on the secondary plug, breakthrough has occurred. The sum of $W_1 + W_2$ must equal W_o, within 25% or the test is invalid. For most compounds tested by this procedure, % RE_d values are generally less than % SE values determined per Section 14.2. The purpose of the static RE_d determination is to establish any loss or gain of analyte unrelated to the flow of nitrogen or air through the PUF plug.

15. Performance Criteria and Quality Assurance

[Note: This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory.]

15.1 Standard Operating Procedures (SOPs)

15.1.1 Users should generate SOPs describing the following activities accomplished in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling cartridges; (3) assembly, calibration, and operation of the analytical system, with make and model of equipment used; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

15.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

15.2 Process, Field, and Solvent Blanks

15.2.1 One PUF cartridge from each batch of approximately twenty should be analyzed, without shipment to the field, for the compounds of interest to serve as a process blank.

15.2.2 During each sampling episode, at least one PUF cartridge should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

15.2.3 Before each sampling episode, one PUF plug from each batch of approximately twenty should be spiked with a known amount of the standard solution. The spiked plug will remain in a sealed container and will not be used during the sampling period. The spiked plug is extracted and analyzed with the other samples. This field spike acts as a quality assurance check to determine matrix spike recoveries and to indicate sample degradation.

15.2.4 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF cartridge included) should be carried through the procedure and analyzed.

15.2.5 All blank levels should not exceed 10 ng/sample for single components or 100 ng/sample for multiple component mixtures (i.e., for organochlorine pesticides and PCBs).

15.3 Sampling Efficiency and Spike Recovery

15.3.1 Before using the method for sample analysis, each laboratory must determine its sampling efficiency for the component of interest as per Section 14.

15.3.2 The PUF in the sampler is replaced with a hexane-extracted PUF. The PUF is spiked with a microgram level of compounds of interest by dropwise addition of hexane solutions of the compounds. The solvent is allowed to evaporate.

15.3.3 The sampling system is activated and set at the desired sampling flow rate. The sample flow is monitored for 24 hours.

15.3.4 The PUF cartridge is then removed and analyzed as per Section 12.

15.3.5 A second sampler, unspiked, is collected over the same time period to account for any background levels of components in the ambient air matrix.

15.3.6 In general, analytical recoveries and collection efficiencies of 75% are considered to be acceptable method performance.

15.3.7 Replicate (at least triplicate) determinations of collection efficiency should be made. Relative standard deviations for these replicate determinations of ±15% or less are considered acceptable performance.

15.3.8 Blind spiked samples should be included with sample sets periodically as a check on analytical performance.

15.4 Method Precision and Bias

15.4.1 Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each compound of concern, and the precision and bias of the sampling process.

15.4.2 Several different parameters involved in both the sampling and analysis steps of this method collectively determine the precision and bias with which each compound is detected. As the volume of air sampled is increased, the sensitivity of detection increases proportionately within limits set by: (a) the retention efficiency for each specific component trapped on the polyurethane foam plug, and (b) the background interference associated with the analysis of each specific component at a given site sampled. The sensitivity of detection of samples recovered by extraction depends on: (a) the inherent response of the particular GC detector used in the determinative step, and (b) the extent to which the sample is concentrated for analysis. It is the responsibility of the analyst(s) performing the sampling and analysis steps to adjust parameters so that the required detection limits can be obtained.

15.4.3 The reproducibility of this method for most compounds for which it has been evaluated has been determined to range from ±5 to ±30% (measured as the relative standard deviation) when replicate sampling cartridges are used (N>5). Sample recoveries for individual compounds generally fall within the range of 90 to 110%, but recoveries ranging from 65 to 125% are considered acceptable. PUF alone may give lower recoveries for more volatile compounds (i.e., those with saturation vapor pressures $>10^{-3}$ mm Hg). In those cases, another sorbent or a combination of PUF and Tenax TA (see Figure 2) should be employed.

15.5 Method Safety

15.5.1 This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use.

15.5.2 It is the user's responsibility to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

16. References

1. "Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyls in Air," *Annual Book of ASTM Standards*, Method D4861-94, ASTM, Philadelphia, PA.

2. Lewis, R., and MacLeod, K., "Portable Sampler for Pesticides and Semi-volatile Industrial Organic Chemicals in Air," *Analytical Chemistry*, Vol. 54, 1982, pp. 310-315.

3. Whitmore R.W., Immerman, F.W., Camann, D.E., Bond, A.E., Lewis, R.G., and Schaum, J.L., "Non-occupational Exposure to Pesticides for Residents of Two U.S. Cities," *Arch. Environ. Contam. Toxicol.*, 26, 47-59 (1994).

4. Lewis, R., and Brown, A., and Jackson, M., "Evaluation of Polyurethane Foam for Sampling of Pesticides, Polychlorinated Biphenyls and Polychlorinated Napththalenes in Ambient Air," *Analytical Chemistry*, Vol. 49, 1977, pp. 1668-1672.

5. Armour, J., and Burke, J., "Method for Separating Polychlorinated Biphenyls from DDT and Its Analogs," *Journal of the Association of Official Analytical Chemists*, Vol. 53, No. 4, 1970, pp. 761-768.

6. *Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples*, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711, Report No. EPA-600/8-80-038, June 1980 (NTIS No. PB82-208752).

7. Kogan, V., Kuhlman, M., Coutant, R., and Lewis, R., "Aerosol Filtration in Sorbent Beds," *Journal of the Air and Waste Management Association*, Vol. 43, 1993, p. 1367-1373.

8. Lewis, R., and Lee, R., "Air Pollution from Pesticide Sources, Occurrences and Dispersion," In: *Air Pollution from Pesticides and Agricultural Processes*, Lee, R., Editor, CRC Press, Boca Raton, FL, 1976, pp. 51-94.

9. Lewis, R., "Problem Associated with Sampling for Semi-volatile Organic Chemicals in Air," *Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants*, Air and Waste Management Association, Pittsburgh, PA, 1986, pp. 134-145.

10. Camann, D., Harding, J., and Lewis, R., "Trapping of Particle-Associated Pesticides in Indoor Air by Polyurethane Foam and Evaporation of Soil Track-In as a Pesticide Source," In: *Indoor Air* '90, Vol. 2, Walkinshaw, D., editor, Canada Mortgage and Housing Corp., Ottawa, 1990, pp. 621-626.

11. Marple, V., Rubow, K., Turner, W., and Spengler, J., "Low Flow Rate Sharp Cut Impactors for Indoor Air Sampling Design and Calibration," *Journal of the Air Pollution Control Association*. Vol. 37, 1987, pp. 1303-1307.

12. Hsu, J., Wheeler, H., Camann, D., Shatterberg, H., Lewis, R., and Bond, A., "Analytical Methods for Detection of Nonoccupational Exposure to Pesticides," *Journal of Chromatographic Science*, Vol. 26, 1988, pp. 181-189.

TABLE 1. COMPOUNDS FOR WHICH PROCEDURE HAS BEEN TESTED[1]

Compound	Recommended Analysis[2]	Compound	Recommended Analyses
Alachlor	GC/ECD	Heptachlor	GC/ECD
Aldrin	GC/ECD	Heptachlor epoxide	GC/ECD
Allethrin	HPLC/UV	Hexachlorobenzene	GC/ECD
Aroclor 1242	GC/ECD	Hexachlorocyclopentadiene[3,4]	GC/ECD
Aroclor 1254	GC/ECD	Lindane (γ-BHC)	GC/ECD
Aroclor 1260	GC/ECD	Linuron	HPLC/UV
Atrazine	GC/NPD	Malathion	GC/NPD or FPD
Bendiocarb	HPLC/UV	Methyl parathion	GC/NPD or FPD
BHC (α- and β-Hexachlorocyclohexanes)	GC/ECD	Methoxychlor	GC/FCD
Captan	GC/ECD	Metolachlor	GC/ECD
Carbaryl	HPLC/UV	Mexacarbate	GC/FCD
Carbofuran	HPLC/UV	Mirex	GC/ECD
Chlordane, technical	GC/ECD	Monuron	HPLC/UV
Chlorothalonil	GC/ECD	Trans-nonachlor	GC/ECD
Chlorotoluron	HPLC/UV	Oxychlordane	GC/ECD
Chlorpyritos	GC/ECD	Pentachlorobenzene	GC/ECD
2,4-D esters and salts	GC/ECD	Pentachlophenol	GC/ECD
Dacthal	GC/ECD	Permethrin (cis and trans)	HPLC/UV
ρ,ρ-'DDT	GC/ECD	o-Phenylphenol	HPLC/UV
ρ,ρ-'DDE	GC/ECD	Phorate	GC/NPD or FPD
Diazinon	GC/NPD or FPD	Propazine	GC/NPD
Dicloran	GC/ECD	Propoxur (Baygon)	HPLC/UV
Dieldrin	GC/ECD	Pyrethrin	HPLC/UV
Dichlorovos (DDVP)	GC/ECD	Resmethrin	HPLC/UV
Dicofol	GC/ECD	Ronnel	GC/ECD
Dicrotophos	HPLC/UV	Simazine	HPLC/UV
Diuron	HPLC/UV	Terbuthiuron	HPLC/UV
Ethyl parathion	GC/NPD or FPD	1,2,3,4-tetrachlorobenzene[3]	GC/ECD
Fenvalerate	HPLC/UV	1,2,3-trichlorobenzene[3]	GC/ECD
Fluometuron	HPLC/UV	2,3,5-trichlorophenol	GC/ECD
Folpet	GC/ECD	Trifluralin	GC/ECD

[1]The following recommendations are specific for that analyte for maximum sensitivity.
[2]GC = gas chromatography; ECD = electron capture detector, FPD = flame photometric detector; HPLC = high performance liquid chromatography; NPD = nitrogen-phosphorus detector; UV = ultraviolet absorption detector, (GC/MS (gas chromatography/mass spectrometry) may also be used).
[3]Using PUF/Tenax-TA "sandwich" trap.
[4]Compound is very unstable in solution.

TABLE 2. SAMPLING EFFICIENCIES FOR SOME ORGANOCHLORINE PESTICIDES

Compound	Quantity Introduced, μg[2]	Air Volume, m^3	Sampling efficiency, %		
			mean	RSD	n
α-Hexachlorocyclohexane (α-BHC)	0.005	0.9	115	8	6
γ-Hexachlorocyclohexane (Lindane)	0.05-1.0	0.9	91.5	8	5
Chlordane, technical	0.2	0.9	84.0	11	8
p,p'-DDT	0.6, 1.2	0.9	97.5	21	12
p,p'-DDE	0.2, 0.4	0.9	102	11	12
Mirex	0.6, 1.2	0.9	85.9	22	7
2,4-D Esters:					
Isopropyl	0.5	3.6	92.0	5	12
Butyl	0.5	3.6	82.0	10	11
Isobutyl	0.5	3.6	79.0	20	12
Isoctyl	0.5	3.6	>80[2]	--	--

[1]Air volume = 0.9 m^3.
[2]Not vaporized. Value base on %RE = 81.0 (RSD = 10%, n = 6).

TABLE 3. SAMPLING EFFICIENCIES FOR ORGANOPHOSPHORUS PESTICIDES

Compound	Quantity Introduced, μg[2]	Sampling efficiency, %		
		mean	RSD	n
Dichlorvos (DDVP)	0.2	72.0	13	2
Ronnel	0.2	106	8	12
Chlorpyrifos	0.2	108	9	12
Diazinon[1]	1.0	84.0	18	18
Methyl parathion[1]	0.6	80.0	19	18
Ethyl parathion[1]	0.3	75.9	15	18
Malathion[1]	0.3	100[3]	--	--

[1]Analyzed by gas chromatography with nitrogen phosphorus detector or flame photometric detector.
[2]Air volume = 0.9 m^3.
[3]Decomposed in generator; value based on %RE = 101 (RDS = 7, n = 4).

TABLE 4. SAMPLING EFFICIENCIES FOR SOME SEMI-VOLATILE ORGANOCHLORINE COMPOUNDS AND PCBs

Compound	Quantity Introduced, μg[1]	Sampling efficiency, %		
		mean	RSD	n
1,2,3-Trichlorobenzene	1.0	6.6[2]	22	8
1,2,3,4-Tetrachlorobenzene	1.0	62.3[2]	33	5
Pentachlorobenzene	1.0	94.0	12	5
Hexachlorobenzene	0.5, 1.0	94.5	8	5
Hexachlorocyclopentadiene	1.0	8.3[2]	12	5
2,4,5-Trichlorophenol	1.0	108	3	5
Pentachlorophenol	1.0	107	16	5
Aroclor 1242	0.1	96.0	15	6
Aroclor 1254	0.1	95.0	7	6
Aroclor 1260	0.1	109	5	11

[1]Air volume = 0.9 m^3.
[2]% SEs were 98, and 97% (n = 2), respectively, for these three compounds by the PUF/Tenax® TA "sandwich" trap.

TABLE 5. SAMPLING EFFICIENCIES FOR CARBAMATES, UREAS, TRIAZINES, AND PYRETHRINS

Compound	Spike Level, µg/plug	Static Recovery, %		n	Retention Efficiency, %		n	Sampling Efficiency, %		n
		mean	RSDP		mean	RSD		mean	RSD	
Carbamates:										
Propoxur	5	61.4	10	6	77.6	37	6	96.7	11	6
Carbofuran	15	55.3	12	6	64.2	46	6	87.2	14	6
Bendicarb	50	57.3	11	6	69.8	43	6	62.1	14	6
Mexacarbate	10	62.8	19	6	62.7	41	6	89.8	14	6
Carbaryl	100	56.6	14	6	63.6	53	6	0	13	6
Ureas:										
Monuron	19	87.0	6	6	91.2	6	5	0		
Diuron	20	84.1	8	6	90.0	2	5	0		
Linuron	20	86.7	8	6	92.5	4	5	0		
Terbuthiuron	18	85.0	8	6	88.8	8	5	0		
Fluometuron	20	91.4	10	6	101	3	5	0		
Chlortoluron	20	86.2	11	6	92.0	7	5	0		
Triazines:										
Simazine	10	103	6	5	101	9	6	0		
Atrazine	10	104	7	5	98.9	7	6	0		
Propazine	10	105	11	5	99.9	14	6	0		
Pyrethrins:										
Pyrethrin I	(9.7)	90.5	10	6	95.6	22	5	0		
Pyrethrin II	(6.1)	88.6	11	6	69.9	29	5	0		
Allethrin	25	69.2	9	5	58.3	12	6	0		
d-trans-Allethrin	25	76.8	9	6	74.4	9	5	0		
Dicrotophos	25	72.0	22	6	71.7	8	5	0		
Resmethrin	25	76.5	14	6	66.7	14	6	0		
Fenvalerate	25	87.9	3	6	57.2	20	3	0		

TABLE 6. EXTRACTION AND 24-H SAMPLING EFFICIENCIES FOR VARIOUS PESTICIDES AND RELATED COMPOUNDS

Compound	Extraction Efficiency[1], %		Sampling Eficiency[2], %, at					
			10 ng/m^3		100 ng/m^3		1,000 ng/m^3	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Chlropyrifos	83.3	11.5	83.7	18.0	92.7	15.1	83.7	18.0
Pentachlorophenol	84.0	22.6	66.7	42.2	52.3	36.2	66.7	42.2
Chlordane	95.0	7.1	96.0	1.4	74.0	8.5	96.0	1.4
o-Phenylphenol	47.0	46.7	46.0	19.1	45.3	29.9	46.0	19.1
Lindane	96.0	6.9	91.7	11.6	93.0	2.6	91.7	11.6
DDVP	88.3	20.2	51.0	53.7	106.0	1.4	51.0	53.7
2,4-D Methyl Ester	--	--	75.3	6.8	58.0	23.6	75.3	6.8
Heptachlor	99.0	1.7	97.3	13.6	103.0	17.3	97.3	13.6
Aldrin	97.7	4.0	90.7	5.5	94.0	2.6	90.7	5.5
Dieldrin	95.0	7.0	82.7	7.6	85.0	11.5	82.7	7.6
Ronnel	80.3	19.5	74.7	12.1	60.7	15.5	74.7	12.2
Diazinon	72.0	21.8	63.7	18.9	41.3	26.6	63.7	19.9
trans-Nonachlor	97.7	4.0	96.7	4.2	101.7	15.3	96.7	4.2
Oxychlorodane	100.0	0.0	95.3	9.5	94.3	1.2	95.3	9.5
α-BHC	98.0	3.5	86.7	13.7	97.0	18.2	86.7	13.7
Bendiocarb	81.3	8.4	59.7	16.9	30.7	23.5	59.7	16.9
Chlorothalonil	90.3	8.4	76.7	6.1	70.3	6.5	76.7	6.1
Heptachlor Epoxide	100.0	0.0	95.3	5.5	97.7	14.2	95.3	5.5
Dacthal	--	--	87.0	9.5	95.3	22.2	87.0	9.5
Aroclor 1242	91.7	14.4	95.0	15.5	94.7	17.5	95.0	15.5

[1]Mean values for one spike at 550 ng/plug and two spikes at 5,500 ng/plug.
[2]Mean values for three determinations.

TABLE 7. EXTRACTION AND 24-H DYNAMIC RETENTION EFFICIENCIES FOR VARIOUS PESTICIDES AND RELATED COMPOUNDS

Compound	Extraction Efficiency[1], %		Sampling Eficiency[2], %, at					
			10 ng/m^3		100 ng/m^3		1,000 ng/m^3	
	mean	RSD	mean	RSD	mean	RSD	mean	RSD
Propoxur	77.5	71.4	92.0	--	91.7	22.8	101.0	18.4
Resmethrin	95.5	71.4	79.0	--	100.7	13.1	107.0	4.4
Dicofol	57.0	8.5	38.0	25.9	65.0	8.7	69.0	--
Captan	73.0	12.7	56.0	--	45.5	64.3	84.3	16.3
Carbaryl	74.0	82.0	102.0	--	61.0	--	113.0	6.1
Malathion	76.5	44.5	108.0	--	54.0	16.0	77.3	7.6
cis-Permethrin	88.7	10.3	101.0	28.5	85.0	26.9	89.0	11.3
trans-Permethrin	88.7	11.0	67.3	34.8	80.7	56.4	108.3	9.5
Methoxychlor	65.5	4.9	--	--	--	--	78.5	2.1
Atrazine	75.0	50.5	--	--	73.0	30.1	83.0	9.5
Folpet	86.7	11.7	--	--	78.0	--	93.0	--
Aroclor 1260	92.0	14.5	88.0	9.6	85.3	9.9	107.1	13.6

[1]Mean values for one spike at 550 ng/plug and two spikes at 5,500 ng/plug.
[2]Mean values for three determinations.

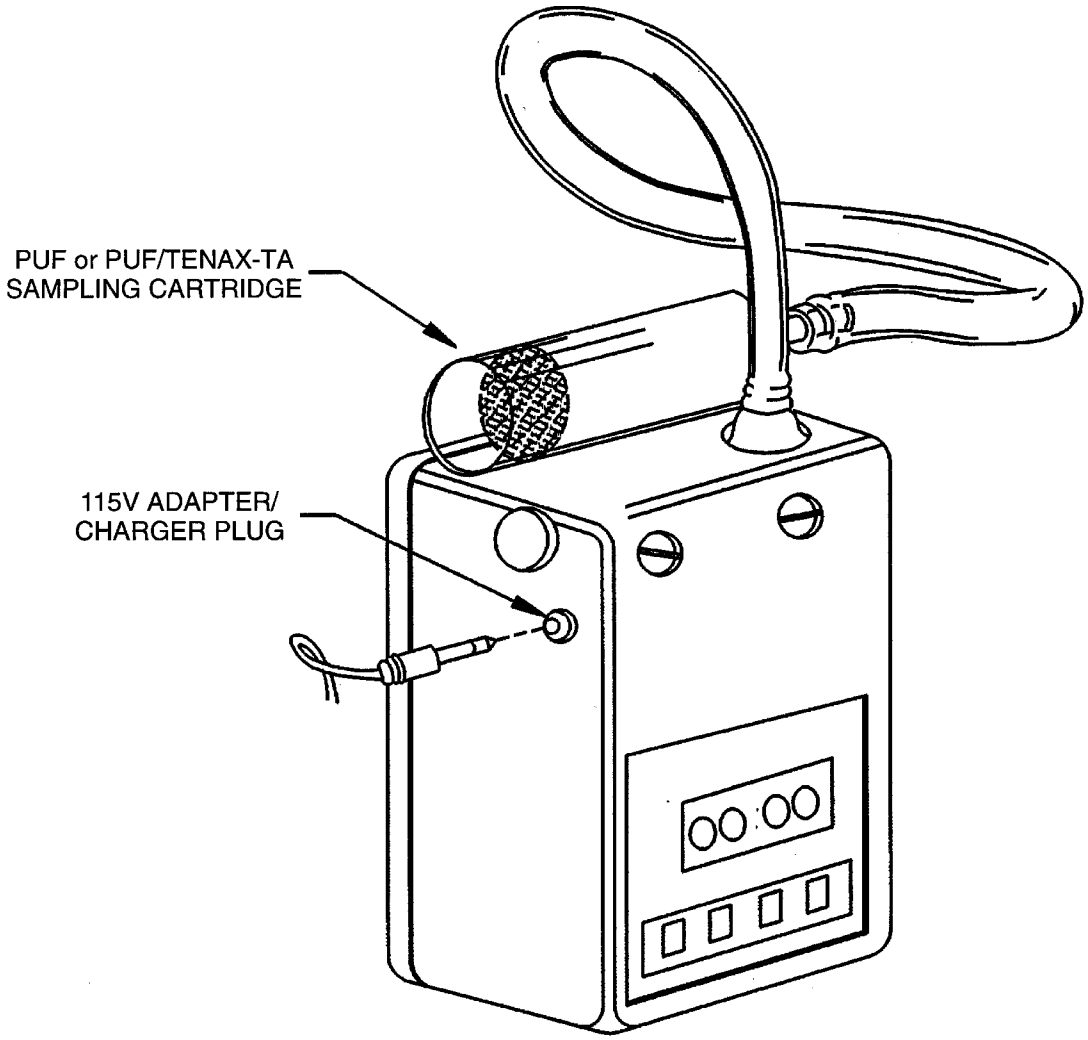


Figure 1. Low volume air sampler.

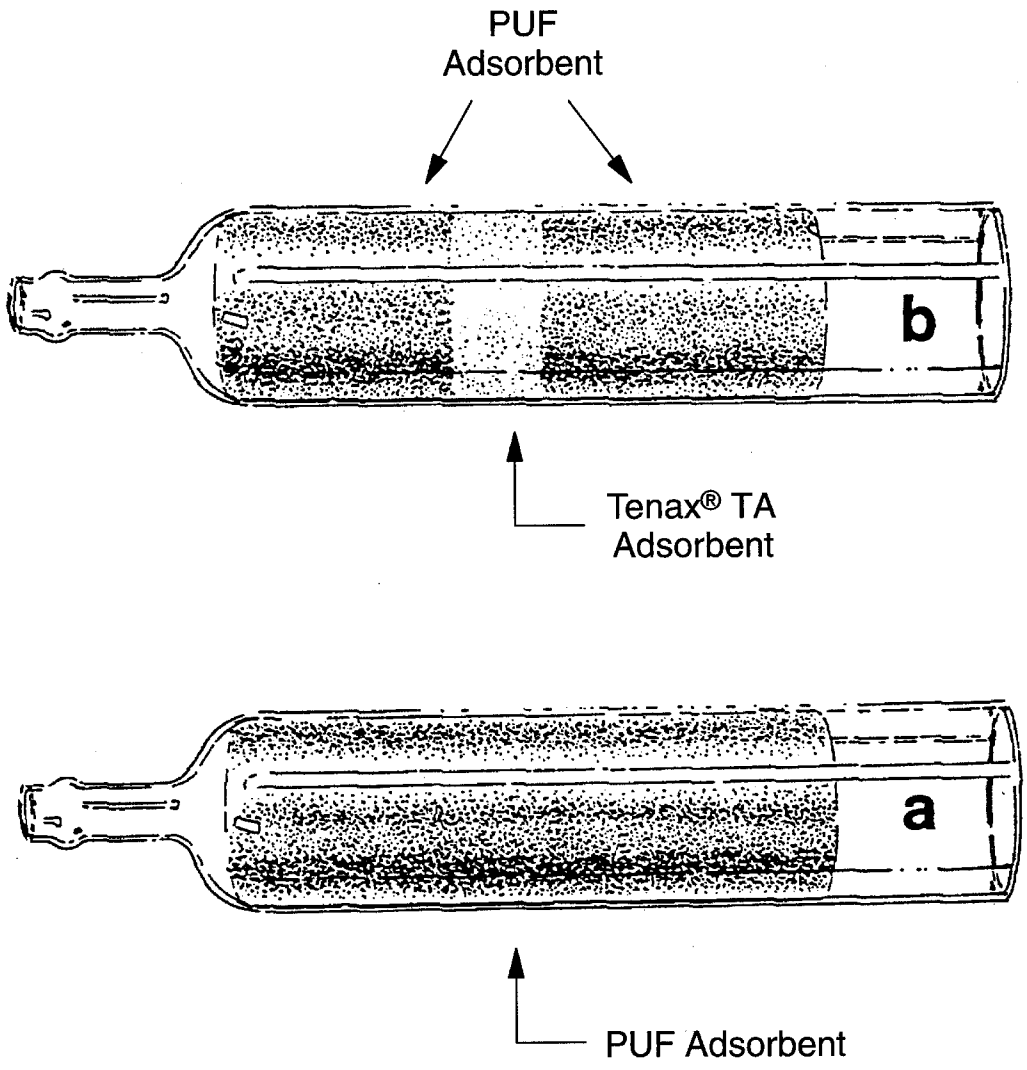


Figure 2. Polyurethane foam (PUF) sampling cartridge (a) and PUF-Tenax® TA "sandwich" sampling cartridge (b).

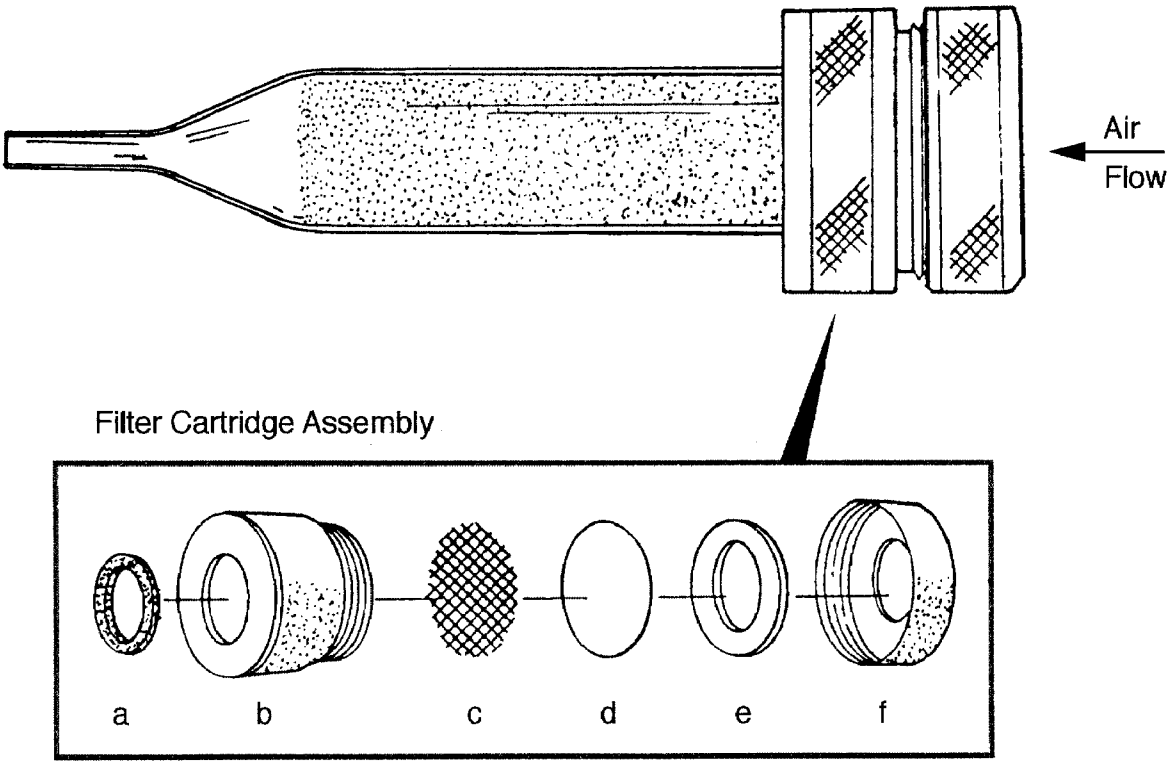


Figure 3. Open-face filter assembly attached to a PUF cartridge:
(a) Inner Viton® o-ring, (b) filter cartridge, (c) stainless steel screen, (d) quartz filter,
(e) filter ring, and (f) cartridge screw cap.

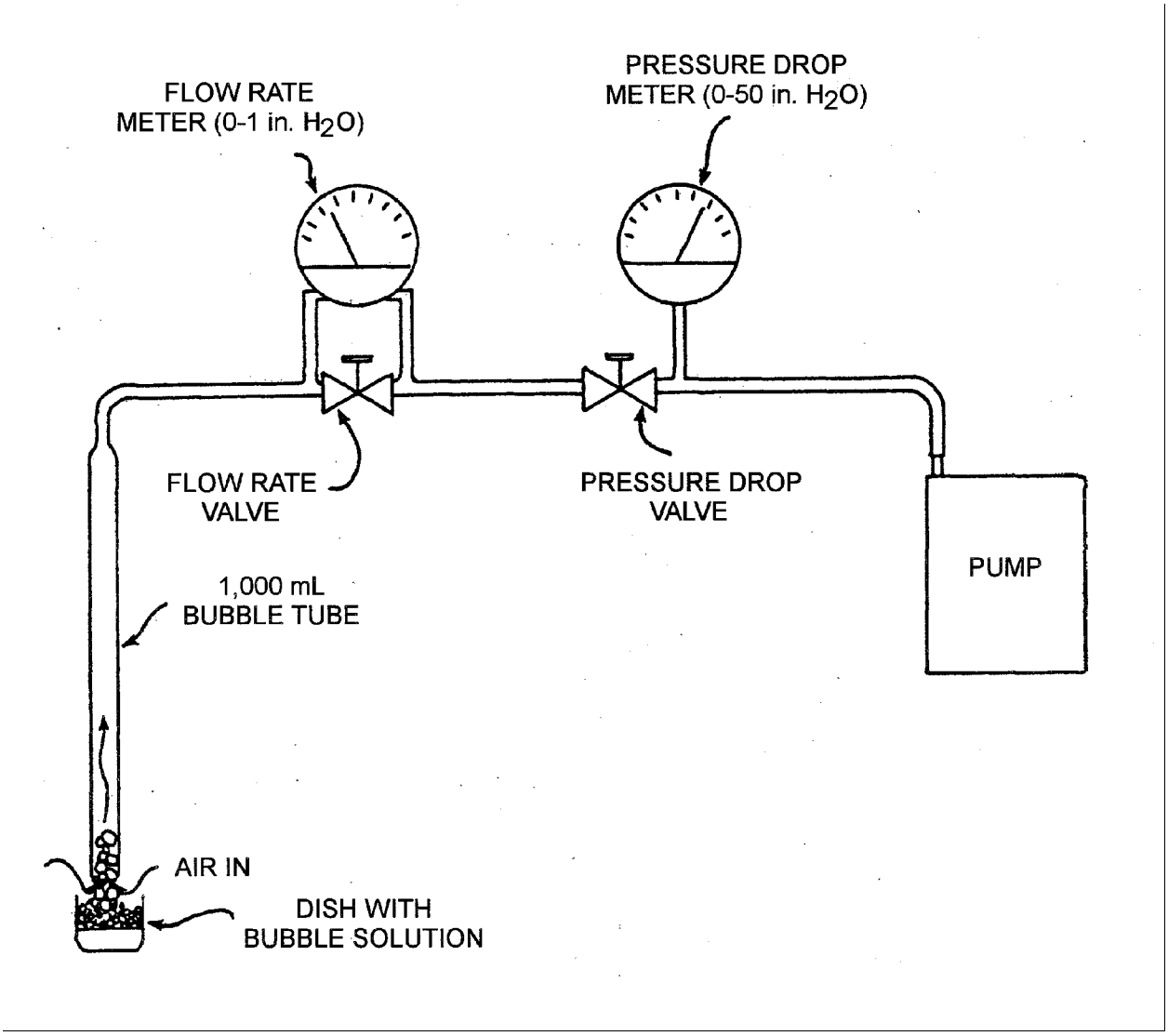


Figure 4. Calibration assembly for air sampler pump.

COMPENDIUM METHOD TO-10A
FIELD TEST DATA SHEET (FTDS)

I. GENERAL INFORMATION

PROJECT:_____ DATE(S) SAMPLED:_____
SITE:_____ TIME PERIOD SAMPLED:_____
LOCATION:_____ OPERATOR:_____
INSTRUMENT MODEL NO.:_____ CALIBRATED BY:_____
PUMP SERIAL NO.:_____ RAIN: ____YES _____NO

ADSORBENT CARTRIDGE INFORMATION:

	Cartridge 1	Cartridge 2	Cartridge 3	Cartridge 4
Type:	_____	_____	_____	_____
Adsorbent:	_____	_____	_____	_____
Serial No.:	_____	_____	_____	_____
Sample No.:	_____	_____	_____	_____

II. SAMPLING DATA

Cartridge Identifi-cation	Sampling Location	Ambient Temp., °F	Ambient Pressure, in Hg	Flow Rate (Q), mL/min		Sampling Period		Total Sampling Time, min.	Total Sample Volume, L
				Cartridge 1	Cartridge 2	Start	Stop		

III. FIELD AUDIT

	Cartridge 1	Cartridge 2	Cartridge 3	Cartridge 4
Audit Flow Check Within 10% of Set Point (Y/N)?	___ pre- _____ post-	_____ pre- _____ post-	_____ pre- _____ post-	_____ pre- _____ post-

CHECKED BY:_____

DATE:_____

Figure 5. Compendium Method TO-10A field test data sheet.

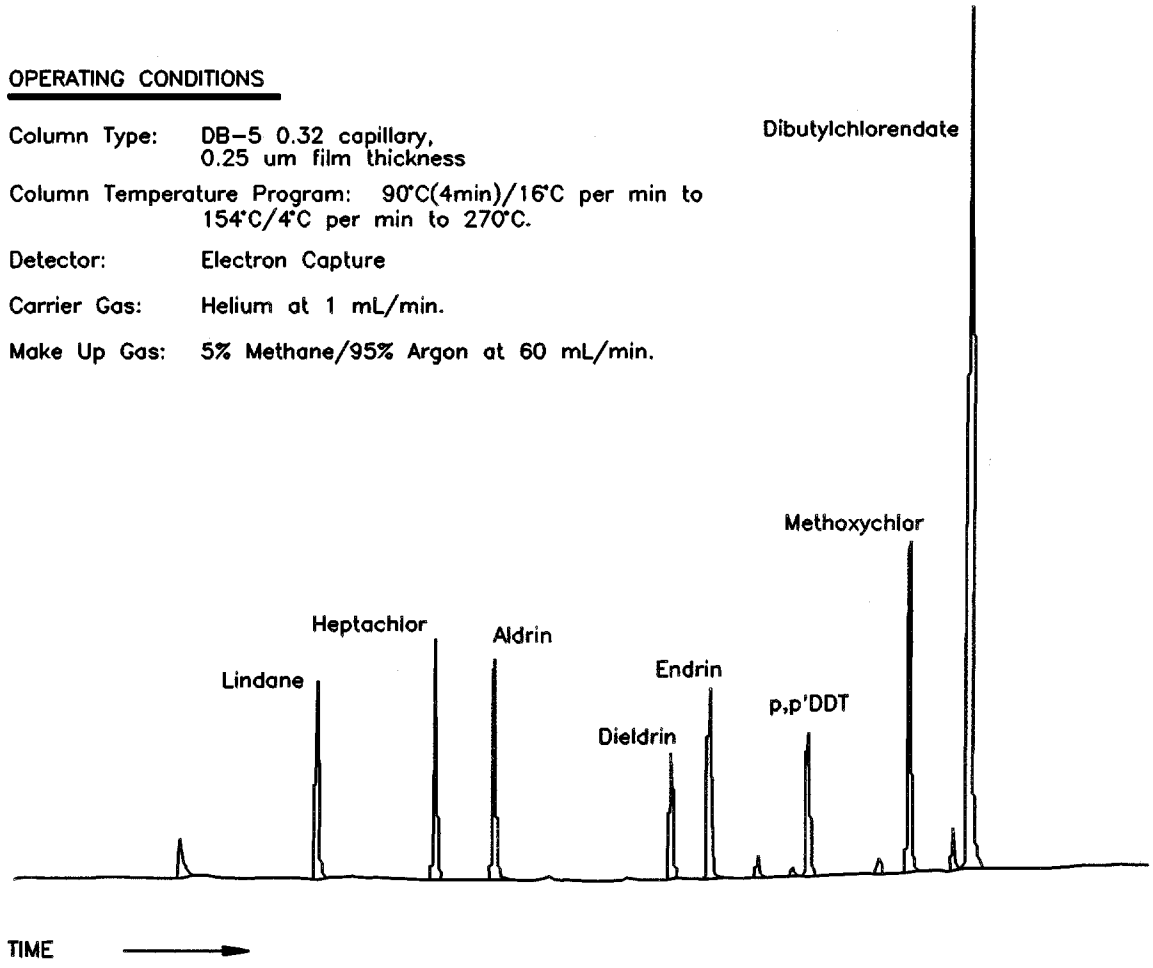


Figure 6. Chromatogram showing a mixture of single component pesticides determined by GC/ECD using a capillary column.

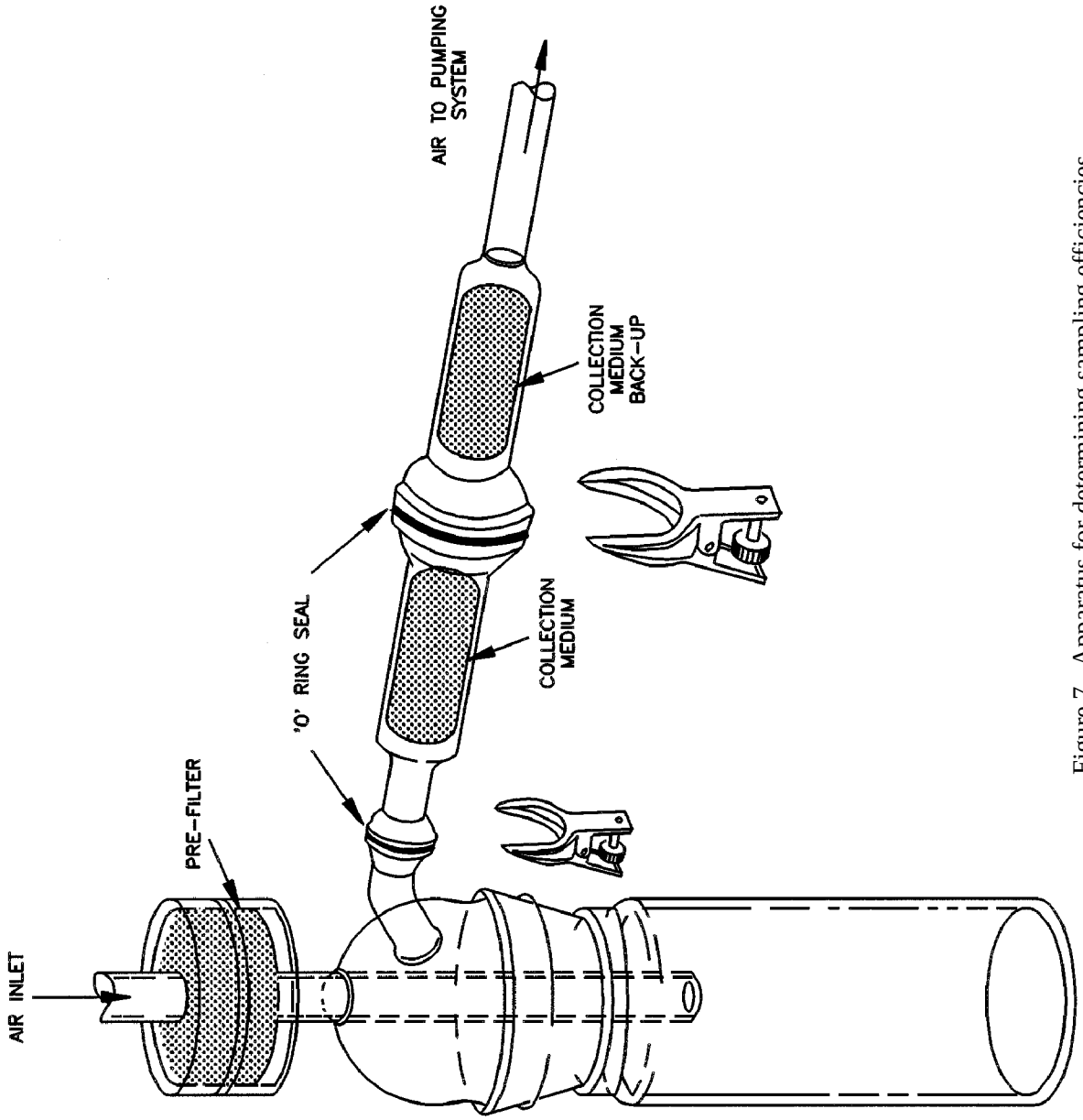


Figure 7. Apparatus for determining sampling efficiencies.

Appendix B3 – Laboratory Reporting Limits: Air, Sediment, and Groundwater

NEA/Pace Analytical Services

Homolog Group	Reporting Limit	Units
Monochlorobiphenyl	0.0050	ug
Dichlorobiphenyl	0.0050	ug
Trichlorobiphenyl	0.0050	ug
Tetrachlorobiphenyl	0.0100	ug
Pentachlorobiphenyl	0.0100	ug
Hexachlorobiphenyl	0.0100	ug
Heptachlorobiphenyl	0.0150	ug
Octachlorobiphenyl	0.0150	ug
Nonachlorobiphenyl	0.0250	ug
Decachlorobiphenyl	0.0250	ug

Con-Test Analytical Laboratory

Analyte	Reporting Limit	Units
Silver, Ag	0.5	ppb
Arsenic, As	0.4	ppb
Barium, Ba	10.0	ppb
Cadium, Cd	0.5	ppb
Chromium, Cr	1.0	ppb
Lead, Pb	1.0	ppb
Mercury, Hg	0.1	ppb
Selenium, Se	5.0	ppb

Appendix B4 – Laboratory Standard Operating Procedures

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE005_06.DOC
REVISION NUMBER: 06

THE EXTRACTION AND CLEANUP OF SOIL, SEDIMENT, AND SOLID SAMPLES BY SOXHLET FOR POLYCHLORINATED BIPHENYL ANALYSIS (PCB)

COPY #___

Property of Northeast Analytical, Inc.

The user of this document agrees not to reproduce, scan, or copy this document. The user also agrees not to disclose or make available this document to other outside parties without the authorization by Northeast Analytical, Inc. All rights reserved.

NORTHEAST ANALYTICAL, INC.
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308
(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE005_06.DOC

REVISION 6 (05/13/2008)

Author:

Mike Glenn
Organic Extractions Department Manager

Reviewed by:

Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 This is the Standard Operating Procedure for the extraction and cleanup of soil, sediment, and solid samples for Polychlorinated Biphenyl (PCB) analysis using the Soxhlet extraction technique by SW-846 Method 3540C for subsequent Analysis by SW-846 Method 8082.

1.2 The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs, in soil/sediment/solid sample, using the soxhlet extraction technique and to perform the subsequent extract volume reduction and cleanup.

2.0 APPLICABLE MATRICES

2.1 This test method is appropriate for soil, sediment, and solid samples. Other extraction methods such as the sonication technique and automated solvent extraction may be used in place of the soxhlet extraction at the discretion of the supervising chemist.

2.2 Time restraints (i.e. requested turn around time) may render this method inapplicable, as it requires 18 +/-2 hours of extraction reflux time.

2.3 Extract cleanup steps employed may vary from sample to sample matrix to matrix. The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3540, 3500, 2500A. An approved instructor must also certify the chemist to perform the procedure.

3.0 DETECTION LIMIT

3.1 Please see determinative method (Lab SOP NE148) for details.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and cleanup of PCBs from soil/sediment/solid samples using the soxhlet extraction method for analysis by SW-846 Method 8082.

5.0 SUMMARY OF TEST METHOD

5.1 Soxhlet extraction: soil/sediment/solid samples are initially dried utilizing sodium sulfate (soil/sediment) or 1:1 magnesium sulfate and sodium sulfate (biota samples). The samples are then loaded into pre rinsed cellulose extraction thimbles. These loaded thimbles are then placed into their own soxhlet extractor apparatus where they are spiked and surrogated. After an 18 hour extraction the derived solvent is exchanged to pure hexane via a TV evaporator system. The extract is then set to volume and undergoes extract clean up. This cleanup is composed of several steps including acid, TBA, florisil and mercury. Following the cleanup procedures the extract is properly diluted and sent for GC analysis.

6.0 DEFINITIONS

6.1 **Method Blank**- A method blank is processed with each batch of samples that are extracted to

assess for contamination during prep and processing steps. The method blank is carried throughout all stages of sample preparation and extraction steps. Organic-free laboratory grade water is processed as the method blank.

6.2 **Lab Control Spike** - A non-site sample which is prepared in the laboratory, to which a known amount of target analyte is added for assessment of laboratory performance. The laboratory control spike sample is composed of sodium sulfate with the spiked target analytes. The Laboratory Control Spike is processed with each batch of samples extracted.

6.3 **Matrix Spike** A site sample to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.4 **Matrix Spike Duplicate** An exact copy of the Matrix Spike utilizing the same site sample and known amount of target analyte for assessment of analyte recovery efficiency.

6.5 **Surrogate Compound Spike**- In chemical composition and chromatography similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, standards, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.6 **QC-Quality Control**- A set of measures for each sample within an analysis methodology to assure that the process is in control.

7.0 INTERFERENCES

7.1 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of certain plastics. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Samples and extracts should not be exposed to plastics such as gloves, tubing, coating on clamps, and pipette bulbs, etc.

8.0 SAFETY

8.1 The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All equipment and solvents should be handled within a lab fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 **Water Cooled Condenser:** Pyrex 45/50 #3840-MCO.

9.2 **250mL Round Bottom Flask:** Pyrex #4100.

9.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M.

9.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)
9.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

9.6 Analytical Balance: Mettler PL-303 used to determine sample mass. (or equivalent)

9.7 Cellulose Extraction Thimble: Contains sample during soxhlet extraction.

9.8 TurboVap Evaporator: Zymark #ZW640-3. (or equivalent)

9.9 TurboVap Evaporator concentrator tubes: Zymark 250mL, 0.5mL endpoint.

9.10 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipette storage.

9.11 Vials: glass, 40mL vials & 4 dram (with Polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

9.12 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.13 Centrifuge: International Equipment Co., Model CL. (or equivalent)

9.14 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88. (or equivalent)

9.15 Pipettes: S/P Disposable Serological Borosilicate Pipettes.

1. **1mL** X 1/10
2. **5mL** X 1/10
3. **10mL** X 1/10

Fisher Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

9.16 4oz. Jars: Industrial Glassware

9.17 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent).

10.0 REAGENTS AND STANDARDS

10.1 Sodium Sulfate: Anhydrous (12-60 Mesh). Used for the laboratory method blank and laboratory control spike.

10.2 Boiling Chips: Chemware PTFE Boiling Stones P#0919120(or equivalent)

10.3 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

10.4 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (or equivalent)

10.5 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

10.6 Florisil: deactivated, see NE094-05.doc, **SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.**

10.7 TBA Reagent: Tetrabutylammonium Hydrogen-Sulfite Reagent. (prepared in the laboratory)

10.8 Mercury: Triple distilled Mercury Waste Solutions, Inc, (or equivalent)

10.9 Sulfuric Acid: Na_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830. (or equivalent)

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 Samples should be collected in 4 oz. Teflon coated jars from the sampling site.

11.2 The samples must be chilled to 4° ± 2 ° C on the day of collection and maintained at that temperature until analysis. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure that they will be at 4 ° C on arrival at the laboratory.

11.3 The Analysis Hold Time for un-preserved samples is 7 days from collection, for preserved samples the Hold Time is 14 days from sample collection.

11.4 The solvent extraction once completed has a hold time of 40 days.

12.0 QUALITY CONTROL

12.1 Every sample set is run with two control samples: the blank standard and the lab control standard.

12.2 Every 20th sample set is run with a Matrix Spike and Matrix Spike Duplicate. The client may also request a Matrix Spike and Matrix Spike Duplicate to be run with their sample set.

13.0 CALIBRATION AND STANDARDIZATION

13.1 The analytical balance should be calibrated daily to ensure accurate measurements are made when weighing out soil samples for extraction.

14.0 PROCEDURES

NOTE: PLEASE REFER TO APPENDIX A FOR ACTIVATING/DEACTIVATING FLORISIL, APPENDIX B FOR CALIBRATION FOR FISH OIL AND CAULKS, APPENDIX C FOR SOXHLET EXTRACTION FOR CAULK AND CLEAN-UP PROCEDURES.

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should **STOP!** Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

14.1.2 Before any steps are taken, the chemist should first review the sample job folder. The chemist should also verify the sample IDs on the bottle against the chain of custody. If there is a discrepancy on either the sample label or the chain of custody, this should brought to the attention of a supervisor.

14.1.3 If the sample is sediment and contains a water layer, decant and discard the layer as aqueous PCB waste. Mix the sample thoroughly in the sample jar; if there is not enough room in the sample container remove sample from container, using a metal spatula, into a mixing tray. Mix the sample thoroughly and discard any foreign objects such as sticks, rocks or leaves then put sample back into sample container and take off sample. **Note** however that the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

14.2 Sample Extraction

14.2.1 Fill a Pyrex pan with ice cubes and cold water about 1/2 inch deep. As the samples are weighed out, place the beakers or 4oz. jars in the Pyrex pan to chill for at least 15 minutes prior to the drying step when doing fish or biota samples.

14.2.2 Rinse all extraction thimbles with Hexane to remove extraneous material. Place thimble into a 4oz. jar (labeled) and allow to dry.

14.2.3 Setup one 250 mL glass beaker or 4oz. jar for each sample. Using the first sample, label a beaker with the sample number, and tare the beaker. Using a metal spatula, add 10 g to 11 g of the wet sample to the beaker. Record the weight in the PCB solid extraction logbook and into the LIMS system hitting F12 (automatically reads scale into LIMS) under sample weight. At this point, a sample for percent total solids may also be taken (see 8.2.4). Place the beaker in the ice bath to chill if fish or biota.

14.2.4 If the PCB concentration is to be determined on a dry weight basis the percent total solid must be determined. Weigh approximately 5 grams of the previously homogenized sample in a previously weighed, aluminum weighing pan. Record the weight of the pan and the weight of the (pan and sample) into the LIMS system. Place the sample in a drying oven at 100 to 110°C for at least 4 hours. Record the time placed in the oven and the oven temperature in the LIMS system. Remove the samples from the drying oven and allow to cool. Weigh the pan and sample.

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIDGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

14.2.5 After the sample has been sufficiently chilled, add approximately 10g of a 1:1 mix of Magnesium Sulfate/Sodium Sulfate to the sample and mix well with a metal spatula. If the sample has not dried after a few minutes, another 10g may be added for fish and biota samples. Soils and Solid samples are mixed with Sodium Sulfate to dry the sample. Once the sample is well-dried and free flowing, transfer the sample to a pre-rinsed extraction thimble. **Be careful not to add too much drying agent to the sample, if too much is added, the sample may not fit completely in the thimble. In this case the sample will have to be split into two different soxhlets.**

14.2.6 Add 200 mL of a 1:1 mixture of Hexane/Acetone to a 250 mL round bottom flask. Add several boiling chips. Place a soxhlet extractor on top of the round bottom flask. Label the round bottom with the sample number. Place the corresponding thimble into the soxhlet extractor. After all samples have been processed, add the specified surrogate and matrix spikes required directly into thimble.

14.2.7 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

14.2.8 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5.5. At this time double check soxhlets for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

14.2.9 The samples should be extracted overnight for a minimum of 16 hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condenser with several pipette volumes of Hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet.

14.2.10 Move soxhlet units into a chemical fume hood and flush the remaining solvent from the soxhlet extractor by tipping the soxhlet. Using a pair of long-handled tweezers, pull the thimbles out of the soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the soxhlets. Once dry; remove the thimbles to an aluminum foil sheet for total solvent evaporation then wrapped up foil and put in solid PCB waste bucket.

14.2.11 Rinse the soxhlet with several pipette full of Hexane and tip again to drain into the round bottom. Set the soxhlet aside at this time. Procure the same number of Turbo Tubes as there are samples. Using an individual Turbo Tube stand, label a TurboTube with the corresponding sample ID number and place in the

holder. Pre-rinse turbo tubes with hexane and allow to dry. Then add a suitable amount of Sodium Sulfate to round bottom flask and swirl around to remove any residual water. Pour the contents of the round bottom into the TurboTube, using a pipette and Hexane to rinse the last drops out of the mouth of the round bottom. Rinse the round bottom with several pipettes full of Hexane, swirl gently, and decant into same TurboTube. Repeat this step twice for same sample then repeat all preceding steps for all other samples.

14.2.12 All glassware must be rinsed with technical grade (tech)-Acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

14.3 Solvent Reduction: TurboVap Evaporator System

14.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The TurboVap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

14.3.2 Turn the unit on (switch is located on the back side of the unit) and allow to heat up to the specified temperature for individual solvent use. This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light.

14.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that gas pressure regulators is off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty TurboTube into the water bath and close the lid. Make sure that the nitrogen gas pressure regulator is turned off. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4. Make sure to wipe down all surfaces with Hexane before concentrating samples. Rinse each tip with solvent then close and turn the pressure up to blow the lines clean.

14.3.4 Place the TurboTube containing the samples into the TurboVap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

14.3.5 The process for solvent (Hexane/Acetone) reduction takes approximately 30-45 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Blow down to approximately 50mL's then recharge with solvent to 200mL's for solvent exchange and blow down to appropriate

concentration. Immediately notify a supervisor if an extract is blown to dryness.

14.3.6 Concentrate the solvent to approximately 10.0 mL. Remove the samples from the TurboVap and place in the rack. **NOTE:** Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 10.0 mL point is achieved Samples, which stop reducing, should be removed as soon as possible.

14.3.7 Quantitatively transfer the sample extract with a Pasteur pipette into an appropriate volumetric flask (25ML for soil extracts). Rinse the TurboTube with 3 Pasteur pipettes of Hexane, and then transfer the Hexane rinse to the volumetric. Repeat the Hexane rinse two more times for a total of three Hexane rinses of the TurboTube. After the sample has been transferred, rinse the Pasteur pipette with 0.5mL of Hexane into the volumetric flask. Add Hexane to the volumetric meniscus mark. Invert the volumetric flask and decant the contents into a pre-labeled 40mL vial.

14.3.8 All dirty glassware must be rinsed with tech-Acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

14.4 Sample Extract Cleanup

14.4.1 Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

14.4.2 Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The sample preparation chemist in the extraction logbook records the sequence and number of repeats of cleanup steps performed. Sample extract cleanups are performed on set volume extracts. The default set volume is 25 mL for soil/sediment/solid samples.

14.4.3 Cleanup procedure will be done in the following order unless otherwise noted, Sulfuric Acid Wash, Florisil Slurry then TBA/Hg Shake.

14.4.3 Sulfuric Acid Wash

14.4.3.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds that are co-extracted with the PCB residues.

14.4.3.2 Add 5.0 mL concentrated H_2S0_4 and shake for 30 seconds by hand, centrifuge for approximately 2 minutes, transfer approximately 20mLs of the Hexane upper layer to an 8 dram vial.

14.4.3.3 Repeat 8.4.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note:** it is entirely possible that all colored material will not be removed from the extract.

14.4.4 Florisil Adsorption (Slurry)

14.4.4.1 The Florisil slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

14.4.4.2 Add approximately 3 grams of tested and approved deactivated Florisil to each vial containing the sample extract. **SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.**

14.4.4.3 Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker.

14.4.4.4 Place the vial(s) into the centrifuge for 2 minutes on setting (½).

14.4.4.5 Transfer the extract to a clean 40mL vial.

14.4.5 Elemental Sulfur Clean-up

14.4.5.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found sediment/soil samples, decaying organic material and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

14.4.5.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

14.4.6 Removal of Sulfur Using Mercury

Note: ***Mercury is a highly toxic metal. All operations involving mercury***

should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

14.4.7.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

14.4.6.2 Transfer the sample extract to a new 8 dram vial.

14.4.6.3 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or Florisil slurry (discussed in 8.8.0).

14.4.6 Removal of Sulfur using TBA Sulfite

14.4.7.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water soluble.

14.4.7.2 Add 2.0mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 1 scoop (using the dedicated dispenser) of sodium sulfite crystals to the extract and shake for at least 45 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more scoops to the extract and observe.

14.4.7.3 Place the samples on the wrist shaker for 45 minutes observing at 15 minute intervals to make sure that the sodium sulfite is not consumed. After the 45 minutes add 5mL's of organic free water and shake for 15 minutes.

14.4.7.4 Place the samples into the centrifuge and spin for approximately 2 minutes on setting #4.

14.4.7.5 Transfer the Hexane layer to a new 40mL vial and cap.

14.5 Extract Screening and Dilution:

14.5.1 *PCB extracts are generally screened by GC to determine the approximate concentration before final analysis. Prior site history and client supplied estimates of sample concentration may be used to determine what, if any, extract dilution is necessary. Extracts of unknown concentration are generally screened at a 10 to 100 fold dilution.*

14.5.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of Hexane. For example, adding 1.0 mL of the extract to 9.0 mL Hexane performs a 1 to 10 dilution. The vial containing the diluted extract is labeled denoting the equivalent extract volume after the dilution; e.g. a 25mL extract diluted 1 to 10 is labeled "250X", an undiluted 25mL extract is labeled "25X". When high dilutions are prepared, secondary (serial) dilutions of the initial diluent are prepared; e.g. a 100 fold dilution is prepared by a 1 to 10 dilution of the initial extract, then a 1 to 10 dilution of the resulting diluent.

14.5.3 Perform the dilution using appropriate class "A" disposable volumetric pipettes to transfer the extract and to add the make-up volume of Hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

14.5.4 Transfer 1 mL of the extract to a labeled 1.5 mL GC autosampler vial. Record the screening dilution on the GC Queue Lab Sheet (LIMS spreadsheet) along with the extract volume, the sample mass, and the percent total solids. Submit the GC Queue Lab Sheet with the sample extracts to the GC analyst.

15.0 CALCULATIONS

15.1 If the PCB concentration is to be determined on a dry weight basis the percent total solid

must be determined. Weigh approximately 5 grams of the previously homogenized sample in a previously weighed, aluminum weighing pan. Record the weight of the pan and the weight of the (pan and sample) into the LIMS system. Place the sample in a drying oven at 100 to 110°C for at least 4 hours. Record the time placed in the oven and the oven temperature in the LIMS system. Remove the samples from the drying oven and allow to cool. Weigh the pan and sample.

15.2 Calculate the **Percent Solids** by:

$$\frac{\{(\text{wt. of pan + dried sample}) - (\text{wt.of pan})\}}{(\text{wt. of wet sample})} \times 100$$

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIDGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

16.0 METHOD PERFORMANCE

16.1 Please see determinative method (Lab SOP NE148) for details

17.0 POLLUTION PREVENTION

17.1 Pollution Prevention: see NEA168.SOP

.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 Please see determinative method (Lab SOP NE148) for details.

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 Please see determinative method (Lab SOP NE148) for details.

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 Please see determinative method (Lab SOP NE148) for details.

21.0 WASTE MANAGEMENT

21.1 Waste Management: see NEA054.SOP, NEA083.SOP, NEA089.SOP.

22.0 REFERENCES

22.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

22.2 "Guide to Environmental Analytical Methods", Third Edition, Genium Publishing Corporation, 1996.

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.1 Appendix A: Activation/Deactivation of Florisil

23.2 Appendix B: Calibration & Analysis for Fish Oil and Caulk

23.3 Appendix C: Soxhlet Extraction for Caulk and Clean-up Procedures

23.4 Appendix D: Outline of PCBs in Soil/Sediment for Soxhlet Extraction

Appendix A:

1.0 Activation and Deactivation of Florisil (For Florisil Columns)

1.1 The Florisil is purchased from US Silica in 500-gram jars. The US Silica lot is tested prior to purchase to check for purity.

1.2 To fully activate the Florisil place jar into a drying oven. Heat the oven to 200°C +/- 5°C, bake for 12 hours. At the end of the 12 hours reduce the temperature to 50°C and remove the jar. **Caution:** the jar will be hot, wear heat resistant gloves to remove from the oven. Place the jar wrapped in aluminum foil into a dessicator while cooling. When the jar is cool remove the aluminum foil and put the cap on. Do not replace cap when the jar and Florisil is hot.

1.3 To deactivate the 500g of activated Florisil to water content of "3%" add 15 mL, for "4 %" add 20 ml of the HPLC OmniSolv Water. Note: you will need two people to do this. Have one person hold the jar at a 45° angle and slowly turn the jar. The second person will slowly add drops of the water to the center of the Florisil. Once this is completed return the cap to the jar.

1.4 *Roll the jar for overnight (12 Hours) on the cell roller.*

Appendix B:

1.0 Preparation of Florisil Column

1.1 Rinse a 1cm x 15cm chromatography column with course glass frit and stopcock with approximately 50mls of acetone and then 50mls of hexane 3 times each.

1.2 Weigh out in a tared aluminum-weighing pan or 10mL glass beaker 8 grams of 4% deactivated Florisil. Pour the Florisil into column and top with a 2-gram layer of sodium sulfate.

1.3 Gently tap the column on the sides and on the clamp with a rubber bulb to pack the Florisil and sodium sulfate for uniformed packing and to eliminate channeling.

2.0 Preparing Calibration Standard for Florisil Column

2.0 Pipette 1 mL of Aroclor 1221 1PPM and 1 mL of Aroclor 1254 1PPM into a 4-dram vial. Add 1ml of the 0.5PPM TCMX/ 5.0PPM DCBP surrogate standards. Hand shake the vial and mix well.

2.2 Using a pipette quantitatively transfer the “Calibrating Standard” to the column.

2.3 Rinse the vial 3 times with hexane, and pipette separately to the column.

2.4 Elute the column with 75 mL of hexane.

3.0 Column Fraction collection

3.1 Fraction 1: Collect the first 30 mL in a graduated cylinder. (0-30mL)

3.2 Fraction 2: Collect the next 10 mL in a graduated cylinder. (30-40mL)

3.3 Fraction 3: Collect the next 10 mL in a graduated cylinder. (40-50mL)

3.4 Fraction 4: Collect the next 10 mL in a graduated cylinder. (50-60mL)

3.5 Fraction 5: Collect the next 10 mL in a graduated cylinder. (60-70mL)

3.6 When the collections are complete pipette 1 mL of each fraction into separate 2mL GC vial for GC analysis.

3.7 The remaining extract for each fraction is transferred to 4 and 8-dram screw top vials for archiving.

4.0 GC Analysis

4.1 The fractions will be analyzed as PCB Aroclor samples on the low level water GC

4.2 Data Assessment and Acceptance Criteria

4.2.1 The GC department/ Ann Casey will approve the batch of Florisil.

4.2.2 The elution volume calibrated will be based on the last fraction that has quantifiable amounts of PCBs. Typically the last fraction to have quantifiable amounts is the 60-70 ml fraction.

4.2.3 If all the PCB peaks have eluted off the Florisil by the 0-30mL or no TCMX and DCBP is in 30-40mL fraction the batch is rejected. The batch of Florisil is removed and reprocessed. To reprocess the Florisil it is retuned to the oven as in step and processed again. If the batch does not pass after reprocessing the Florisil is rejected and not used for sample processing.

4.2.4 If fraction 7 contains quantifiable amounts of PCBs the batch is re tested with the calibration standards and rerun. If the same results are obtained the batch of Florisil is removed and reprocessed fully. If it does not pass after reprocessing, the Florisil is rejected and not used for sample processing.

4.2.5 The CCV check standard response must be within +/- 15% of the known value for each Aroclor.

4.3 Calibrated Florisil Approval

4.3.1 The GC department will approve the batch of Florisil and will generate a label.

4.3.2 The Label will be as follows:

500g DEACTIVATED FLORISIL @ 4%

US SILICA LOT #
ACTIVATED: 11/29/07
DEACTIVATED:11/30/07 with 20mL H2O
GC Analysis:
USE 8g of Florisil
ELUTE with 70mL Hexane
Collect 60mL of Hexane

Tech: GC Analyst: Approved: A. Casey

Appendix C:

1.0 Soxhlet Extraction

1.1 Caulking material itself is made of several different polymer components, many of which can interfere with the extraction and detection of PCBs.

1.2 NEA normal extraction by Soxhlet 3540 NEA SOP 005_06. The Soxhlet extraction SOP should be followed with these modifications:

1.2.1 Since Caulking can be highly contaminated with PCB Aroclors and have several polymer/oils that interfere with the extraction/cleanup and analysis sample size should be no greater than 5-grams.

1.2.2 Weight out the caulk sample (Warning caulk may also contain Lead and or Asbestos) if possible cut the caulk into small pieces and mix with Na2SO4. For dry and brittle caulk carefully mix.

1.2.3 Transfer the sample to a prep rinsed thimble and top with Na2SO4.

1.2.3.1 Added 0.5mL of TCMX Tetrachlorometaxylene @ 0.5 PPM and DCBP Decachlorobiphenyl @5.0 PPM surrogate in hexane to all samples.

1.2.3.2 Lab Control samples B & LCS made with Na2SO4 Aroclor 1254 is the Aroclor of choice for control spikes.

1.3 Extract the samples with 1:1 Hexane : Acetone for 14+ hours.

1.4 When the extraction cycle is complete transfer the sample extract to a turbo tube for blow down and solvent exchange.

1.5 Solvent switch the extracts to hexane and set to approximately 25mls in an 8-dram vial for clean ups.

NOTE: THIS IS NOT YOUR SET VOLUME.

2.0 Caulk Sample Clean-up

2.1 Acid clean-up (3 to 4 may be needed)

2.1.1 Chill samples for at least 5 minutes by placing into freezer.

2.1.2 Add Slowly 3.0 ml concentrated sulfuric acid (H2SO4) to sample or until you see a color change stop.

2.1.3 Shake vigorously by hand.

2.1.4 Centrifuge in bench top centrifuge at ¾ speed 2min.

2.1.5 Transfer solvent (top) layer to clean 8-dram vial.

2.1.6 Backwash acid vial with 1mL of Hexane x3 transfer Hexane to 8-dram.

2.1.7 Repeat this 1 more time.

2.1.8 3rd Acid wash

2.1.8.1 Shake vigorously by hand.

2.1.8.2 Place sample sonication water bath, sonicate for 2 min.

2.1.8.3 Centrifuge in bench top centrifuge at ¾ speed 2min.

2.1.9 Transfer solvent (top) layer to clean ACE vial.

2.1.10 Backwash acid vial with 1mL of Hexane x3 transfer Hexane to the ACE vial.

2.1.11 Do acid washes until extract is clear.

2.1.12 If extract will not clear try 10% slurry shake and transfer to ACE vial 1mL of Hexane x3 transfer.

2.1.13 Using the blow down apparatus, concentrate samples down to 2-4 ml in Hexane.

2.2 Florisil Clean-up Columns

2.2.1 Rinse a 1cm x 15cm chromatography column with course glass frit and stopcock with approximately 50mls of acetone and then 50mls of hexane 3 times each.

2.2.2 Weigh out in a tared aluminum-weighing pan or 10mL glass beaker 8 grams of 4% deactivated Florisil. Pour the Florisil into column and top with a 2-gram layer of sodium sulfate.

2.2.3 Gently tap the column on the sides and on the clamp with a rubber bulb to pack the Florisil and sodium sulfate for uniformed packing and to eliminate channeling.

2.2.4 Using a pipette quantitatively transfer the sample to the column.

2.2.5 Rinse the vial 3 times with hexane, and pipette separately to the column.

2.2.6 Elute the column with 60 mL of hexane. (DO NOT LET THE Column go dry).

2.2.7 Collect the amount of Hexane listed on the calibrated Florisil jar (50ml) into a graduated cylinder.

2.2.8 Quantitatively transfer the sample from the graduated cylinder to an ACE Vial rinse the graduated cylinder time 3 with hexane.

2.2.9 Using the blow down apparatus, concentrate samples down to 10 ml in Hexane. Rinse times 3 with hexane for transfer.

2.2.10 Transfer sample to a 25ml volumetric flasks and set to volume.

Appendix D

Outline for PCBs IN SOIL/SEDIMENT
For Soxhlet Extraction

1. **PREPARE SAMPLE FOR PREPARATION**
2. **RINSE EXTRACTION THIMBLES**
3. **WEIGH SAMPLE AND RECORD WEIGHT**
4. **DRY SAMPLES**
5. **ADD SAMPLE TO THIMBLES**
6. **SET UP SOXHLET EXTRACTOR APPARATUS**
7. **ADD SURROGATES AND/OR MATRIX SPIKE**
8. **EXTRACT SAMPLE FOR APPROXIMATELY 18 HOURS**
9. **BREAKDOWN SOXHLET EXTRACTOR APPARATUS**
10. **TRANSFER SOLVENT TO TURBOTUBE**

11. **SOLVENT REDUCTION, USING THE ZYMARK TURBOVAP EVAPORATION SYSTEM**

12. **TRANSFER AND SET VOLUME**

13. **EXTRACT CLEANUP (ACID, MERCURY OR TBA, FLORISIL)**

14. **EXTRACT DILUTION**

15. **GC SCREENING/ ANALYSIS**

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE118_08.DOC
REVISION NUMBER: 08

EXTRACTION AND CLEANUP OF AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS USING THE CONTINUOUS LIQUID / LIQUID EXTRACTION METHOD (SW-846 METHOD 3520C) FOR SUBSEQUENT ANALYSIS BY METHODS SW-846 8082 OR EPA 680

COPY #___

Property of Northeast Analytical, Inc.

The user of this document agrees not to reproduce, scan, or copy this document. The user also agrees not to disclose or make available this document to other outside parties without the authorization by Northeast Analytical, Inc. All rights reserved.

NORTHEASTANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE118_08.DOC

REVISION 8 (07/01/2008)

Author: Carrie Barss
Title: Aqueous Extraction Supervisor

Reviewed by:

Carrie Barss
Aqeous Lab Supervisor

Reviewed by:

Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

Table of Contents

Section 1: Identification of Test Method	pg. 3
Section 2: Applicable Matrix or Matrices	pg. 3
Section 3: Detection Limit	pg. 3
Section 4: Scope and Application, Including Components to be Analyzed	pg. 3
Section 5: Summary of the Test Method	pg. 3-4
Section 6: Definitions	pg. 4
Section 7: Interferences	pg. 4
Section 8: Safety	pg. 4
Section 9: Equipment and Supplies	pg. 4-6
Section 10: Reagents and Standards	pg. 6
Section 11: Sample collection, Preservation, Shipment and Storage	pg. 6
Section 12: Quality Control	pg. 6
Section 13: Calibration and Standardization	pg. 6
Section 14: Procedure	pg. 6-11
Section 15: Calculations	pg. 11
Section 16: Method Performance	pg. 11
Section 17: Pollution Prevention	pg. 11
Section 18: Data Assessment and Acceptance Criteria for Quality Control Measures	pg. 11
Section 19: Corrective Action for Out-Of-Control Data	pg.11
Section 20: Contingencies for Handling Out-Of-Control or Unacceptable Data	pg. 11
Section 21: Waste Management	pg.11
Section 22: References	pg.11-12
Section 23: Tables, Diagrams, Flowcharts and Validation Data	pg.13

1.0 IDENTIFICATION OF TEST METHOD

1.1 Standard Operating Procedure for the Extraction and Cleanup procedures of aqueous samples for Polychlorinated Biphenyl (PCB) Analysis using the Continuous Liquid/Liquid Extraction (CLLE) Technique SW-846 EPA Method 3520C.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This method is applicable to surface water, groundwater, wastewater and other aqueous samples. Samples containing a high concentration of particulate, organic product or other interferences may require separatory funnel extraction in lieu of this procedure.

3.0 DETECTION LIMITS

3.1 Refer to determinative method (EPA Method 8082 for PCB Analysis) for Detection Limits.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and Cleanup of PCBs from aqueous samples using the Continuous Liquid/Liquid Extraction by SW-846 EPA Method 3520C.

5.0 SUMMARY OF TEST METHOD

5.1 A measured volume of sample (usually 1 liter) is adjusted to the appropriate pH. The sample is placed into a continuous liquid liquid extractor and extracted with dichloromethane for 2 hours.

5.2 The extract solvent is exchanged to Hexane utilizing a liquid-vapor evaporation system.

5.3 The extract is set to a final volume. The default set volume is 10mL. The client and/or project specifications may dictate an alternative set volume.

5.3 The extract proceeds through several cleaning procedures including an acid wash, florisil cleanup, and elemental sulfur removal with mercury.

5.4 The extract solvent is presented for GC analysis.

6.0 DEFINITIONS

6.1 **Matrix Spike (MS):** An aliquot of sample, fortified with a known quantity of the analyte(s) of interest, used to indicate the assessment of the analyte(s) recovery efficiency.

6.2 **Surrogate Compound Spike:** A chemical composition similar to the analytes of interest. This is usually not found in the environmental samples. These compounds are spiked into all samples, standards, blanks, and matrix spike(s) samples prior to analysis. Percent recoveries are calculated for each surrogate (refer to **Section 15.0** in NE013 SOP).

6.3 **Quality Control samples:** A set of measures for each sample within an analysis to assure that the process is in control.

6.4 **Internal Standard:** A pure compound added to a sample just before instrumental analysis, used to permit corrections for inefficiencies.

7.0 INTERFERENCES

7.1 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters into the samples through the use of certain plastics. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Samples and extracts should not be exposed to plastics such as gloves, tubing, coating on clamps, and pipette bulbs, etc.

8.0 SAFETY

8.1 The extraction technician should have received in-house safety training and should know the location of first aid equipment and emergency spill / clean-up equipment, before handling any apparatus or equipment.

8.2 Polychlorinated biphenyls should be treated with extreme caution; as a class of chemical compounds they possess both toxic and suspected carcinogenic properties. Refer to MSDS for further details.

8.3 Safety glasses and gloves must be worn when handling glassware and samples. Polychlorinated biphenyls (PCBs) have been tentatively classified as known or suspected carcinogens. The extraction technician must review the Material Safety Data Sheet (MSDS) for PCBs and all reagents used in the procedure before beginning the extractions. All equipment and solvents should be handled within a lab fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 Accelerated One-Step Extractor/Concentrator*;* Corning # 3915-C consisting of:

a) **Jacketed Concentrator Tube**; Corning # 2157-100TJ
b) **Membrane Assembly**, 47 mL; Corning # 3918-47
c) **Extractor Body**, Corning # 3915-MBO
d) **Extractor Cup**; Corning # 3915-ECO
e) **Snyder Sidearm**; Corning # 3915-MSCO
f) **Coupler Assembly**; Corning # 3915-CAO
g) **Photoceram Membrane Support**; Corning # 3918-47MS
h) **Stopcock Assembly**; Corning # 3915-SCA
i) **Connectors/Washers for Stopcock Assembly**; Corning # 3915-CW
j) **35/25 Joint O-Ring, Viton**; Corning # 3915-35VO
k) **Coupler O-Ring**; Corning # 3915-CVO
l) **35/25 Joint Clamp**; Corning # 2140-35
m) **Hose Connectors for Jacketed Concentrator Tube**; Corning # 158-CO
n) **24/40Ttaper Joint Clamp**
o) **Stainless Steel Ball-Joint Clamp**

9.2 **Allihn Condenser;** medium, Corning # 3480-MCO

9.3 **Constant Temperature Circulator;** VWR Scientific and Lauda (one unit each)

9.4 **Neslab Chiller;** CFT-33

9.5 **Graduated Cylinder;** 100 mL; Kimble # 20011-100 or equivalent

9.6 **Beakers;** assorted Pyrex 600 mL and 1000 mL, used for solvent containment and pipette storage.

9.7 **Glass Wool;** Silanized, Supelco #2-0410, solvent washed as per NE159.doc

9.8 **Glass Beads**

9.9 **Disposable Pasteur pipettes (9”);** Krackeler #67-450-900-CS or equivalent

9.10 **pH Indicator Strips;** EM Science# 9590 or equivalent

9.11 **Microliter Gastight Syringes;** 500 and 1000 µL; Hamilton

9.12 **TurboVap Evaporator concentrator tubes (TurboTubes);** Zymark 250 mL, 0.5 mL endpoint.

9.13 **TurboVap Evaporator;** Zymark #ZW640-3

9.14 **Class A volumetric flasks with stoppers;** 5 and 10 mL; Pyrex #5640

9.15 **15mL vials and 40 mL vials** with polyseal caps

9.16 **Vial rack;** plastic rack used to hold vials during all phases of the extract processing.

9.17 **Centrifuge;** International Equipment Co., Model CL (or equivalent)

9.18 **Wrist Shaker;** Burrel wrist action shaker, Model 75 and 88 (or equivalent)

9.19 **Auto sampler vials;** Scientific Resource Inc., # 99468-A or equivalent

10.0 REAGENTS AND STANDARDS

10.1 **1N Sodium Hydroxide;** J.T. Baker #5671-03, UN#1824 or equivalent

10.2 **Dichloromethane;** High purity solvent; Burdick/Jackson, #UN1593

10.3 **Hexane;** High purity solvent; Burdick/Jackson, #UN1208 or equivalent

10.4 **Acetone;** High purity solvent; Burdick/Jackson, #UN 1090 or equivalent

10.5 **Toluene;** High Purity Solvent; Burdick/Jackson, #UN1294 or equivalent

10.6 **1:1 Sulfuric Acid;** Mallinckrodt #2468, #UN1830, for pH adjustment (1:1 H_2SO_4 preparation: To a beaker containing 500mL cold DI water, slowly and under constant stirring, add 500mL concentrated H_2SO_4. Allow the mixture to cool after preparation.)

10.7 **Concentrated Sulfuric Acid;** Solvent washed as per NE174.doc, Mallinckrodt #2468, #UN1830 or equivalent

10.8 **Florisil;** J.T. Baker #M368-08. Solvent washed per NE094-05.doc
SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.

10.9 **Mercury;** Triple distilled, solvent washed as per NE175.doc, Mercury Waste Solutions Inc. (or equivalent)

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

11.1 The samples should be collected in unpreserved 1 liter glass bottles with Teflon lined cap. Samples should be delivered to the laboratory on ice and should be chilled to 4ºC ± 2ºC. Samples are stored in refrigerator at the laboratory at 4ºC ± 2ºC. The sample extraction hold time for this method is five days from the date the samples were collected.

12.0 QUALITY CONTROL

12.1 The extraction technician should have completed an acceptable demonstration of precision and accuracy before performing the method without supervision. The addition of spiking material to a sample or blank must be witnessed by another extraction technicain and noted in LIMS. All surrogates and matrix spikes must meet acceptable QC limits. An approved instructor must also certify the technician to perform the procedure.

12.2 A Method Blank sample and Lab Control Spike (LCS) must be prepared per each extraction batch or 1 per 20 site samples whichever is more frequent. A matrix spike/matrix spike duplicate (or lab duplicate) should be prepared for every 20 site samples or as per client specified quality assurance project plan (QAPP). The spike concentration for LCS, MS, MSD is 1.0 mL for A1242 at 0.5ppm. Client and/or project specifications may dictate and alternate spike amount or Aroclor.

12.3 PCB Surrogate TCMX and DCBP are added to each sample prior to extraction, in order to measure extraction and cleanup efficiency. Default surrogate concentration is: 1.0mL of 0.05ppmTCMX / 0.5ppm DCBP. Client and/or project specifications may dictate an alternate surrogate concentration.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Refer to determinative method (PCB Analysis EPA Method 8082) for Calibration and Standardization.

14.0 PROCEDURE

14.1 SAMPLE PREPARATION

Note: Unless otherwise noted, when rinsing is referred to in this SOP, it will be with a Teflon squirt bottle. A solvent followed by a (b) will be used to designate solvent from a beaker.

14.1.1 Throughout the entire process it should be noted that if the extraction chemist encounters any problems or difficulties with any samples or steps involved, all work should **STOP!!!** Any problems should be brought to the attention of the supervisor and documented in LIMS.

14.1.2 Before any steps are taken; the extraction chemist should first review the sample identification on the labels against the chain of custody in the job folder. Any discrepancies should be noted in LIMS.

14.1.3 Bring samples to room temperature by letting the samples warm up in the laboratory for a minimum of 30 minutes.

14.1.4 Mark the level of the sample on the outside of the sample container with a paint pen. Determine the pH of the sample by removing a small amount of sample with a disposable Pasteur pipette (approximately 0.1 mL) and wet a pH indicator strip. The pH should be between 5 and 9. Adjust the pH with 1:1 sulfuric acid if the pH is greater than 9 or 5N sodium hydroxide if the pH is less than 5. Record the original pH in LIMS.

14.1.5 Using 1 liter precleaned amber bottles; measure out two 1-liter aliquots of DI water to be used as an extraction blank and a laboratory control spike.

14.2 ASSEMBLY OF PYREX ACCELERATED ONE STEP EXTRACTOR / CONCENTRATOR

14.2.1 See NEA233.SOP

14.3 EXTRACTION

14.3.1 **Observe sample:** In case of a high amount of sediment or very fine particles, place glass wool and some glass beads on top of membrane assembly. This will prevent the obstruction of the membrane.

Note: DO NOT pack the glass wool down, otherwise you will obstruct the flow through the membrane.

14.3.2 Pour 55mL Dichloromethane (b) into extractor body. Check extractor for leaks which will most likely occur between the extractor body and cup assembly.

14.3.3 Add sample to the extractor unit. Rinse sample bottle with 55mL Dichloromethane (b) and add to extractor unit.

14.3.4 Add surrogate and matrix spike compound solutions directly into sample in the extractor body.

14.3.5 Place condenser into top of extractor body.

14.3.6 Open stopcock when both the chiller and constant temperature circulator have reached proper operating temperature (~5° for chiller and 79° for heater). Solvent will begin to flow from extractor body into concentrator tube and immediately begin to boil.

14.3.7 Periodically verify that the boiling rate of the solvent is approximately 900 mL per hour (once the unit is running and stabilized) as follows:

14.3.7.1 Note solvent level in concentrator tube.

14.3.7.2 Close stopcock and record how long it takes to boil 50 mL of solvent over into extractor body.

14.3.7.3 The solvent should boil off in approximately 3 to 3.5 minutes, if the boiling rate is correct.

14.3.7.4 If **boiling rate** is too **slow**: Increase the temperature of the hot water circulator bath. If **boiling rate** is too **fast**: Decrease the temperature of the hot water circulator bath.

14.3.8 Allow extraction to proceed for 2 hours.

14.3.9 Fill up sample bottle with water to previous level. Pour water into a 1 liter graduated cylinder and record sample volume in LIMS. Discard sample container according to guidelines in Chemical Hygiene Plan.

14.4 SAMPLE EXTRACT CONCENTRATION

14.4.1 Close stopcock and allow solvent in concentrator tube to boil down.

14.4.2 When desired concentration volume of less than 10mL is reached, disconnect the concentrator tube from the hot water flow.

Note: Sample will continue to boil while apparatus is cooling down. Sample extract will reflux from Snyder sidearm, which will increase the extract volume.

14.4.3 Attach the cold-water tubing to the concentrator tube.

14.4.4 Start cold water flow and cool for 10 to 15 minutes.

Note: Make sure extract is cold before disconnecting concentrator tube or loss of analytes may occur.

14.5 DISASSEMBLY

14.5.1 See NEA233.SOP.

14.6 SAMPLE TRANSFER

14.6.1 Using a pre-rinsed Pasteur pipette transfer the sample extract into a correctly labeled and Hexane pre-rinsed TurboTube or 40mL vial.

14.6.2 Rinse inside of concentrator tube with 3 Pasteur pipette volumes of Hexane and add to the sample extract. Repeat this step twice. Rinse down the inside walls of the Turbo Tube. Add enough Hexane to the extract to get a total volume of approximately 100mL in the TurboTube OR in the case of the 40mL vial add enough Hexane for a total of approximately 20mL.

14.7 SOLVENT REDUCTION: TURBOVAP EVAPORATOR SYSTEM

14.7.1 The TurboVap evaporator system is used to reduce the sample volume. The TurboVap uses a heated water bath and positive pressure nitrogen flow with vortex action. The unit maintains a slight equilibrium imbalance between the liquid and the gaseous phase of the solvent extract, which allows fractional reduction of the solvent without loss of higher boiling point analytes.

14.7.3 Turn the Turbo Vap allowing it to heat up to 40º C ± 2º C.

14.7.3 As a precaution the TurboVap system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples. Make sure that the lid and the nitrogen gas pressure regulator are closed, and that the cells or rows are turned on. Bleed any residual gas until the regulator gauge reads "0" psi.

14.7.4 If the sample was initially stored in a 40mL vial, pour sample into a hexane pre-rinsed and correctly labeled TurboTube. To complete the transfer, rinse the threads with one disposable pipette volume of hexane. Rinse the 40mL vial with three pipette volumes of hexane. Add this to the TurboTube. Repeat this twice. Rinse down the inside walls of the TurboTube. Bring the volume up to approximately 100 mL with hexane.

14.7.5 Add 200 uL of toluene to the sample extract (6-8 drops from a disposable pipette) for 8082 analysis. No toluene is added for 680 analysis.

14.7.6 Wipe down the inside of the TurboVap with a Hexane wetted paper towel including top lid and pins. Place turbo tubes containing the sample extract into TurboVap and close lid. Slowly open the pressure regulator. Keep the gas pressure very low to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

14.7.7 The process for solvent (dichloromethane/hexane) reduction takes approximately 30 minutes. **DO NOT** leave the unit unattended as extracts may be blown to dryness and loss of PCB, surrogate, or matrix spike may occur. Immediately notify the extraction supervisor if an extract is blown to dryness and note the incident in LIMS.

14.7.8 Concentrate the solvent to approximately ½ the set volume. Remove the samples from the TurboVap and place into tube rack.

14.7.9 Using a disposable pipette quantitatively transfer the sample extract into a hexane pre-rinsed volumetric. Use hexane (b) to rinse the TurboTube and set to volume. Invert the volumetric with a prerinsed stopper several times to mix completely.

14.7.10 Transfer sample from the volumetric to a correctly labeled 15mL vial .

14.7.11 All dirty glassware must be rinsed with acetone and dried in the fume hood before being washed with warm water, rinsed with RO water, and muffled.

14.8 SAMPLE EXTRACT CLEAN-UP PROCEDURE

Note: Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances, which must be removed before accurate chromatographic analysis can be performed. Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the extract technician combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The extraction technician records the sequence and number of repeats of cleanup steps performed in LIMS. Sample extract cleanups are performed on set volume extracts. The set volume is 5mL or 10mL for water/wastewater samples.

14.8.1 Sulfuric Acid Wash

14.8.1.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds which are co-extracted with the PCB residues.

14.8.1.2 Add one Pateur pipette volume full of solvent washed concentrated sulfuric acid (NE174.doc) to each extract vial and shake by hand in a fume hood for 30 seconds. Then centrifuge for at least 1 minute on setting #4. Transfer the hexane (upper) layer to a correctly labeled, pre-rinsed, 15mL vial.

14.8.1.3 Repeat 14.8.1.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required.

***Note*: It is entirely possible that all colored material will not be removed from the extract.**

14.8.2 Florisil Absorption (Slurry)

14.8.2.1 The florisil slurry removes co-extracted polar compounds, residual water and residual acid.

14.8.2.2 Add one spatula of florisil to each extract vial

***Note*: See supervisor for the appropriate florisil deactivation concentration to be used.**

14.8.2.3 In a fume hood vigorously shake the vial for approximately 30 seconds by hand. Swirl to get any florisil off the walls of the vial, then allow to settle.

14.8.2.4 Transfer the hexane (upper) layer to a correctly labeled, pre-rinsed, 15mL vial.

14.8.3 Removal of Sulfur Using Mercury

NOTE: Mercury is a highly toxic metal; all operations involving mercury should be performed within a fume hood. Prior to using mercury, the extraction chemist should become aquatinted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the Material Safety Data Sheet (MSDS).

14.8.3.1 Add 1-3 drops of solvent washed mercury (NE175.doc) to the sample extracts and cap. Handshake for 15-30 seconds. If the mercury changes color, or breaks up into tiny balls and will not reform the original ball, change the mercury. To change the mercury transfer extract into a new correctly labeled and hexane pre-rinsed 15mL vial and add new mercury to it. Repeat previous step. Place on wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

14.8.3.2 Remove the sample extracts from the wrist shaker.

14.9 Final Extract Preparation

14.9.1 Label 15mL vials with the client, test, dilution factor, date and sample ID number. Transfer the extract to the hexane pre-rinsed, correctly labeled final 15mL vial.

14.9.2 Transfer approximately 1.0 mL into a labeled 1.5 mL GC autosampler vial.

14.9.3 Submit all final vials along with the project folder containing the Extraction Log and GC Queue Lab Sheet to the analyst.

15.0 CALCULATIONS

15.1 Please consult determinative method (PCB Analysis, EPA Method 8082) for calculations**.**

16.0 METHOD PERFORMANCE

16.1 Please consult determinative methods (EPA Method 8082 (NE148.doc) and EPA Method 680 (NE040.doc) for Method Performance details.

17.0 POLLUTION PREVENTION

17.1 Refer to NEA168.SOP for pollution prevention measures

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

18.1 Please consult determinative methods (EPA Method 8082 (NE148.doc) and EPA Method 680 (NE040.doc) for Data Assessment and Acceptance Criteria for Quality Control Measures.

19.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA

19.1 Please consult determinative methods (EPA Method 8082 (NE148.doc) and EPA Method 680 (NE040.doc) for Corrective Action for Out-Of-Control Data

20.0 CONTIGENCIES FOR HANDLING OUT-OF-CONTROL DATA

20.1 Please consult determinative methods (EPA Method 8082 (NE148.doc) and EPA Method 680 (NE040.doc) for Contingencies for Handling Out-Of-Control or Unacceptable Data

21.0 WASTE MANAGEMENT

21.1 Please see NEA054.SOP, NEA083.SOP and NEA089.SOP

22.0 REFERENCES

22.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

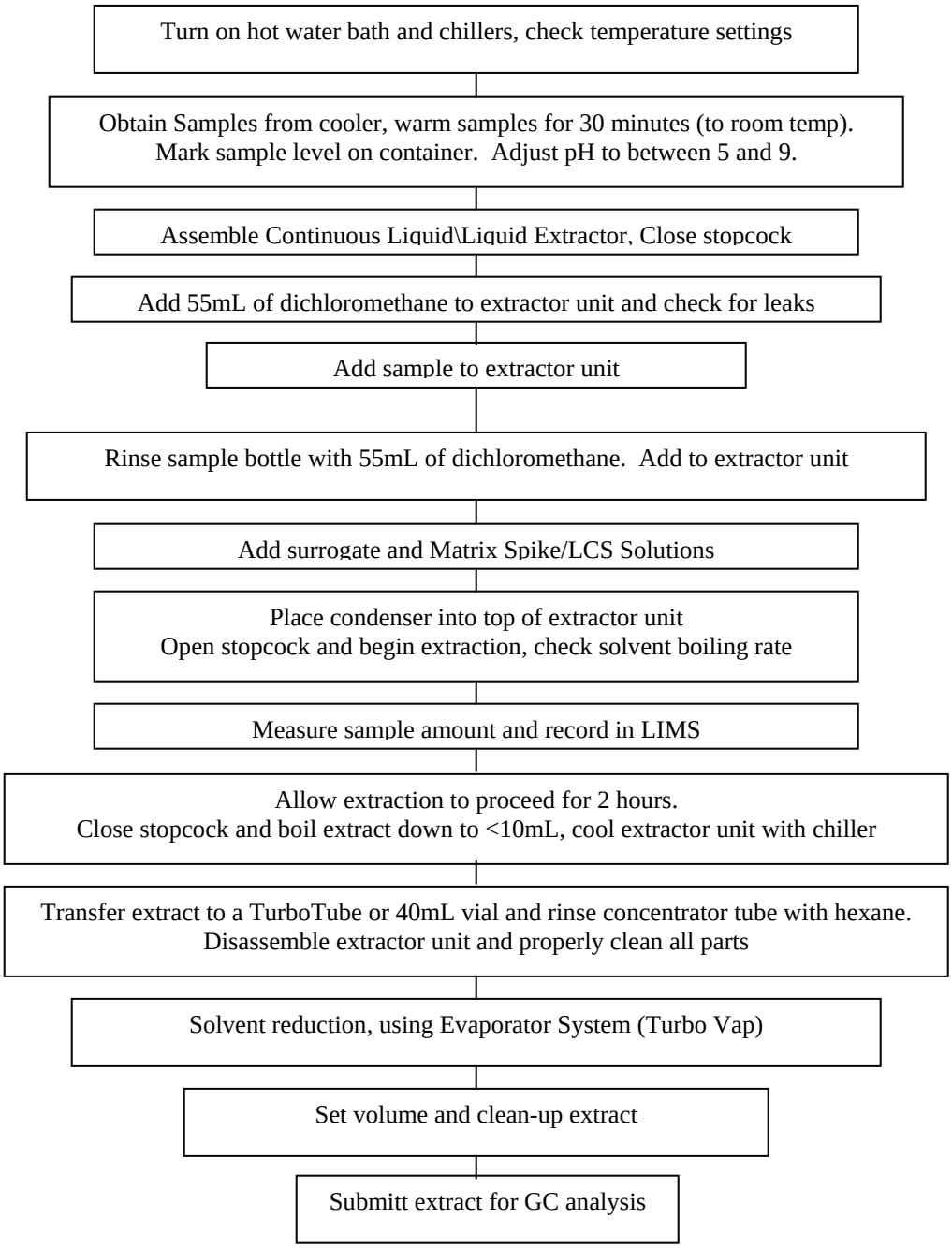
22.2. "Guide to Environmental Analytical Methods", Fourth Edition, Genium Publishing Corporation, 1998.

22.3 EPA Method 680 –EMSL Cincinnati, Ohio: Ann Alford-Stevens, Thomas A. Bellar, James W. Eichelberger, William L. Budde. November 1985.

23.0 ATTACHMENTS

23.1 Attachment A: Flowchart for the extraction and cleanup procedures for CLLE setup

23.1


Turn on hot water bath and chillers, check temperature settings
Obtain Samples from cooler, warm samples for 30 minutes (to room temp).
Mark sample level on container. Adjust pH to between 5 and 9.
Assemble Continuous Liquid\Liquid Extractor, Close stopcock
Add 55mL of dichloromethane to extractor unit and check for leaks
Add sample to extractor unit
Rinse sample bottle with 55mL of dichloromethane. Add to extractor unit
Add surrogate and Matrix Spike/LCS Solutions
Place condenser into top of extractor unit
Open stopcock and begin extraction, check solvent boiling rate
Measure sample amount and record in LIMS
Allow extraction to proceed for 2 hours.
Close stopcock and boil extract down to <10mL, cool extractor unit with chiller
Transfer extract to a TurboTube or 40mL vial and rinse concentrator tube with hexane.
Disassemble extractor unit and properly clean all parts
Solvent reduction, using Evaporator System (Turbo Vap)
Set volume and clean-up extract
Submitt extract for GC analysis

Northeast Analytical, Inc.
2190 Technology Drive
Schenectady, NY 12308

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) AROCLORS BY US-EPA SW-846 METHOD 8082

SOP Name: NE148_06.SOP
Revision: 06
Date Effective: February 19,2009
Issuing Section: GC Analysis

Controlled Copy #____

Reviewed and Approved By:

Chemist :

_____ Date: 02/19/09

Kari Lantiegne

Laboratory Director:

_____ Date: 02/19/09

Robert E. Wagner

QA/QC Director:

_____ Date: 02/19/09

Christina L. Braidwood

Property of Northeast Analytical Inc.

The user of this document agrees not to reproduce, scan, or copy this document. The user also agrees not to disclose or make available this document to other outside parties without the authorization by Northeast Analytical, Inc.

Northeast Analytical, Inc. All rights reserved

Table of Contents

Section 1:	Identification of Test Method	pg. 3
Section 2:	Applicable Matrix or Matrices	pg. 3
Section 3:	Detection Limit	pg. 3
Section 4:	Scope and Application, Including Components to be Analyzed	pg. 3
Section 5:	Summary of the Test Method	pg. 4
Section 6:	Definitions	pg. 4-6
Section 7:	Interferences	pg. 6
Section 8:	Safety	pg. 6
Section 9:	Equipment and Supplies	pg. 7
Section 10:	Reagents and Standards	pg. 7-8
Section 11:	Sample collection, Preservation, Shipment and Storage	pg. 8-9
Section 12:	Quality Control	pg. 9-13
Section 13:	Calibration and Standardization	pg. 14-15
Section 14:	Procedure	pg. 15-17
Section 15:	Calculations	pg. 17-18
Section 16:	Method Performance	pg. 18-19
Section 17:	Pollution Prevention	pg. 19
Section 18:	Data Assessment and Acceptance Criteria for Quality Control Measures	pg. 20
Section 19:	Corrective Action for Out-Of-Control Data	pg. 20-22
Section 20:	Contingencies for Handling Out-Of-Control or Unacceptable Data	pg. 22
Section 21:	Waste Management	pg. 23
Section 22:	References	pg. 23
Section 23:	Tables, Diagrams, Flowcharts and Validation Data	pg. 23-49

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) AROCLORS BY US-EPA SW-846 METHOD 8082

1.0 Identification of Test Method

1.1 This method is used to determine Polychlorinated Biphenyl (PCB) by gas chromatography with electron capture detection and Total Aroclor Quantification using EPA SW 846 Method 8082- Polychlorinated Biphenyl (PCB) Aroclors by Capillary Column GC.

2.0 Applicable Matrix

2.1 This SOP is applicable in the determination and quantification of PCBs as outlined in EPA SW-846 Method 8082. It is applicable to the following matrices: water, soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, tissue samples, caulk, and air cassette samples including polyurethane foam (PUF) and associated filters for EPA Methods TO-4A and TO-10A.

3.0 Detection Limit

3.1 Detection Limit: Reporting Limits (RLs) and Method Detection Limits (MDLs) vary for each compound.

3.1.1 The following are default Reporting Limits based on the lowest calibration standard and global MDL /Reporting Limits based on MDL studies performed by NEA used for EPA Method 8082. See attachment G for example of MDL study. Reporting Limits (PQLs) are based on the Lowest Calibration Standard.

Matrix	Sample Mass/Volume Extracted	Calibration Curve Low Standard	Extract Volume	Global MDL* (All Aroclors)	RL (PQL) (all Aroclors)
Soil/Sediment Solid	10 g	20 ng/ml	25 mL	0.0115 mg/kg	0.050 mg/kg
Water	1 Liter	5 ng/ml	10 mL	0.0075 ug/L	0.050 ug/L
Biota	10 g (wet weight basis)	20 ng/mL	25 mL	0.0104 mg/kg	0.050 mg/kg
Polyurethane Foam Cassette (TO-4A/TO 10A)	1 PUF	20 ng/ml	5 mL	0.021 ug/Puf	0.100 ug/Puf
Waste Oil	0.5 g	20 ng/ml	25 mL	0.200 mg/kg	1.00 mg/kg
Wipe	1 Wipe	20 ng/ml	25 mL	0.115 ug/Wipe	0.500 ug/wipe

3.2 Individual MDLs and RLs are determined every two years for each instrument with matrix specific MDL studies for each extraction methodology. MDLs must be determined again whenever a major change in instrumentation or extraction methodology occurs.

3.3 MDLs are verified annually by the extraction and analysis of a low level MDL verification check sample. The Aroclor must be observed qualitatively in the MDL verification check sample

4.0 Scope and application, including components to be analyzed

4.1 This SOP is applicable in the determination and quantification of PCB as outlined in EPA SW-846 Method 8082. : water, soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, tissue samples, caulk, wipes and air cassette samples including polyurethane foam (PUF) and associated filters for EPA Methods TO-4A and TO-10A.

4.2 In general, samples are extracted, or in the case of oils and waste solvent diluted, with a pesticide grade solvent. Applicable extraction methods for solids and animal tissues include: SW-846 Method 3540 (Soxhlet), SW-846 Method 3545 (Pressurized Fluid Extraction), or SW-846 Method 3550 (Ultrasonic Extraction). Extraction methods for aqueous samples include SW-846 Method 3510 (Separatory Funnel), and SW-846 Method 3520 (Continuous Liquid Liquid Extraction). The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of clean-up techniques. Applicable cleanup techniques include SW-846 Method 3620 (Florisil Cleanup), SW-846 Method 3660 (Sulfur Cleanup) and SW-846 Method 3665 (Sulfuric Acid/Permanganate Cleanup). The sample is then analyzed by direct injection onto a gas chromatographic system and detected by an electron capture detector.

4.3 This method provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCB by capillary column gas chromatography. Each matrix requires different sample handling or special preparation procedure before analysis can be performed. Each sample matrix will be covered separately in the extraction standard operating procedures.

5.0 Summary of Test Method

5.1 Samples are extracted with a pesticide analytical grade solvent. The extracts are further processed by concentration and a series of clean-up procedures. The sample extracts are then analyzed by injecting onto a gas chromatographic system and with an electron capture detector in series.

5.2 This purpose of this SOP is to provide a detailed written document for quantification of PCB according to SW-846 Method 8082 specification.

5.3 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs by gas chromatography. Sample extraction and cleanup procedures are described separately in additional laboratory Standard Operating Procedures.

5.4 The following PCB Aroclors can be determined by this method*:

Compound	CAS Number
Aroclor 1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

*Note: Additional PCB Aroclor mixtures including Aroclor 1262 and Aroclor 1268 may be analyzed by this method with minor modifications

5.4 Extensive knowledge of this SOP and EPA Method 8082 is required. The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

6.0 Definitions

6.1 Accuracy – The nearness of a result or the mean of a set to the true value. Accuracy is assessed by analysis of references samples and percent recoveries.

6.2 Analytical Batch –The basic unit for analytical quality control is the analytical batch, which is defined as samples which are analyzed together with the sample method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar matrices (e.g. water, sediment, soil, etc.).

6.3 Blank – A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix, however, a universal blank matrix does not exist for solid samples, but sometimes sodium sulfate is used as a blank matrix. The blank is taken through the appropriate steps of the process. A

reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field is sealed containers and transported back to the laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

6.4 Continuing Calibration Check Standard (CCCS) –The continuing calibration check standard contains all target analytes found in the calibration standards and is used to verify that the initial calibration is prepared correctly and that the instrument system is correctly calibrated. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards

6.5 Calibration Standard (ICAL)– A series of known standard solutions used by the analyst for instrument calibration. Calibration standards are prepared from primary standard and/or stock standard solutions.

6.6 CAS Number – An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012, Columbus, OH 43210: [614] 447-3600).

6.7 Duplicate– A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

6.10 Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination as requested or required.

6.11 Initial Calibration – Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

6.12 Instrument Calibration – Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

6.13 Laboratory Control Sample (LCS) – Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot or reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

6.14 Laboratory Method Blank – An analytical control consisting of all reagents and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

6.15 Matrix – The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

6.16 Matrix Spike – Aliquot of sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

6.17 Matrix Spike Duplicate – A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

6.18 Method Detection Limit (MDL) – The minimum constituent concentration that can be measured and reported with 99% confidence that the signal produced is different from the blank in a given matrix. The MDL is determined from a minimum

of seven replicate samples, taken through the entire preparation and analysis procedure. The standard deviation, *s*, of those replicates is multiplied by a student's t factor in order to calculate the MDL.

6.19 MSDS – Material Safety Data Sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs.

6.20 PCB Polychlorinated biphenyls (PCBs) are a class of 209 individual chemical compounds (congeners), in which one to ten chlorine atoms are attached to biphenyl. Use of PCBs has made them a frequent environmental pollutant.

6.21 Precision – The agreement between a set of replicate measurements without assumption of knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis.

6.22 Quality Control – Set of measures within a sample analysis methodology to assure that the process is in control.

6.23 Standard Curve – A standard curve is a curve which plots concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by diluting the stock analyte solution in graduated amounts which cover the expected range of the samples being analyzed. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

6.24 Stock Solution – Standard solution which can be diluted to derive the other standards.

6.25 Surrogate – Organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference sample) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.26 Surrogate Standard – A pure compound added to a sample in the laboratory just before processing so that the overall efficiency of a method can be determined.

7.0 Interferences

7.1 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Laboratory method blanks must be thoroughly reviewed for presence of non-target peaks and comparison of samples with blank chromatographic patterns.

7.2 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

7.3 Polychloroterphenyls (PCTs), polybrominatedbiphenyls (PBB), polychlorinated napthalenes (PCN), as well as dioxins can co-elute with PCBs. Carry-over from these compounds, when in high concentration, is common if clean-up procedures are not followed. These materials may be removed through the use of specified clean-up procedures.

7.4 Pesticides can be a source of contamination through breakdown into components such as hexachlorobenzene (HCB). This chlorinated compound can carry-over on the GC column, and contaminate samples. Specified clean-up procedures should be followed to eliminate this as a source of contamination when analyzing PCBs. High concentrations of pesticides can cause carry-over on GC columns.

8.0 Safety

8.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

8.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. Manipulation of sample extracts outside of a fume hood should be minimized by the analyst.

8.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions for handling solvents and chemicals used to process samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

8.4 Samples remaining after analysis should either be returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance and also standard operating procedure NEO54, disposal of laboratory waste.

9.0 Equipment and Supplies

9.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use a Varian Model 3400 or 3800 (or equivalent) gas chromatograph (or equivalent), equipped with a Model 1077 or 1177 split/splitless injector (or equivalent), temperature programmable oven, Varian Model 8200, Varian Model 8400, or LEAP GC pal automatic sampler (or equivalent), and electron capture detector (or equivalent). A data system and integration of detector signal is interfaced to the gas chromatograph.

9.2 Chromatographic Data System: A data system for measuring peak height and peak area. An Empower computer network based workstation (Waters Corporation), will be employed to capture detector response and digitally store the chromatographic, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

9.3 Column (Primary): ZB-1, Phenomenex Cat. No. 7HG-G001-11; 30 m x 0.25mm x 0.25 um ; DB-1, J&W Part No. 122-1032; 30 m x 0.25 mm x 0.25 um ; or equivalent.

9.4 Column (Secondary): ZB-5, Phenomenex Cat. No. ZB-5-G002-11; 30m x 0.25mm x 0.25 um ; DB-5, J&W Part No. 122-5032; 30m x 0.25 mm x0.25 um; or equivalent.

9.5 Class A volumetric flasks: 5.0 – 100mL.

9.6 8 dram vials and 4 vials dram for sample extract storage.

9.7 Pasteur pipettes.

9.8 250ml and 100ml beakers, glass.

9.9 Disposable 1.0, 5.0, and 10.0 ml pipettes.

9.10 Hexane, Burdick and Jackson-Pest Grade.

9.11 Acetone, Burdick and Jackson.-Pest Grade

9.12 Toluene, Baker, (Cat.No. 9336-03)

9.13 Methylene Chloride, Burdick and Jackson, (Cat. No. 300-4)

9.13 Ferrules: 0.4mm graphite/vespel, Restek 20229, and ¼" graphite ferrules, Restek 20210 or equivalent.

9.14 Injector septa: Thermolite Septa, Restek 20365 or equivalent.

9.15 Injector liner: Low Pressure Drop Liner w/Glass Wool, Restek 21033 or equivalent.

9.16 SGE Injector Syringe 10.0 µL: SGE 002987 or equivalent

9.17 Auto sampler vials: Snap vial 12x32mm Clear w/P, Microliter 11-5200

9.18 Snap Caps: 11mm Natural Snap Cap PTFE, Microliter 11-0051N-B.

10.0 Reagents and Standards

10.1 Analytical Standard Solutions.

10.1.1 Aroclor Stock Standard Solutions

10.1.1.1 Polychlorinated Biphenyls - Neat commercial material for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as electric power transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the trade name Aroclor. These standards should be compared to PCB reference materials to verify commercial materials. To be used as calibration standards, they must have the same pattern and congener distribution.

10.1.1.2 Stock standards are prepared from individual Aroclor formulations by weighing an exact amount of the neat material to the nearest 0.1 g, and dissolving and diluting to volume in a 100 mL volumetric flask with hexane. See Attachment A, Table 1 for exact weights of each compound.

10.1.1.3 The stock standards are transferred into Boston bottles and stored in a refrigerator at 0-6°C, protected from light.

10.1.1.4 The stock standards are transferred into screw-cap boston bottles and stored in a freezer 0°C , protected from light. Stock standards should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards. Stock PCB standards must be replaced after one year, or sooner if a problem with instrument calibration is detected.

10.2 Calibration Standards

10.2.1 Calibration standards are prepared at five concentration levels using a prepared working standard. See Attachment A, Tables 2 and 3A AND 3B for the preparation and exact concentrations of the working standards. The following five standards make up the initial calibration curve standard set for a High Level curve : 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, 1000 ng/mL. The following five standards make up the initial calibration curve set for a Low Level curve: 5 ng/mL, 10 ng/mL, 20 ng/mL, 50 ng/mL, 100 ng/mL.

10.2.1 The two surrogates Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) are included in the A1254 calibration standards. The standard for TCMX/DCBP is prepared by diluting 1 mL of TCMX/DCBP custom standard solution (ULTRA, cat.#CUS-4911, at 500/5000 ng/mL) into a 1000 mL volumetric flask resulting in a solution of TCMX/DCBP at 0.5/5.0 PPM

10.2.2 Refer to Attachment A, Tables 4A and 4B for instructions on preparation of the calibration standards containing A1254 and the surrogates. Refer to Attachment A, Tables 3A and 3B for instructions on preparing the remaining calibration standards.

10.2.3 Transfer all calibration standards to ASE vials and store in a refrigerator at 0-6°C, protected from light. Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

10.3 Continuing Calibration Standards:

10.3.1 The surrogate compounds Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) are included in all Continuing Calibration Check Standards at a concentration near the mid-point of the surrogate calibration curve sequence. All continuing calibration standards are prepared independently from calibration standards, by using an alternate source purchased from standard vendors. Refer to Attachment B, Tables 1-3 for instructions on preparation of these standards.

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 Sample Collection and Preservation:

11.1.1 Routine soil, sediment, sludge, solid, caulk, and concentrated liquid samples should be collected in 8 oz clear glass wide-mouth jars, fitted with a Teflon-lined cap. Aqueous samples should be collected in 1 liter amber glass bottles with a Teflon-lined cap. Project specific protocols may require that containers be pre-cleaned to EPA specification protocol A –. Protect samples from light.

11.1.2 All samples must be placed on ice or refrigerated at >0-6°C from the time they are collected until delivery to the lab.). Samples that are collected within driving distance of the laboratory and delivered the same day may not have reached temperature acceptance limits. These samples are deemed acceptable if evidence of cooling is present (i.e. they are received with ice in the cooler)

11.2 Sample Shipment:

11.2.1 Sample Shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

11.3 Sample Storage:

11.3.1 The samples must be protected from light and refrigerated at >0-6°C from time of receipt until they are removed from storage for extraction. Remaining sample material will be stored protected from light and refrigerated at >0-6°C. Sample will be disposed of or stored / archived according to project specifications.

11.3.2 Routine soil, sediment, sludge, solid, liquid and concentrated liquid samples are stored in a refrigerator dedicated for this type of sample.

11.4 Sample Extract Storage:

11.4.1 Sample extracts must be protected from light and refrigerated at >0-6°C during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements.

11.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

11.5 Required Hold Times

11.5.1 Extraction of solid samples by appropriate technique must be completed within fourteen days from sample collection.

11.5.2 Extraction of aqueous samples by appropriate technique must be completed within seven days from sample collection.

11.5.3 Sample extracts must be analyzed within forty days of sample extraction.

12.0 Quality Control

12.1 This section outlines the necessary quality control samples that need to be generated at the time of sample extraction. The results of the quality control measurement samples document the quality of the data generated.

The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Method Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Cont Cal Check Std	Analyzed prior to each sample batch and at a frequency or one per ten injections. Each analytical sequence must close with a Continuing Calibration Check Standard (CCCS).
Duplicate Analysis	Field generated sample – analyzed at discretion of client.
Matrix Spike	One matrix spike per 20 field samples or designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

12.2 Method Blank

12.2.1 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples and organic-free reagent water blank is processed. The method blank must exhibit PCB levels less than the matrix defined reporting limit (RL). If the method blank exhibits PCB contamination above the reportable RL, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

12.3 Laboratory Control Spike

12.3.1 A Laboratory Control Spike (LCS), also referred to as a QC reference check standard, is extracted with each batch of samples at a rate of one per 20 samples. For water sample, spike one liter of laboratory organic free water, extract and analyze. For solid and tissue samples spike 10 grams of sodium sulfate, extract and analyze. For oil samples spike 1 gram of PCB free oil, extract and analyze. An Aroclor is chosen for the LCS analyte, typically based on program requirements or expected sample contamination. Calculate the percent recovery for the PCB spike. If the percent recovery for the LCS is out of criteria, (70%-130%) the analysis is out of the control and the problem should be immediately corrected.

12.3.2 The following are default Laboratory Spikes Concentrations:

Aqueous Samples: .1.0 mL of A1242 @ 0.5 ug/mL (ppm) yielding a final sample concentration of 0.500 ug/L

Solid Samples: 1.0 mL of A1242 @ 12.5 ug/mL (ppm) yielding a final sample concentration of 10 ug/g

Note: Alternate spike concentrations and selection of Aroclors may be applicable based on project specific requirements.

12.4 Duplicate Analysis

12.4.1 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike/matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

RPD = (DUP1-DUP2)/AVG x 100

Where: RPD = Relative Percent Difference
DUP1 = The greater of the measured values
DUP2 = The lesser of the measured values
AVG = Average of the two analysis

The relative percent difference must be less than or equal to 30%.

12.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.5.1 A matrix spike is to be analyzed at a rate of one matrix spike per every 20 samples. Also matrix spike duplicate or duplicate sample is to be analyzed at a rate of one per every 20 samples. Duplicate samples may be appropriate in place of matrix spike duplicate, for soil and waste samples, where detectable amounts of organics are present.

12.5.2 The following are default Laboratory Matrix Spike Concentrations:

Aqueous Samples: .1.0 mL of A1242 @ 0.5 ug/mL (ppm) yielding a final sample added concentration of 0.500 ug/L

Solid Samples: 1.00 mL of A1242 @ 100 ug/mL (ppm) yielding a final sample added concentration of 10 ug/g

Note: Alternate spike concentrations and selection of Aroclors may be applicable based on project specific requirements.

12.5.3 Analyze one unspiked and one spiked sample. Calculate the percent recovery based on PCB concentration of both samples as follow:

P = A-B/T x 100

Where: P = Percent recovery, %
A = concentration of analyte in the spike sample aliquot
T = Know true values of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

12.5.4 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 70% and less than or equal to 130% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

12.6 Surrogates

12.6.1 A surrogate compound is added to each sample, matrix spike, matrix spike duplicate, duplicate, method blank, and LCS at time of extraction. The surrogate compounds chosen for this method are Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP). The following are typical surrogate amounts added to normal encountered matrices. These amounts can be adjusted if the PCB background levels are high and the surrogate is being diluted out of analysis range.

12.6.1.1 Soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, tissue samples: 0.5ml of 0.5ppm TCMX/ 5.0ppm DCBP set to 25ml final extract volume.

12.6.1.2 Water: 1.0ml of 0.05ppm TCMX/ 0.5ppm DCBP set to 10ml final extract volume.

12.6.2 Only one surrogate analyte needs to meet established control limits for the analysis to be valid. The recovery must fall within lab established limits of 60-140% if lab limits are not available for the analysis to be valid. If percent surrogate recovery is not within laboratory established limits for either surrogate, the following steps are required.

12.6.2.1 Review calculations that were used to generated surrogate percent recovery values to make certain there are no errors.

12.6.2.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

12.6.2.3 Review data for chromatographic interferences.

12.6.2.4 Re-extraction and/or re-analysis of samples may be indicated if problems persist with surrogate recoveries. If the surrogate percent recovery is out of limits on the re-extracted samples, low or high surrogate recovery is due to matrix affects and the data can be reported as estimated. If above steps do not lead to satisfactory results then consult with organics manager to resolve the situation.

12.7 Continuing Calibration Check Standard (CCCS)

12.7.1 The initial CCCS is from an alternative source independent of the calibration check standards. It is prepared at a concentration approximately equal to the midlevel standard. This standard is analyzed after the initial calibration standards, every tenth injection, and at the end an analytical sequence. One check standards must be run with a 24 hour time period. The percent recover must be ±15% of the true value.

12.7.2 If the criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can proceed. Note that all samples which are not bracketed by valid check standards must be re-analyzed when the system is in-control.

12.8 Retention Time

12.8.1 The retention time (RT) windows are established from the Continuing Calibration Check Standard (CCS) peak retention times. The CCS is analyzed three times over a 72-hour period and the standard deviation is calculated from the three retention time measurements. The standard deviation is multiplied by three and this establishes the retention time window for each quantified peak (±3SD). Use the retention time for a peak in the continuing calibration check standard to determine the mid point of the retention time window for the analysis sequence. If the continuing calibration checks fall outside of these windows update the windows using the previous check standard. If the retention times are still outside the established windows instrument maintenance must be performed and recalibration may be required.

12.8.2 This function is performed in the chromatography software graphically as vertical dropdown retention time markers with retention time window brackets. Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-response sample analysis.

12.8.2 See attachment F for an example of calculated retention time windows.
Retention Time Window Study for GC18F Column DB-1

12.9 Analytical Sequence Queue:

12.9.1 The following is an example of the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run after every nine samples in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples. Below is an example of an analytical sequence:

Injections	Material Injected
1	Hexane Blank
2-36	Initial Calibration Standards
37-43	Continuing Calibration Check Standard
44-52	Samples analyses, including method blanks, matrix spikes, matrix duplicates, matrix spike duplicates, and QC reference check standard. A maximum of nine samples between continuing calibration check standards.
53	Continuing calibration check standard
54 and higher	repeat inject. 44-53 sequence

12.10 PCB Aroclor Qualitative Identification and Secondary GC Column Confirmation:

12.10.1 Positive identification of PCB Aroclors is based on comparison of retention time of the five selected quantitation peaks and major non-quantitation peaks for the unknown sample with retention time of reference standards (continuing calibration verification standards). Additionally pattern recognition is used for comparison of unknown samples with reference standards for positive identification. Confirmation of Aroclor presence by secondary GC column analysis may be necessary for highly altered/degraded PCB patterns or for programs including PCB air monitoring, US-EPA CLP protocol and other projects as specified in the site sampling and analysis quality assurance plan.

12.10.1.1 Dual Column/Confirmatory Column Analysis by GC:

Inject samples under same operating conditions and analytical run QA/QC parameters on a secondary GC column of dissimilar phase (e.g ZB-1 and ZB-5). Note: If using dual GC column system, samples are injected sequentially through separate injection ports onto both columns. Samples are analyzed and concentration results are reported.

12.10.1.2 Dual Column/Confirmatory Column Laboratory Default by SW-846:

12.10.1.2. 1 Report **highest** concentration of the 2 column results for each individual Aroclor on the merged EDD, Form 1 or Certificate of Analysis (Note: This is appropriate for Aroclor regulated projects. E.g. Air Monitoring for EPA TO-10A alternative reporting may be based upon total PCB values for PCB- Total regulated projects).

12.10.1.2.2 If **RPD percent** exceeds 40% report the highest concentration result of the two analyses unless observed chromatographic interference or instrumental analysis QA/QC indicates the lower value may be more accurate. P-flag all excursions > 40% and describe interferences or rationale for reporting lower value in Data Narrative.

12.10.1.2.3 If a concentration is above the PQL on one column and below the PQL on the second column, the qualitative presence is not confirmed and the sample is reported as not detected. **Note: If reporting to the MDL is required do the following:**

For reporting the MDL:

a) If one result is greater than the PQL and other result is < PQL (J-flag) Report the **highest** result as confirmed (*unless interference or QC reasons indicate lower value*)

b) If one result is above MDL (J-Flag) and second is Not Detected report the concentration as **not detected**. (Presence not confirmed).

c) If both results are J-Flag values (< PQL) report the **highest** value of the two.

12.10.1.3 **USEPA-CLP/ASP Program Protocols**

a) Report **Lowest** Value of the 2 column results for each individual Aroclor on the merged EDD, Form 1 or Certificate of Analysis (Note: This is appropriate for Aroclor regulated projects. E.g. Air Monitoring for EPA TO-10A alternative reporting may be based upon total PCB values for PCB- Total regulated projects).

b) If **Percent Difference** (not RPD%) exceeds 25% then P-flag all excursions > 25%. Note any chromatographic interferences present in Case Narrative.

c) If one result is greater than PQL and other result is < PQL (J-Flag) Report the **lowest** result (J-Flagged) value (*confirmed hit*).

d) If one result is above MDL (J-Flag) and second is Not detected, report the concentration as **not detected** (*presence not confirmed*).

13.0 Calibration and Standardization

13.1 Gas chromatographic operation parameters: See Attachment C

13.3 Initial GC Calibration

13.3.1 GC calibration is performed by the internal standard calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

13.3.2 Establish the gas chromatographic operating parameters outlined in the Procedure section and prepare the calibration standards at the five concentrations outlined in the Reagent and Standard section. Inject each calibration standard using the GC Autosampler and the parameters outlined in the Procedure section. Note: The same parameters are used for actual samples.

13.3.3 For each Aroclor, 5 peaks are selected to prepare calibration curves. The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (i.e., minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with

organochlorine pesticides. The determined area of the five peaks selected for calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and the peak numbers used.

Aroclor	Peak Numbers
A1016	6 , 7 , 8 , 9 , 10
A1221	1 , 2 , 3 , 4 , 5
A1232	5 , 7 , 8 , 9 , 10
A1242	6 , 7 , 8 , 9 , 10
A1248	11 , 12 , 13 , 14 , 15
A1254	16 , 17 , 18 , 19 , 20
A1260	20 , 21 , 22 , 23 , 24

13.3.4 For the initial calibration curve to be considered valid, the percent relative standard deviation of response factors must be less than 20% over the working range if average calibration factor quantitation is used. Note: the % RSD is a useful check for linearity through the origin and is used as a data quality indicator. In general an inverse weighted linear calibration curve with intercept is used for quantitation and is not replaced with the average calibration factor. For linear calibration curve the Correlation Coefficient R must be greater than 0.99.

13.3.5 Our laboratory uses a computer based chromatography software module (Water Corporation, Empower software) interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. Integration of peak areas and production of chromatograms is performed in the Empower software. All data analysis will be carried out on specialized software developed at Northeast Analytical including calculating calibration curves/response factors, report generation, and archival of data.

13.3.6 If a re-calibration is performed, the CCCS must be analyzed again and values calculated using the new relative response factors. If the CCCS fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.,* GC gas leak, autosampler lines plugged, broken injector liner).

13.4 Retention Time Windows

13.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Select a calibration standard and inject three times within a 72-hour time period.

13.4.2 For each peak calculate the standard deviation resulting from the variation in the three retention times for that peak.

13.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determination.

13.5.3 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that the zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

14.0 Procedure

14.1 Sample Extraction and Preparation

14.1.1 The following SOP's detail sample extraction procedures that are utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE	EPA Method
NE005	Soxhlet Extraction/ Extract Prep	8082, 3540C
NE017	Fish and Biota Extraction	8082
NE088	PCB Extraction Of Wipe	8082, 3540A
NE111	Waste Dilution EPA 3580 for PCB 8082	8082, 3580A
NE120	Extraction and cleanup of PCB by SW-846 3550B	8082, 3550B
NE140	PCB Screening by GC	3510C, 3520C, 3545
NE141	SW-846 3510C H2O PCB extraction	8082, 608, 3510C
NE143	EPA 3545 extraction for 8082 PCB	8082, 3545
NE144	EPA 3545 extraction of wipe for 8082 PCB	8082, 3545
NE151	PUF Extraction for 8082 analysis	8082, 3540C/ TO-10A
NE158	% Lipid Determination Fish & Biota	3540, 3500, 2500A
NE194	High Level PCB extraction for 8082 by SepFunnel	8082, 3510C

14.2 Gas Chromatographic Procedures

14.2.1 Prescreening of sample extracts: See standard operating procedure NE140 for details on the PCB screening procedures used prior to final analysis by this method. Prescreening is a fast and effective way to determine if re-extracts are required and dilutions for over ranged samples. The GC will be standardized by using Aroclor 1221, Aroclor 1242, and Aroclor 1260. These three Aroclor formulations incorporate most environmental PCBs found in sample extracts and provide a good estimate of PCB amount for final dilution for this determinative method. A three level calibration curve is utilized (0.50ug/ml, 2.5ug/ml, and 5.0ug/ml standards). The concentration of each Aroclor (grouped as Aroclor 1221, Aroclor 1242, and Aroclor 1260 only) in a sample will be calculated based on the extract volume (not the sample weight or volume) to supply solution concentration values that show if the extract needs to be diluted for final capillary GC analysis. If a dilution is necessary, sample extracts are diluted to a solution concentration near 0.500ug/g, so ensuring each sample quantifies in the middle of the calibration curve.

14.2.2 Approximately 1.0ml of the final dilution extract is then transferred into a labeled autosampler vial.

14.2.3 The sequence of the analytical queue is set up in the NEA LIMS as a unique batch file. This file contains the exact order in which standards, instrument blanks, and samples will be analyzed. Once the sample set is uploaded into the Empower acquisition/run screen and saved, the sample set is printed and the samples are loaded into the GC autosampler tray in the order specified by the sample set queue.

14.2.4 The following labeling will be used on the autosampler vial and for the sample set file created for the analytical queue.

14.2.4.1 The initial calibration standard will be labeled as 040516A, 040516B, etc. Substitute the actual date of analysis and the Aroclor used in the file name.

14.2.4.2 The instrument blanks will be labeled 070405B01, B02, B03, etc. Substitute the actual date of analysis in the file name.

14.2.4.3 The Continuing calibration check standards will be labeled CS160405A CS160405B, etc. Substitute the actual date of analysis and the Aroclor used in the file name.

14.2.4.4 Samples are labeled with the laboratory identification number on the autosampler vial. In the sample set file the laboratory identification number, along with the client identification, sample weight, set volume and dilution are entered.

14.2.5 At this point the chromatography software can be initiated to start data collection. The gas chromatograph is placed into run mode and sample analysis is performed until the analytical queue is complete.

14.2.6 Peak Identification

14.2.6.1 Target peaks are identified in unknown samples based upon Retention Time (RT). The retention time of an unknown peak must fall within the retention time windows established.

14.2.6.2 Besides using retention time windows to assign peak IDs, the analyst should also rely on their own experience in recognition of multi-response PCB chromatograms. Caution should be exercised when identifying peaks which elute near interferences present in samples and blanks. Comparison of sample chromatograms with method blank and field blank chromatograms is useful in determining chromatographic interferences.

14.2.6.3 This method should be applied with caution when used in determining PCB of interest in unknown sample for which no prior historical information exists. In this case confirmatory column analysis or confirmation by GC/MS analysis may be advised.

14.3 Data Reduction/Reporting

14.3.1 Final peak assignments and quantitation calculations are performed within the software along with the current instrument calibration. The final concentration results are provided in the reporting section of the software. Final concentration results are reviewed by QA department or other approved manager before release to the client.

14.3.2 Data Qualifiers:

Sample Concentration Reports (Certificates of Analysis, Data Package Form 1's and Electronic Data Deliverables (EDDs) are generated using the appropriate data qualifiers as follows:

U – Denotes analyte not detected at concentration greater than or equal to the Practical Quantitation Limit (PQL). Note: PQLs are adjusted for sample weight/volume and dilution factors.

J - Denotes an estimated concentration. The concentration result is greater than or equal to the Method Detection Limit (MDL) but less than the Practical Quantitation Limit (PQL).

P - Indicates relative percent difference between primary and secondary GC column analysis exceeds 40 %.

C- Denotes analyte confirmed by secondary GC column analysis.

B - Denotes analyte observed in associated method blank. Analyte concentration should be considered as estimated.

E - Denotes analyte concentration exceeded calibration range of instrument. Sample could not be re-analyzed at secondary dilution due to insufficient sample amount, quick turn-around request, sample matrix interference or hold time excursion. Concentration result should be considered as estimated.

Z - Laboratory Reserved Qualifier (explained in associated Case Narrative)

15.0 Calculations

15.1 Calibration curve calculation:

15.1.1 PCB Solution concentration calculation from initial Calibration by Linear Regression $Y_i = aX_i + b$

Xi = Calibrated Solution Concentration (ng/mL)
Yi = total area response of 5 PCB quant. peaks (uV-Sec.)
a = slope
b = intercept

Unknown Solution Conc. X = (Y –b) a

Y = Total area response of PCB Chromatogram (uV-Sec.)
a = slope of ICAL by linear regression
b = intercept of ICAL by linear regression

15.2 Capillary GC: Sample calculations

15.2.1 The concentration of each identified PCB Aroclor in a sample will be calculated based on the sample weight or volume.

15.2.2 The PCB solution concentration of the extract is calculated as follows:

Solution Conc. = (Y –b)/a

Where:

Y = Total area response of PCB Chromatogram (uV-Sec.)
a = slope of ICAL by linear regression
b = intercept of ICAL by linear regression

15.3 Final concentration of samples:

15.3.1 Calculations of final PCB concentrations will vary upon matrix, calculations are as follows:

(1.) Soil/Sediment/Solids:

Final Conc. = (Sol. Conc.) * (V)*DF/ (M)* (%Total Solids) (1/1000) ug/g

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

(2.) Water:

Final Conc.= (Sol. Conc.) * V*DF/[(Vt)](1/1000) ug/L

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
Vt= Total Volume Extraction (L)

(3.) Biota Tissue

Final Conc. = (Sol. Conc.) * (V)*DF/(M)(1/1000) ug/g

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor

M = mass extracted (g)

(4.) PUF Cassette

Final Conc. = (Sol. Conc.) * (V)*DF/ (Va) ng/cubic meter

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
Va = volume of air sampled (cubic meters)

(5.) Waste Oil

Final Conc. = (Sol. Conc.) * (V)*DF/ (M)*(%Total Solids) (1/1000) ug/g

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

15.3 The calculated concentration for each PCB aroclor will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results with concentrations at or above the MDL but below RL will be reported as detects and flagged as estimated J. The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

16.0 Method Performance
Method Performance is Assessed by Initial/Continuing Demonstration of Proficiency Studies and MDL Determinations

16.1 Initial Demonstration of Performance (IDOP) Procedure:

16.1.1 Prepare 4 replicates of a fortified laboratory blank sample (using laboratory reagent water or sodium sulfate) by spiking each sample with 1.0 mL of 0.500 ug/mL Aroclor solution (typically Aroclor 1242) for water samples and 0.100 mL of 100 ug/mL Aroclor 1242 solution for solid samples. Prepare one method blank sample with the batch. Extract and analyze each aliquot according to procedures beginning in Section 14.0 below.

16.1.2 For each replicate the recovery value of the sample must fall in the range of 70±30 % (or established lab limits) and the percent RSD must be < 20 % for the method performance to be considered acceptable. See Section 23 Attachment G for example IDOP study.

16.1.3 This procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated. The initial demonstration of capability is used primarily to preclude the laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

16.2 Continuing Demonstration of Performance Procedure:

16.2.1 Annual continuing demonstration of performance may be satisfied by a repeat Initial Demonstration of Performance, the acceptable analysis of an unknown samples (for example PT test sample), or the acceptable analysis of 4 consecutive Laboratory Control Spike samples. Records of continuing demonstration of performance are maintained by the laboratory Quality Assurance Department.

16.2.2 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples an organic-free reagent water blank is processed.

16.2.3 The method blank should exhibit PCB levels less than the practical quantification limit or reporting limt (PQL or RL). If the method blank exhibits PCB contamination above the reportable quantitation limit, the samples associated with the contaminated blank should be re-extracted and analysis repeated when appropriate. If there is no original sample available for re-extraction or if the associated sample concentrations greatly exceed the blank concentration, then all positive concentration results for the associated samples should be flagged with a "B" indicating blank contamination and a case narrative describing the situation prepared.

16.2.4 A matrix spike is to be analyzed at a rate of 1 matrix spike per every 10 samples. A duplicate sample may be prepared in lieu of a matrix spike when detectable PCB concentrations are known to be present.

16.3 Method Detection Limit

16.3.1 A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples or sodium sulfate will be prepared and spiked with chlorinated PCB methyl esters mixture, at a low level and taken through all extraction and analytical procedures.

$MDL = S * t_{(n-1,\ 1-alpha=0.99)}$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1-alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)}$ = 2.998

16.3.2 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

17.0 Pollution Prevention

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols and ASE and Soxhlet extractions for solid matrices.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 Data Assessment and Acceptance Criteria for Quality Control Measures

18.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

18.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

18.4 Please see Table 19.1 below for specific Quality Assurance Acceptance Criteria.

19.0 Corrective Action for Out-Of-Control Data

19.1 The table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	The five point calibration is analyzed initially and when Continuing Calibration Check standard fails criteria.	- %RSD≤20% for the relative response factors for the calibration standards if using average response factor calibration. Correlation Coefficient R must be >0.99 for Linear Regression.	- Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria.
Continuing Calibration Check Standard (CCCS)	- Initially analyze a CCCS immediately following an initial calibration. - After the initial CCCS of the sequence, a CCCS must be analyzed after 9 samples. - Analytical sequence must end with analysis of a CCCS.	- Calibration factor for the continuing calibration check must ±15% of the true value. - Retention time of all quantitated peaks must be within RT window (reset with each initial CCCS of a sequence). - All samples must be bracketed by a CCCS that meet all criteria stated above.	- If the reason for the failure of the CCCS appears to be a poor injection (or a degraded standard solution), the CCCS will be re-injected (or re-prepared and re-injected) immediately following the failed CCCS. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCCS meets all the acceptance criteria and there is no apparent impact on the sample data the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. - If CCCS failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCCS failure, correct system, if necessary, and recalibrate. Initial calibration and CCS criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCSs must be reanalyzed. -If acceptable CCCSs are observed later in the sequence, samples bracketed by acceptable CCCSs will be reported. Samples between the failed CCS and prior/ subsequent complaint CCCS will be re-analyzed.

-Retention Time (RT)	- Use the retention time for peak in the CCSs to determine midpoint of the relative retention time window for the analysis sequence. -Each sample analysis: Rely on RT windows to identify PCB Aroclor to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because compound composition may shift RT for GC peaks.	- Each quantitated peak and surrogate peak should be with established windows.	-Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	-One per extraction batch of ≤20 samples of the same matrix per day. -Must be analyzed on each instrument used to analyze associated samples. -Must undergo all sample preparative procedures.	- Concentration does not exceed the RL for any PCB Aroclor. - Must meet surrogate criteria of 60-140% recovery.	- Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. -If method blank is found to contain PCB contamination above the RL for any PCB Aroclor compound , then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data B flagged to indicate method blank contamination.
Laboratory Control Spike (LCS)	- One per extraction batch of ≤20 samples per matrix per day.	-Percent recovery must be within method limits. - Must meet Aroclor spike criteria of 70-130% recovery -Must meet surrogate criteria of 60-140% recovery.	-Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. -If LCS recovery is still out of limits, the re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate LCS failed recovery.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	-Normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. -If requested, an MSD can be extracted and analyzed. The MSD would follow the above criteria as for the MS.	- Percent recovery for MS must be within method limits - If MS/MSD is analyzed, relative percent difference (RPD) should be within 30%. - Must meet Aroclor spike criteria of 70-130% recovery -Must meet surrogate criteria of 60-140% (unless original unspiked sample is also outside of criteria)	-Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. -Check for errors such as calculations and spike preparation. -Check original unspiked sample results and surrogate recovery for indications of matrix effects. -If no errors are found, and the associated LCS is within limits, then sample matrix effects are likely the cause. Note exceedance in case narrative.
Surrogates	-Surrogates are added to all samples and QC samples.	- Percent recovery for the surrogate should be 60-140%.	-Re-analyze the affected sample or QC sample to

	Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) solution.		determine if instrument was the cause. If surrogate passes, then report samples. -Check for errors in surrogate calculation and surrogate solutions. -If no problem is found, then re-extract and re-analyze the sample. -If re-extraction is within limits and sample extract holding time, then report only the re-analysis. -If the re-extraction is within limits, but out of extraction holding time, then report both sets of data. -If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. -If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have a client re-sample.

20.0 Contingencies for Handling Out-Of-Control or Unacceptable Data

20.1 Data that is detected to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

20.1.1 If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operation condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

20.1.2 If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is control.

20.1.3 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

20.1.4 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

21.0 Waste Management

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

21.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 References:

22.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

22.2 U.S. EPA 40 CFP Part 136, "Guidelines Establishing Test Procedures of the Analysis of Pollutants", July, 1988.

22.3 "Standard Methods for the Examination of Water and Waste Water", 19th Edition 1995, American Public Health Association, American Water Works Association, Water Pollution Control Federation.

22.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1996.

22.5 Guide to Environmental Analytical Methods", third edition, Genium Publishing Corporation, 1997.

23.0 Tables, Diagrams, Flowcharts and Validation Data

Attachment A: PCB Stock Standard/Calibration Standard Preparation

Attachment B: Continuing Calibration Check Standard Preparation

Attachment C: GC Operating Parameters

Attachment D: Chromatograms

Attachment E: Example Retention Time Window Study

Attachment F: Example MDL Studies

Attachment A-PCB Stock Standards Prep Table:

Table 1

PCB Stock Standard Preparation Table

PCB Formulation	Supplier	Catalog #	Standard weight(mg)	Conc. (PPM)
A1016	Monsanto Neat Archive	NA	100.0	1000.0
A1221	Monsanto Neat Archive	NA	100.0	1000.0
A1232	Monsanto Neat Archive	NA	100.0	1000.0
A1242	Monsanto Neat Archive	NA	100.0	1000.0
A1248	AccuStandard	C-248N-50mg	100.0	1000.0
A1254	Monsanto Neat Archive	NA	100.0	1000.0
A1260	Monsanto Neat Archive	NA	100.0	1000.0
TCMX/DCBP (Surrogate)	Ultra Scientific	CUS-4911*	0.5/5.0	500/5000

Unless otherwise noted hexane is the solution used to make all dilutions. *Custom Order

Table 2

PCB Calibration Standard Preparation Table (High Level Calibration Curve)

Initial Volume (mL)	Initial Conc. (ug/mL)	Final Volume (mL)	Final Concentration (PPM)					
			A1016	A1221	A1232	A1242	A1248	A1260
5.0	(10.0)	50.0	1.000	1.000	1.000	1.000	1.000	1.000
2.5	(10.0)	50.0	0.500	0.500	0.500	0.500	0.500	0.500
1.25	(10.0)	50.0	0.250	0.250	0.250	0.250	0.250	0.250
1.00	(10.0)	50.0	0.200	0.200	0.200	0.200	0.200	0.200
0.500	(10.0)	50.0	0.100	0.100	0.100	0.100	0.100	0.100
5.0	(0.200)	50.0	0.020	0.020	0.020	0.020	0.020	0.020

Actual Concentration, see Table 1 for actual working standard concentrations for each Aroclor.
See Table 3 for A1254 Standard Preparation (high level)

Table 2A

PCB Calibration Standard Preparation Table (Low Level Calibration Curve)

Init. Volume (mL)	Initial Conc. (ug/ml)	Final Volume (mL)	Final Concentration (PPM)					
			A1016	A1221	A1232	A1242	A1248	A1260
0.5	(10.0)	50.0	0.100	0.100	0.100	0.100	0.100	0.100
2.5	(1.0)	50.0	0.050	0.050	0.050	0.050	0.050	0.050
1.0	(1.0)	50.0	0.020	0.020	0.020	0.020	0.020	0.020
1.0	(0.500)	50.0	0.010	0.010	0.010	0.010	0.010	0.010
0.50	(0.500)	50.0	0.005	0.005	0.005	0.005	0.005	0.005

Actual Concentration, see Tables 1 and 2 for actual working standard concentrations for each Aroclor.
See Table 3A for A1254 Standard Preparation (low level)

Table 3

PCB A1254 Calibration Standard Preparation Table (for High Level Curve)

Initial Volume (mL) A1254	Initial Conc. (ug/mL) A1254	Initial Volume (mL) 0.5/5.0 -PPM Surrogate	Final Volume (mL)	Final Concentration (PPM)		
				A1254	TCMX	DCBP
5.0	10.0	0	50	1.000	0	0
2.5	10.0	0	50	0.500	0	0
10.0	10.00	4.0	100	1.000	0.020	0.200
25.0*	1.000		50	0.500	0.010	0.100
1.25	10.0	0.800	50	0.250	0.008	0.080
0.500	10.0	0.500	50	0.100	0.005	0.050
1.000**	1.000	0.200	50	0.020	0.002	0.020

*This initial volume is of the A1254 1.000 ppm calibration standard WITH surrogates.
**This initial volume is of the A1254 1.000 ppm secondary stock solution WITHOUT surrogates.

Table 3A
PCB A1254, TCMX and DCBP Calibration Standard Preparation Table (for Low Level Curve)

Initial Volume A1254 (mL)	Initial Conc. A1254 (ug/mL)	Initial Volume (mL) 0.5/5.0 -PPM Surrogate	Final Volume (mL)	Final Concentration (PPM)		
				A1254	TCMX	DCBP
5.00	1.000	0.80	50	0.100	0.00800	0.0800
2.50	1.000	0.50	50	0.050	0.00500	0.0500
1.0	1.000	0.40	50	0.020	0.00400	0.0400
1.0	0.500	0.250	50	0.010	0.00250	0.0250
0.50	0.500	0.100	50	0.005	0.00100	0.0100

ATTACHMENT B: PCB Continuing Calibration Standards

Table 1
PCB Continuing Calibration Working Standards
prepared from 1000 PPM Stock Standards

PCB	Stock Source	Initial Volume (mL)	Final Volume (mL)	Concentration (PPM)
A1016	Chem Service Cat # F107AS	1.0	100	10.0
A1221	Chem Service Cat # F108AS	1.0	100	10.0
A1232	Chem Service Cat# F113AS	1.0	100	10.0
A1242	Chem Service Cat# F109AS	1.0	100	10.0
A1248	Chem Service Cat# F110AS	1.0	100	10.0
A1254	Chem Service Cat# F111AS	1.0	100	10.0
A1260	Chem Service Cat# F112AS	1.0	100	10.0

ATTACHMENT B cont'd

Table 2
PCB Continuing Calibration Standards (High Level)
prepared from 10 PPM CCV Working Standards and all contain surrogates

PCB	Surr. Volume* (mL)	Initial Volume (mL)	Final Volume (mL)	Surrogate Concentration TCMX/DCBP (PPM)	Aroclor Concentration (PPM)
A1016	2.0	5.0	100	0.010/0.100	0.500
A1221	2.0	5.0	100	0.010/0.100	0.500
A1232	2.0	5.0	100	0.010/0.100	0.500
A1242	2.0	5.0	100	0.010/0.100	0.500
A1248	2.0	5.0	100	0.010/0.100	0.500
A1254	2.0	5.0	100	0.010/0.100	0.500
A1260	2.0	5.0	100	0.010/0.100	0.500

*Surrogate stock solution 0.500 PPM TCMX and 5.0 PPM DCBP

Table 3
PCB Continuing Calibration Standards (low Level)
prepared from 10.0 PPM CCV Working Standards and all contain surrogates.

PCB	Surr. Volume* (mL)	Initial Volume (mL)	Final Volume (mL)	Surrogate Concentration TCMX/DCBP (PPM)	Aroclor Concentration (PPM)
A1016	1.0	0.500	100	0.005/0.050	0.050
A1221	1.0	0.500	100	0.005/0.050	0.050
A1232	.1.0	0.500	100	0.005/0.050	0.050
A1242	.1.0	0.500	100	0.005/0.050	0.050
A1248	.1.0	0.500	100	0.005/0.050	0.050
A1254	1.0	0.500	100	0.005/0.050	0.050
A1260	1.0	0.500	100	0.005/0.050	0.050

*Surrogate stock solution 0.500 PPM TCMX and 5.0 PPM DCBP

Attachment C: GC Operating Parameters

GC-19 Low Level PCB Method

GC #:	**19**
Method:	**608/8082 Low Level PCB**
GC Method #:	**5**
Date:	**10/27/2006**
Analyst:	**AJM**
File Name:	**S:\FORMS\LOG\GC\[GC19_Parameters.xls]8082 LL M5**
Column:	**19F ZB-1**
	19B ZB-5

Sample Delivery:

Single Method **Method 5**

CP-8400

Injection Mode:	**User**		
Sample Penetration Depth (%)	95	Viscosity Delay (sec)	1.0
Solvent Penetration Depth (%)	95	Plunger Speed During Fill (ul/sec)	1.0
		Plunger Speed During Injection (ul/sec)	5.0
Air Plug after Sample (ul)	1.0	Pre Injection Delay (sec)	3.0
Sample Air Gap	No	Post Injection Delay (sec)	3.0
Number of Fill Strokes	0		
Fill Volume for Fill Strokes	5.0		

Default Clean

Default Clean Vial	I
Default Clean Volume (ul)	5
Number of Clean Strokes	1
Default Clean Drawup Spped (ul/sec)	5

Clean Mode

Number of Pre-Injection Solvent Clean Flushes	1
Number of Post-Injection Solvent Clean Flushes	1
Number of Pre-Injection Sample Clean Flushes	0
Clean Solvent Source Vial	I+II

Solvent Plug

Vial for Solvent Plug	III
Solvent Plug Size (ul)	0.2
Solvent Drawup Speed (ul/sec)	5.0
Solvent Pause Time	1.0
Solvent Air Gap	NO

Select Edit

Select Automation Mode:	Single Method		
Edit Single Method Automation			
Method:	5		
Initial Sample:	0	Injection Possition	Both
Final Sample:	99	First Injector used	Pos. 1
Injections / Sample:	1	Use Injection Delay	No
First Injection Volume (ul):	1.1*	Delay between Injections	0.5
Second Injection Volume (ul):	1.3*	Advance Carrousel between Injections	No
	*can vary	Clean between Injections	Yes

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.23	30.23

Stabilization Time (min): 0.20

Injector Front CP-

1177 Oven	O
1177 Temperature	30

Tim	Split State	Split Ratio
Initial	ON	20

Flow/PSI (Front EFC, Type

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*23.1**	-------	30.30	30.30

*last

Constant Flow Mode	N
Column Flow Rate	1.

Injector Middle CP-

1177 Oven	O
1177 Temperature	30

Tim	Split State	Split Ratio
Initial	ON	20

Flow/PSI (Front EFC, Type

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*29.5**	-------	30.30	30.30

Constant Flow Mode	N
Column Flow Rate	1.

Detector

	Front	Middle
ECD Oven	O	**OF**
Temperature	30	5
Electronics	O	O
Range	1	1

Tim	Range	Autozero
Initial	1	YE

Tim	Range	Autozero
Initial	1	YE

Front ECD

Time Constant:	Fas	Fas
Cell Current:	CAP	CAP
Contact Potential (mV):	-	-
Date of last adjustment	5/2/200	5/2/200
Make-Up Flow (ml/min):	manually set and measured.	

Analog

Detectors Front:
Middle:
Rear:

Tim	Signal Source	Attenuation
Initial	Front Detector	1
Tim	Signal Source	Attenuation
Initial	Middle Detector	1
Tim	Signal Source	Attenuation
Initial	Rear Detector	1

Valve

Time	1 Non	2 Non	3 Non	4 Non	5 Non	6 Non	7 None
Initia	----	----	----	----	----	----	-----

Initial valve

GC-19 8082 High Level PCB Method

GC #:	**19**
Method:	**8082 High Level PCB**
GC Method #:	**7**
Date:	**2/15/2006**
Analyst:	**KLL**
File Name:	**S:\FORMS\LOG\GC\[GC19_Parameters.xls]8082 HL M7**
Column:	**19F ZB-1**
	19B ZB-5

Sample Delivery:

Single Method **Method 7**

CP-8400

Injection Mode:	**User**		
Sample Penetration Depth (%)	95	Viscosity Delay (sec)	1.0
Solvent Penetration Depth (%)	95	Plunger Speed During Fill (ul/sec)	1.0
		Plunger Speed During Injection (ul/sec)	5.0
Air Plug after Sample (ul)	1.0	Pre Injection Delay (sec)	3.0
Sample Air Gap	No	Post Injection Delay (sec)	3.0
Number of Fill Strokes	0		
Fill Volume for Fill Strokes	5.0		

Default Clean

Default Clean Vial	I
Default Clean Volume (ul)	5
Number of Clean Strokes	1
Default Clean Drawup Spped (ul/sec)	5

Clean Mode

Number of Pre-Injection Solvent Clean Flushes	1
Number of Post-Injection Solvent Clean Flushes	1
Number of Pre-Injection Sample Clean Flushes	0
Clean Solvent Source Vial	I+II

Solvent Plug

Vial for Solvent Plug	III
Solvent Plug Size (ul)	0.2
Solvent Drawup Speed (ul/sec)	5.0
Solvent Pause Time	1.0
Solvent Air Gap	NO

Select Edit

Select Automation Mode:	Single Method		
Edit Single Method Automation Method:	7		
Initial Sample:	0	Injection Possition	Both
Final Sample:	99	First Injector used	Pos. 1
Injections / Sample:	1	Use Injection Delay	No
First Injection Volume (ul):	1	Delay between Injections	0.5
Second Injection Volume (ul):	1	Advance Carrousel between Injections	No
		Clean between Injections	Yes

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.23	30.23

Stabilization Time (min): 0.20

Injector: **Front CP-1177**

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	35

Flow/PSI(Front EFC, Type 1):

Injector: **Middle CP-1177**

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	35

Flow/PSI(Front EFC, Type 1):

Leap GC Pal Parameters 3/9/2007					
Sample injection Methods					
Method	**GC Dual**	**GC Duals**		**Method**	**GC Inj s**
Cylcle	GC Dual	GC Dual		**Cylcle**	GC Inj S
Syringe	10 ul	10 ul		**Syringe**	10 ul
1. Sample Vol	1.0 ul	1.0 ul		**1. Sample Vol**	1.0 ul
1. Air Vol	1.0 ul	1.0 ul		**Solvent Plug**	200 nl
1. Inject to	GC Inj 1	GC Inj 1		**Slv Source**	Standard
Inj Time Diff	0s	0s		**Int Standard**	0 nl
2. Sample Offs	1	0		**Std Source**	Standard
2. Sample Vol	1.0 ul	1.0 ul		**Air Gap (s)**	1.0 ul
2. Air Vol	1.0 ul	1.0 ul		**1. Air Vol Ndl**	1.1 ul
2. Inject to	GC Inj 2	GC Inj 2		**Pre Cln Slv 1**	2
Pre Cln Slv 1	2	2		**Pre Cln Slv 2**	2
Pre Cln Slv 2	2	2		**Fill Speed**	5.0 ul/s
Pre Cln Sp 1	0	0		**Pull Up Delay**	1.0 s
Int Cln Slv 1	2	2		**Inject to**	GC Inj 1
Int Cln Slv 2	2	2		**Inject Speed**	5.0 ul/s
Pst Cln Slv 1	2	2		**Pre Inj Del**	0 ms
Pst Cln Slv 2	2	2		**Pst Inj Del**	0 ms
Fill Volume	10 ul	10 ul		**Pst Cln Slv 1**	2
Fill Speed	2.5 ul/s	2.5 ul/s		**Pst Cln Slv 2**	2
Fill Stroke	0	0			
Pull Up Delay	500ms	500ms			
Inject Speed	10 ul/s	10 ul/s			
Pre Inj Del	0 ms	0 ms			
Pst Inj Del	0 ms	0 ms			

ATTACHMENT D ZB5 Chromatograms

FIGURE 1. A1016 @ 0.500PPM PLOT

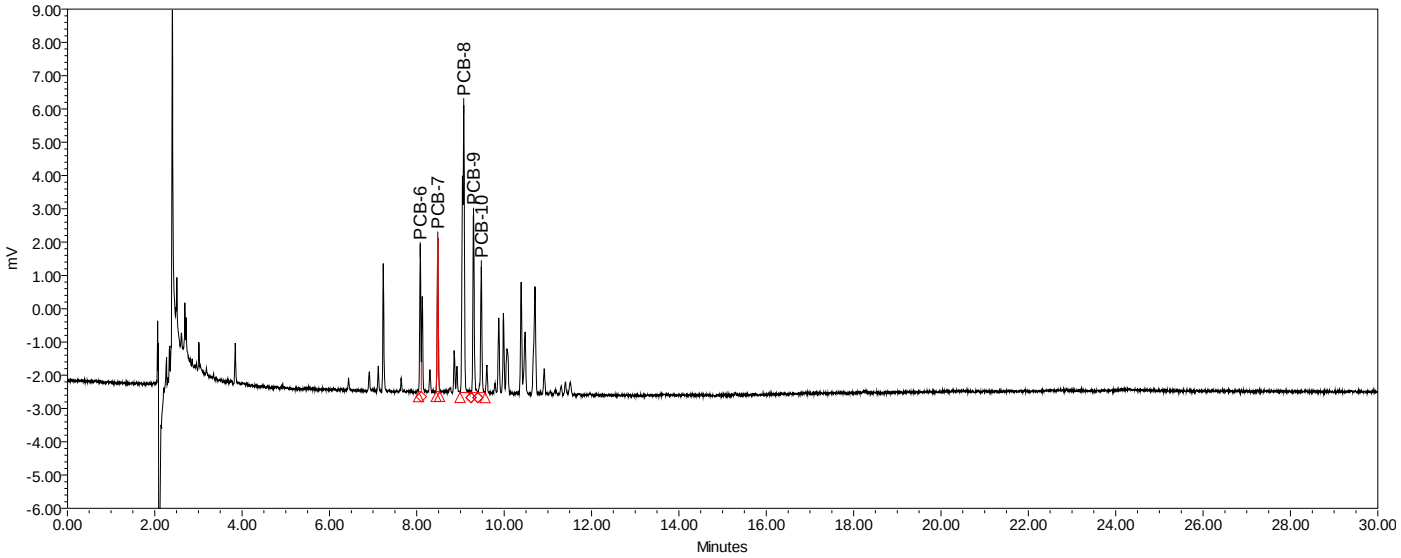


FIGURE 2. A1221 @ 0.500PPM PLOT

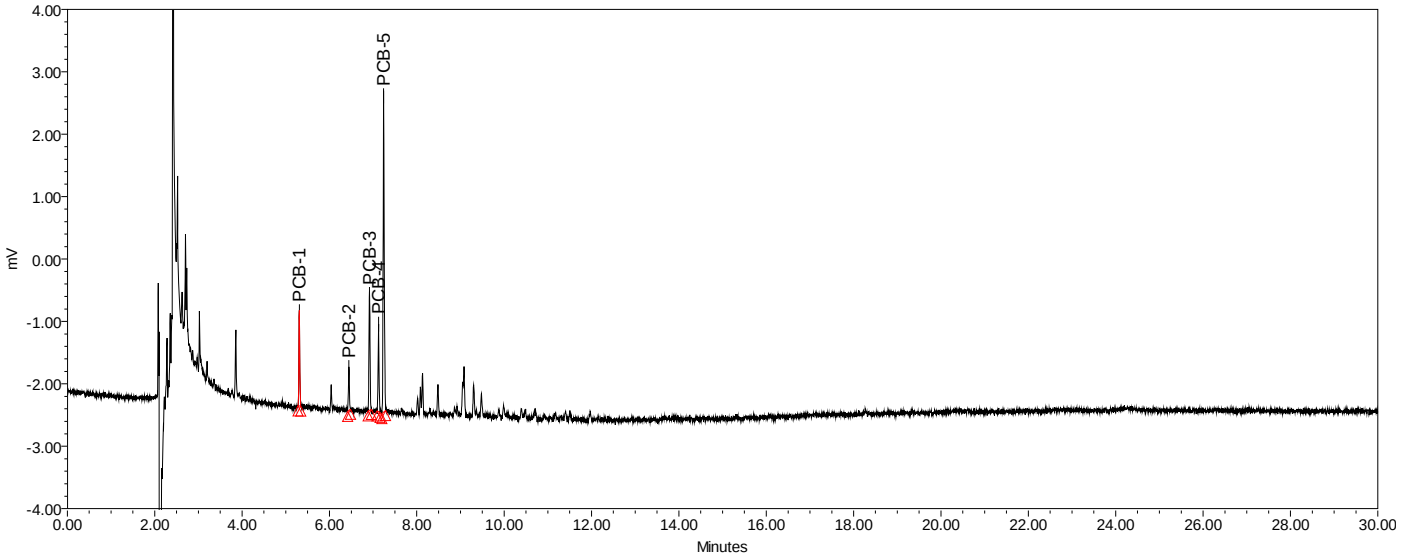


FIGURE 3. A1232 @ 0.500PPM PLOT

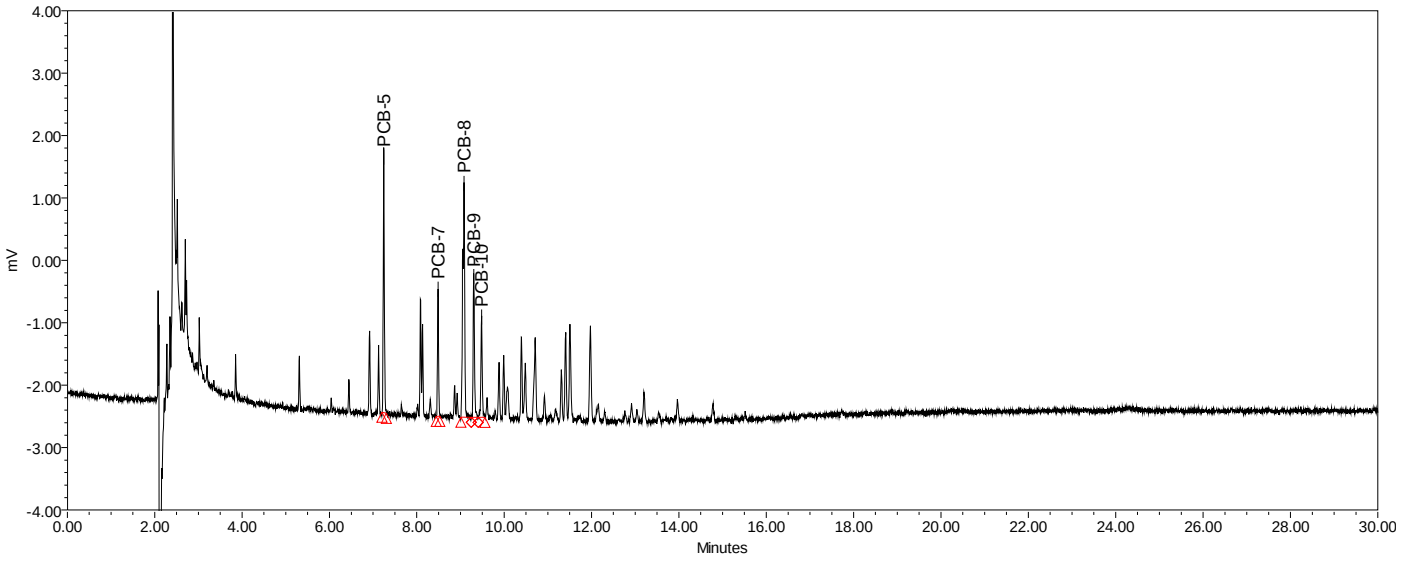


FIGURE 4. A1242 @ 0.500PPM PLOT

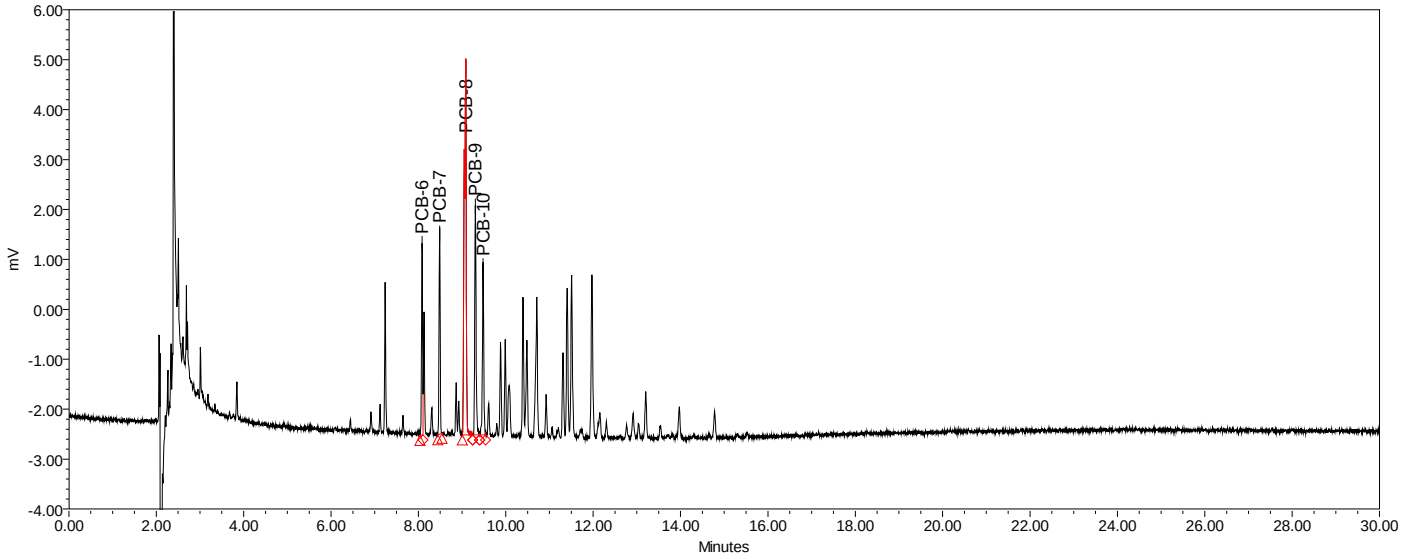


FIGURE 5. A1248 @ 0.500PPM PLOT

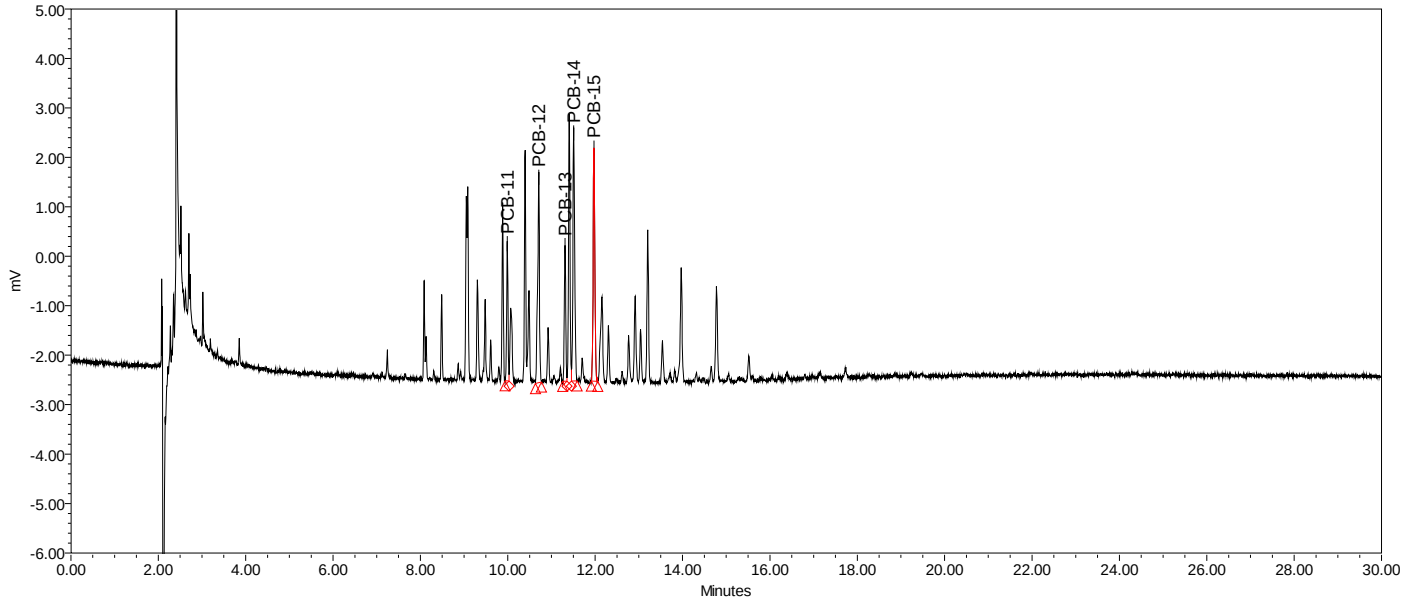


FIGURE 6. A1254 @ 0.500PPM w/ TCMX & DCBP @ 10/100PPB PLOT

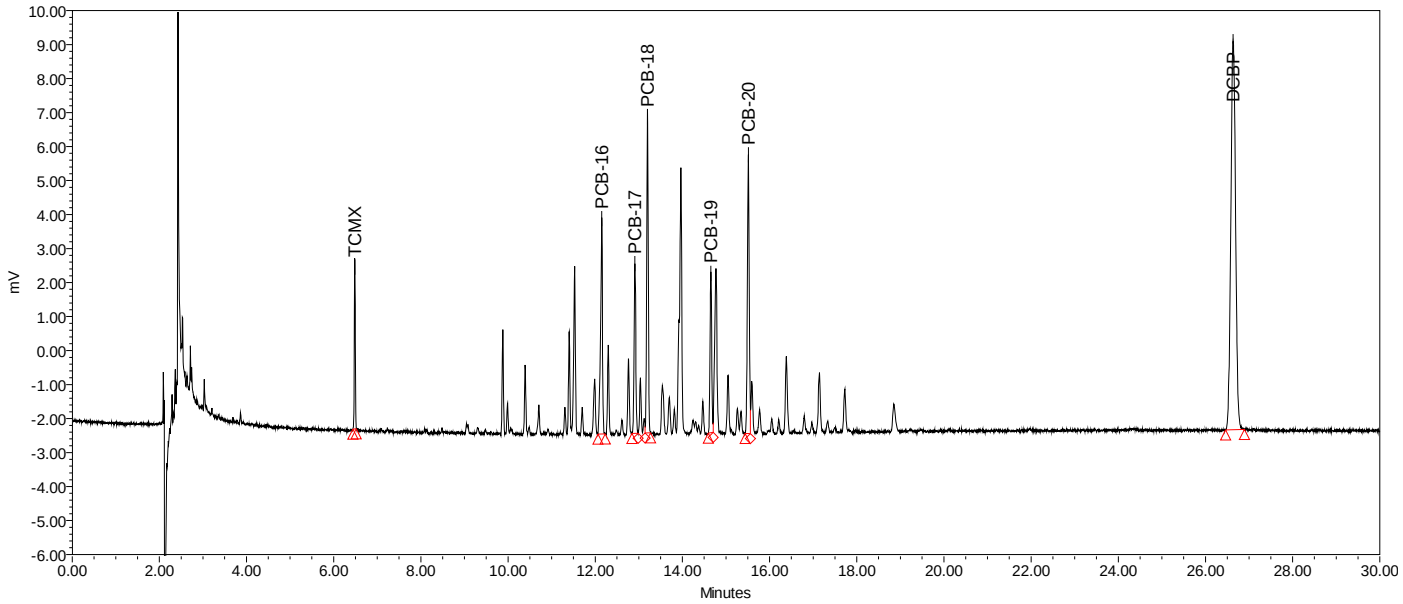
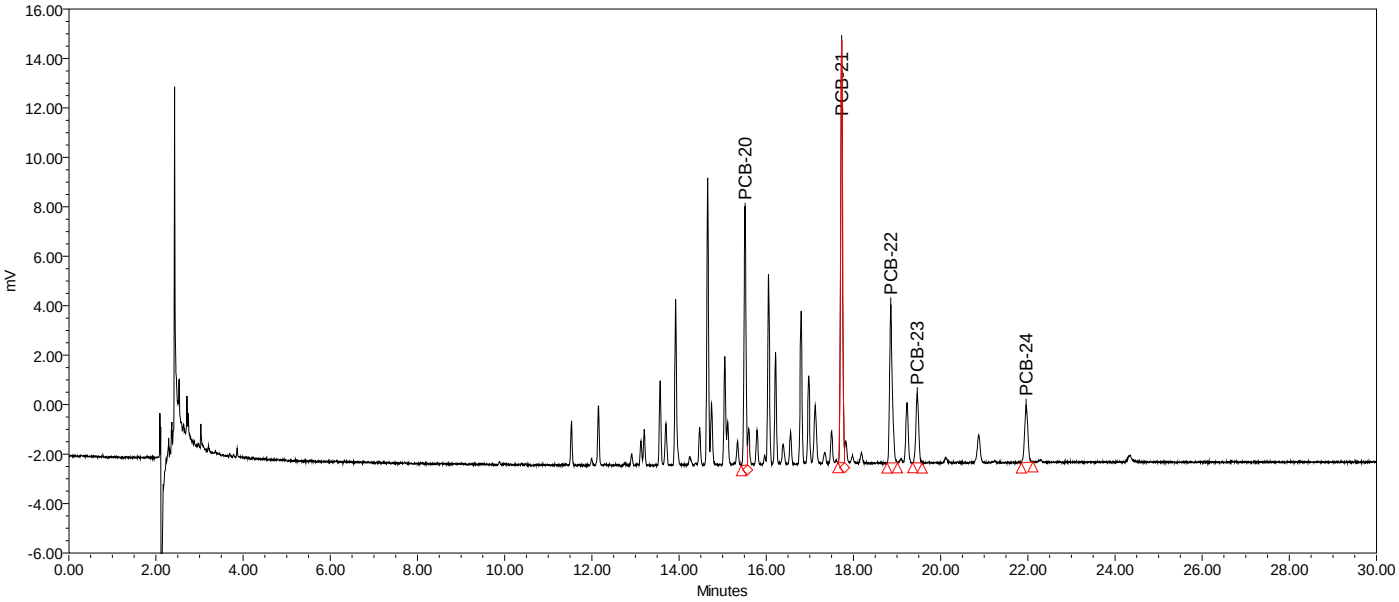


FIGURE 7. A1260 @ 0.500PPM PLOT



ATTACHMENT D cont' ZB1 Chromatograms

FIGURE 1. A1016 @ 0.500PPM PLOT

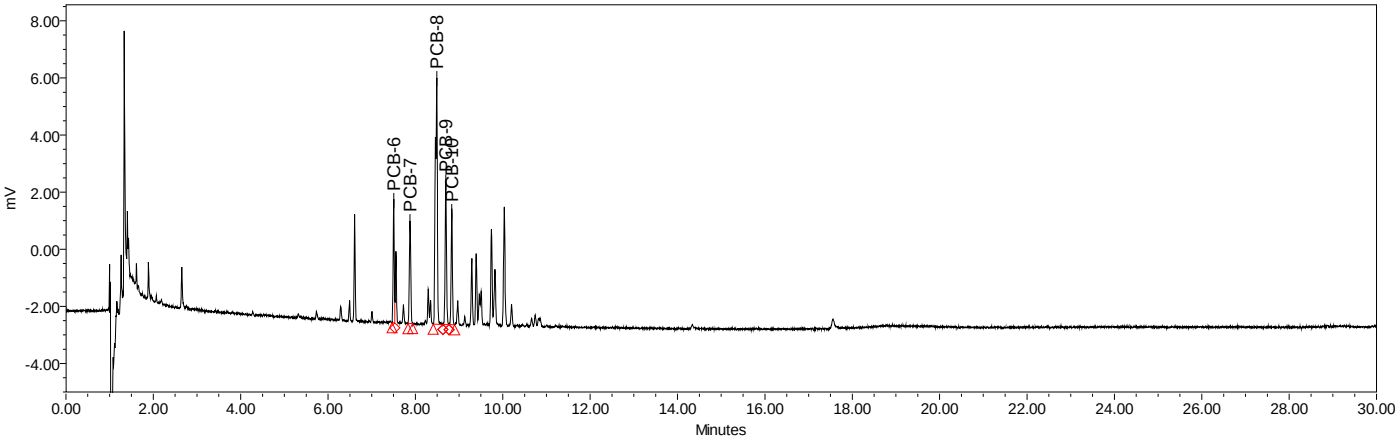


FIGURE 2. A1221 @ 0.500PPM PLOT

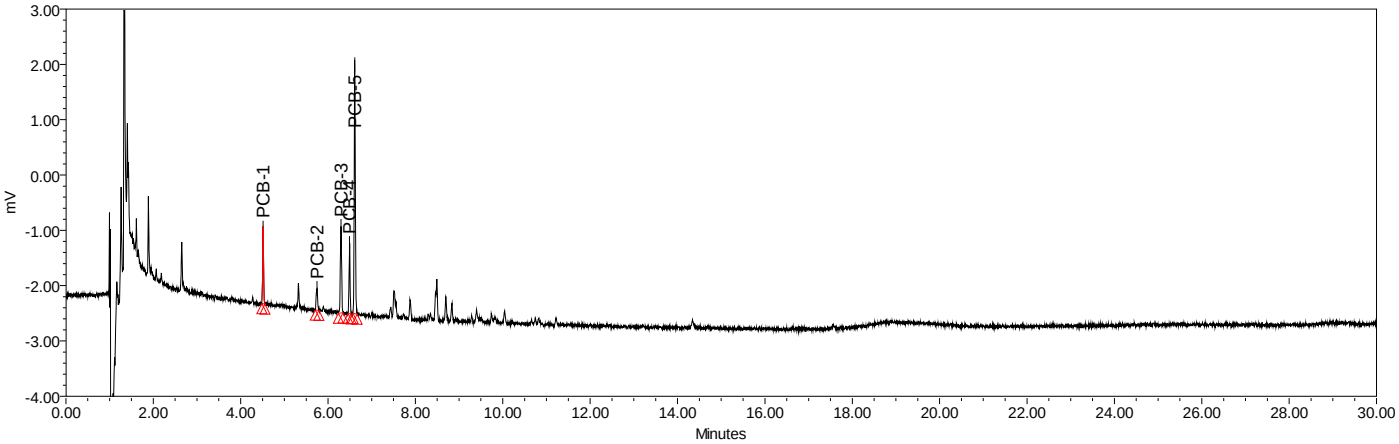


FIGURE 3. A1232 @ 0.500PPM PLOT

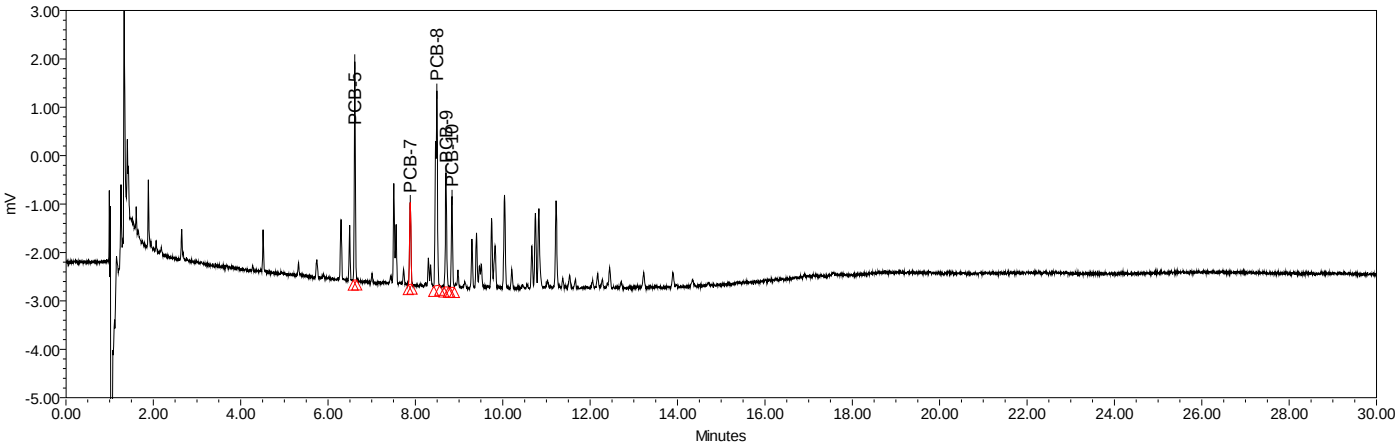


FIGURE 4. A1242 @ 0.500PPM PLOT

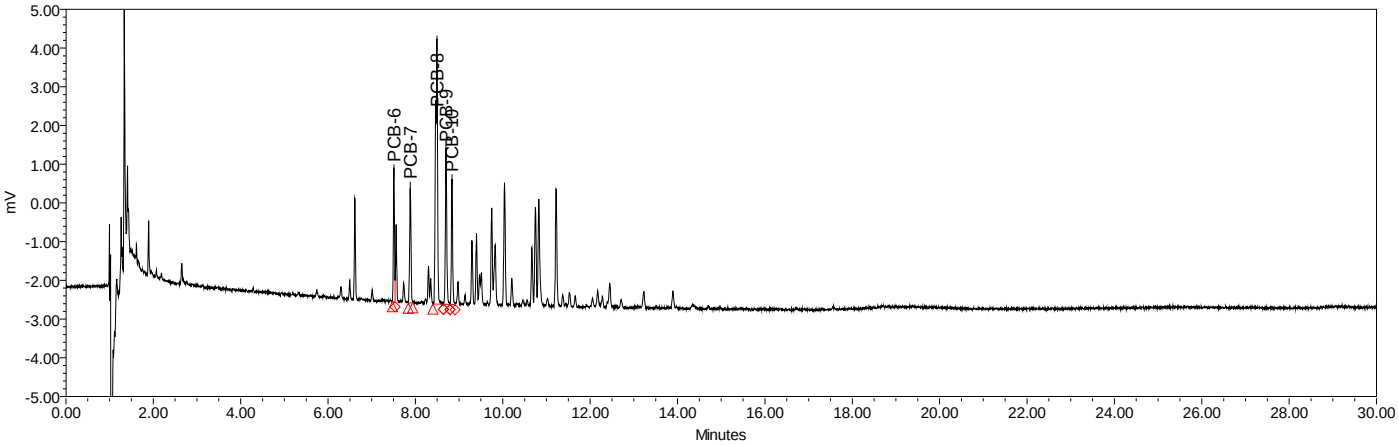


FIGURE 5. A1248 @ 0.500PPM PLOT

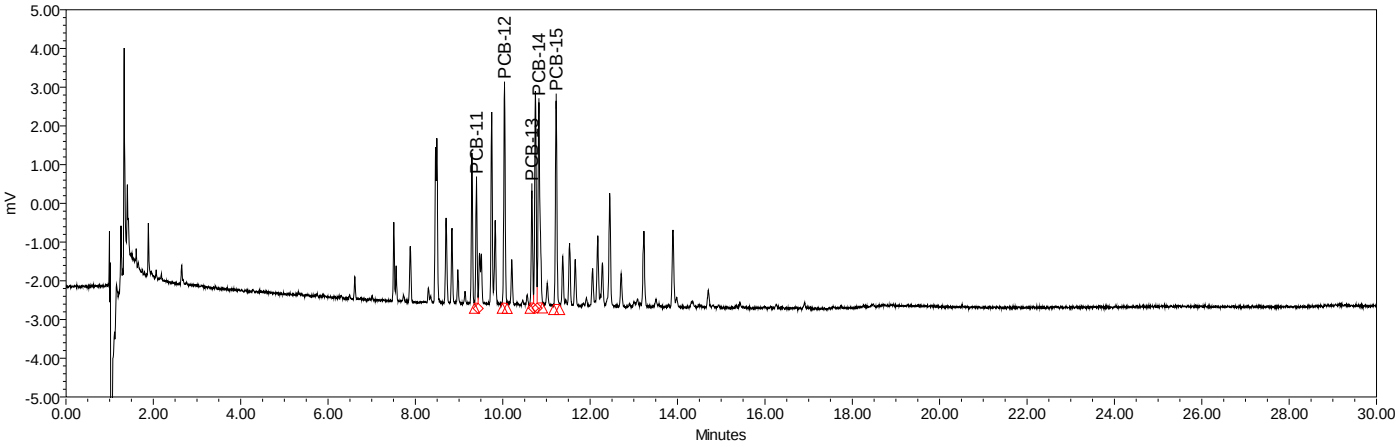


FIGURE 6. A1254 @ 0.500PPM w/ TCMX & DCBP @ 10/100PPB PLOT

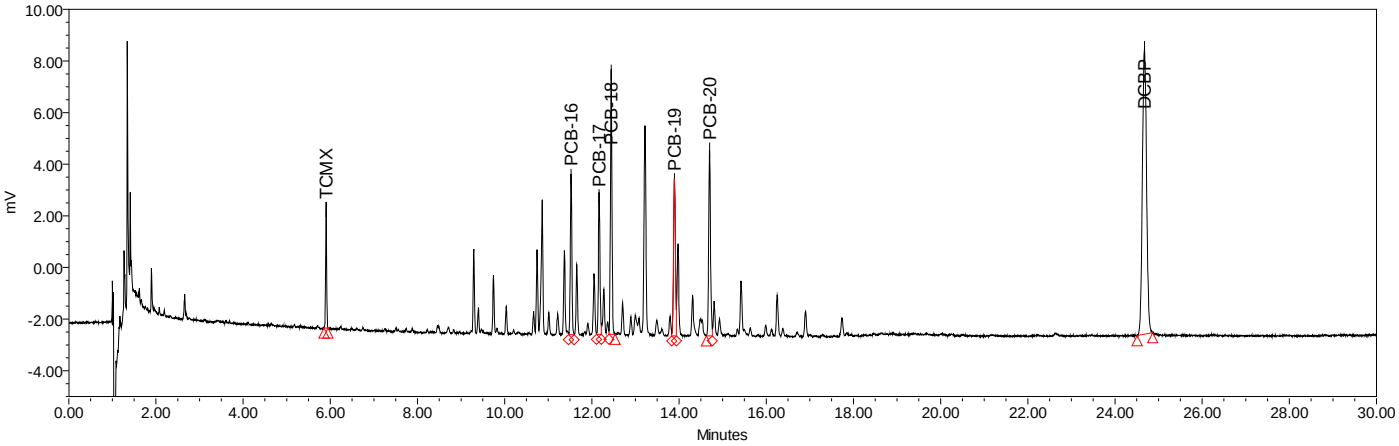
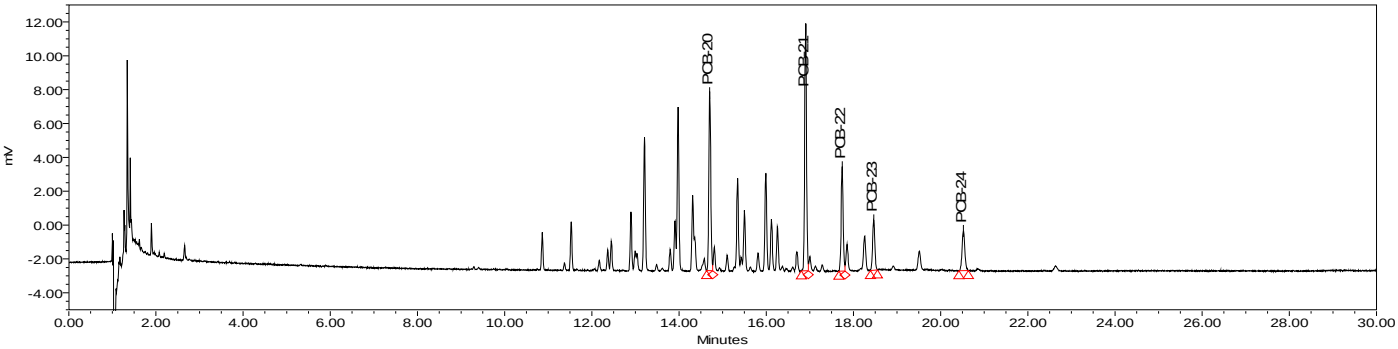


FIGURE 7. A1260 @ 0.500PPM PLOT



Attachment E Retention Time Windows: ZB-1 Column

Attachment E Retention Time Windows: ZB-1

Retention Time Window Study
for Aroclors (PCB) by GC/ECD

Instrument: GC 19F
Column: ZB-1

Analyte	PEAK	Standard 1 500 PPB R.T. Min	Standard 2 50/500 PPB R.T. Min	Standard 3 500 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS_0327B/A	CS_0328A	CS_0329A			
Aroclor 1016	6	7.927	7.922	7.921	0.0032	0.0406	0.010
	7	8.317	8.312	8.312	0.0029	0.0347	0.009
	8	8.961	8.956	8.956	0.0029	0.0322	0.009
	9	9.178	9.172	9.172	0.0035	0.0378	0.010
	10	9.321	9.317	9.317	0.0023	0.0248	0.007
Aroclor 1221	1	4.894	4.892	4.893	0.0010	0.0204	0.003
	2	6.142	6.142	6.145	0.0017	0.0282	0.005
	3	6.706	6.703	6.705	0.0015	0.0228	0.005
	4	6.904	6.900	6.902	0.0020	0.0290	0.006
	5	7.024	7.021	7.023	0.0015	0.0218	0.005
Aroclor 1232	5	7.025	7.026	7.022	0.0021	0.0296	0.006
	7	8.315	8.318	8.312	0.0030	0.0361	0.009
	8	8.961	8.963	8.957	0.0031	0.0341	0.009
	9	9.178	9.179	9.173	0.0032	0.0350	0.010
	10	9.322	9.324	9.318	0.0031	0.0328	0.009
Aroclor 1242	6	7.925	7.928	7.922	0.0030	0.0379	0.009
	7	8.314	8.318	8.311	0.0035	0.0422	0.011
	8	8.959	8.963	8.956	0.0035	0.0392	0.011
	9	9.176	9.180	9.173	0.0035	0.0383	0.011
	10	9.320	9.324	9.317	0.0035	0.0377	0.011
Aroclor 1248	11	9.906	9.900	9.901	0.0032	0.0325	0.010
	12	10.577	10.573	10.571	0.0031	0.0289	0.009
	13	11.231	11.225	11.225	0.0035	0.0309	0.010
	14	11.396	11.390	11.390	0.0035	0.0304	0.010
	15	11.808	11.803	11.803	0.0029	0.0245	0.009
Arolcor 1254	16	12.121	12.116	12.115	0.0032	0.0265	0.010
	17	12.793	12.786	12.785	0.0044	0.0341	0.013
	18	13.075	13.069	13.070	0.0032	0.0246	0.010
	19	14.572	14.567	14.566	0.0032	0.0221	0.010
	20	15.394	15.389	15.389	0.0029	0.0188	0.009
Arolcor 1260	20	15.396	15.398	15.392	0.0031	0.0198	0.009
	21	17.668	17.670	17.664	0.0031	0.0173	0.009
	22	18.611	18.613	18.606	0.0036	0.0194	0.011
	23	19.417	19.421	19.415	0.0031	0.0157	0.009
	24	21.729	21.731	21.722	0.0047	0.0218	0.014
TCMX (SURROGATE)	Surr.	6.311	6.307	6.307	0.0023	0.0366	0.007
DCB (SURROGATE)	Surr.	26.432	26.421	26.421	0.0064	0.0240	0.019

Attachment E cont' Retention Time Windows: ZB-5 Column

Retention Time Window Study
for Aroclors (PCB) by GC/ECD

Instrument: GC 19B
Column: ZB-5

Analyte	PEAK	Standard 1 500 PPB R.T. Min	Standard 2 500 PPB R.T. Min	Standard 3 500 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS_0327B/A	CS_0328A	CS_0329A			
Aroclor 1016	6	8.260	8.256	8.256	0.0023	0.0280	0.007
	7	8.669	8.665	8.665	0.0023	0.0266	0.007
	8	9.277	9.272	9.272	0.0029	0.0311	0.009
	9	9.502	9.498	9.498	0.0023	0.0243	0.007
	10	9.685	9.680	9.679	0.0032	0.0332	0.010
Aroclor 1221	1	5.480	5.479	5.476	0.0021	0.0380	0.006
	2	6.618	6.615	6.611	0.0035	0.0531	0.011
	3	7.086	7.084	7.084	0.0012	0.0163	0.003
	4	7.291	7.289	7.288	0.0015	0.0210	0.005
	5	7.410	7.406	7.407	0.0021	0.0281	0.006
Aroclor 1232	5	7.408	7.412	7.409	0.0021	0.0281	0.006
	7	8.667	8.671	8.667	0.0023	0.0266	0.007
	8	9.278	9.278	9.274	0.0023	0.0249	0.007
	9	9.502	9.505	9.501	0.0021	0.0219	0.006
	10	9.684	9.686	9.681	0.0025	0.0260	0.008
Aroclor 1242	6	8.258	8.261	8.255	0.0030	0.0363	0.009
	7	8.667	8.670	8.664	0.0030	0.0346	0.009
	8	9.275	9.279	9.272	0.0035	0.0379	0.011
	9	9.501	9.506	9.498	0.0040	0.0425	0.012
	10	9.682	9.686	9.679	0.0035	0.0363	0.011
Aroclor 1248	11	10.202	10.196	10.198	0.0031	0.0300	0.009
	12	10.936	10.930	10.932	0.0031	0.0279	0.009
	13	11.545	11.540	11.541	0.0026	0.0229	0.008
	14	11.748	11.743	11.742	0.0032	0.0274	0.010
	15	12.219	12.215	12.217	0.0020	0.0164	0.006
Arolcor 1254	16	12.402	12.397	12.397	0.0029	0.0233	0.009
	17	13.175	13.170	13.168	0.0036	0.0274	0.011
	18	13.469	13.463	13.461	0.0042	0.0309	0.012
	19	14.942	14.935	14.934	0.0044	0.0292	0.013
	20	15.812	15.805	15.805	0.0040	0.0256	0.012
Arolcor 1260	20	15.808	15.810	15.804	0.0031	0.0193	0.009
	21	18.082	18.085	18.079	0.0030	0.0166	0.009
	22	19.272	19.274	19.268	0.0031	0.0159	0.009
	23	19.911	19.910	19.912	0.0010	0.0050	0.003
	24	22.558	22.557	22.552	0.0032	0.0143	0.010
TCMX (SURROGATE)	Surr.	6.658	6.653	6.653	0.0029	0.0434	0.009
DCB (SURROGATE)	Surr.	27.519	27.509	27.498	0.0105	0.0382	0.032

Attachment F Example of MDL Study: ZB-1 Column

Compound:	Aroclor 1254		Analysis:	SW-846 8082	
Matrix:	Solid		Instrument:	GC-19F	
Extraction:	Ase		Column:	DB-1	
Spike conc:	75.0	ug/Kg	Detector:	ECD	
			LRF:	09010025	

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/Kg	Percent Recovery (%)
AM00103	01/08/09	1221/1254 #1 ASE	01/23/09	68.9	91.9%
AM00104	01/08/09	1221/1254 #2 ASE	01/23/09	70.2	93.5%
AM00105	01/08/09	1221/1254 #3 ASE	01/23/09	76.8	102.4%
AM00106	01/08/09	1221/1254 #4 ASE	01/23/09	67.0	89.4%
AM00107	01/08/09	1221/1254 #5 ASE	01/23/09	75.2	100%
AM00108	01/08/09	1221/1254 #6 ASE	01/23/09	67.3	89.7%
AM00109	01/08/09	1221/1254 #7 ASE	01/23/09	69.9	93.2%
AM00110	01/08/09	1221/1254 #8 ASE	01/23/09	69.3	92.4%
			Number (n):	8	
One sided Student's t values (t)			AVG:	70.6	ug/Kg
at the 99% confidence level.			STD (s):	3.55	ug/Kg
Number (n)	(t) value		%RSD:	5.04%	
7	3.143		MDL:	10.7	ug/Kg
8	2.998		PQL:	53.3	ug/Kg
			VALID:	valid	

Attachment F cont' Example of MDL Study: ASE extraction ZB-5 Column

Compound:	Aroclor 1254		Analysis:	SW-846 8082	
Matrix:	Solid		Instrument:	GC-19B	
Extraction:	Ase		Column:	ZB-5	
Spike conc:	75.0	ug/Kg	Detector:	ECD	
			LRF:	09010025	
NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/Kg	Percent Recovery (%)
AM00103	01/08/09	1221/1254 #1 ASE	01/23/09	73.9	98.5%
AM00104	01/08/09	1221/1254 #2 ASE	01/23/09	74.8	99.7%
AM00105	01/08/09	1221/1254 #3 ASE	01/23/09	79.9	107%
AM00106	01/08/09	1221/1254 #4 ASE	01/23/09	75.8	101%
AM00107	01/08/09	1221/1254 #5 ASE	01/23/09	78.6	105%
AM00108	01/08/09	1221/1254 #6 ASE	01/23/09	77.7	104%
AM00109	01/08/09	1221/1254 #7 ASE	01/23/09	70.1	93.5%
AM00110	01/08/09	1221/1254 #8 ASE	01/23/09	78.9	105%
			Number (n):	8	
One sided Student's t values (t)			AVG:	76.2	ug/Kg
at the 99% confidence level.			STD (s):	3.24	ug/Kg
Number (n)	(t) value		%RSD:	4.25%	
7	3.143		MDL:	9.72	ug/Kg
8	2.998		PQL:	48.6	ug/Kg
			VALID:	valid	

Attachment F cont' Example of MDL Study: SOX extraction ZB-1 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	SOIL/SOLID	Instrument:	GC-18F/LEAP GC PAL
Extraction:	SOX	Column:	ZB-1
Spike conc:	75.00 ug/kg		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/kg	Percent Recovery (%)
AJ00234	01/17/06	1221/1254 #1 SOX	04/19/06	81.0	108.0%
AJ00235	01/17/06	1221/1254 #2 SOX	04/19/06	79.4	106%
AJ00236	01/17/06	1221/1254 #3 SOX	04/19/06	77.0	102.7%
AJ00237	01/17/06	1221/1254 #4 SOX	04/19/06	81.1	108.1%
AJ00238	01/17/06	1221/1254 #5 SOX	04/19/06	77.1	102.8%
AJ00239	01/17/06	1221/1254 #6 SOX	04/19/06	73.7	98%
AJ00240	01/17/06	1221/1254 #7 SOX	04/19/06	71.8	95.7%
AJ00241	01/17/06	1221/1254 #8 SOX	04/19/06	77.4	103%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	77.31	ug/kg
STD (s):	3.293	ug/kg
%RSD:	4.26%	
MDL:	9.871	ug/kg
PQL:	49.36	ug/kg
VALID:	valid	

Attachment F cont' Example of MDL Study: SOX extraction ZB-5 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	SOIL/SOLID	Instrument:	GC-18B/LEAP GC PAL
Extraction:	SOX	Column:	ZB-5
Spike conc:	75.00 ug/kg		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/kg	Percent Recovery (%)
AJ00234	01/17/06	1221/1254 #1 SOX	07/01/06	79.2	105.7%
AJ00235	01/17/06	1221/1254 #2 SOX	07/01/06	74.7	100%
AJ00236	01/17/06	1221/1254 #3 SOX	07/01/06	80.2	107.0%
AJ00237	01/17/06	1221/1254 #4 SOX	07/01/06	79.8	106.3%
AJ00238	01/17/06	1221/1254 #5 SOX	07/01/06	81.9	109.2%
AJ00239	01/17/06	1221/1254 #6 SOX	07/01/06	78.3	104%
AJ00240	01/17/06	1221/1254 #7 SOX	07/01/06	85.2	113.6%
AJ00241	01/17/06	1221/1254 #8 SOX	07/01/06	82.6	110%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	80.23	ug/kg
STD (s):	3.146	ug/kg
%RSD:	3.92%	
MDL:	9.432	ug/kg
PQL:	47.16	ug/kg
VALID:	valid	

Attachment F cont' Example of MDL Study: PUF extraction ZB-1 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	PUF	Instrument:	GC-19F/8400
Extraction:	SOX	Column:	ZB-1
Spike conc:	0.150 ug		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug	Percent Recovery (%)
AJ00508	02/08/06	TO-10A 1221/1254 #1	02/10/06	0.138	91.8%
AJ00509	02/08/06	TO-10A 1221/1254 #2	02/10/06	0.130	86.8%
AJ00510	02/08/06	TO-10A 1221/1254 #3	02/10/06	0.141	93.7%
AJ00511	02/08/06	TO-10A 1221/1254 #4	02/10/06	0.150	99.8%
AJ00512	02/08/06	TO-10A 1221/1254 #5	02/10/06	0.135	90.2%
AJ00513	02/08/06	TO-10A 1221/1254 #6	02/10/06	0.142	94.6%
AJ00514	02/08/06	TO-10A 1221/1254 #7	02/10/06	0.140	93.1%
AJ00515	02/08/06	TO-10A 1221/1254 #8	02/10/06	0.134	89.2%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	0.139	ug
STD (s):	0.006	ug
%RSD:	4.25%	
MDL:	0.018	ug
PQL:	0.088	ug
VALID:	valid	

Attachment F cont' Example of MDL Study: PUF extraction ZB-5 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	PUF	Instrument:	GC-19B/8400
Extraction:	SOX	Column:	ZB-5
Spike conc:	0.150 ug		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug	Percent Recovery (%)
AJ00508	02/08/06	TO-10A 1221/1254 #1	02/10/06	0.143	95.3%
AJ00509	02/08/06	TO-10A 1221/1254 #2	02/10/06	0.127	84.8%
AJ00510	02/08/06	TO-10A 1221/1254 #3	02/10/06	0.135	90.2%
AJ00511	02/08/06	TO-10A 1221/1254 #4	02/10/06	0.134	89.0%
AJ00512	02/08/06	TO-10A 1221/1254 #5	02/10/06	0.134	89.1%
AJ00513	02/08/06	TO-10A 1221/1254 #6	02/10/06	0.136	90.4%
AJ00514	02/08/06	TO-10A 1221/1254 #7	02/10/06	0.143	95.2%
AJ00515	02/08/06	TO-10A 1221/1254 #8	02/10/06	0.140	93.3%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	0.136	ug
STD (s):	0.005	ug
%RSD:	3.91%	
MDL:	0.016	ug
PQL:	0.080	ug
VALID:	valid	

STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE148_06	01	Kari Lantiegne Christina L. Braidwood Robert E. Wagner	Chemist QAO Lab Director	Christina Braidwood	02/19/09

ICP-MS

Inductively Coupled Plasma –Mass spectroscopy

6020A

Non-potable Water and Soil

Approved:

Michael Erickson Laboratory Director	Katherine F. Allen QA Officer

Revision Number: 1

NON-CONTROLLED COPY

Controlled Copy Number:_____

Change Record

Revision	Date	Responsible Person	Description of Change
0	01/30/08	Andrea Palpini	Original
1	10/21/10	Andrea Palpini	Modification of reference dates (Sec. 12.1). Addition of soil analysis. Add. Argon gas (Sec 4.14) Cal Std 5 remake (5.11) Changes to diln test Sec 8.2g.Stds made volumetrically

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE, AND APPLICATION

This method describes the multi-element determination of trace elements by ICP-MS. Sample material is introduced by pneumatic nebulization into a radio-frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier and the ion information processed by a data handling system. Interferences must be recognized and corrected. Such corrections include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by sample matrix must be corrected for by the use of internal standards.

When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, soil/sediment and industrial waste, for which total (acid-leachable) elements are required.

2.0 INTERFERENCES

2.1 Isobaric Elemental Interference

Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

2.2 Isobaric Molecular and Doubly Charged Ion Interference

Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the Cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standing solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) = (m/z 75 signal) – (3.13) (m/z 77 signal) + (2.73) (m/z) (82 signal), (where the final term adjust for any selenium contribution at 77 m/z)

Note: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^{+}$, (e.g. $^{81}BrH^{+}$ from bromine waste)

Similarly, corrected cadmium signal (using natural isotopes abundances for coefficient approximations) = (m/z 114 signal) – (0.027) (m/z 118 signal) – (1.63) (m/z 108 signal), (where the last two terms adjust for any tin or MoO^{+} contributions at m/z 114).

Note: Cadmium values will be biased low by this type of equation when $^{92}ZrO^{+}$ ions contribute at m/z 108, but use of the m/z 111 for Cd is even subject to direct ($^{94}ZrOH^{+}$) and indirect ($^{90}ZrO^{+}$) additive interferences when Zr is present.

Note: As for the arsenic equation above, the coefficients in the Cd equation are for only illustrative purposes. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g. oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent –to-oxide ion intensities, the correction must be adjusted for the degree of outside formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported for oxide-ion corrections using ThO^{+}/Th for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas has been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met

2.3 Physical Interference

Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for the physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by the matrix change. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

2.4 Memory Interference

Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interferences.

2.4.1 Consistent flushing with blank reagent will minimize memory effects in most cases, and the Perkin Elmer Elan 9000 is capable of adding extended rinse periods should an analyte exceed a prescribed concentration.

2.4.2 Routine rinse times are determined by the regular analysis of blanks after Quality control samples containing high concentrations of metals and their subsequent passing.

3.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

3.1 Holding time = 6 months.

3.2 Aqueous samples are preserved with metals grade nitric acid before the appropriate digestion procedure to pH <2.

3.3 Dissolved samples are filtered prior to preservation through a 0.45-micron filter within 24 hours of sampling. Samples may then be digested for analysis, or if not, turbidity determined, and if acceptable, analyzed directly 16 hours after preservation to pH <2.

3.4 Aqueous samples are held in storage for a minimum of 30 days before disposal.

3.5 Solid samples are refrigerated at 4 ± 2 °C upon receipt, and are digested within 90 days of collection.

4.0 EQUIPMENT & SUPPLIES

4.1 Perkin Elmer Elan 9000 Inductively Coupled Plasma Mass Spectrometer
4.2 Elan version 3.0 software and accompanying computer
4.3 Cetac ASX-520 plus autosampler with probe
4.4 14mL polypropylene disposable sample cups
4.5 Orange-Green pump tubing for internal standard introduction
4.6 Black-Black pump tubing for sample introduction
4.7 Black-White pump tubing for drainage
4.8 PE mixing block for the internal standard and sample combination before delivery to the nebulizer
4.9 CrossFlow nebulizer
4.10 Ryton Scott Spray chamber
4.11 Polyscience Re-circulator
4.12 50-mL disposable hot block tubes, with certificate of analysis for trace impurities
4.13 Hot Block, certified calibration at 95°C
4.14 Argon Gas – High Purity (99.99%)

5.0 REAGENTS & STANDARDS

5.1 Conc. Trace-Grade Nitric Acid

5.2 2% Nitric Acid rinse

5.3 Conc. Trace-Grade Hydrochloric Acid

5.4 0.5% Hydrochloric Acid rinse

5.5 Type II water (ASTM D1193) for preparation of all reagents and standards

5.6 Internal Standard Stock solution, 10 ppm Li-6,Sc,Ge,Y,In,Tb and Bi traceable ultra-High purity metals grade, purchased from a reputable vendor, with a certificate of traceability (Perkin Elmer stock # N9303832, or equivalent)

5.7 Working internal standard solution, 50 ppb Li-6,Sc,Ge,In,Tb and Bi made up in 1% nitric acid by adding 5 mls of the stock to 1000mls volumetrically

5.8 10 ppm tune stock solution: Contains Ba,Be,Ce,Co,In,Li,Mg,Pb,Rh,Tl,U and Y. 0.25ml of tune stock solution up to a volume of 250ml in 1% Nitric Acid. (Spex cat # CL-TUNE-1, or equivalent)

5.9 Dual detector calibration solution: 20ppm Ca,Fe,K,Mg,Na and Sr. 200ppb of Ag,Al,As,Ba,Be,Cd,Co,Cr,Cu,Mn,Mo,Ni,Pb,Sb,Se,Tl,V,Zn,Th and U. 50ppb of IS solution , Li-6,Sc,Ge,Y,In,Tb,Bi in a 1% HCL matrix.

To make this standard, pipet 2mL of the 10ppm Ag,Al,As,Ba,Be,Cd,Co,Cr,Cu,Mn,Ni,Pb,Sb,Se,Tl,V,Zn,Th,U and 1000ppm Fe,K,Ca,Na,Mg and Sr Initial Calibration Verification Standard, (Perkin Elmer # N9303825, or equivalent). Add 0.5mL of the 10ppm IS stock standard (Perkin Elmer stock # N9303832, or equivalent).

5.10 Stock Standard ICP-MS Calibration Standards: 20 ppm (20000ppb) traceable ultra-high purity standards purchased from a reputable vendor, with a certificate of traceability (Perkin Elmer #N9303816, or equivalent). This standard contains Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V, and Zn.

5.10 Calibration standards are made volumetrically daily in 1% Nitric Acid:

Cal. Std. #1	**0.2ppb**	10mL of	1ppb (std #3) to a final volume of 50mL
Cal. Std. #2	**0.5ppb**	2.5mL of	10ppb (std #4) to a final volume of 50mL
Cal. Std. #3	**1.0ppb**	5.0mL of	10ppb (std #4) to a final volume of 50mL
Cal. Std. #4	**10.0ppb**	5.0mL of	100ppb (std #6) to a final volume of 50mL
Cal. Std. #5	**50ppb**	20 mL of	100 ppb (std #6) to a final volume of 40 mL
Cal. Std #6	**100ppb**	0.25mL of	20000ppb (std stock) to a final volume of 50mL

5.12 Continuing Calibration Standard (CCV) 50.0 ppb: 20 mL of 100 ppb Cal Std #6 diluted to a volume of 40mL.

5.13 Initial Calibration Verification Stock Standard: 1000ppm and 10ppm (10000ppb) traceable ultra-high purity second source standard purchased form a reputable vendor., with a certificate of traceability. This standards contains 1000ppm of Fe,K, Ca, Na, Mg, Sr and 10ppm of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th, and U. (Perkin Elmer #N9303825, or equivalent)

5.14 Initial Calibration Verification Standard (ICV/QCS): 4ppm Fe, K, Ca, Na, Mg, Sr and 40ppb Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th, and U.

Volumetrically add 0.20 mLs of the ICV stock standard to a final volume of 50mLs in 1% Trace Acid.

5.15 Inter-element Interference Check Stock Solution A, ultra-pure High metals grade, purchased from a reputable dealer. (Perkin Elmer #N9303828, or equivalent)

Analyte	Concentration mg/L
Mo	20
Ti	20
Al	1000
Ca	1000
Fe	1000
K	1000
Na	1000
S	1000
Cl	10000
C	2000
Mg	1000
P	1000

5.16 Inter-element Interference Check Stock Solution B, ultra-pure High metals grade, purchased from a reputable dealer. (Perkin Elmer #N9303829, or equivalent)

Analyte	Concentration mg/L
Ag	5.0
Cd	10.0
Co	20.0
Cr	20.0
Cu	20.0
Mn	20.0
Ni	20.0
V	20.0
As	10.0
Se	10.0
Zn	10.0

5.17 IEC Check A, made in 2% nitric acid, by adding 2.5 mLs stock A volumetrically to a final volume of 25 mLs then diluting 1:5 prior to analysis.

Analyte	Concentration mg/L
Mo	1.0
Ti	1.0
Al	50.0
Ca	50.0
Fe	50.0
K	50.0
Na	50.0
S	50.0
Cl	500.0
C	100.0
Mg	50.0
P	50.0

5.18 IEC check AB, made in 2% nitric acid, by adding 2.5 mLs stock A, and 0.25 mLs stock B volumetrically to a final volume of 25 mLs then diluting 1:5 prior to analysis.

Analyte	Concentration mg/L
Mo	1.0
Ti	1.0
Al	50.0
Ca	50.0
Fe	50.0
K	50.0
Na	50.0
S	50.0
Cl	500.0
C	100.0
Mg	50.0
P	50.0
Ag	0.025
Cd	0.05
Co	0.10
Cr	0.10
Cu	0.10
Mn	0.10
Ni	0.10
V	0.10
As	0.05
Se	0.05
Zn	0.05

5.19 Standard Reference Material (SRM) , used for solid matrix LFB/LFBdup purchased from a reputable dealer

5.20 Teflon Chips, used as a control blank for preparation of method blanks when preparing solid matrices.

6.0 SAFETY

See Material Safety Data Sheets (MSDS) and Con-Test Chemical Hygiene Plan.

7.0 PROCEDURE

7.1 Elan 9000 – Turning on the Instrument and Instrument Warm Up

7.1.1 Open up the vent

7.1.2 Turn on the chiller

7.1.3 Turn on the instrument. The switches are located on the left side of the instrument. They should be turned on in the following order. 2,4,1,3 (System, Electrical, RF Generator, Rough Pump). **Under normal circumstances the instrument, chiller and vacuum pump are left on 24/7.**

7.1.4 Change the pump tubing (a good time to do this is while the vacuum is being established)

7.1.5 Turn on the Computer

7.1.5.1 Click on the Elan Icon
7.1.5.2 Click on the Instrument Icon
7.1.5.3 Click on the Vacuum Icon on the Instrument. When the Vacuum Icon turns from **Yellow to Green** then the vacuum has been established. This takes about 15 minutes.
7.1.5.4 Click on the Plasma Icon. The Plasma will turn from **Yellow to Green**. Let the machine warm up for a minimum 30 minutes

7.1.6 Fill the rinse blank (2% Nitric Acid, 0.5% Hydrochloric Acid)

7.1.7 Fill the Internal Standard (IS)

7.2 Tuning and Performance Check Criteria

Note: Tuning the Instrument should only be performed by an experienced operator. The steps given here assume that the tune and the performance check pass. The user should have read and understood the Elan 9000 user manual and specifically Chapter 3 in the manual. Many factors can contribute to a poor tune, dirty sample introduction system, dirty cones, and a dirty torch. When the system has been cleaned the torch will need to be re-aligned and optimized. The lens voltages will need to be re-calibrated, and the nebulizer flow will need to be re-calculated for optimum conditions. System maintenance is crucial for keeping the instrument in good operational condition.

7.2.1 Open Instrument Workspace folder

7.2.2 Open EPA Tuning folder

7.2.3 Place A/S probe and IS line in the Tuning solution. Wait 2 minutes for full aspiration.

7.2.4 In the EPA Tune folder, Click **Tune MS**

7.2.5 When the Tune is complete and it has passed method 6020A criteria, then the tune should be saved. (see table 1)

7.2.5.1 go to **File, Save As**
7.2.5.2 Save As Tune /date (Tune/yymmdd) log the tune in the run log book
7.2.5.3 Go back and Save As: **EPA default file** (This will apply the tune to that days run)

7.2.6 Go Back to Open Workspace, and open **Daily Performance Check**

7.2.7 Click on **Analyze sample**

7.2.8 When the analysis is complete, evaluate data against method 6020A/MCP/RCP criteria found in table I.

7.2.9 Print the tune and the performance check and keep with that day's data set.

7.3 Instrument Calibration and Sample Analysis

7.3.1 Open analyze sample workspace
7.3.2 Click open icon dataset
7.3.3 Go to file and new, enter today's date in the format (yymmdd)
7.3.4 Place probe in the instrument rinse on the Auto Sampler. Allow the instrument to rinse for about 30 minutes to 1 hour. Place the tune line in the tune solution.
7.3.5 Make the instrument standards and the QC standards.
7.3.6 Set up the calibration and QC standards in the Auto Sampler rack
7.3.7 Click on the **Analyze batch**, you will see a prompt that will ask you if you want to erase previous calibration standards and blanks, say **YES.**
7.3.8 Analyze samples under the batch mode. Use the 1st option default which is to run the calibration.
7.3.9 Highlight the calibration standards, blanks and sample QC to be run
7.3.10 Click on **Run Blanks Standards and Samples**
7.3.11 Evaluate the calibration curves, according to Table I. Evaluate method QC after the calibration.
7.3.12 Save the calibration and QC in the cal. File in the format (yymmdd)
7.3.13 Fill out the ID weight file for the samples to be run.
7.3.14 In the **Analyze Samples** under the batch mode, highlight all samples to be run, then click on **Build Run List**
7.3.15 A prompt will come up asking if you want to clear the QC data, click **NO**
7.3.16 Pour out Samples and check carefully with the ID weight file
7.3.17 Click on **Analyze Batch**

7.4 Aqueous and Soil Sample Digestion- Total Recoverable Analytes

7.3.1 Prepare samples for analysis according to SOP 3005 for the Acid Digestion of Waters, SOP 3050 for Acid Digestion of Soils and SOP3051 for Microwave Digestion of Soils.

7.3.2 A sample batch should contain no more than 20 samples. All samples and QC should be matrix matched. A batch should contain the samples, LRB, LFB, LFM and a Duplicate.

8.0 QUALITY CONTROL

8.1 Definitions

For definitions and explanations of quality control measures (blanks, LCS/QC Reference, LFB, Duplicates, MS/MSD, etc.) refer to section 4.0 of the Con-Test Analytical Quality Assurance Manual.

8.2 Quality Control Measures & Acceptance Criteria

8.2a Calibration Blank (ICB/CCB)

8.2a1 Analyzed as part of the calibration curve, at the beginning and end of sample analysis, and in between every 10 samples to determine any bias associated with drift at the RL portion of the curve. Results should

be less than the ±RL. Additional CCBs may be run after 5 samples at the prerogative of the analyst. The CCB should be run after the CCV (see 8.2i below). If the CCB for an element(s) are outside of the limits, the CCB should be re-run. If the CCB still fails for the element(s) in question then the operator has two options. The instrument can continue to run, and those element(s) that are outside of the specifications will need to be run during a different calibration, or the instrument is stopped, the problem corrected and the instrument is re-calibrated and the samples are re-analyzed.

8.2a2 CCBs should be analyzed after the ICV and CCVs

8.2b Laboratory Reagent Blank/Method Blank (LRB/MB)

8.2b1 Matrix matched samples brought through the digestion procedure. At least 1 is prepped per digestion batch of 20, and results should be less than the RL. For dissolved samples, TYPE II water filtered through the same type filters the dissolved samples were filtered through, and if the samples are digested, so will the MB. If the MB is above the RL, but the samples are below the RL, then the data may be reported.

If the concentration of the analyte is greater than 10X the concentration of the positive LRB, then the data may be reported. If the concentration of the sample is less than 10X the concentration of the positive method blank than the sample must be re-digested for those out of control element(s).

8.2c Initial Calibration Verification (ICV)

8.2c1 Also known as the external standard or reference standard. Analyzed after the calibration to ensure proper standard make-up and detect any analytical biases. The ICV is made from a secondary source (different Lot # or a different vendor) than the standards from which the curve is comprised. The range is +/- 10%.

8.2d Lab Fortified Blanks (LFB)/Laboratory Control Samples (LCS), LFB/LCS Duplicates

8.2d.1 Matrix matched blanks are spiked at a frequency of 2 per batch of 20 samples or less for matrix that cannot be spiked, and 1 per digestion batch of 20 for those that can. It is the analyst's prerogative to prepare additional LFBs.

8.2d.2 LFBs are carried through the entire preparation process, and spiked with a separate source from the calibration.

8.2d.3 Limits for waters by 6020A are 80-120% for both MA DEP DE and CT RCP.

8.2.d.4 For solid matrices a SRM is used. Control limit criteria are established by the manufacturer.

8.2d.5 LCS/LFB duplicates must be performed for all MA Data Enhancement projects:

RPD Limits: Aqueous <20% Soil <30%

8.2e Matrix Duplicates (DUPS)

Analyzed to assess precision by use of a calculated RPD. Limits are dependent on the matrix. Matrix duplicates are prepared 1 per 20 samples or less.

If result is > 5x RL: aqueous RPD limit is +/- 20%, soil RPD limit is +/- 35%

If result is < 5x RL: aqueous and soil RPD limit is "difference" < RL

Samples that are totally consumed during digestion cannot be duplicated, are read twice by the instrument to confirm precision.

8.2f Matrix Spikes (MS)

Spiking occurs prior to sample preparation, and is carried through the entire preparation process, then analyzed with the samples. Spikes are performed on 1 per 20 samples or less and recovery limits are 75-125%R

Internal laboratory control limits are generated through a charting program. The recoveries must fall within the limits listed above.

Samples that are totally consumed during digestion cannot be spiked.

For all Massachusetts and Connecticut samples, if the matrix spike falls below 30% recovery, redigest and reanalyze. (Per EPA Region 1 data validation guidance). Narrate further nonconformance.

8.2f1 **Matrix Spike Duplicates (MSDs)** are prepared in addition to DUPS. Because of the multi-element component of ICPMS analysis, DUPS are primarily used over the MSDs due to the abundancy of metals with hits > 5x the RL, unless an MSD is requested by the client.

8.2f1.1 MSDs have the same recovery limits as DUPS. (see 8.2e above)

8.2f2 The concentration of Ca, Mg, and Na, and to some degree Fe, Mn and Al, in environmental water samples, along with Fe, and Al in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at typical spiking concentrations may prove to be of little use in assessing data quality for these analytes.

8.2g Dilution Test

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (**analyte concentration must be > 100X the RL of the element for 6020 and RCP or >50x the RL for MCP**) a 5X dilution of the sample is required. A difference criterion ±15% (for RCP) or +/-10% (for 6020 and MCP) must be between the dilution and the native sample. If this criterion is not met then the recommended corrective action for the non-compliance is to narrate on the final report. This test should be performed every 20 samples. It is preferred that the test is performed on the same sample for which the MS and DUP is performed.

8.2h Post Digestion Spike Addition

An analyte spike added to a portion of a prepared sample, (analyte concentration must be <100X the RL of the element) is performed on the QC sample. This is the same sample for which the MS, DUP and Dilution Test is performed. The recovery of the test should be within 80-120% of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If this criterion is not met then the recommended corrective action for the non-compliance is to narrate on the final report. This test should be performed every 20 samples.

8.2i Continuing Calibration Verification (CCV)

Analyzed after every 10 samples, and at the conclusion of analysis, with a range of 90% - 110%. The CCV known value should be in the center of the calibration curve.

8.2j Interference Check Standard A and AB (ICSA/ICSAB)

Verify the magnitude of elemental and molecular-ion interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, which ever is more frequent. Do these by analyzing the interference check solution A (5.17) and AB (5.18). The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to section 2.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed. The ICSA and ISCAB should have a recovery of 80-120%. If the standard does not meet this requirement, than corrective action is not required, because instrumental conditions are based on natural isotope abundances that can not be changed. Narrate the non-compliance. If the IS recoveries (30-120%) are within the acceptable range than the data is acceptable.

8.2k Internal Standards (IS)

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30-120% of any field sample, based on the intensity of that internal standard in the initial calibration blank, the following procedure is followed. The sample must be diluted fivefold (1 + 4) and reanalyzed with the addition of appropriate amounts of IS. This procedure must be repeated until the internal-standards intensities fall within the prescribed window. The intensity levels of the IS for the ICV, ICB, CCV and CCB should fall within ±20% of the intensity level of the IS in the calibration blank. If they do not agree, terminate the analysis, correct the problem and recalibrate the instrument. Verify the instrument calibration and re-analyze all affected samples back to the last passing instrument QC sample. If the IS recoveries of the ICSA and ICSAB are not within 30-120%, then the calibration should be terminated and the instrument recalibrated.

8.2l Linear Dynamic Range Analysis (LDR)

A linear dynamic range study is analyzed annually for each wavelength. It is determined by analyzing three concentrations of the analyte until the observed recovery is no more than 10% below the stated concentration of the standard.

Determined sample concentrations that exceed 90% of the LDR should be diluted and reanalyzed. The generated limits are posted at the instrument for reference.

8.2m Method Detection Limit Studies (MDLs)

MDLs are conducted annually, when a new analyst begins performing analysis on that particular instrument, or when conditions are changed, due to major maintenance or service. (See the Con-Test Analytical Quality Assurance Manual)

8.2n Instrument Detection Limit Studies (IDLs)

IDLs are conducted quarterly, or when conditions are changed, due to major maintenance or service. (See the Con-Test Analytical Quality Assurance Manual). 7 replicates of Instrument blanks are analyzed on 3 non- consecutive days. The averages of each days standard deviations are computed. The IDL must be less than the elements MDL.

8.2o Reporting Limit (RL) Calibration Check Standard (Low-Level, LL, Check Standard)

This standard verifies the instrument sensitivity, to support the RL. **Only required if the RL standard is not part of the initial calibration curve.**

Required daily, following initial calibration. Must be at the level of the RL for all analytes (RL must be $\leq$1/2 MCP Method 1 Clean-up Standard for each metal; or < applicable site-specific RL (based on project DQO's).

Criteria = 70-130% of true value.

9.0 CORRECTIVE ACTIONS/ CONTINGENCIES OF HANDLING OUT-OF-CONTROL DATA

9.1 Refer to Con-Test Quality Assurance Manual, section 3.3.3.
9.2 Refer to Con-Test Corrective Action SOP.

10.0 POLLUTION PREVENTION

10.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

11.0 WASTE MANAGEMENT

11.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

11.2 Acidic samples and waste are dumped into satellite waste containers.

12.0 REFERENCES

12.1 USEPA "Test Methods for Evaluating Solid Waste, Physical / Chemical Methods" SW-846 Method 6020A, update I, 02/2007

12.2 Quality Assurance and Quality Control Requirements and Performance for SW846 Method 6020A, Trace Metals by Inductively Coupled Plasma- Mass Spectroscopy – (ICP-MS) for the MCP. Massachusetts DEP WSC-CAM-IIID. Revision #1. July 1 2010.

12.3 CT DEP "Recommended Reasonable Confidence Protocols and Quality Assurance and Quality Control Requirements, Determination of Trace Metals by SW-846 Method 6020 Inductive Coupled Plasma-Mass Spectrometry" Version 2.0, July 2006

12.4 Con-Test Analytical Quality Assurance Manual

12.5 Con-Test Analytical Chemical Hygiene Plan

12.6 Con-Test Analytical Corrective Action SOP

12.7 Con-Test Analytical Procedure for Maintaining Controlled Documents SOP

12.8 Perkin Elmer Instrument Manual Elan 9000 ICPMS, 2003 edition

12.9 Con-Test Analytical SOP # 16 Turbidity Determination of Metals Samples

12.10 Con-Test Analytical SOP # 39 Preservation and Digestion of Aqueous samples

12.11 Con-Test Analytical SOP # 29 Acid Digestion of Solid Materials.

12.12 Con-Test Analytical SOP #135 Microwave Assisted Digestion of Soils, Sediments, Sludge's and Oils.

TABLE I.

Quality Control	6020A	MCP 6020A	RCP 6020A
Daily Performance Standard	1. Perform Daily, before instrument tune. 2. Should be a 10ug/L standard of 3 or more elements that bracket the mass ranges of interest. 3. Oxide and double charge should be <3%.	4. Perform Daily, before instrument tune. 5. Should be a 10ug/L standard of 3 or more elements that bracket the mass ranges of interest. 6. Oxide and double charge should be <3%.	1. Perform Daily, before instrument tune. 2. Should be a 10ug/L standard of 3 or more elements that bracket the mass ranges of interest. 3. Oxide and double charge should be <3%.
Mass Calibration	±0.1amu	±0.1amu	±0.1amu
Resolution*	<0.9amu full width a 10% peak height	<0.9amu full width a 10% peak height	<0.9amu full width a 10% peak height
Tune	1. Elements should bracket the masses of interest. 2. Analyze at least 4 times with a RSD of ≤5% for the elements contained in the tuning solution.	1. Elements should bracket the masses of interest. 2. Analyze at least 4 times with a RSD of ≤5% for the elements contained in the tuning solution.	1. Elements should bracket the masses of interest. 2. Analyze at least 4 times with a RSD of ≤5% for the elements contained in the tuning solution.

* ELAN measures at 5% peak height. Equivalent to <0.7amu full width at 5% peak height.

Quality Control	6020A	MCP 6020A	RCP 6020A
Initial Calibration	1. The calibration blank should be less than 3X the current IDL for each element. 2. Calibrate for the elements of interest. Use a calibration blank and at least one standard 3. Use the average of at least 3 integrations for all standards and sample analysis. 4. Linear curve fit with correlation coefficient of r>0.998	1. Frequency-daily following tuning of the ICP-MS and before sample analysis 2. Minimum of 3 non blank points that may include the RL and the LR. If the RL and LR are not included in the calibration then a RL and LR standard must be run. 3. Minimum of 3 integrations for the calibration and sample analysis 4. Linear curve fit with correlation coefficient of r>0.998	1. Frequency-daily following tuning of the ICP-MS and before sample analysis 2. Minimum of 3 non blank points that may include the RL and the LR. If the RL and LR are not included in the calibration then a RL standard must be run. 3. Minimum of 3 integrations for the calibration and sample analysis 4. Linear curve fit with correlation coefficient of r>0.995
Initial Calibration Verification (ICV)	1. Frequency-Daily immediately following calibration. And following the last sample 2. Separate source (independent) from calibration standards. Matrix- matched (same acid concentration as the standards and samples). Near the mid-point of the calibration curve 3. ICV recovery must be 90-110%	1. Frequency-Daily immediately following calibration 2. Separate source (independent) from calibration standards. Matrix- matched (same acid concentration as the standards and samples). Near the mid-point of the calibration curve 3. ICV recovery must be 90-110%	1. Frequency-Daily immediately following calibration 2. Separate source (independent) from calibration standards. Matrix- matched (same acid concentration as the standards and samples). Near the mid-point of the calibration curve 3. ICV recovery must be 90-110%
Initial Calibration Blank (ICB)	1. Immediately following the ICV and the quality control check standard (ICV/CCV) at the end of the analysis. 2. The calibration blank should be less than 3X the IDL for each element	1. Frequency-immediately following the ICV 2. Must be matrix- matched (same acid concentration as the standards and samples) 3. ICB must be <RL	1. Frequency-immediately following the ICV 2. Must be matrix- matched (same acid concentration as the standards and samples) 3. ICB must be <RL

Reporting Limit Check standard	Not required Not needed if RL is in the ICAI, otherwise ± 30% of True Value Recommended.	1. Frequency- Daily following the ICB. 2. This standard is **not need** if the RL is included in the calibration. (note; for MCP projects, the RL is defined as being ½ of the method 1 cleanup standard or < applicable site specific RL (based on project DQOs) 3. criteria: %recovery 70-130%	1. Frequency- Daily following the ICB. 2. This standard is **not needed** if the RL is included in the calibration. 3. Criteria: %recovery 70-130%

Quality Control	6020A	MCP 6020A	RCP 6020A
Continuing Calibration Verification (CCV)	1. Analyze Instrument check standard (ICV), 3rd part source 2. Every 10 analytical samples, and at the end of the run. 3. CCV% recovery must be 90-110%	1. Every 10 analytical samples, and at the end of the analysis. 2. Same source as the calibration standards, and at the mid-point of the curve. 3. CCV % recovery must be 90-110%	1. Every 10 analytical samples, and at the end of the analysis. 2. Same source as the calibration standards, and at the mid-point of the curve. 3. CCV % recovery must be 90-110%
Continuing Calibration Blank (CCB)	1. CCB must be less than 3X the IDL of each element 2. Follows the CCV and at the end of the analysis.	1. Every 10 analytical samples, immediately following the CCV and at the end of the analysis. 2. Must be matrix-matched (same concentration of acid that is in the standards and the samples). 3. CCB must be within the limits of ± RL per element	1. Every 10 analytical samples, immediately following the CCV and at the end of the analysis. 2. Must be matrix-matched (same concentration of acid that is in the standards and the samples). 3. CCB must be within the limits of ± RL per element
Linear Range Standard	1. Not required 2. Dilute samples that are over the LDR of the element in question	1. Frequency- required Daily following the RL standard. 2. This standard is only necessary if the LR is not contained in the calibration curve. 3. LR % recovery is 90-110%	1. Frequency- Annually 2. Determine the upper limit of the Linear Dynamic Range for each m/z (mass/charge) ratio
Interference Check Solutions ICSA and ICSAB	1. Must be run and monitored at the start of the run and every 12 hours	1. Frequency- at the start of the analytical run 2. ICSA and ICSAB must have known amounts of analytes. 3. Criteria: % recovery 80-120% Otherwise narrate	1. Frequency- at the start of the analytical run 2. ICSA and ICSAB must have known amounts of analytes. 3. Criteria: % recovery ±20% or within 2X the RL, whichever is greater. If the analyte is not present then the concentration of the analyte is zero. Narrate non-conformance
Method blank	Method blank must be carried through the complete process. It should contain the same amount of acid that is in the samples	1. Frequency- one per digestion batch of ≤20 field samples. Undigested samples use the ICB/CCB as the method blank. 2. Must be matrix-matched 3. Method Blank must be < RL	1. Frequency- one per digestion batch of ≤20 field samples. Undigested samples use the ICB/CCB as the method blank. 2. Must be matrix-matched 3. Method Blank must be < RL

Quality Control	6020A	MCP 6020A	RCP 6020A
Laboratory Control Sample (LCS)	LCS must be carried through the complete process. It should contain the same amount of acid that is in the samples. Employ QA/QC procedures	1. Frequency- one per digestion batch of ≤20 field samples. Undigested samples use the ICV/CCV as the LCS. 2. Must be matrix-matched 3. LCS %recovery is 80-120% for aqueous samples, and vendor control limits of 95% percentile for standard reference material for solids.	1. Frequency- one per digestion batch of ≤20 field samples. Undigested samples use the ICV/CCV as the LCS. 2. Must be matrix-matched 3. LCS %recovery is 80-120% for aqueous samples, and vendor control limits of 95% percentile for standard reference material for solids.
Laboratory Control Sample Duplicate (LCSD)	Not required	1. Frequency- one per digestion batch of ≤20 field samples. Undigested samples use the ICV/CCV as the LCS. 2. Must be matrix-matched 3. Prepared using the same standard source as the LCS 4. Run immediately after the LCS in the analytical sequence 5. Relative Percent Difference (RPD) must be ≤20% for aqueous samples and ≤30% for solid samples	Not required
Matrix Spike (MS)	1. Every 20 samples or per batch 2. % recoveries are 75-125%.	1. Project Specific. Should be selected by the data user. One MS per ≤20 field samples 2. MS recoveries for all media 75-125%. (If recovery is < 30%, reprepare and reanalyze as directed in the MCP 6020A Method.)	1. Every 20 samples or per batch 2. % recoveries are 75-125%. (If recovery is < 30%, reprepare and reanalyze as directed in the RCP 6020a Method.)
Matrix Spike Duplicate (MSD)	Not required	1. Project Specific. If requested by the data user. One MSD or Duplicate per ≤20 field samples 2. RPD aqueous samples; >5X RL; ±20%, <5X RL difference ≤RL. Solid samples >5X RL ±35%, <5X RL difference ≤2XRL	Not Required
Duplicate (MD)	Analyze one duplicate sample for every matrix in a batch. Frequency: 1 matrix duplicate for every 20 samples.	1. Project Specific. If requested by the data user. 1 MD or Duplicate per ≤20 field samples 2. RPD aqueous samples; >5X RL; ±20%, <5X RL difference ≤RL. Solid samples >5X RL ±35%, <5X RL difference ≤2XRL	1. Every 20 samples or per batch RPD aqueous samples; >5X RL; ±20%, <5X RL difference ≤RL. Solid samples >5X RL ±35%, <5X RL difference ≤2XRL

Quality Control	6020A	MCP 6020A	RCP 6020A
Dilution test	1. If the analyte concentration is within the LDR, and the analyte concentration is 100X greater than the MDL, than perform a fivefold dilution (1+4) dilution. 2. The resulting dilution must be ±10% of the original determination. If not, interference must be suspected. 3. One serial dilution must be performed for every 20 samples or less of each matrix in a batch	1. Frequency- 1 dilution test for every 20 field samples. Only if the analyte is >50X the RL 2. Dilution test=5X dilution 3. Difference criterion ±10% 4. Narrate non-conformance	1. Frequency- 1 dilution test for every 20 field samples. Only if the analyte is >100X the RL 2. Dilution test=5X dilution 3. Difference criterion ±15% 4. Narrate non-conformance
Post digestion Spike	1. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80-120% of the known value or within laboratory derived acceptance criteria. 2. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and re-analyzed to compensated for the matrix effect.	Not Required	Not Required

Quality Control	6020A	MCP 6020A	RCP 6020A
Internal Standards	If the intensity of any internal standard in a field sample falls below 30% of the intensity of the internal standard in the calibration blank, a significant matrix effect must be suspected. Under these conditions, the detection limit has degraded and the correction ability of the internal standardization technique becomes questionable. **Follow the following procedures**. 1. Make sure that the instrument has not drifted by examining the last CCBs/ICB. If the degradation is seen in the last CCV, stop the analysis find and correct the problem. • Re-calibrate the instrument, and verify the calibration by running all QC needed to assure the instrument is calibrated. • Re-analyze all samples that were effected by the bad CCB If drift has not occurred then a matrix effect has occurred, and the sample must be diluted. • A five fold dilution (1+4) is performed on the effected sample, • The sample is re-analyzed at dilution with the appropriate amount of IS. If this dilution does not correct the problem (IS recovery>30%), then further dilution is necessary until the effect is eliminated. (IS recovery.30%) • Results and DLs must be adjusted for dilution.	1. Frequency- Internal standards (IS) must be added to all field and QC samples 2. Field samples. Relative Intensity of the (IS) must be 30-120% of IS in the Calibration Blank 3. QC Samples. 80-120% of IS in the Calibration Blank 4. Optimize mass and ionization potential mass of the IS to the elements to be quantitated by the MS-ICP 5. **Action**: dilute the field sample until the IS recoveries are acceptable. If not met, terminate the analysis and recalibrate the instrument	1. Frequency- Internal standards (IS) must be added to all field and QC samples 2. Field samples. Relative Intensity of the (IS) must be 30-120% of IS in the Calibration Blank 3. QC Samples. 80-120% of IS in the Calibration Blank 4. Optimize mass and ionization potential mass of the IS to the elements to be quantitated by the MS-ICP 5. **Action**: dilute the field sample until the IS recoveries are acceptable. If not met, terminate the analysis and recalibrate the instrument

MERCURY (COLD VAPOR TECHNIQUE)
EPA 245.1
SW 846-7470A/7471A and 7471B

Approved:

Michael Erickson
Laboratory Director

Katherine F. Delisle
QA Officer

Revision Number: 10

NON-CONTROLLED COPY

Controlled Copy Number_____

Change Record

Revision	Date	Responsible Person	Description of change
1	02/20/2002	KRL	Updates for NELAC format
2	12/06/2002	PM	MA MCP Data Enhancement Program compliance
3	01/08/2004	PM	Changes/updates, per AZ audit: section 7.3, references on title page
4	02/05/2005	PM	Updates for AZ/MA audits (12/04, 01/05)
5	01/03/2006	KD	Updates for "Controlled Document Status"; sections 12.0 (corrective action SOP), and 14.0 (ref. Addition).
6	06/02/2006	KD	Updates due to internal audit and CT RCP ref.'s Sections; 3.0 (storage), 4.2.5 (vortex), 10.2.6 (freq. of dup's), 10.2.7 (freq. of MS's and RCP ref.), 10.2.8 (freq. of MSD's), 10.2.9 (RCP ref.,and freq. of LFB's), 10.2.10 (RCP ref.), and 14.0 (CT RCP ref. addition).Limits added in new appendix.
7	06/21/07	SLS	Update due to MA DEP audit: section 10.2.7, matrix spikes for EPA 245.1 must be performed at a 10% frequency.
8	04/03/08	MTM, KSH	Added requirements and information from new PE instrument. Updates for new FIMS Hg Analyzer and RL changed to 0.1ppb
9	03/30/2009	JMM/AMP	Updates due to annual review; Grammatical edits made throughout document. Sec4.0 FIMS-100 added. Sec5.0 updates and 3%HCl prep added. Sec 8.0, Leeman instrument setup and operation removed. Sec8.0 FIMS-100 instrument setup updated including psigs updates. Sec8.0 FIMS-100 instrument operation updated adding instructions to flush tubing. Sec10.0 add note to ICB section to auto-zero, recalibrate and rerun if ICB fails.
10	10/13/09	AMP	Update References to include 7471B

Distribution/Training List

See Employee Training Record File for signed training statements for trained users.

1.0 SUMMARY, SCOPE, AND APPLICATION

This method is applicable to drinking, surface, and saline waters along with domestic and industrial wastes. In addition to inorganic forms of mercury, organic mercury may also be present in these matrices. All samples and standards are digested with Nitric acid, Sulfuric acid, potassium permanganate, and potassium persulfate and any organic-mercury compounds (such as phenyl mercuric acetate and methyl mercuric chloride) are transformed to the mercuric ion, which is then quantitated. Heating the samples after the addition of these chemicals insures that any methyl mercuric chloride is oxidized to the mercuric ion. Mercury absorption is at a wavelength of 253.7 nm. Possible interference from sulfides is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of additional inorganic mercury from distilled water.

Copper has also been reported to interfere; copper concentrations as high as 10 mg/L have no effect on the recovery of mercury from spiked samples. Sea water, brines and industrial effluents high in chlorides also require additional potassium permanganate. Excess hydroxylamine hydrochloride solution is used to tie up free chlorine generated by the addition of the potassium permanganate. The dead air space must be purged before the addition of stannous chloride solution. Interference from certain volatile organic materials, which absorb at the same wavelength as mercury, is also possible. Running the sample without reagents will determine if this type of interference is present.

Method Detection Limit = 0.10 ug/L.

2.0 INTERFERENCES

Interferences have been reported for waters containing sulfides, chloride, and tellurium. Interference from these sources may vary according to concentration. Organic compounds with broad band UV absorbencies are confirmed as interference.

These interferences are typically diluted out with the resulting higher detection limit. In other cases, a sample is analyzed without using stannous chloride, and any resulting peak is deemed to be an interferant, and subtracted from the true result, or diluted.

3.0 SAMPLE PRESERVATION/STORAGE/HOLDING TIME

Preserve to a pH < 2.0 with trace metals-grade nitric acid.
Dissolved samples are filtered prior to preservation through a 0.45-micron filter within 24 hours of sampling and before preservation. Samples may then be digested for analysis, or if not, turbidity determined, and if acceptable, analyzed directly 16 hours after preservation to pH <2.
Waste waters to be analyzed by method 245.1 must be preserved for 24 hours prior to digestion.
Holding time = 28 days.
Samples are stored for a minimum of 30 days.

4.0 EQUIPMENT & SUPPLIES

4.1 Water bath set at a constant 95.0°C

4.2 Computer controlled FIMS-100 Mercury Analysis System, and associated consumables:
- 4.2.1 Mercury lamp
- 4.2.2 Pump tubing
  - 4.2.2.1 Reductant Tubing – 1.14 x 0.86 mm red/red 3-bridged
  - 4.2.2.2 Rinse and Waste – 1.52 x 0.86 mm yellow/blue/yellow 3-bridged
  - 4.2.2.3 Liquid-Gas Separator and Waste – 3.17 x 0.85 mm black/white 3 bridged
- 4.2.3 Perkin Elmer S-10 Autosampler and probe
- 4.2.4 Vortex mixer
- 4.2.5 Absorption cell

4.3 Argon gas supply
4.4 15mL plastic tubes and caps.
4.5 50 mL centrifuge tubes and caps
4.6 Volumetric flasks
4.7 Starch-Iodine paper
4.8 Analytical balance capable of weighing to the nearest 0.01 g.

5.0 REAGENTS & STANDARDS

5.1 Concentrated Sulfuric Acid – metals ultra-pure grade

5.2 Concentrated Nitric Acid – trace grade

5.3 Concentrated Hydrochloric Acid – trace grade

5.4 Deionized water - Type II water (ASTM D1193) for preparation of all reagents and standards

5.5 Potassium Persulfate – Under a hood, Add 50 g of potassium persulfate (ACS grade) to a 1-Liter volumetric flask containing 500 mL of deionized water. Fill to final volume with deionized water. Under a hood, heat the solution in a hot water bath until dissolved.

5.6 Hydroxylamine Hydrochloride-Sodium Chloride- Under a hood, add 120g of hydroxylamine hydrochloride (ACS grade) and 120g of sodium chloride (ACS grade) to a 1-Liter volumetric flask containing 500 mLs of deionized water. Fill to final volume with deionized water.

*NOTE – Loosen the hydroxylamine crystals under a hood while wearing gloves and avoid breathing crystals.

5.7 Stock Mercury Reference QC/LCS Solution (second source) – Metals ultra-pure grade 100 mg/L Atomic Absorption Standard, from a different source than Stock Mercury Solution.

5.8 Hg Stock Standard Solution, 10 mg/l – Ultra-pure metals grade obtained from reputable vendor. Used to make calibration standards, aqueous and solids standards.

5.9 Working Standard Mercury Solution – 1.0 mg/L – Add 5mL of 10 mg/mL Hg stock standard solution to a 50 mL volumetric flask containing 25 mLs of deionized water and 1 mL of conc. Nitric acid. Fill to volume with deionized water.

5.10 Working Mercury Reference QC Solution (IPC) -1.0 mg/L - Add 0.25 mL of 100mg/L stock reference solution to a 25-mL volumetric flask containing 0.5 mL of conc. Nitric acid and 10 mLs of deionized water. Fill to volume with deionized water.

5.11 Aqueous Standard-0.3mg/L - Used for spiking. Add 3mL of 10 mg/mL stock standard solution to a 100 mL volumetric flask containing 50 mLs of deionized water and 2 mL of conc. Nitric acid. Fill to volume with deionized water.

5.12 Solids Standard –2.0mg/L - Used for spiking. Add 10mL of 10 mg/mL stock standard solution to a 50 mL volumetric flask containing 25 mLs of deionized water and 1 mL of conc. Nitric acid. Fill to volume with deionized water.

5.13 10% Hydrochloric rinse- Under a hood add 100mL cHCl to a 1L volumetric flask containing 500mL deionized water. Filled to a volume.

5.14 3% HCl Rinse for FIMS-100- Under a hood add 30mL of cHCl to a 1L volumetric flask containing 500mL deionized water. Fill to volume with deionized water.

5.15 Potassium Permanganate –Under a hood, add 50g of potassium permanganate (ACS grade) to a 1L volumetric flask containing 500mL deionized water. Fill to volume with deionized water. Under a hood, warm in a water bath until dissolved.

5.15 Stannous Chloride – Add 50.0g of $SnCl_2$ (ACS grade) into 500 mL of 0.5N sulfuric acid. Shake gently until dissolved.

5.16 0.5N sulfuric acid solution – 14mLs concentrated Sulfuric acid added to a 1-liter volumetric flask containing 500 mLs of deionized water. Bring up to volume with deionized water.

6.0 SAFETY

See Material Safety Data Sheets (MSDS) and CON-TEST Chemical Hygiene Plan.

7.0 CALIBRATION & STANDARDIZATION

Prepare working standards daily:

7.1 Prepare 2.0ug/L- IPC (Initial Performance Check) / QC Reference solution- add 0.05mL of QC reference stock into a 25 mL volumetric flask and bring to volume.
Add reagents ***** (see below section 7.2 a – e)

7.2 The normal sequence of standards run is 0.0, 0.10, 0.50, 1.00, 2.00, 5.00 ug/L. A linear calibration formula is used. Make up the standards as follows:

CONCENTRATION (ug/L)	MLS OF WORKING STANDARD (1 mg/L)	FINAL VOLUME (mL)*
Auto-zero	0	25
0.10	0.5 mL of 5.0 ppb Cal. Std.	25
0.50	0.0125	25
1.00	0.025	25
2.00	0.05	25
5.00	0.125	25

*NOTE – All standards, reference QC and blanks are made in 2 % nitric acid.

***Add to 25mL portions of blanks, standards and QC's:**

a. 1.25mLs of concentrated sulfuric acid, 0.625 mLs of concentrated nitric acid and 3.75 mLs of potassium permanganate solution.

b. Make sure potassium permanganate stays in solution.

c. Add 2mLs of potassium persulfate solution.

d. Digest by placing in a well ventilated hot bath set at 95°C for 2 hours.

e. After cooling under a hood to room temperature, add 1.5mLs of hydroxylamine hydrochloride-sodium chloride.

7.4 Correlation Coefficient must be 0.995 or higher.

7.5 The RL is incorporated into the curve as the low standard.

7.6 See initial quality control requirements in section 10.

8.0 PROCEDURE

8.1 SAMPLE PREPARATION: WATERS

8.1.1 Homogenize samples by shaking and transfer 6mLs of sample to 15mL plastic tubes.

8.1.2 Add 0.30mLs of concentrated H_2SO_4, 0.15mLs of concentrated HNO_3 and 0.90 mLs of potassium permanganate solution. Let stand for 15 minutes. If any samples do not remain purple in color for 15 minutes add more potassium permanganate solution until they do.

8.1.3 Add 0.48 mLs of potassium persulfate. Cap tubes and place the samples in a hot water bath at 95°C for 2 hours. Record initial water bath temperature and start time in the prep log.

8.1.4 Remove samples from hot water bath and place in hood. Record final water bath temperature and end time in the prep log. Allow samples to cool to room

temperature before proceeding.

8.1.5 Under a hood, add 0.36mLs of hydroxylamine hydrochloride-sodium chloride solution to each sample. If more is needed to reduce the potassium permanganate add until the sample turns clear (or until the sample attains its original color).

8.1.6 If chloride is suspected to be present in the sample:
Use starch-iodine paper to test sample. The paper will turn blue or brown if chloride is present.

8.1.7 If chloride is present then the sample must be analyzed twice. Analyze one portion as normal. Analyze one portion without adding any stannous chloride (insert stannous chloride tube into the rinse water reservoir during analysis). The actual mercury present is found by subtracting the concentration that is found in the portion without stannous chloride from the concentration found in the run where stannous chloride was added.

8.2 SAMPLE PREPARATION: SOLIDS/ SOILS/ SLUDGE

8.2.1 Weigh 0.100 – 0.300g of homogenized sample into a 50 mL centrifuge tube.

Add to each sample:

8.2.2 25mLs of DI water
8.2.3 1.25mLs conc. Sulfuric acid
8.2.4 0.625mLs conc. Nitric acid
8.2.5 3.75mLs potassium permanganate. Wait 15 minutes to see if the sample remains purple. If not, additional Potassium Permanganate may be added.
8.2.6 2.00mLs potassium persulfate solution
8.2.7 Cap and place samples into a well-ventilated 95 degrees C hot water bath for 2 hours. Record the temperature of the water bath and the amount of time in bath, in the prep log.
8.2.8 Remove samples from hot water bath and place under hood. Allow them to cool to room temperature before proceeding.
8.2.9 Add 1.50 mLs of Hydroxylamine hydrochloride-sodium chloride solution and vortex to clear samples.

8.3 FIMS-100 INSTRUMENT SETUP

8.3.1 Turn on FIMS instrument, computer, monitor, printer and argon 70-110 psig on tank gauge. Let FIMS warm up for 45min. Make sure gas flow gauge on FIMS-100 reads pressure at 50-100 psig.

8.3.2 Fill a bottle with stannous chloride, and fill rinse bottles.

8.3.3 Make sure waste is less than 75% full.

8.3.4 Setup cassettes by swinging pump pressure levers over the pump magazines against the rollers.

8.3.5 Tighten auto sampler magazine by pushing lever up.

8.3.6 Check all pump tubing and capillary tubing; change if necessary.

8.3.7 Double click on “AA WinLab32 for FIMS” icon on the computer screen.

8.3.8 If system status check passes click on the Workspace icon.

8.3.9 Click “Sample Info” icon.

8.3.10 Set up run. Make sure to fill in location with the cup #, initial sample weight if sample is a solid, the sample ID, and add QCs every 10 samples (CCB is QC 5, CCV is QC 4 for method 245.1 and QC 6 for methods 7470/7471) Include sample prep volume.

8.3.11 Save by clicking on “File”. Then select “Save as”. Then select “Sample Info File”. Save the file as the date. (example:090909)

8.3.12 Click on tools then, “Automated Analysis Control” window and the “set-up” tab.

8.3.13 Select appropriate “sample info file” (should be today’s date).

8.3.14 Under “Results Data Set Name” click on “Open” change to today’s date and save.

8.3.15 Click on the method you wish to use.

8.3.16 Make sure “Print log During Analysis” is checked.

8.4 FIMS INSTRUMENT OPERATION

8.4.1 In the Automated Analysis Control window, click the “Analyze” tab. Look over the run sequence.

8.4.2 Click the “FIAS” icon.

8.4.3 Click on the “Pump1” button and allow the pump tubing to condition for 30 min.

8.4.4 Click back on the “Automated Analysis Control” window.

8.4.5 Click the “Calibrate” button.

8.4.6 After Calibration, if the Correlation Coefficient is 0.995 or better, click on “Analyze Sample” button. If Correlation Coefficient is lower than 0.995 recalibrate after checking system.

8.4.7 After sampling is done, flush reductant tubing by running rinse solution through is for 10mins. Remove weighted tubes from rinse and allow air to pass through system for 10mins. Then turn off pump

8.4.8 To raise tip from rinse, click on “Analysis” on the tool bar, select “Autosampler” the select A/S Probe Up/Down.

8.4.9 Close gas valve on tank.

8.4.10 Loosen cassettes by swinging pump pressure levers off of the pump magazines.

8.4.11 Loosen cassettes of auto sampler pump by pushing lever down.

8.4.12 Next click "File" the select "Exit".

8.4.13 Shut computer off.

8.4.14 Turn off FIMS instrument.

9.0 CALCULATIONS

Mercury, mg/L = (Ax B)/1000

Where:
A = Direct reading from instrument (ppb)
B = Dilution factor (if necessary)

10.0 QUALITY CONTROL MEASURES

10.1 Definitions

For definitions and explanations of quality control measures, refer to section 4.0 of the Con-Test Quality Assurance Manual.

10.2 Quality Control Measures & Acceptance Criteria

***Note-**All calibration and check standards must be brought through the digestion process before analysis.

10.2.1 Calibration

Calibrate each batch with a minimum of five working standards and a blank over the appropriate working range. Correlation coefficient for the calibration curve must be 0.995 or better.

10.2.2 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Analyzed as part of the calibration curve, at the beginning and end of sample analysis, and in between every 10 samples to determine any bias associated with drift at the RL portion of the curve. Results should be less than the RL. If the CCB fails, it will be run again according to the method. If it fails twice, an auto-zero will be performed and the samples run since the last CCB within control limits will be rerun. Additional CCBs may be run after 5 samples at the prerogative of the analyst. The CCB should be run after the CCV.

CCBs should be analyzed after the ICV and CCVs

10.2.4 Method (Preparation) Blank

Matrix matched samples brought through the digestion procedure. At least 1 is prepped per digestion batch of 20, and results should be less than the RL. If the MB fails after two attempts, we narrate in LIMS for MCP DE and RCP jobs. If the sample results are >10x the level of contamination detected in the method blank, the data is considered valid and unbiased. If the samples are not >10x the level of contamination but are non detect, the data is considered valid. If the samples are detected and are not >10x the level of contamination the sample batch will be re-prepped or the out of control event will be narrated.

10.2.5 Initial Calibration Verification (ICV) / Instrument Performance Check (IPC)

Also known as the external standard, QC reference standard. Analyzed after the calibration to ensure proper standard make-up and detect any analytical biases. The ICV is made from a different Lot # (separate source) than the calibration standards. ICV recovery must be 90-110%.

An Instrument performance check standard (2.0 ppb) same source, is also analyzed after initial calibration according to method 245.1 EMMC, and must be 90-110%R.

10.2.6 Matrix Duplicates (DUPS)

Analyzed 1 per batch of 20 samples or less for solids and 1 per batch of 10 samples or less for aqueous, to assess precision by use of a calculated RPD.

Limits:	Aqueous	+/- 20%
	Solid	+/- 35%

10.2.7 Matrix Spikes (MS)

Spiking occurs prior to sample preparation, and is carried through the entire process, and analyzed with the samples. Spikes are done at a frequency of 1 per batch of 10 samples or less for EPA 245.1, and a frequency of 1 per batch of 20 samples or less for other methods.

Limits: 75-125%R For all MA MCP and CT RCP matrices and data types.
70-130% for Method 245.1

Internal laboratory control limits are generated through a charting program. The recoveries must fall within the tighter of the two limit sets.

For all Massachusetts and Connecticut samples, if the matrix spike falls below 30% recovery re-digest and reanalyze. (Per EPA Region 1 data validation guidance) Narrate further nonconformance.

10.2.8 Matrix Spike Duplicates (MSD)

Analyzed per client requests or in lieu of a sample duplicate.

RPD Limits:	Aqueous	+/- 20%
	Solid	+/- 35%

Matrix Spike Duplicates are prepared instead of DUPS if the analyte of concern is believed to have a high probability of non-detection.

10.2.9 Lab Fortified Blanks (LFB)/Laboratory Control Samples (LCS)

Matrix matched blanks are spiked at a frequency of 1 per batch of 20 samples or less. LFBs are carried through the entire preparation process, and spiked with a separate source from the calibration.

245.1 Limits:	Aqueous	85-115%R
7470 / 7471 / MA MCP + CT RCP Limits:		
	Aqueous/Leachates	80-120%R
	Solid	Vendor supplied limits

10.2.10 Lab Fortified Blank (LFB) Duplicates/ Laboratory Control Sample (LCS) Duplicates

Duplicates are analyzed for all MA Data Enhancement samples.

Limits:	Aqueous/Leachates	80 – 120%
	Solid: Vendor supplied limits.	

RPD Limits:	Aqueous	$\leq$ 20%
	Solids	$\leq$ 30%

10.2.11 Continuing Calibration Verification (CCV)

Analyzed after every 10 samples, and at the conclusion of analysis, with a range of 90-110%R for 245.1 and 80%-120%R for solids, leachates, MCP DE, and RCP. The CCV known value is to be in the center of the calibration curve.

10.2.11 Linear Dynamic Range Analysis (LDR)

Determined sample concentrations that exceed 90% of the LDR should be diluted and reanalyzed. The generated limits are posted at the instrument for reference.

A linear dynamic range study is analyzed annually. It is determined by analyzing three concentrations of the analyte until the observed recovery is no more than 10% below the stated concentration of the standard.

QUALITY CONTROL MEASURES

Quality Control Type	Concentration	Limits/range	Frequency	Corrective Actions
Initial Calibration Blank (ICB)	0	<RL	Just after ICV	Auto-zero, recalibrate, and rerun
Continuing Calibration Blank (CCB)	0	<RL	10% and at end after CCV	Auto-zero, rerun from last passing CCB
Method Blank (MB)	0	<RL	Prepped at 5%	Narrate
Initial Calibration Verification (ICV)/ Instrument Performance Check (IPC)	2.00 ppb	+/- 5% +/- 10% for 245.1	After calibration	Recalibrate and rerun
Matrix Duplicates (DUPS) aqueous	N/A	+/- 20%	10%	Re-Prep and Rerun
solids	N/A	+/- 35%	10%	Re-prep and rerun
Matrix Spikes (MS) aqueous	2.00 ppb	70-130% for 245.1	5%	Dilution/PDS/Re-prep and rerun
aqueous solids	2.00 ppb	75-125 % 75 – 125%	10%	
Matrix Spike Dups (MSDs) solids	2.00 ppb	+/- 35%	If no dups	Re-prep and rerun
Aqueous	2.00 ppb	+/- 20%	If no dups	Re-prep and rerun
Lab-Fortified Blank/Lab-Control Sample (LFB/LCS)		Method 245.1 85-115% Methods 7471/7470 and MCP DE + CT RCP Aqueous/ Leachates 80-120% Solids – Vendor Control limits.	10%	Re-prep and rerun
Continuing Cal. Verification (CCV)	2.00 ppb	Method 245.1 90 – 110% Methods 7471/7470 MCP DE , and RCP 80-120%	10% and at end	Recal., rerun from last passing CCV

11.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all federal, state, and local regulations governing the waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

12.0 CORRECTIVE ACTIONS / CONTINGENCIES OF HANDLING OUT OF CONTROL DATA

12.1 Refer to Con-Test Quality Assurance Manual, section 3.3.3
12.2 Refer to Con-Test Corrective Action SOP.

13.0 POLLUTION PREVENTION

13.1 The smallest volume of standard is made up to avoid unnecessary waste.

13.2 Acidic samples and waste are dumped in an appropriate satellite waste container.

13.3 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option.

14.0 REFERENCES

14.1 APHA - "Standard Methods for the Examination of Water and Wastewater", 18/19th edition, 1992/1995, Method 3500 Hg B.

14.2 US EPA - "Methods for the Determination of Metals in Environmental Samples" EPA 600/4-91/010, Revision 3.0 May 1994. Method 245.1, SW846 7470 and 7471

14.3 USEPA - "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW846, 3rd edition, November 1986, Methods 7470 & 7471.

14.4 MA DEP, "Quality Assurance and Quality Control Requirements and Performance Standards for SW846 Methods 7470A and 7471A, Mercury in Liquid, Solid, or Semi-Solid Waste", Revision 4, May 1, 2003.

14.5 Con-Test Analytical Quality Assurance Manual

14.6 Con-Test Analytical Hygiene Plan

14.7 FIMS Flow Injection Mercury Setting Up and Performing Analyses Manual, 07/2003

14.8 FIMS Flow Injection Mercury System Hardware Guide, 01/2002

14.9 WinLab32 for AA, Version 6.5.0.0266, Copyright 2007 Perkin Elmer

14.8 Con-Test Analytical Corrective Action SOP.

14.9 Con-Test Analytical Procedure for Maintaining Controlled Documents SOP.

14.10 CT DEP “Recommended Reasonable Confidence Protocols and Quality Assurance and Quality Control Requirements for Determination of Mercury by SW-846 Methods 7470/7471 Cold Vapor Atomic Absorption Spectroscopy”, Version 1.0, July 2005.

14.11 US EPA - "Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)” Method 7471B, Rev 2, February 2007.

APPENDIX C:

RISK-BASED AIR CONCENTRATION CALCULATIONS

RISK-BASED COMPARISON CRITERIA FOR PCBS

In 2005, two PCB risk-based air concentrations (RBACs) were developed for the KMS, assuming occupational exposures to adult school employees within the school (BETA, 2006). The first RBAC is the Action Level (AL; 0.05 ug/m^3). The AL is set at the lesser of a target cancer risk of 1×10^{-6} or a hazard index of 0.2 and is used as an initial indicator that PCB air concentrations above background levels have been detected. The second RBAC is the Acceptable Long-Term Average Exposure Concentration (ALTAEC; 0.3 ug/m^3). The ALTAEC is set at the lesser of a target cancer risk of 1×10^{-5} or a hazard index of 1 and is indicative of the maximum acceptable air concentration that should not be exceeded for an extended time period. The RBACs were developed considering carcinogenic and non-carcinogenic endpoints using the following general equations and assumptions:

$$RBAC_{cancer} = \frac{\text{Target Risk} \times AP}{EF \times ED \times EP \times CF \times UR}$$

$$RBAC_{non\text{-}cancer} = \frac{\text{Target HI} \times AP \times RfC}{EF \times ED \times EP \times CF}$$

Where:

RBCA	=	Risk-Based Air Concentration (mg/m^3)
Target Risk	=	Target Risk Level (1×10^{-5} for ALTAEC; 1×10^{-6} for AL)
Target HI	=	Target Hazard Index (1 for ALTAEC; 0.2 for AL)
AP	=	Averaging Period (70 years for cancer; 25 years for noncancer)
EF	=	Exposure Frequency (250 days/year)
ED	=	Exposure Duration (8 hours/day)
EP	=	Exposure Period (25 years)
CF	=	Conversion Factor (1.14×10^{-4} year/hour)
UR	=	Unit Risk (0.1 $(mg/m^3)^{-1}$)
RfC	=	Reference Concentration (7E-05 mg/m^3)

Both RBACs are based on noncarcinogenic effects as the most sensitive endpoint. The risk basis for the AL is a noncarcinogenic hazard index of approximately 0.2 while the risk basis for the ALTAEC is a noncarcinogenic hazard index of 1. Although the ALTAEC is indicative of the maximum acceptable air concentration that should not be exceeded for an extended time period, the ALTAEC could be exceeded over the short-term and still result in acceptable risk levels.

Both RBACs were developed to be applied to a total PCB air concentration. PCB homologues have been quantified and summed to generate total PCB air concentrations at the KMS.

In September 2009, EPA published Public Health Levels (PHLs) for PCBs which are calculated indoor air concentrations that maintain PCB exposures below a level that EPA believes does not cause harm (USEPA, 2009). PHLs were calculated for all ages of children from toddlers in day

care to adolescents in high school as well as for adult school employees. For the KMS, indoor air PCB concentrations are compared to the PHL (0.453 ug/m^3) for adult school employees. The PHL for adult employees is slightly less than the PHL developed for children 12 to <15 years old, representative of the middle school age range (0.468 ug/m^3). Using the lower of the applicable PHLs for the KMS results in a health-protective evaluation. In calculating the PHL, EPA considered average PCB exposures from both school (e.g., school indoor and outdoor air, indoor dust and nearby outside soils) and non-school (e.g., diet, outside soils, indoor dust, and indoor and outdoor air) environments. EPA assumed that middle school children spend 6.5-hours per day at school (with 6 hours spent inside the school) for a 180-day school year. For the adult school employee, EPA assumed an 8-hour school day (8 hours spent inside the school) and a 185-day school year.

References

BETA Group, Inc. (BETA). 2006. Final Completion and Inspection Report: Long-Term Monitoring and Maintenance Plan. McCoy Field/Keith Middle School, 225 Hathaway Boulevard, New Bedford, Massachusetts. Prepared for the City of New Bedford. October 4, 2006.

United States Environmental Protection Agency (USEPA). 2009. Public Health Levels for PCBs in Indoor School Air. http://www.epa.gov/pcbsincaulk/ September 2009.

APPENDIX D:

EPA REGION I LOW STRESS (LOW FLOW) PURGING AND SAMPLING PROCEDURE FOR THE COLLECTION OF GROUNDWATER SAMPLES FROM MONITORING WELLS

U.S. ENVIRONMENTAL PROTECTION AGENCY REGION I

LOW STRESS (low flow) PURGING AND SAMPLING PROCEDURE FOR THE COLLECTION OF GROUNDWATER SAMPLES FROM MONITORING WELLS

Quality Assurance Unit
U.S. Environmental Protection Agency – Region 1
11 Technology Drive
North Chelmsford, MA 01863

The controlled version of this document is the electronic version viewed on-line only. If this is a printed copy of the document, it is an uncontrolled version and may or may not be the version currently in use.

This document contains direction developed solely to provide guidance to U.S. Environmental Protection Agency (EPA) personnel. EPA retains the discretion to adopt approaches that differ from these procedures on a case-by-case basis. The procedures set forth do not create any rights, substantive or procedural, enforceable at law by party to litigation with EPA or the United States.

Prepared by: Charles Porfert 1/19/10
(Charles Porfert, Quality Assurance Unit) Date

Approved by: Gerard Sotolongo 1-19-10
(Gerard Sotolongo, Quality Assurance Unit) Date

Revision Page

Date	Rev #	Summary of changes	Sections
7/30/96	2	Finalized	
01/19/10	3	Updated	All sections

TABLE OF CONTENTS

	Page
USE OF TERMS	4
SCOPE & APPLICATION	5
BACKGROUND FOR IMPLEMENTATION	6
HEALTH & SAFETY	7
CAUTIONS	7
PERSONNEL QUALIFICATIONS	9
EQUIPMENT AND SUPPLIES	9
EQUIPMENT/INSTRUMENT CALIBRATION	13
PRELIMINARY SITE ACTIVITIES	13
PURGING AND SAMPLING PROCEDURE	14
DECONTAMINATION	19
FIELD QUALITY CONTROL	21
FIELD LOGBOOK	21
DATA REPORT	22
REFERENCES	22
APPENDIX A PERISTALTIC PUMPS	24
APPENDIX B SUMMARY OF SAMPLING INSTRUCTIONS	25
LOW-FLOW SETUP DIAGRAM	29
APPENDIX C EXAMPLE WELL PURGING FORM	30

USE OF TERMS

Equipment blank: The equipment blank shall include the pump and the pump's tubing. If tubing is dedicated to the well, the equipment blank needs only to include the pump in subsequent sampling rounds. If the pump and tubing are dedicated to the well, the equipment blank is collected prior to its placement in the well. If the pump and tubing will be used to sample multiple wells, the equipment blank is normally collected after sampling from contaminated wells and not after background wells.

Field duplicates: Field duplicates are collected to determine precision of the sampling procedure. For this procedure, collect duplicate for each analyte group in consecutive order (VOC original, VOC duplicate, SVOC original, SVOC duplicate, etc.).

Indicator field parameters: This SOP uses field measurements of turbidity, dissolved oxygen, specific conductance, temperature, pH, and oxidation/reduction potential (ORP) as indicators of when purging operations are sufficient and sample collection may begin.

Matrix Spike/Matrix Spike Duplicates: Used by the laboratory in its quality assurance program. Consult the laboratory for the sample volume to be collected.

Poteniometric Surface: The level to which water rises in a tightly cased well constructed in a confined aquifer. In an unconfined aquifer, the potentiometric surface is the water table.

QAPP: Quality Assurance Project Plan

SAP: Sampling and Analysis Plan

SOP: Standard operating procedure

Stabilization: A condition that is achieved when all indicator field parameter measurements are sufficiently stable (as described in the "Monitoring Indicator Field Parameters" section) to allow sample collection to begin.

Temperature blank: A temperature blank is added to each sample cooler. The blank is measured upon receipt at the laboratory to assess whether the samples were properly cooled during transit.

Trip blank (VOCs): Trip blank is a sample of analyte-free water taken to the sampling site and returned to the laboratory. The trip blanks (one pair) are added to each sample cooler that contains VOC samples.

SCOPE & APPLICATION

The goal of this groundwater sampling procedure is to collect water samples that reflect the total mobile organic and inorganic loads (dissolved and colloidal sized fractions) transported through the subsurface under ambient flow conditions, with minimal physical and chemical alterations from sampling operations. This standard operating procedure (SOP) for collecting groundwater samples will help ensure that the project's data quality objectives (DQOs) are met under certain low-flow conditions.

The SOP emphasizes the need to minimize hydraulic stress at the well-aquifer interface by maintaining low water-level drawdowns, and by using low pumping rates during purging and sampling operations. Indicator field parameters (e.g., dissolved oxygen, pH, etc.) are monitored during purging in order to determine when sample collection may begin. Samples properly collected using this SOP are suitable for analysis of groundwater contaminants (volatile and semi-volatile organic analytes, dissolved gases, pesticides, PCBs, metals and other inorganics), or naturally occurring analytes. This SOP is based on Puls, and Barcelona (1996).

This procedure is designed for monitoring wells with an inside diameter (1.5-inches or greater) that can accommodate a positive lift pump with a screen length or open interval ten feet or less and with a water level above the top of the screen or open interval (Hereafter, the "screen or open interval" will be referred to only as "screen interval"). This SOP is not applicable to other well-sampling conditions.

While the use of dedicated sampling equipment is not mandatory, dedicated pumps and tubing can reduce sampling costs significantly by streamlining sampling activities and thereby reducing the overall field costs.

The goal of this procedure is to emphasize the need for consistency in deploying and operating equipment while purging and sampling monitoring wells during each sampling event. This will help to minimize sampling variability.

This procedure describes a general framework for groundwater sampling. Other site specific information (hydrogeological context, conceptual site model (CSM), DQOs, etc.) coupled with systematic planning must be added to the procedure in order to develop an appropriate site specific SAP/QAPP. In addition, the site specific SAP/QAPP must identify the specific equipment that will be used to collect the groundwater samples.

This procedure does not address the collection of water or free product samples from wells containing free phase LNAPLs and/or DNAPLs (light or dense non-aqueous phase

liquids). For this type of situation, the reader may wish to check: Cohen, and Mercer (1993) or other pertinent documents.

This SOP is to be used when collecting groundwater samples from monitoring wells at all Superfund, Federal Facility and RCRA sites in Region 1 under the conditions described herein. Request for modification of this SOP, in order to better address specific situations at individual wells, must include adequate technical justification for proposed changes. All changes and modifications must be approved and included in a revised SAP/QAPP before implementation in field.

BACKGROUND FOR IMPLEMENTATION

It is expected that the monitoring well screen has been properly located (both laterally and vertically) to intercept existing contaminant plume(s) or along flow paths of potential contaminant migration. Problems with inappropriate monitoring well placement or faulty/improper well installation cannot be overcome by even the best water sampling procedures. This SOP presumes that the analytes of interest are moving (or will potentially move) primarily through the more permeable zones intercepted by the screen interval.

Proper well construction, development, and operation and maintenance cannot be overemphasized. The use of installation techniques that are appropriate to the hydrogeologic setting of the site often prevent "problem well" situations from occurring. During well development, or redevelopment, tests should be conducted to determine the hydraulic characteristics of the monitoring well. The data can then be used to set the purging/sampling rate, and provide a baseline for evaluating changes in well performance and the potential need for well rehabilitation. Note: if this installation data or well history (construction and sampling) is not available or discoverable, for all wells to be sampled, efforts to build a sampling history should commence with the next sampling event.

The pump intake should be located within the screen interval and at a depth that will remain under water at all times. It is recommended that the intake depth and pumping rate remain the same for all sampling events. The mid-point or the lowest historical midpoint of the saturated screen length is often used as the location of the pump intake. For new wells, or for wells without pump intake depth information, the site's SAP/QAPP must provide clear reasons and instructions on how the pump intake depth(s) will be selected, and reason(s) for the depth(s) selected. If the depths to top and bottom of the well screen are not known, the SAP/QAPP will need to describe how the sampling depth will be determined and how the data can be used.

Stabilization of indicator field parameters is used to indicate that conditions are suitable for sampling to begin. Achievement of turbidity levels of less than 5 NTU, and stable drawdowns of less than 0.3 feet, while desirable, are not mandatory. Sample collection

may still take place provided the indicator field parameter criteria in this procedure are met. If after 2 hours of purging indicator field parameters have not stabilized, one of three optional courses of action may be taken: a) continue purging until stabilization is achieved, b) discontinue purging, do not collect any samples, and record in log book that stabilization could not be achieved (documentation must describe attempts to achieve stabilization), c) discontinue purging, collect samples and provide full explanation of attempts to achieve stabilization (note: there is a risk that the analytical data obtained, especially metals and strongly hydrophobic organic analytes, may reflect a sampling bias and therefore, the data may not meet the data quality objectives of the sampling event).

It is recommended that low-flow sampling be conducted when the air temperature is above 32°F (0°C). If the procedure is used below 32°F, special precautions will need to be taken to prevent the groundwater from freezing in the equipment. Because sampling during freezing temperatures may adversely impact the data quality objectives, the need for water sample collection during months when these conditions are likely to occur should be evaluated during site planning and special sampling measures may need to be developed. Ice formation in the flow-through-cell will cause the monitoring probes to act erratically. A transparent flow-through-cell needs to be used to observe if ice is forming in the cell. If ice starts to form on the other pieces of the sampling equipment, additional problems may occur.

HEALTH & SAFETY

When working on-site, comply with all applicable OSHA requirements and the site's health/safety procedures. All proper personal protection clothing and equipment are to be worn. Some samples may contain biological and chemical hazards. These samples should be handled with suitable protection to skin, eyes, etc.

CAUTIONS

The following cautions need to be considered when planning to collect groundwater samples when the below conditions occur.

If the groundwater degasses during purging of the monitoring well, dissolved gases and VOCs will be lost. When this happens, the groundwater data for dissolved gases (e.g., methane, ethene, ethane, dissolved oxygen, etc.) and VOCs will need to be qualified. Some conditions that can promote degassing are the use of a vacuum pump (e.g., peristaltic pumps), changes in aperture along the sampling tubing, and squeezing/pinching the pump's tubing which results in a pressure change.

When collecting the samples for dissolved gases and VOCs analyses, avoid aerating the groundwater in the pump's tubing. This can cause loss of the dissolved gases and VOCs in

the groundwater. Having the pump's tubing completely filled prior to sampling will avoid this problem when using a centrifugal pump or peristaltic pump.

Direct sun light and hot ambient air temperatures may cause the groundwater in the tubing and flow-through-cell to heat up. This may cause the groundwater to degas which will result in loss of VOCs and dissolved gases. When sampling under these conditions, the sampler will need to shade the equipment from the sunlight (e.g., umbrella, tent, etc.). If possible, sampling on hot days, or during the hottest time of the day, should be avoided. The tubing exiting the monitoring well should be kept as short as possible to avoid the sun light or ambient air from heating up the groundwater.

Thermal currents in the monitoring well may cause vertical mixing of water in the well bore. When the air temperature is colder than the groundwater temperature, it can cool the top of the water column. Colder water which is denser than warm water sinks to the bottom of the well and the warmer water at the bottom of the well rises, setting up a convention cell. "During low-flow sampling, the pumped water may be a mixture of convecting water from within the well casing and aquifer water moving inward through the screen. This mixing of water during low-flow sampling can substantially increase equilibration times, can cause false stabilization of indicator parameters, can give false indication of redox state, and can provide biological data that are not representative of the aquifer conditions" (Vroblesky 2007).

Failure to calibrate or perform proper maintenance on the sampling equipment and measurement instruments (e.g., dissolved oxygen meter, etc.) can result in faulty data being collected.

Interferences may result from using contaminated equipment, cleaning materials, sample containers, or uncontrolled ambient/surrounding air conditions (e.g., truck/vehicle exhaust nearby).

Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment and/or proper planning to avoid ambient air interferences. Note that the use of dedicated sampling equipment can also significantly reduce the time needed to complete each sampling event, will promote consistency in the sampling, and may reduce sampling bias by having the pump's intake at a constant depth.

Clean and decontaminate all sampling equipment prior to use. All sampling equipment needs to be routinely checked to be free from contaminants and equipment blanks collected to ensure that the equipment is free of contaminants. Check the previous equipment blank data for the site (if they exist) to determine if the previous cleaning procedure removed the contaminants. If contaminants were detected and they are a concern, then a more vigorous cleaning procedure will be needed.

PERSONNEL QUALIFICATIONS

All field samplers working at sites containing hazardous waste must meet the requirements of the OSHA regulations. OSHA regulations may require the sampler to take the 40 hour OSHA health and safety training course and a refresher course prior to engaging in any field activities, depending upon the site and field conditions.

The field samplers must be trained prior to the use of the sampling equipment, field instruments, and procedures. Training is to be conducted by an experienced sampler before initiating any sampling procedure.

The entire sampling team needs to read, and be familiar with, the site Health and Safety Plan, all relevant SOPs, and SAP/QAPP (and the most recent amendments) before going onsite for the sampling event. It is recommended that the field sampling leader attest to the understanding of these site documents and that it is recorded.

EQUIPMENT AND SUPPLIES

A. Informational materials for sampling event

A copy of the current Health and Safety Plan, SAP/QAPP, monitoring well construction data, location map(s), field data from last sampling event, manuals for sampling, and the monitoring instruments' operation, maintenance, and calibration manuals should be brought to the site.

B. Well keys.

C. Extraction device

Adjustable rate, submersible pumps (e.g., centrifugal, bladder, etc.) which are constructed of stainless steel or Teflon are preferred. Note: if extraction devices constructed of other materials are to be used, adequate information must be provided to show that the substituted materials do not leach contaminants nor cause interferences to the analytical procedures to be used. Acceptance of these materials must be obtained before the sampling event.

If bladder pumps are selected for the collection of VOCs and dissolved gases, the pump setting should be set so that one pulse will deliver a water volume that is sufficient to fill a 40 mL VOC vial. This is not mandatory, but is considered a "best practice". For the proper operation, the bladder pump will need a minimum amount of water above the pump; consult the manufacturer for the recommended submergence. The pump's recommended submergence value should be determined during the planning stage, since it may influence well construction and placement of dedicated pumps where water-level fluctuations are significant.

Adjustable rate, peristaltic pumps (suction) are to be used with caution when collecting samples for VOCs and dissolved gases (e.g., methane, carbon dioxide, etc.) analyses. Additional information on the use of peristaltic pumps can be found in Appendix A. If peristaltic pumps are used, the inside diameter of the rotor head tubing needs to match the inside diameter of the tubing installed in the monitoring well.

Inertial pumping devices (motor driven or manual) are not recommended. These devices frequently cause greater disturbance during purging and sampling, and are less easily controlled than submersible pumps (potentially increasing turbidity and sampling variability, etc.). This can lead to sampling results that are adversely affected by purging and sampling operations, and a higher degree of data variability.

D. Tubing

Teflon or Teflon-lined polyethylene tubing are preferred when sampling is to include VOCs, SVOCs, pesticides, PCBs and inorganics. Note: if tubing constructed of other materials is to be used, adequate information must be provided to show that the substituted materials do not leach contaminants nor cause interferences to the analytical procedures to be used. Acceptance of these materials must be obtained before the sampling event.

PVC, polypropylene or polyethylene tubing may be used when collecting samples for metal and other inorganics analyses.

The use of 1/4 inch or 3/8 inch (inside diameter) tubing is recommended. This will help ensure that the tubing remains liquid filled when operating at very low pumping rates when using centrifugal and peristaltic pumps.

Silastic tubing should be used for the section around the rotor head of a peristaltic pump. It should be less than a foot in length. The inside diameter of the tubing used at the pump rotor head must be the same as the inside diameter of tubing placed in the well. A tubing connector is used to connect the pump rotor head tubing to the well tubing. Alternatively, the two pieces of tubing can be connected to each other by placing the one end of the tubing inside the end of the other tubing. The tubing must not be reused.

E. The water level measuring device

Electronic "tape", pressure transducer, water level sounder/level indicator, etc. should be capable of measuring to 0.01 foot accuracy. Recording pressure transducers, mounted above the pump, are especially helpful in tracking water levels during pumping operations, but their use must include check measurements with a water level "tape" at the start and end of each sampling event.

F. Flow measurement supplies

Graduated cylinder (size according to flow rate) and stopwatch usually will suffice.

Large graduated bucket used to record total water purged from the well.

G. Interface probe

To be used to check on the presence of free phase liquids (LNAPL, or DNAPL) before purging begins (as needed).

H. Power source (generator, nitrogen tank, battery, etc.)

When a gasoline generator is used, locate it downwind and at least 30 feet from the well so that the exhaust fumes do not contaminate samples.

I. Indicator field parameter monitoring instruments

Use of a multi-parameter instrument capable of measuring pH, oxidation/reduction potential (ORP), dissolved oxygen (DO), specific conductance, temperature, and coupled with a flow-through-cell is required when measuring all indicator field parameters, except turbidity. Turbidity is collected using a separate instrument. Record equipment/instrument identification (manufacturer, and model number).

Transparent, small volume flow-through-cells (e.g., 250 mLs or less) are preferred. This allows observation of air bubbles and sediment buildup in the cell, which can interfere with the operation of the monitoring instrument probes, to be easily detected. A small volume cell facilitates rapid turnover of water in the cell between measurements of the indicator field parameters.

It is recommended to use a flow-through-cell and monitoring probes from the same manufacturer and model to avoid incompatibility between the probes and flow-through-cell.

Turbidity samples are collected before the flow-through-cell. A "T" connector coupled with a valve is connected between the pump's tubing and flow-through-cell. When a turbidity measurement is required, the valve is opened to allow the groundwater to flow into a container. The valve is closed and the container sample is then placed in the turbidimeter.

Standards are necessary to perform field calibration of instruments. A minimum of two standards are needed to bracket the instrument measurement range for all parameters except ORP which use a Zobell solution as a standard. For dissolved oxygen, a wet sponge used for the 100% saturation and a zero dissolved oxygen solution are used for the calibration.

Barometer (used in the calibration of the Dissolved Oxygen probe) and the conversion formula to convert the barometric pressure into the units of measure used by the Dissolved Oxygen meter are needed.

J. Decontamination supplies

Includes (for example) non-phosphate detergent, distilled/deionized water, isopropyl alcohol, etc.

K. Record keeping supplies

Logbook(s), well purging forms, chain-of-custody forms, field instrument calibration forms, etc.

L. Sample bottles

M. Sample preservation supplies (as required by the analytical methods)

N. Sample tags or labels

O. PID or FID instrument

If appropriate, to detect VOCs for health and safety purposes, and provide qualitative field evaluations.

P. Miscellaneous Equipment

Equipment to keep the sampling apparatus shaded in the summer (e.g., umbrella) and from freezing in the winter. If the pump's tubing is allowed to heat up in the warm weather, the cold groundwater may degas as it is warmed in the tubing.

EQUIPMENT/INSTRUMENT CALIBRATION

Prior to the sampling event, perform maintenance checks on the equipment and instruments according to the manufacturer's manual and/or applicable SOP. This will ensure that the equipment/instruments are working properly before they are used in the field.

Prior to sampling, the monitoring instruments must be calibrated and the calibration documented. The instruments are calibrated using U.S Environmental Protection Agency Region 1 *Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction [ORP], and turbidity),* January 19, 2010, or latest version or from one of the methods listed in 40CFR136, 40CFR141 and SW-846.

The instruments shall be calibrated at the beginning of each day. If the field measurement falls outside the calibration range, the instrument must be re-calibrated so that all measurements fall within the calibration range. At the end of each day, a calibration check is performed to verify that instruments remained in calibration throughout the day. This check is performed while the instrument is in measurement mode, not calibration mode. If the field instruments are being used to monitor the natural attenuation parameters, then a calibration check at mid-day is highly recommended to ensure that the instruments did not drift out of calibration. Note: during the day if the instrument reads zero or a negative number for dissolved oxygen, pH, specific conductance, or turbidity (negative value only), this indicates that the instrument drifted out of calibration or the instrument is malfunctioning. If this situation occurs the data from this instrument will need to be qualified or rejected.

PRELIMINARY SITE ACTIVITIES (as applicable)

Check the well for security (damage, evidence of tampering, missing lock, etc.) and record pertinent observations (include photograph as warranted).

If needed lay out sheet of clean polyethylene for monitoring and sampling equipment, unless equipment is elevated above the ground (e.g., on a table, etc.).

Remove well cap and if appropriate measure VOCs at the rim of the well with a PID or FID instrument and record reading in field logbook or on the well purge form.

If the well casing does not have an established reference point (usually a V-cut or indelible mark in the well casing), make one. Describe its location and record the date of the mark in the logbook (consider a photographic record as well). All water level measurements must be recorded relative to this reference point (and the altitude of this point should be determined using techniques that are appropriate to site's DQOs.

If water-table or potentiometric surface map(s) are to be constructed for the sampling event, perform synoptic water level measurement round (in the shortest possible time) before any purging and sampling activities begin. If possible, measure water level depth (to 0.01 ft.) and total well depth (to 0.1 ft.) the day before sampling begins, in order to allow for re-settlement of any particulates in the water column. This is especially important for those wells that have not been recently sampled because sediment buildup in the well may require the well to be redeveloped. If measurement of total well depth is not made the day before, it should be measured after sampling of the well is complete. All measurements must be taken from the established referenced point. Care should be taken to minimize water column disturbance.

Check newly constructed wells for the presence of LNAPLs or DNAPLs before the initial sampling round. If none are encountered, subsequent check measurements with an interface probe may not be necessary unless analytical data or field analysis signal a worsening situation. This SOP cannot be used in the presence of LNAPLs or DNAPLs. If NAPLs are present, the project team must decide upon an alternate sampling method. All project modifications must be approved and documented prior to implementation.

If available check intake depth and drawdown information from previous sampling event(s) for each well. Duplicate, to the extent practicable, the intake depth and extraction rate (use final pump dial setting information) from previous event(s). If changes are made in the intake depth or extraction rate(s) used during previous sampling event(s), for either portable or dedicated extraction devices, record new values, and explain reasons for the changes in the field logbook.

PURGING AND SAMPLING PROCEDURE

Purging and sampling wells in order of increasing chemical concentrations (known or anticipated) are preferred.

The use of dedicated pumps is recommended to minimize artificial mobilization and entrainment of particulates each time the well is sampled. Note that the use of dedicated sampling equipment can also significantly reduce the time needed to complete each

sampling event, will promote consistency in the sampling, and may reduce sampling bias by having the pump's intake at a constant depth.

A. Initial Water Level

Measure the water level in the well before installing the pump if a non-dedicated pump is being used. The initial water level is recorded on the purge form or in the field logbook.

B. Install Pump

Lower pump, safety cable, tubing and electrical lines slowly (to minimize disturbance) into the well to the appropriate depth (may not be the mid-point of the screen/open interval). The Sampling and Analysis Plan/Quality Assurance Project Plan should specify the sampling depth (used previously), or provide criteria for selection of intake depth for each new well. If possible keep the pump intake at least two feet above the bottom of the well, to minimize mobilization of particulates present in the bottom of the well.

Pump tubing lengths, above the top of well casing should be kept as short as possible to minimize heating the groundwater in the tubing by exposure to sun light and ambient air temperatures. Heating may cause the groundwater to degas, which is unacceptable for the collection of samples for VOC and dissolved gases analyses.

C. Measure Water Level

Before starting pump, measure water level. Install recording pressure transducer, if used to track drawdowns, to initialize starting condition.

D. Purge Well

From the time the pump starts purging and until the time the samples are collected, the purged water is discharged into a graduated bucket to determine the total volume of groundwater purged. This information is recorded on the purge form or in the field logbook.

Start the pump at low speed and slowly increase the speed until discharge occurs. Check water level. Check equipment for water leaks and if present fix or replace the affected equipment. Try to match pumping rate used during previous sampling event(s). Otherwise, adjust pump speed until there is little or no water level drawdown. If the minimal drawdown that can be achieved exceeds 0.3 feet, but remains stable, continue purging.

Monitor and record the water level and pumping rate every five minutes (or as appropriate) during purging. Record any pumping rate adjustments (both time and flow rate). Pumping rates should, as needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. Adjustments are best made in the first fifteen minutes of pumping in order to help minimize purging time. During pump start-up, drawdown may exceed the 0.3 feet target and then "recover" somewhat as pump flow adjustments are made. Purge volume calculations should utilize stabilized drawdown value, not the initial drawdown. If the initial water level is above the top of the screen do not allow the water level to fall into the well screen. The final purge volume must be greater than the stabilized drawdown volume plus the pump's tubing volume. If the drawdown has exceeded 0.3 feet and stabilizes, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump's tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are collected.

Avoid the use of constriction devices on the tubing to decrease the flow rate because the constrictor will cause a pressure difference in the water column. This will cause the groundwater to degas and result in a loss of VOCs and dissolved gasses in the groundwater samples.

Note: the flow rate used to achieve a stable pumping level should remain constant while monitoring the indicator parameters for stabilization and while collecting the samples.

Wells with low recharge rates may require the use of special pumps capable of attaining very low pumping rates (e.g., bladder, peristaltic), and/or the use of dedicated equipment. For new monitoring wells, or wells where the following situation has not occurred before, if the recovery rate to the well is less than 50 mL/min., or the well is being essentially dewatered during purging, the well should be sampled as soon as the water level has recovered sufficiently to collect the volume needed for all anticipated samples. The project manager or field team leader will need to make the decision when samples should be collected, how the sample is to be collected, and the reasons recorded on the purge form or in the field logbook. A water level measurement needs to be performed and recorded before samples are collected. If the project manager decides to collect the samples using the pump, it is best during this recovery period that the pump intake tubing not be removed, since this will aggravate any turbidity problems. Samples in this specific situation may be collected without stabilization of indicator field parameters. Note that field conditions and efforts to overcome problematic situations must be recorded in order to support field decisions to deviate from normal procedures described in this SOP. If this type of problematic situation persists in a well, then water sample collection should be changed to a passive or no-purge method, if consistent with the site's DQOs, or have a new well installed.

E. Monitor Indicator Field Parameters

After the water level has stabilized, connect the "T" connector with a valve and the flow-through-cell to monitor the indicator field parameters. If excessive turbidity is anticipated or encountered with the pump startup, the well may be purged for a while without connecting up the flow-through-cell, in order to minimize particulate buildup in the cell (This is a judgment call made by the sampler). Water level drawdown measurements should be made as usual. If possible, the pump may be installed the day before purging to allow particulates that were disturbed during pump insertion to settle.

During well purging, monitor indicator field parameters (turbidity, temperature, specific conductance, pH, ORP, DO) at a frequency of five minute intervals or greater. The pump's flow rate must be able to "turn over" at least one flow-through-cell volume between measurements (for a 250 mL flow-through-cell with a flow rate of 50 mLs/min., the monitoring frequency would be every five minutes; for a 500 mL flow-through-cell it would be every ten minutes). If the cell volume cannot be replaced in the five minute interval, then the time between measurements must be increased accordingly. Note: during the early phase of purging emphasis should be put on minimizing and stabilizing pumping stress, and recording those adjustments followed by stabilization of indicator parameters. Purging is considered complete and sampling may begin when all the above indicator field parameters have stabilized. Stabilization is considered to be achieved when three consecutive readings are within the following limits:

Turbidity (10% for values greater than 5 NTU; if three Turbidity values are less than 5 NTU, consider the values as stabilized),
Dissolved Oxygen (10% for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized),
Specific Conductance (3%),
Temperature (3%),
pH (± 0.1 unit),
Oxidation/Reduction Potential (±10 millivolts).

All measurements, except turbidity, must be obtained using a flow-through-cell. Samples for turbidity measurements are obtained before water enters the flow-through-cell. Transparent flow-through-cells are preferred, because they allow field personnel to watch for particulate build-up within the cell. This build-up may affect indicator field parameter values measured within the cell. If the cell needs to be cleaned during purging operations, continue pumping and disconnect cell for cleaning, then reconnect after cleaning and continue monitoring activities. Record start and stop times and give a brief description of cleaning activities.

The flow-through-cell must be designed in a way that prevents gas bubble entrapment in the cell. Placing the flow-through-cell at a 45 degree angle with the port facing upward can help remove bubbles from the flow-through-cell (see Appendix B Low-Flow Setup Diagram). All during the measurement process, the flow-through-cell must remain free of any gas bubbles. Otherwise, the monitoring probes may act erratically. When the pump is turned off or cycling on/off (when using a bladder pump), water in the cell must not drain out. Monitoring probes must remain submerged in water at all times.

F. Collect Water Samples

When samples are collected for laboratory analyses, the pump's tubing is disconnected from the "T" connector with a valve and the flow-through-cell. The samples are collected directly from the pump's tubing. Samples must not be collected from the flow-through-cell or from the "T" connector with a valve.

VOC samples are normally collected first and directly into pre-preserved sample containers. However, this may not be the case for all sampling locations; the SAP/QAPP should list the order in which the samples are to be collected based on the project's objective(s). Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

If the pump's flow rate is too high to collect the VOC/dissolved gases samples, collect the other samples first. Lower the pump's flow rate to a reasonable rate and collect the VOC/dissolved gases samples and record the new flow rate.

During purging and sampling, the centrifugal/peristaltic pump tubing must remain filled with water to avoid aeration of the groundwater. It is recommended that 1/4 inch or 3/8 inch (inside diameter) tubing be used to help insure that the sample tubing remains water filled. If the pump tubing is not completely filled to the sampling point, use the following procedure to collect samples: collect non-VOC/dissolved gases samples first, then increase flow rate slightly until the water completely fills the tubing, collect the VOC/dissolved gases samples, and record new drawdown depth and flow rate.

For bladder pumps that will be used to collect VOC or dissolved gas samples, it is recommended that the pump be set to deliver long pulses of water so that one pulse will fill a 40 mL VOC vial.

Use pre-preserved sample containers or add preservative, as required by analytical methods, to the samples immediately after they are collected. Check the analytical methods (e.g. EPA SW-846, 40 CFR 136, water supply, etc.) for additional information on preservation.

If determination of filtered metal concentrations is a sampling objective, collect filtered water samples using the same low flow procedures. The use of an in-line filter (transparent housing preferred) is required, and the filter size (0.45 μm is commonly used) should be based on the sampling objective. Pre-rinse the filter with groundwater prior to sample collection. Make sure the filter is free of air bubbles before samples are collected. Preserve the filtered water sample immediately. Note: filtered water samples are not an acceptable substitute for unfiltered samples when the monitoring objective is to obtain chemical concentrations of total mobile contaminants in groundwater for human health or ecological risk calculations.

Label each sample as collected. Samples requiring cooling will be placed into a cooler with ice or refrigerant for delivery to the laboratory. Metal samples after acidification to a pH less than 2 do not need to be cooled.

G. Post Sampling Activities

If a recording pressure transducer is used to track drawdown, re-measure water level with tape.

After collection of samples, the pump tubing may be dedicated to the well for re-sampling (by hanging the tubing inside the well), decontaminated, or properly discarded.

Before securing the well, measure and record the well depth (to 0.1 ft.), if not measured the day before purging began. Note: measurement of total well depth annually is usually sufficient after the initial low stress sampling event. However, a greater frequency may be needed if the well has a "silting" problem or if confirmation of well identity is needed.

Secure the well.

DECONTAMINATION

Decontaminate sampling equipment prior to use in the first well and then following sampling of each well. Pumps should not be removed between purging and sampling operations. The pump, tubing, support cable and electrical wires which were in contact with the well should be decontaminated by one of the procedures listed below.

The use of dedicated pumps and tubing will reduce the amount of time spent on decontamination of the equipment. If dedicated pumps and tubing are used, only the initial sampling event will require decontamination of the pump and tubing.

Note if the previous equipment blank data showed that contaminant(s) were present after using the below procedure or the one described in the SAP/QAPP, a more vigorous procedure may be needed.

Procedure 1

Decontaminating solutions can be pumped from either buckets or short PVC casing sections through the pump and tubing. The pump may be disassembled and flushed with the decontaminating solutions. It is recommended that detergent and alcohol be used sparingly in the decontamination process and water flushing steps be extended to ensure that any sediment trapped in the pump is removed. The pump exterior and electrical wires must be rinsed with the decontaminating solutions, as well. The procedure is as follows:

Flush the equipment/pump with potable water.

Flush with non-phosphate detergent solution. If the solution is recycled, the solution must be changed periodically.

Flush with potable or distilled/deionized water to remove all of the detergent solution. If the water is recycled, the water must be changed periodically.

Optional - flush with isopropyl alcohol (pesticide grade; must be free of ketones {e.g., acetone}) or with methanol. This step may be required if the well is highly contaminated or if the equipment blank data from the previous sampling event show that the level of contaminants is significant.

Flush with distilled/deionized water. This step must remove all traces of alcohol (if used) from the equipment. The final water rinse must not be recycled.

Procedure 2

Steam clean the outside of the submersible pump.

Pump hot potable water from the steam cleaner through the inside of the pump. This can be accomplished by placing the pump inside a three or four inch diameter PVC pipe with end cap. Hot water from the steam cleaner jet will be directed inside the PVC pipe and the pump exterior will be cleaned. The hot water from the steam cleaner will then be pumped from the PVC pipe through the pump and collected into another container. Note: additives or solutions should not be added to the steam cleaner.

Pump non-phosphate detergent solution through the inside of the pump. If the solution is recycled, the solution must be changed periodically.

Pump potable water through the inside of the pump to remove all of the detergent solution. If the solution is recycled, the solution must be changed periodically.

Pump distilled/deionized water through the pump. The final water rinse must not be recycled.

FIELD QUALITY CONTROL

Quality control samples are required to verify that the sample collection and handling process has not compromised the quality of the groundwater samples. All field quality control samples must be prepared the same as regular investigation samples with regard to sample volume, containers, and preservation. Quality control samples include field duplicates, equipment blanks, matrix spike/matrix spike duplicates, trip blanks (VOCs), and temperature blanks.

FIELD LOGBOOK

A field log shall be kept to document all groundwater field monitoring activities (see Appendix C, example table), and record the following for each well:

Site name, municipality, state.

Well identifier, latitude-longitude or state grid coordinates.

Measuring point description (e.g., north side of PVC pipe).

Well depth, and measurement technique.

Well screen length.

Pump depth.

Static water level depth, date, time and measurement technique.

Presence and thickness of immiscible liquid (NAPL) layers and detection method.

Pumping rate, drawdown, indicator parameters values, calculated or measured total volume pumped, and clock time of each set of measurements.

Type of tubing used and its length.

Type of pump used.

Clock time of start and end of purging and sampling activity.

Types of sample bottles used and sample identification numbers.

Preservatives used.

Parameters requested for analyses.

Field observations during sampling event.

Name of sample collector(s).

Weather conditions, including approximate ambient air temperature.

QA/QC data for field instruments.

Any problems encountered should be highlighted.

Description of all sampling/monitoring equipment used, including trade names, model number, instrument identification number, diameters, material composition, etc.

DATA REPORT

Data reports are to include laboratory analytical results, QA/QC information, field indicator parameters measured during purging, field instrument calibration information, and whatever other field logbook information is needed to allow for a full evaluation of data usability.

Note: the use of trade, product, or firm names in this sampling procedure is for descriptive purposes only and does not constitute endorsement by the U.S. EPA.

REFERENCES

Cohen, R.M. and J.W. Mercer, 1993, *DNAPL Site Evaluation*; C.K. Smoley (CRC Press), Boca Raton, Florida.

Robert W. Puls and Michael J. Barcelona, *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, April 1996 (EPA/540/S-95/504).

U.S. Environmental Protection Agency, 1992, *RCRA Ground-Water Monitoring: Draft Technical Guidance*; Washington, DC (EPA/530-R-93-001).

U.S. Environmental Protection Agency, 1987, *A Compendium of Superfund Field Operations Methods*; Washington, DC (EPA/540/P-87/001).

U.S Environmental Protection Agency, Region 1, *Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction [ORP], and turbidity),* January 19, 2010 or latest version.

U.S Environmental Protection Agency, EPA SW-846.

U.S Environmental Protection Agency, 40 CFR 136.

U.S Environmental Protection Agency, 40 CFR 141.

Vroblesky, Don A., Clifton C. Casey, and Mark A. Lowery, Summer 2007, Influence of Dissolved Oxygen Convection on Well Sampling, *Ground Water Monitoring & Remediation* 27, no. 3: 49-58.

APPENDIX A
PERISTALTIC PUMPS

Before selecting a peristaltic pump to collect groundwater samples for VOCs and/or dissolved gases (e.g., methane, carbon dioxide, etc.) consideration should be given to the following:

- The decision of whether or not to use a peristaltic pump is dependent on the intended use of the data.
- If the additional sampling error that may be introduced by this device is NOT of concern for the VOC/dissolved gases data's intended use, then this device may be acceptable.
- If minor differences in the groundwater concentrations could effect the decision, such as to continue or terminate groundwater cleanup or whether the cleanup goals have been reached, then this device should NOT be used for VOC/dissolved gases sampling. In these cases, centrifugal or bladder pumps are a better choice for more accurate results.

EPA and USGS have documented their concerns with the use of the peristaltic pumps to collect water sample in the below documents.

- "Suction Pumps are not recommended because they may cause degassing, pH modification, and loss of volatile compounds" *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001, December 1987.
- "The agency does not recommend the use of peristaltic pumps to sample ground water particularly for volatile organic analytes" *RCRA Ground-Water Monitoring Draft Technical Guidance*, EPA Office of Solid Waste, November 1992.
- "The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and volatiles loss", *Low-flow (Minimal drawdown) Ground-Water Sampling Procedures*, by Robert Puls & Michael Barcelona, April 1996, EPA/540/S-95/504.
- "Suction-lift pumps, such as peristaltic pumps, can operate at a very low pumping rate; however, using negative pressure to lift the sample can result in the loss of volatile analytes", USGS Book 9 Techniques of Water-Resources Investigation, Chapter A4. (Version 2.0, 9/2006).

APPENDIX B

SUMMARY OF SAMPLING INSTRUCTIONS

These instructions are for using an adjustable rate, submersible pump or a peristaltic pump with the pump's intake placed at the midpoint of a 10 foot or less well screen or an open interval. The water level in the monitoring well is above the top of the well screen or open interval, the ambient temperature is above 32°F, and the equipment is not dedicated. Field instruments are already calibrated. The equipment is setup according to the diagram at the end of these instructions.

1. Review well installation information. Record well depth, length of screen or open interval, and depth to top of the well screen. Determine the pump's intake depth (e.g., mid-point of screen/open interval).

2. On the day of sampling, check security of the well casing, perform any safety checks needed for the site, lay out a sheet of polyethylene around the well (if necessary), and setup the equipment. If necessary a canopy or an equivalent item can be setup to shade the pump's tubing and flow-through-cell from the sun light to prevent the sun light from heating the groundwater.

3. Check well casing for a reference mark. If missing, make a reference mark. Measure the water level (initial) to 0.01 ft. and record this information.

4. Install the pump's intake to the appropriate depth (e.g., midpoint) of the well screen or open interval. Do not turn-on the pump at this time.

5. Measure water level and record this information.

6. Turn-on the pump and discharge the groundwater into a graduated waste bucket. Slowly increase the flow rate until the water level starts to drop. Reduce the flow rate slightly so the water level stabilizes. Record the pump's settings. Calculate the flow rate using a graduated container and a stop watch. Record the flow rate. Do not let the water level drop below the top of the well screen.

If the groundwater is highly turbid or colored, continue to discharge the water into the bucket until the water clears (visual observation); this usually takes a few minutes. The turbid or colored water is usually from the well being disturbed during the pump installation. If the water does not clear, then you need to make a choice whether to continue purging the well (hoping that it will clear after a reasonable time) or continue to

the next step. Note, it is sometimes helpful to install the pump the day before the sampling event so that the disturbed materials in the well can settle out.

If the water level drops to the top of the well screen during the purging of the well, stop purging the well, and do the following:

> Wait for the well to recharge to a sufficient volume so samples can be collected. This may take awhile (pump maybe removed from well, if turbidity is not a problem). The project manager will need to make the decision when samples should be collected and the reasons recorded in the site's log book. A water level measurement needs to be performed and recorded before samples are collected. When samples are being collected, the water level must not drop below the top of the screen or open interval. Collect the samples from the pump's tubing. Always collect the VOCs and dissolved gases samples first. Normally, the samples requiring a small volume are collected before the large volume samples are collected just in case there is not sufficient water in the well to fill all the sample containers. All samples must be collected, preserved, and stored according to the analytical method. Remove the pump from the well and decontaminate the sampling equipment.

If the water level has dropped 0.3 feet or less from the initial water level (water level measure before the pump was installed); proceed to Step 7. If the water level has dropped more than 0.3 feet, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump's tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are be collected.

7. Attach the pump's tubing to the "T" connector with a valve (or a three-way stop cock). The pump's tubing from the well casing to the "T" connector must be as short as possible to prevent the groundwater in the tubing from heating up from the sun light or from the ambient air. Attach a short piece of tubing to the other end of the end of the "T" connector to serve as a sampling port for the turbidity samples. Attach the remaining end of the "T" connector to a short piece of tubing and connect the tubing to the flow-through-cell bottom port. To the top port, attach a small piece of tubing to direct the water into a calibrated waste bucket. Fill the cell with the groundwater and remove all gas bubbles from the cell. Position the flow-through-cell in such a way that if gas bubbles enter the cell they can easily exit the cell. If the ports are on the same side of the cell and the cell is cylindrical shape, the cell can be placed at a 45-degree angle with the ports facing upwards; this position should keep any gas bubbles entering the cell away from the monitoring probes and allow the gas bubbles to exit the cell easily (see Low-Flow Setup Diagram). Note,

make sure there are no gas bubbles caught in the probes' protective guard; you may need to shake the cell to remove these bubbles.

8. Turn-on the monitoring probes and turbidity meter.

9. Record the temperature, pH, dissolved oxygen, specific conductance, and oxidation/reduction potential measurements. Open the valve on the "T" connector to collect a sample for the turbidity measurement, close the valve, do the measurement, and record this measurement. Calculate the pump's flow rate from the water exiting the flow-through-cell using a graduated container and a stop watch, and record the measurement. Measure and record the water level. Check flow-through-cell for gas bubbles and sediment; if present, remove them.

10. Repeat Step 9 every 5 minutes or as appropriate until monitoring parameters stabilized. Note at least one flow-through-cell volume must be exchanged between readings. If not, the time interval between readings will need to be increased. Stabilization is achieved when three consecutive measurements are within the following limits:

Turbidity (10% for values greater than 5 NTUs; if three Turbidity values are less than 5 NTUs, consider the values as stabilized),
Dissolved Oxygen (10% for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized),
Specific Conductance (3%),
Temperature (3%),
pH (± 0.1 unit),
Oxidation/Reduction Potential (±10 millivolts).

If these stabilization requirements do not stabilize in a reasonable time, the probes may have been coated from the materials in the groundwater, from a buildup of sediment in the flow-through-cell, or a gas bubble is lodged in the probe. The cell and the probes will need to be cleaned. Turn-off the probes (not the pump), disconnect the cell from the "T" connector and continue to purge the well. Disassemble the cell, remove the sediment, and clean the probes according to the manufacturer's instructions. Reassemble the cell and connect the cell to the "T" connector. Remove all gas bubbles from the cell, turn-on the probes, and continue the measurements. Record that the time the cell was cleaned.

11. When it is time to collect the groundwater samples, turn-off the monitoring probes, and disconnect the pump's tubing from the "T" connector. If you are using a centrifugal or peristaltic pump check the pump's tubing to determine if the tubing is completely filled with water (no air space).

All samples must be collected and preserved according to the analytical method. VOCs and dissolved gases samples are normally collected first and directly into pre-preserved sample containers. However, this may not be the case for all sampling locations; the SAP/QAPP should list the order in which the samples are to be collected based on the project's objective(s). Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

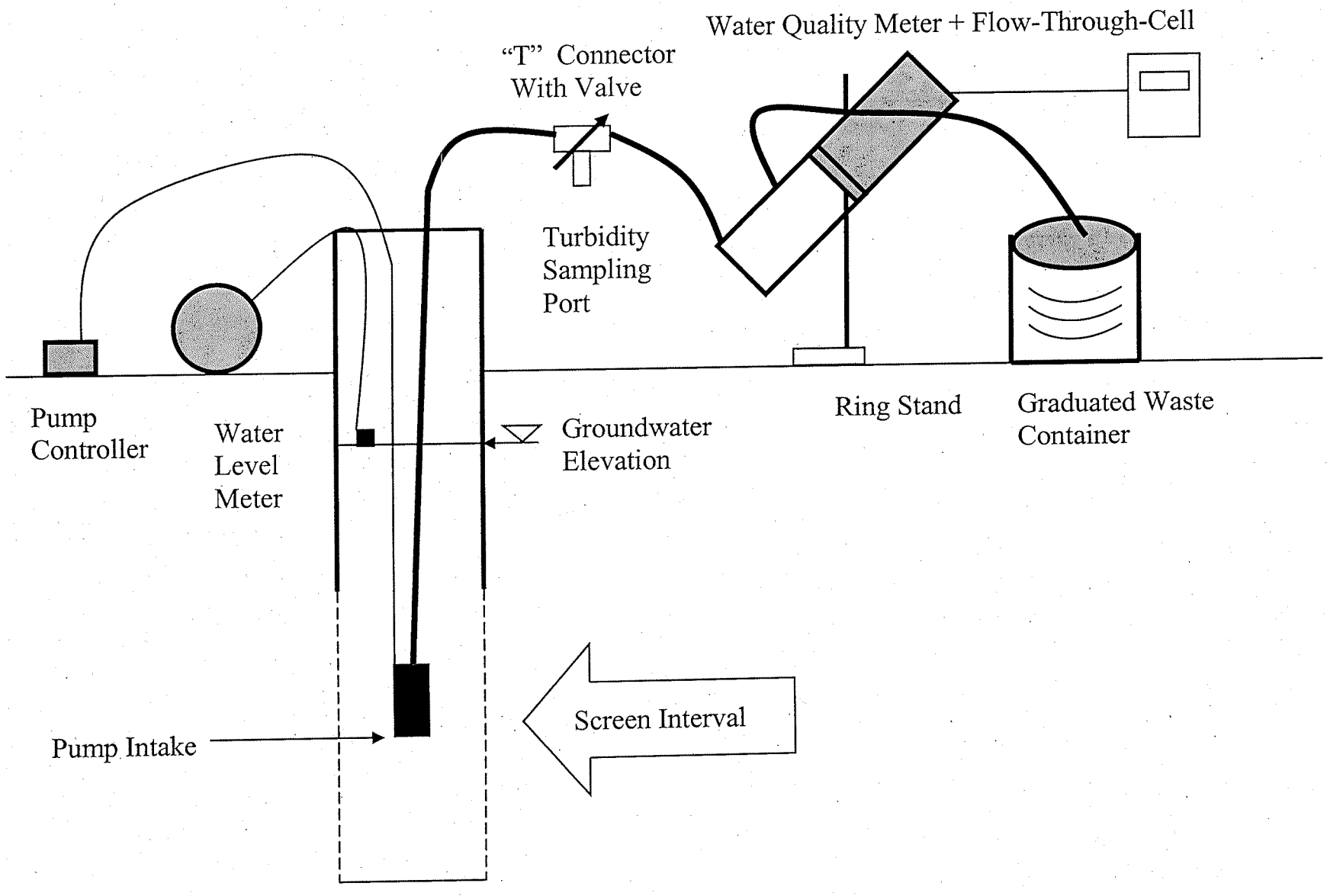
If the pump's tubing is not completely filled with water and the samples are being collected for VOCs and/or dissolved gases analyses using a centrifugal or peristaltic pump, do the following:

> All samples must be collected and preserved according to the analytical method. The VOCs and the dissolved gases (e.g., methane, ethane, ethene, and carbon dioxide) samples are collected last. When it becomes time to collect these samples increase the pump's flow rate until the tubing is completely filled. Collect the samples and record the new flow rate.

12. Store the samples according to the analytical method.

13. Record the total purged volume (graduated waste bucket). Remove the pump from the well and decontaminate the sampling equipment.

Low-Flow Setup Diagram



APPENDIX C
EXAMPLE (Minimum Requirements)
WELL PURGING-FIELD WATER QUALITY MEASUREMENTS FORM

Location (Site/Facility Name)_____
Well Number_____ Date_____
Field Personnel_____
Sampling Organization_____
Identify MP_____

Depth to _____/_____ of screen
(below MP) top bottom
Pump Intake at (ft. below MP)_____
Purging Device; (pump type)_____
Total Volume Purged _____

Clock Time 24 HR	Water Depth below MP ft	Pump Dial[1]	Purge Rate ml/min	Cum. Volume Purged liters	Temp. °C	Spec. Cond.[2] µS/cm	pH	ORP[3] mv	DO mg/L	Turb-idity NTU	Comments
Stabilization Criteria					3%	3%	±0.1	± 10 mv	10%	10%	

1. Pump dial setting (for example: hertz, cycles/min, etc).
2. µSiemens per cm(same as µmhos/cm)at 25 °C.
3. Oxidation reduction potential (ORP)

Title: **Groundwater Sampling**	Procedure Number: **001**
Supersedes:	Revision Number: **0**
Reason for Revision:	Effective Date: **September 2004**

Authorization Signatures		
Author: Charles Foster — Date: 9/20/04	Technical Review: Dorothy McGlincy — Date: 9/20/04	Quality Assurance Review: Elizabeth Denly — Date: 9/22/04

TABLE OF CONTENTS

Page No.

1.0 INTRODUCTION 4
1.1 Scope & Applicability 4
1.2 Summary of Method 4
1.3 Equipment 4
1.4 Definitions 6
1.5 Health & Safety Warnings 7
1.6 Cautions & Potential Problems 7
1.6.1 Pre-Sampling Issues 7
1.6.2 General Purging and Sampling Issues 8
1.7 Personnel Qualifications 9
2.0 PROCEDURES 9
2.1 Pre-Sampling Activities 9
2.2 Groundwater Purging Activities 10
2.2.1 Purging with a Submersible Pump or Peristaltic Pump 10
2.2.2 Purging with a Bailer 12
2.3 Groundwater Sample Collection 13
2.4 Post-Sampling Activities 14
3.0 INVESTIGATION-DERIVED WASTE DISPOSAL 15
4.0 QUALITY ASSURANCE/QUALITY CONTROL 15
4.1 Field Duplicates 15
4.2 Equipment Blanks 15
4.3 Trip Blanks 16
4.4 Matrix Spikes/Matrix Spike Duplicates (MS/MSDs) and MS/Duplicates 16
4.5 Temperature Blanks 16
5.0 DATA MANAGEMENT AND RECORDS MANAGEMENT 16
6.0 REFERENCES 17

ATTACHMENTS

ATTACHMENT A GROUNDWATER FIELD DATA RECORD 18

1.0 INTRODUCTION

1.1 Scope & Applicability

This Standard Operating Procedure (SOP) was prepared to direct TRC personnel in groundwater sampling activities. This SOP details equipment and sampling procedures for low-flow sampling and bailer sampling from monitoring wells (overburden and bedrock wells). This SOP assumes wells have been installed and developed in accordance with TRC SOPs 009 and 010, respectively. Various regulatory agencies and project-specific workplans may have specific requirements (e.g., equipment/instrument, flow rate, etc.) that may be applicable, depending on the program.

The objective of groundwater sampling is to obtain a representative sample of water from the groundwater aquifer with minimum disturbance. This requires that the sample being collected is representative of groundwater as opposed to stagnant water which is contained in the well casing.

1.2 Summary of Method

In order to obtain a representative groundwater sample for chemical analysis, it is important to remove the stagnant water in the well casing and the water immediately adjacent to the well before collection of the sample. This may be achieved with one of a number of instruments. The most common of these are the submersible pump, peristaltic pump, and bailer. Once purging is completed and the correct laboratory-cleaned sample containers have been prepared, sampling may proceed. Sampling may be conducted with any of the above instruments and need not be the same as the device used for purging. Care should be taken when choosing the sampling device as some will affect the integrity of the sample. Sampling should occur from the least to most contaminated well, if this information is known.

1.3 Equipment

The following equipment should be used when sampling a monitoring well. Site-specific conditions may warrant the use of additional equipment or deletion of items from this list.

- Appropriate level of personal protection
- Water level measuring device, capable of measuring to 0.01 foot accuracy
- Oil/water interface probe
- Submersible pump with low-flow capabilities (less than 1 liter/min), constructed of inert materials (i.e., stainless steel and Teflon®)
- Peristaltic pump
- Source of power for use with submersible pump (e.g., compressor, generator, nitrogen tanks, etc.)
- Bottom-filling bailer, constructed of inert materials (i.e., stainless steel and Teflon®)
- Bailer cord or wire (recommended Teflon®-coated stainless steel cable, bailer wire, contaminant-free rope)

- Teflon® or Teflon®-lined polyethylene tubing (polyethylene tubing allowed if sampling only for inorganics): 1/4 inch or 3/8 inch inner diameter (preferred)
- Multi-parameter water quality instrument outfitted with an in-line flow-through cell (must be capable of measuring: pH, temperature, conductivity, oxidation-reduction potential [ORP], and dissolved oxygen [DO]): recommended threaded flow-through cell, when possible.
- Turbidity meter
- Well keys
- Map of well locations and well construction data
- Container for purge water
- Stopwatch or timer
- pH test strips
- Sample bottle labels
- Chain-of-custody forms
- Five-gallon bucket
- Sample cooler(s)
- Photoionization detector (PID) or flame ionization detector (FID) for well mouth monitoring
- Sample containers (may be supplied by the laboratory, depending upon the program, but must be I-Chem Series 300, or equivalent). Sample containers for groundwater samples may include:
  - Volatile Organic Compounds (VOCs) and Volatile Petroleum Hydrocarbons (VPH)*: Two to three 40 mL VOC vials with Teflon®-lined septum caps, pre-preserved with 2-3 drops of 1:1 hydrochloric acid (must contain enough acid to yield pH < 2)
  - Extractable Petroleum Hydrocarbons (EPH)*: Two 1-liter amber glass bottles with Teflon®-lined caps, pre-preserved with 1:1 hydrochloric acid (must contain enough acid to yield pH < 2)
  - Semivolatile Organic Compounds (SVOCs), Pesticides, Polychlorinated Biphenyls (PCBs), Dioxins: For each parameter, two 1-liter amber glass bottles with Teflon®-lined caps
  - Metals*: 1 500 mL to 1-liter polyethylene bottle pre-preserved with nitric acid (must contain enough acid to yield pH < 2)
  - Cyanide*: 1 500 mL to 1-liter polyethylene bottle pre-preserved with 10N (10 Normal) sodium hydroxide (must contain enough sodium hydroxide to yield pH > 12)
  - Hexavalent chromium: 1 500 mL polyethylene bottle

    * Preservative may be added by laboratory prior to sending bottles to the field or may be added by the field team before sampling, depending on the project requirements.
- Field Logbook and/or Groundwater Field Data Record
- Filtration equipment, if needed

- Sample preservative kit (includes preservatives for each specific analysis)
- Bubble wrap/Bubble wrap bags
- In-line filter (0.45 micron)
- Graduated cylinder (1000 ml)
- Teflon® bailer
- Lint-free, non-abrasive, disposable towels (e.g., Kimwipes®)
- Indelible marking pens
- Ice
- Teflon® tape
- Polyethylene sheeting

1.4 Definitions

Bailer	A cylindrical hollow device constructed of inert materials with a check valve (ball on the inside).
Borehole	A hole drilled into the soil or bedrock using a drilling rig, or similar equipment.
Dense Non-Aqueous Phase Liquid (DNAPL)	Separate phase product that is denser than water and therefore sinks to the bottom of the well or aquifer.
Depth To Water (DTW)	The distance to groundwater from an established measuring point.
Drawdown	The lowering of groundwater from the water column in the well or in an aquifer.
Flame Ionization Detector (FID)	An instrument that uses a flame to break down VOCs into ions that can be measured.
I-Chem Series 300 Sample Containers	Bottles that are prepared to meet or exceed all analyte specifications established in the latest U.S. EPA "Specifications and Guidance for Contaminant-Free Sample Containers" document. Bottles are accompanied by Certificates of Analysis demonstrating the achievement of these specifications.
Light Non-Aqueous Phase Liquid (LNAPL)	Separate phase product that is less dense than water and therefore floats on the surface of the water table.
Monitoring Well	A well used to measure groundwater levels and sample groundwater.
Photo Ionization Detector (PID)	An instrument that uses an ultraviolet light source to break down VOCs into ions that can be measured.
Piezometer	A well primarily installed to monitor changes in the potentiometric surface.

Potentiometric Surface	A surface representing the hydraulic head of groundwater.
Recharge Rate	The rate at which groundwater returns to the water column in the well.
Separate Phase Product	A liquid that does not easily dissolve in water due to differences in specific gravity. Separate phase product can be denser (DNAPL) or less dense (LNAPL) than water and therefore can be found at different depths in the water column.
Static Water Level	Level at which water resides in a well when the water level is at equilibrium with atmospheric pressures.

1.5 Health & Safety Warnings

TRC employees will be on site when implementing this SOP. Therefore, TRC personnel shall follow the site-specific Health & Safety Plan (HASP). TRC personnel will use the appropriate level of personal protective equipment (PPE), which includes (at a minimum) the following: 1) hardhat; 2) safety boots (steel toe/steel shank); 3) safety glasses; and 4) chemical-resistant gloves.

The well mouth should be pre-screened using a PID/FID to avoid inhalation of contaminants venting from the well. If monitoring results indicate sustained elevated concentrations of organic contaminants, the level of PPE will need to be increased in accordance with the HASP or work should be conducted upwind of the well.

Implementing this SOP may require the use of reagents and/or compressed gases for the calibration and operation of field equipment. These substances may be hazardous materials and TRC personnel must appropriately handle and store them at all times. Skin contact with water from preserved sample bottles must be avoided. When filling bottles pre-preserved with acid (e.g., hydrochloric acid, nitric acid, sulfuric acid), acid fumes may be released and should not be inhaled.

1.6 Cautions & Potential Problems

1.6.1 Pre-Sampling Issues

(a) If the screen or open borehole is greater than 10 feet, consult the project-specific workplans.

(b) The need for redevelopment of the monitoring wells should be evaluated. This is performed by comparing the measured depth of the well with the constructed depth. If the measured depth is less than the constructed depth, this may indicate siltation of the well and/or a clogged well screen. If it is determined that redevelopment is necessary, it must be performed in accordance with TRC SOP 010, *Well Development.* The time for a well to restabilize after redevelopment will be determined on a project-specific basis and may be up to two weeks, depending on regulatory requirements.

(c) During total well depth measurement there is the potential for sediment present at the bottom of the well to be stirred up when making the measurement and thereby increasing the turbidity of the groundwater.

(d) Avoid placing the submersible pump at the measured depth of the monitoring well or piezometer at the beginning of development, as this could result in plugging or damage to the pump as well as a possible increase in turbidity.

(e) Use caution if using nitrogen cylinders for purging/sampling of groundwater. Check for leaks around regulator connections by spraying soapy water on the connections. If a leak is discovered, the connection to the regulator should be disassembled, wrapped with Teflon® tape, and reconnected to the cylinder. If the leak continues, the regulator should be replaced. It should be noted that Department of Transportation (DOT) regulations apply to the transportation and handling of compressed gas cylinders (see 49 CFR 171).

(f) All field personnel must be made aware of the measurement reference point being used at a site for water level measurement in order to ensure collection of comparable data.

1.6.2 General Purging and Sampling Issues

(a) Prior to pump installation, make sure the tubing and the pump are securely fastened together to avoid losing the pump down the well. Never lower pumps into well only using tubing. A security line attached to the pump should be considered.

(b) Start with the lowest pumping rate possible and increase it until the desired rate is reached. Avoid high pumping rates (> 1 liter/min) as this could lead to damage of the well filter pack.

(c) Make sure monitoring instruments (i.e., multi-parameter water quality instrument, turbidity meter, water level measuring device) are maintained in good condition and properly calibrated to ensure accurate readings.

(d) It should be noted that peristaltic pumps are not preferred when sampling for VOCs due to the potential for degassing during sampling which can alter the sample pH and alkalinity, and cause loss of VOCs.

(e) During purging and sampling, the tubing should remain filled with water to minimize possible changes in water chemistry due to contact with the atmosphere. All flow-through cells should be shaded from direct sunlight to minimize the potential for offgassing and temperature fluctuations.

(f) In the event that a well will not be purged with a submersible pump, the alternative to pumping may be the use of a bottom-filling bailer. A bailer may be made in varying diameters; however a bailer that fits in a two-inch well is the most common. In some instances a < 1-inch diameter bailer (a.k.a. pencil bailers) is used for small diameter wells (e.g., piezometers).

(g) Disposal of the groundwater collected during purging must be in accordance with all applicable regulations and site-specific workplans.

(h) Several procedures should be established to minimize cross-contamination. For example:

- Wrap monitoring and sampling equipment with protective material (i.e., aluminum foil, polyethylene sheeting, ziploc bags) between sampling locations to minimize contamination during well purging.

- Use dedicated sampling equipment when appropriate to minimize the need for decontamination and minimize turbulence in the well.

- Protect sampling equipment from blowing soil and dust by covering with plastic sheeting, as needed.

(i) Clear tape should not be used to cover labels for 40 ml vials for VOC and VPH analysis as the tape can interfere with the analytical instrumentation robotics.

1.7 Personnel Qualifications

Since this SOP will be implemented at sites or in work areas that entail potential exposure to toxic chemicals or hazardous environments, all TRC personnel must be adequately trained. Before implementing this SOP alone, TRC personnel must be trained in these procedures by a senior staff member with experience sampling groundwater. In addition, all personnel utilizing this SOP must have completed the following:

- OSHA 40-hour Health and Safety Training for Hazardous Waste Workers (HAZWOPER)
- 8-hour annual refresher training

In addition to the 40-hour initial OSHA training (and annual 8-hour refresher training), all TRC field staff will complete 24 hours of supervised field experience that contribute toward the 24-hour field supervised requirement in compliance with OSHA regulation: 29 CFR 1910.120(e)(4).

2.0 PROCEDURES

Procedures for sampling monitoring wells and piezometers are described below.

When sampling with equipment that is not dedicated or disposable, sampling should begin at the monitoring well with the least contaminated groundwater and systematically proceed to the well with the most contaminated groundwater, if possible.

It should be noted that there is the potential requirement to determine static water level measurements on <u>all</u> wells at the site, regardless if the well is being sampled.

2.1 Pre-Sampling Activities

(a) Calibrate all field monitoring equipment before collecting groundwater samples. Refer to TRC SOP 012, *Water Level and Product Measurement,* TRC SOP 024, *Calibration of Field Instruments for Water Quality Parameters,* and manufacturer's equipment calibration instructions.

(b) Record the location, time, and date in the field logbook and/or on the Groundwater Field Data Record.

(c) On the Groundwater Field Data Record note the physical condition of the well, including damage, deterioration, and signs of tampering, if any.

(d) Lay polyethylene sheeting around the well. Place monitoring, purging, and sampling equipment on the polyethylene sheeting.

(e) Unlock the protective cap on the well.

(f) Open the well cap and stay upwind. Note any unusual odors, sounds, or difficulties in opening the well and, if required, measure the organic vapor reading at the rim of the well with a suitable organic vapor screening device, (i.e., PID or FID) and record the reading in the field logbook and/or on the Groundwater Field Data Record.

(g) If appropriate for site conditions, check for the presence of non-aqueous phase liquid (NAPL), LNAPL or DNAPL, using an oil/water interface probe (refer to TRC SOP 012, *Water Level and Product Measurement*). If LNAPL or DNAPL are detected, contact the project manager before proceeding with purging and sampling activities.

(h) Gently lower a clean, decontaminated water level measuring device into the well to determine the static water level. Record the information on depth to groundwater to the nearest 0.01 feet, the depth to LNAPL or DNAPL, and/or the thickness of NAPL in the field logbook and/or the Groundwater Field Data Record. Refer to TRC SOP 012, *Water Level and Product Measurement*, for proper procedures in performing these measurements. Be sure to record the reference measuring point used on the well casing or polyvinylchloride (PVC). If no reference point exists, make one as described below and describe its location in the field logbook and/or on the Groundwater Field Data Record.

(i) Creation of Reference Measuring Point: A survey mark should be placed on top of the riser pipe with a black marker (or notched with a handsaw or file) as a reference point for groundwater level measurements. If the lip of the riser pipe is not flat, then the reference point may be the tallest point on the riser pipe. Alternatively, the northern-most direction of the riser pipe may also be marked for use as the reference point. The measurement reference point should be documented in the field logbook and/or on the Groundwater Field Data Record used to record observations during water level measurements. All field personnel must be made aware of the measurement reference point being used at a site in order to ensure collection of comparable data.

(j) Measure the depth to the bottom of the well to assist in calculating the well volume of the well. If NAPL is suspected, use a decontaminated oil/water interface probe for this measurement. If the measured depth is less than the constructed depth, this may indicate that the well needs to be redeveloped (see TRC SOP 010, *Well Development*).

2.2 Groundwater Purging Activities

2.2.1 Purging with a Submersible Pump or Peristaltic Pump

(a) Non dedicated vs. dedicated systems.

- Non-dedicated systems: Determine the required depth of the pump intake (midpoint of the well screen or the midpoint of the water column; a pre-determined location based on the depth and length of the screen interval; see well construction data or the workplan). Slowly lower the pump and tubing into the well to the pre-determined pump intake location. The tubing should be cut to the desired length to assist in installing the pump. Measure the depth of the pump intake while lowering the pump

into location. Record the pump location in the field logbook and/or on the Groundwater Field Data Record.

- Dedicated systems: Pump has already been installed. Refer to historical monitoring well information and record the depth of the pump intake in the field logbook and/or on the Groundwater Field Data Record.

(b) It is recommended that 1/4 inch or 3/8 inch (inner diameter) tubing be used to help ensure that the sample tubing remains filled with water and prevent water from being aerated as it flows through the tubing. If the pump tubing is not completely filled with water to the sampling point, use one of the following procedures to collect samples: (1) add clamp, connector (Teflon® or stainless steel) or valve to constrict sampling end of tubing; (2) insert smaller diameter Teflon® tubing into the water filled portion of the pump tubing allowing the end to protrude beyond the end of the pump tubing, and collect the sample from smaller diameter tubing.

(c) If the measured water level from Section 2.1 is lower than the top of the well screen, position the pump intake at the midpoint of the standing water. The intake should be at least 2 feet above the bottom of the well to minimize mobilization of settled sediment, the risk of the pumping suction being broken, or the entrainment of air in the pump tubing and resulting sample.

(d) Connect the discharge line from the pump to the flow-through cell. Use a "T" connection or valve prior to the flow-through cell to allow for collection of water for turbidity measurements. Direct the discharge line from the flow-through cell to a 5-gallon bucket to contain the purge water for proper disposal.

(e) Commence purging at the slowest possible flow rate and slowly increase the rate until discharge occurs. Discharge the purge water in accordance with regulatory requirements or containerize per project requirements.

(f) Measure the flow rate of the pump with a graduated cylinder and stop watch. Record the volume of water collected for a period of one minute and calculate the flow rate as follows.

$$Flowrate(L/min) = \frac{volume\ collected\ (mL)}{1\ minute} \times \frac{1\ L}{1000\ mL}$$

Measure the water level and record the flow rate and the water level. This should be performed every three to five minutes during purging. The flow rate should be adjusted to result in a rate between 0.1 to 0.4 L/min.

(g) Continue to monitor the water level and flow rate during the purging. Monitor the drawdown (water level elevation) within the well using the water level meter or oil/water interface meter to ensure that minimal drawdown occurs. The flow rate should be lowered if drawdown is greater than 0.3 feet. Note any flow rate adjustments on the Groundwater Field Data Record.

Under no circumstances should the well be pumped dry. If drawdown cannot be maintained below 0.3 feet and the water level is approaching the top of the screened interval, perform the following steps:

- Reduce the flow rate, or turn the pump off for 15 minutes and allow for recovery. (The pump must have a check valve to prevent backflow if it is shut off).
- Begin pumping again at a lower flow rate.
- If water draws down to the top of the screened interval again, turn pump off and allow for recovery.
- If two tubing volumes (including volume of water in pump and flow cell) have been removed during purging, sampling should proceed the next time the pump is turned on without waiting for indicator field parameters to stabilize (see Section 2.2.1 [i]).
- If this procedure is used, this should be recorded in the field logbook and/or on the Groundwater Field Data Record.

(h) Prior to recording the water quality indicator parameters, a minimum of one tubing volume must be purged.

(i) Using the water quality meter, take an initial reading of the indicator parameters: temperature, pH, specific conductance, DO, turbidity, and ORP. All measurements, except turbidity, must be obtained using a transparent flow-through cell. Initially, turbidity may be elevated. Once visual estimates (e.g., clear) indicate that turbidity has decreased to a measurable range (<100 nephelometric turbidity units [NTUs]), begin monitoring indicator parameters as frequently as possible (approximately every 3 to 5 minutes, or as appropriate). Record the readings on the Groundwater Field Data Record. The monitoring probes must be submerged in water at all times. Record the water level along with the indicator parameters, as described in Step (g) above.

Parameters are considered to have stabilized if, over three consecutive readings, all of the following criteria are met.

- pH ± 0.1 unit
- specific conductance and temperature within 3%
- turbidity less than 5 NTUs or within 10% for values greater than 1 NTU
- DO ± 10%
- ORP ±10 mv

NOTE: If parameters do not stabilize, or turbidity remains greater than 5 NTUs within the project-determined time range (EPA recommends up to 4 hours), contact the project manager to develop a modified sampling approach.

(j) Record the disposition of the purge water in the field logbook.

2.2.2 Purging with a Bailer

(a) Use a decontaminated bailer or an unused, disposable bailer.

(b) Attach a bailing line, Teflon-coated bailing wire or rope with appropriate length to reach the bottom of the well. Use a secure knot or series of knots to the top of the bailer. Be sure to have additional length of line to facilitate handling of the bailer at the surface (typically 10 ft).

(c) Lower the bailer gently into the well until it reaches the water column and fills with water from the bottom. Note: It is recommended that the bailer be lowered into the water to a depth that prevents the water from entering the top of the bailer. This is done to prevent excess turbulence caused by filling from the bottom and the top simultaneously. Controlling the line attached to the bailer as it is lowered into the well is also important to prevent degassing of the water as the bailer impacts the water. In shallow wells, controlling the line is not too difficult, however, for wells of greater depths it is common to utilize a hand over hand (windmill) approach using both hands to control longer lengths of line and prevent the loops in the line from tangling with one another. This procedure is simple to learn and saves a good deal of time by preventing tangles. Do not allow bailing line or rope to become contaminated by surface soil.

(d) Once the bailer is full of water, gently withdraw the bailer from the well until it comes out of the top of the well. Be sure to control excess line in your hands to prevent the rope and bailer from touching the ground, and then grasp the bailer as it appears at the top of the well.

(e) Immediately pour the water into a vessel for water quality measurements and record them on the field log (if required after each successive well volume is purged) otherwise, pour water into a 5-gallon bucket or other vessel to keep track of the volume purged. As a general rule, bailers are able to hold about one liter of water when full. This process will have to be repeated several times to complete adequate purging of the well. (e.g., 3 to 5 well volumes)

(f) Once the required volume of water is removed (typically 3 to 5 well volumes) from the well, and parameters are stabilized to the satisfaction of the site-specific work plan, sampling the water from the well should commence.

2.3 Groundwater Sample Collection

(a) If using a submersible pump or peristaltic pump, maintain the same pumping rate as used during purging. Disconnect the pump tubing from the flow-through cell. Samples must be collected directly from the discharge port of the pump tubing prior to passing through the flow-through cell.

(b) If using bottom-filling bailers,

- Slowly lower the bailer into the well until it is submerged to the point where water does not go into the top (i.e., bottom-filling).
- Retrieve the bailer. The first bailer recovered after well purging must be used for sample collection.

(c) Fractions of the groundwater sample should be collected in the following order (i.e., decreasing volatility):

- VOCs;
- SVOCs;
- Unfiltered inorganic compounds; and
- Filtered inorganic compounds.

During sample collection, allow the water to flow directly down the side of the sample container without allowing the tubing to touch the inside of the sample container or lid, in

order to minimize aeration and turbulence and maintain sample integrity. The tubing should remain filled with water.

(d) Collection of VOCs/VPH: Samples for volatile organics will be collected first, and the sample vial must be filled so a meniscus forms over the mouth of the vial. This ensures no air bubbles or headspace will be formed after it has been capped. Ensure the lack of air bubbles and headspace by turning the vial upside down and tapping it lightly. If any bubbles are observed, discard the sample and collect a new sample.

Preservation of VOCs/VPH in the field: A "test" vial may be collected first to determine the amount of preservative (hydrochloric acid [HCl]) needed to reduce the pH to less than 2. The pH of the test sample will be determined; then HCl will be incrementally added one drop at a time to the sample until the pH is less than 2. The volume of HCl added to the test vial will be recorded and that amount will be used in each of the remaining sample vials. The test vial will not be submitted to the laboratory for analysis. The determination of when to collect a "test" vial will be determined on a project-specific basis but should be considered for all groundwater samples with elevated pH (>9).

In some cases 40 ml VOC vials come pre-preserved. If the test vial effervesces upon addition of sample, no preservatives will be added to the VOC fraction of the sample. If a pre-preserved vial effervesces upon the addition of sample, contact the laboratory for more information.

When acid preservation is used for the collection of VOCs, the acid must be added to the vials before sample collection.

(e) Fill the remaining sample containers at least 3/4 full for all non-VOC analyses.

(f) Preserve the non-VOC samples in accordance with method and project-specific requirements following sample collection if the sample containers are not pre-preserved. (NOTE: Pre-preserved vials may also be supplied by the laboratory, depending on the program). Check the pH of the non-VOC samples which are chemically preserved to ensure adequate amount of preservative has been added.

(g) Depending upon project requirements, filtering may be performed. An in-line filter should be fitted at the end of the discharge tubing and the sample will be collected after the filter. Pre-rinse the in-line filter by allowing a minimum of 0.5 to 1 liter of groundwater from the well to pass through the filter prior to sampling. Preserve the filtered water sample immediately, if required.

2.4 Post-Sampling Activities

(a) Cease pumping and, if system is non-dedicated, disassemble and decontaminate the purging and sampling equipment. (See TRC SOP 004, *Equipment Decontamination Procedures*).

(b) Dispose of the bailer (if disposable), and/or rope in accordance with the site-specific workplan or store the bailer in a plastic bag for transport to the site decontamination area.

(c) Replace the protective/locking cover on the well and lock the outer casing (if present).

(d) Label each sample and cover the label with clear tape unless the bottle is being submitted for VOC analysis (see Section 1.6.2). Refer to TRC SOP 014, *Packaging and Shipping of Environmental Samples* and TRC SOP 018, *Sample Chain-of-Custody* for proper labeling and packaging procedures. Place all samples in a cooler with ice.

3.0 INVESTIGATION-DERIVED WASTE DISPOSAL

All investigation-derived wastes (IDW) generated during groundwater sampling must be disposed in accordance with federal, state, local, and project-specific requirements.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

The collection of quality control (QC) samples is dependent upon the data quality objectives. Site-specific plans should be consulted to determine the required frequency of QC sample collection.

4.1 Field Duplicates

The following procedures should be used for collecting field duplicates of groundwater samples:

(a) For quality control purposes, each duplicate sample will be submitted to the laboratory as a "blind" duplicate sample, in that a non-existing sample identification will be assigned in labeling the duplicate. All labeling procedures used for groundwater sampling will be employed and all parameters measured will also be recorded. Since the duplicate is collected simultaneously with the actual sample, a "blind" sample time, within one hour of the actual time, will also be assigned. The actual source and collection time of the duplicate sample will be recorded in the field logbook and/or on the Groundwater Field Data Record.

(b) Each duplicate sample will be collected simultaneously with the actual sample by alternately filling sample and duplicate bottles. Following the order of collection specified for each set of containers (VOCs, SVOCs, unfiltered inorganic compounds, and filtered inorganic compounds), the duplicate sample containers will be alternately filled with each parameter.

(c) All collection and preservation procedures outlined for groundwater sampling will be followed for each duplicate sample.

4.2 Equipment Blanks

Equipment blanks include reagent water that is run through the pump and the pump's tubing and collected and preserved in the same sample containers as field samples. If dedicated systems are used, equipment blanks are not required although an initial blank could be performed to demonstrate that the dedicated equipment is clean prior to use. If only dedicated tubing is used, the equipment blank will include only the pump in subsequent sampling events.

Ideally, the reagent water should come from the laboratory and be certified clean. If not certified and/or if not from the laboratory performing the analyses, a separate water blank that has not run through the sampling equipment should be sent to the laboratory for analysis.

4.3 Trip Blanks

Trip blanks will check for potential contamination of VOCs via migration during storage and shipping. Trip blanks consist of two to three 40 mL VOC vials filled with analyte-free water and preserved with HCl to pH <2. Trip blanks are submitted to the laboratory at a frequency of one per cooler for coolers which contain samples for VOC and/or VPH analysis. Trip blanks are analyzed by the laboratory for VOCs and/or VPH, depending on field sample analyses.

4.4 Matrix Spikes/Matrix Spike Duplicates (MS/MSDs) and MS/Duplicates

Matrix spikes (MSs) are an additional analysis of a sample spiked with a subset or all of the target analytes and are used to demonstrate the accuracy of analytical methods for a given matrix. Matrix spike duplicates (MSDs) are an additional analysis of a sample spiked with a subset or all of the target analytes and are also used to demonstrate the accuracy of analytical methods for a given matrix. MS/MSDs also provide a measure of analytical precision for a given matrix. Duplicates are an additional analysis of a sample and are used to demonstrate the precision of analytical methods for a given matrix.

Triplicate volume of a field sample must be collected in order for the laboratory to have enough volume to perform the MS/MSD analyses for organic parameters. Duplicate volume of a field sample must be collected in order for the laboratory to have enough volume to perform MS/Duplicate analyses for inorganic parameters. The sample designated for MS/MSD or MS/Duplicate analyses should be noted in the Comments column of the chain-of-custody.

4.5 Temperature Blanks

Temperature blanks consist of a sample container filled with non-preserved water (potable or distilled) and are included in all coolers which contain samples which require temperature preservation. These should be added to the coolers by the field team if not provided by the laboratory. Temperature blanks must remain inside the coolers on ice during the sampling process.

5.0 DATA MANAGEMENT AND RECORDS MANAGEMENT

Record the sample location, sample identification, and date and time of collection in the field logbook or the Groundwater Field Data Record. The Groundwater Field Data Record (Attachment A) should be used to record the following:

- Volume of each sample
- Sample identification number
- Sample location (sketch of the sample point)
- Time and date sample was taken
- Personnel performing the task
- Volume of water removed
- Purging time
- Flow rate during purging and sampling

- Weather conditions during sampling
- Field parameters such as water level, pH, temperature, conductivity, turbidity, oxidation-reduction potential, and dissolved oxygen
- Sample collection equipment and method used
- Decontamination procedure
- Analytical parameters
- Preservation method and amount of preservative added

Any deviations from the record management procedures specified in the Field Sampling Plan or Quality Assurance Project Plan, if applicable, must be approved by the Quality Assurance (QA) Officer and Project Manager and documented in the field logbook.

6.0 REFERENCES

A Compendium of Superfund Field Operations Methods. EPA/540/P-87/001.

Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers. EPA 542-S-02-001. US EPA Office of Solid Waste and Emergency Response. May 2002.

Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. Ground Water Issue. EPA/540/S-95/504. US EPA Office of Solid Waste and Emergency Response. April 1996.

Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells. U.S. EPA, Rev. 2. July 30, 1996.

RCRA Ground-Water Monitoring: Draft Technical Guidance. EPA/530-R-93-001. US EPA Office of Solid Waste. November 1992.

TRC SOP 004, *Equipment Decontamination Procedures,* Revision 0, August 2003.

TRC SOP 009, *Ground Water Monitoring Well Installation,* Revision 2, October 1999.

TRC SOP 010, *Ground Water Monitoring Well Development,* Revision 2, October 1999.

TRC SOP 012, *Water Level and Product Measurement,* Revision 0, August 2003.

TRC SOP 014, *Packaging and Shipping of Environmental Samples,* Revision 0, April 2003.

TRC SOP 018, *Sample Chain-of-Custody,* Revision 0, May 2003.

TRC SOP 024, *Calibration of Field Instruments for Water Quality Parameters,* Revision 0, November 2003.

ATTACHMENT A
GROUNDWATER FIELD DATA RECORD

TRC

Groundwater Sampling Data Record

Project: | Project No.: | Date/Time: | Sheet ___ of ___

TRC Personnel:

Well Identification:

WELL INTEGRITY

	YES	NO
Protect. Casing Secure	☐	☐
Concrete Collar Intact	☐	☐
PVC Stick-up Intact	☐	☐
Well Cap Present	☐	☐
Security Lock Present	☐	☐

Protective Casing Stick-up _____ ft. (from grout(d))

Riser Stick-up (from ground) _____ ft.

WELL DIAMETER ☐ 2 inch ☐ 4 inch ☐ 6 inch ☐ ___

WELL MATERIAL ☐ PVC ☐ SS ☐ ___

Well Depth _____ ft. ☐ top of riser ☐ top of casing ☐ _____ ☐ measured ☐ historical

Water Depth _____ ft.

Height of Water Column _____ ft. x ☐ .16 gal/ft (2 in.) ☐ .65 gal/ft (4 in.) ☐ 1.5 gal/ft (6 in.) ☐ ___ gal/ft (___ in.)

Depth of pump intake _____

Volume of Water in Well = _____ gallon(s)

[Vol. = r^2 h(0.163)]

_____ Total gallons purged

PID SCREENING MEAS.

Background		
Well Mouth		(if required)

Depth to NAPL _____

Thickness of NAPL _____

FIELD WATER QUALITY MEASUREMENTS

Time or Volume Purged										
pH (Std. Units)										
Eh (millivolts)										
Conduct. (µmhos/cm)										
Temp. (C)										
Turb. (NTU)										
DO (mg/l)										
Flow (ml/min)										
Depth To Water (ft)										
Time										
pH (Std. Units)										
Eh (millivolts)										
Conduct. (µmhos/cm)										
Temp. (C)										
Turb. (NTU)										
DO (mg/l)										
Flow (ml/min)										
Depth To Water (ft)										

Pump Type	Purge	Sample
Peristaltic Pump	☐	☐
Submersible Pump	☐	☐
Bladder Pump	☐	☐
Other: _____	☐	☐

Description of Sampling Equipment and Flow Rate:

Analytical Parameter	Filtered (Y/N)	Preservation	Volume/Containers	Time Collected	Sample ID

Signed:_____ Rev. 0 Sept. 2004

APPENDIX E:

CALIBRATION OF FIELD INSTRUMENTS (TEMPERATURE, pH, DISSOLVED OXYGEN, CONDUCTIVITY/SPECIFIC CONDUCTANCE, OXIDATION/REDUCTION POTENTIAL [ORP], AND TURBIDITY).

STANDARD OPERATING PROCEDURE
CALIBRATION OF FIELD INSTRUMENTS
(temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction potential [ORP], and turbidity)

Quality Assurance Unit
U.S. Environmental Protection Agency – Region 1
11 Technology Drive
North Chelmsford, MA 01863

The controlled version of this document is the electronic version viewed on-line only. If this is a printed copy of the document, it is an uncontrolled version and may or may not be the version currently in use.

This document contains direction developed solely to provide guidance to U.S. Environmental Protection Agency (EPA) personnel. EPA retains the discretion to adopt approaches that differ from these procedures on a case-by-case basis. The procedures set forth do not create any rights, substantive or procedural, enforceable at law by party to litigation with EPA or the United States.

Prepared by: Charles Porfert 1/19/10
(Charles Porfert, Quality Assurance Unit) Date

Approved by: Gerard Sotolongo 1-19-10
(Gerard Sotolongo, Quality Assurance Unit) Date

Revision Page

Date	Rev #	Summary of changes	Sections
6/03/98	1	Draft	
01/19/10	2	Finalized	

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION....4

2.0 HEALTH AND SAFETY WARNINGS....4

3.0 GENERAL....4

4.0 FREQUENCY OF CALIBRATION....5

5.0 CALIBRATION PROCEDURES....5

5.1 TEMPERATURE....6

5.2 pH (electrometric)....7

5.3 DISSOLVED OXYGEN....8

5.4 SPECIFIC CONDUCTANCE....10

5.5 OXIDATION/REDUCTION POTENTIAL (ORP)....11

5.6 TURBIDITY....12

6.0 POST CALIBRATION CHECK....14

7.0 DATA MANAGEMENT AND RECORDS MANAGEMENT....15

8.0 REFERENCES....15

Table 1 INSTRUMENT CALIBRATION LOG....16

OXYGEN SOLUBILITY....17

1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to provide a framework for calibrating field instruments used to measure water quality parameters for groundwater and surface water. Water quality parameters include temperature, pH, dissolved oxygen, specific conductance, oxidation/reduction potential [ORP], and turbidity. This SOP supplements, but does not replace, EPA analytical methods listed in 40 CFR 136 and 40 CFR 141 for temperature, dissolved oxygen, conductivity/specific conductance, pH and turbidity.

This SOP is written for instruments that measure temperature, pH, dissolved oxygen, specific conductance, turbidity, and/or oxidation/reduction potential [ORP] and the probe readings for pH, dissolved oxygen, and specific conductance are automatically corrected for temperature.

For groundwater monitoring, the instrument must be equipped with a flow-through-cell and the display/logger or computer display screen needs to be large enough to simultaneously contain the readouts of each probe in the instrument. Turbidity is measured using a separate instrument. It must not be measured in a flow-through-cell because the flow-through-cell acts as a sediment trap. This procedure is applicable for use with the *EPA Region 1 Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells.*

2.0 HEALTH AND SAFETY WARNINGS

Read all labels on the standards and note any warnings on the labels. Wear appropriate personal protection equipment (e.g., gloves, eye shields, etc.) when handling the standards. If necessary, consult the Material Safety Data Sheets (MSDS) for additional safety information on the chemicals in the standards.

3.0 GENERAL

All monitoring instruments must be calibrated before they are used to measure environmental samples. For instrument probes that rely on the temperature sensor (pH, dissolved oxygen, specific conductance, and oxidation/reduction potential [ORP]), each temperature sensor needs to be checked for accuracy against a thermometer that is traceable to the National Institute of Standards and Technology (NIST). Before any instrument is calibrated or used to perform environmental measurements, the instrument must stabilize (warm-up) according to manufacturer's instructions and must have no air bubbles lodged between the probe and probe guard.

Most projects will require at least two standards to bracket the expected measurement range. This means that one standard is less than the expected value and one is higher. When an environmental sample measurement falls outside the calibration range, the instrument must be re-calibrated to bracket the new range before continuing measurements. Otherwise, the measurements that are outside the calibration range will need to be qualified.

This SOP requires that the manufacturer's instruction manual (including the instrument specifications) accompany the instrument into the field.

4.0 FREQUENCY OF CALIBRATION

At a minimum, the instrument is calibrated prior to use on the day the measurements are to be performed. A post calibration check at the end of the day is performed to determine if the instrument drifted out of calibration. Some projects may require more frequent calibration checks throughout the day in addition to the check at the end of the day. For these checks, the instrument can be recalibrated during the day if the instrument drifted out of calibration and only the data measured prior to the check would need to be qualified. The calibration/post calibration data information is recorded in Table 1.

Instruments (e.g., sonde) that monitor continuously over a period of time are calibrated before deployment. When these instruments are recovered, the calibration is checked to determine if any of them drifted out of calibration.

Some instruments lose their calibration criteria when they are turned off. Those instruments can either be left on all day (battery dependent) or calibrated at each sampling location. If they are calibrated at each sampling location, a post calibration check is not needed.

Ideally, the temperature of the standards should be close to the temperature of the ambient water that is being measured.

5.0 CALIBRATION PROCEDURES

Prior to calibration, all instrument probes and cable connections must be cleaned and the battery checked according to the manufacturer's instructions. Failure to perform these steps (proper maintenance) can lead to erratic measurements.

If a multi-probe instrument is to be used, program the instrument to display the parameters to be measured (e.g., temperature, pH, percent dissolved oxygen, mg/L dissolved oxygen, specific conductance, and ORP).

The volume of the calibration solutions must be sufficient to cover both the probe and temperature sensor (see manufacturer's instructions for the volume to be used).

Check the expiration date of the standards. Do not use expired standards.

All standards are stored according to manufacturer instructions.

5.1 TEMPERATURE

Most instrument manuals state there is no calibration of the temperature sensor, but the temperature sensor must be checked to determine its accuracy. This accuracy check is performed at least once per year and the accuracy check date/information is kept with the instrument. If the accuracy check date/information is not included with the instrument or the last check was over a year, the temperature sensor accuracy needs to be checked at the beginning of the sampling event. If the instrument contains multiple temperature sensors, each sensor must be checked. This procedure is not normally perform in the field. If the instrument is obtained from a rental company, the rental company should performed the calibration check and include with the instrument documentation that it was performed.

Verification Procedure

1. Fill a container with water and adjust the water temperature to below the water body's temperature to be measured. Use ice or warm water to adjust the temperature.

2. Place a thermometer that is traceable to the National Institute of Standards and Technology (NIST) and the instrument's temperature sensor into the water. Wait for both temperature readings to stabilize.

3. Compare the two measurements. The instrument's temperature sensor must agree with the reference thermometer measurement within the accuracy of the sensor (e.g., $\pm 0.2\,^{\circ}C$). If the measurements do not agree, the instrument may not be working properly and the manufacturer needs to be consulted.

4. Adjust the water temperature to a temperature higher than the water body to be measured.

5. Compare the two measurements. The instrument's temperature sensor must agree with the reference thermometer measurement within the accuracy of the sensor (e.g.,

±0.2°C). If the measurements do not agree, the instrument may not be working properly and the manufacturer needs to be consulted.

5.2 pH (electrometric)

The pH of a sample is determined electrometrically using a glass electrode.

Choose the appropriate buffered standards that will bracket the expected values at the sampling locations. If the water body's pH is unknown, then three standards are needed for the calibration: one close to seven, one at least two pH units below seven, and the other at least two pH units above seven. Instruments that will not accept three standards will need to be re-calibrated if the water sample's pH is outside the initial calibration range described by the two standards.

Calibration Procedure

1. Allow the buffered standards to equilibrate to the ambient temperature.

2. Fill calibration containers with the buffered standards so each standard will cover the pH probe and temperature sensor.

3. Remove probe from its storage container, rinse with deionized water, and remove excess water.

4. Select measurement mode. Immerse probe into the initial standard (e.g., pH 7).

5. Wait until the readings stabilize. If the reading does not change within 30 seconds, select calibration mode and then select "pH". Enter the buffered standard value into instrument.

6. Remove probe from the initial standard, rinse with deionized water, and remove excess water.

7. Immerse probe into the second standard (e.g., pH 4). Repeat step 5.

8. Remove probe from the second standard, rinse with deionized water, and remove excess water. If instrument only accepts two standards, the calibration is complete. Go to step 11. Otherwise continue.

9. Immerse probe in third buffered standard (e.g., pH 10) and repeat step 5.

10. Remove probe from the third standard, rinse with deionized water, and remove excess water.

11. Select measurement mode, if not already selected. To ensure that the initial calibration standard (e.g., pH 7) has not changed, immerse the probe into the initial standard. Wait for the readings to stabilize. The reading should read the initial standard value within the manufacturer's specifications. If not, re-calibrate the instrument. If re-calibration does not help, the calibration range may be too great. Reduce calibration range by using standards that are closer together.

12. The calibration is complete. Rinse the probe with deionized water and store the probe according to manufacturer's instructions.

13. Record the calibration information on Table 1.

5.3 DISSOLVED OXYGEN

Dissolved oxygen (DO) content in water is measured using a membrane electrode. To insure proper operation, the DO probe's membrane and electrolyte should be replaced prior to calibration for the sampling event. The new membrane may need to be conditioned before it is used; consult manufacturer's manual on how the conditioning is to be performed. Failure to perform this step may lead to erratic measurements. Before performing the calibration/measurements, inspect the membrane for air bubbles and nicks.

Note: some manufacturers require an altitude correction instead of a barometric correction. In that case, enter the altitude correction according to the manufacturer's directions in Step 5 and then proceed to Step 6.

Note: some instruments have a built-in barometer. Follow the manufacturer's instructions for entering the barometric value in step 5.

<u>Calibration Procedure</u>

1. Gently dry the temperature sensor and remove any water droplets from the DO probe's sensor membrane according to manufacturer's instructions. Note that the evaporation of moisture on the temperature sensor or DO probe may influence the readings during calibration.

2. Create a 100 percent water-saturated air environment by placing a wet sponge or a

wet paper towel on the bottom of the DO calibration container. Place the DO probe into the calibration container. The probe is loosely fitted into the calibration container to prevent the escape of moisture evaporating from the sponge or paper towel while maintaining ambient pressure (see manufacturer's instructions). Note that the probe and the temperature sensor must not come in contact with these wet items.

3. Allow the confined air to become saturated with water vapor (saturation occurs in approximately 10 to 15 minutes). During this time, turn on the instrument to allow the DO probe to warm-up. Select the measurement mode. Check the temperature readings. Readings must stabilize before continuing to the next step.

4. Select calibration mode; then select "DO %".

5. Enter the local barometric pressure (usually in mm of mercury) for the sampling location into the instrument. This measurement must be determined from an on-site barometer. Do not use barometric pressure obtained from the local weather services unless the pressure is corrected for the elevation of the sampling location. [Note: inches of mercury times 25.4 mm/inch equals mm of mercury or consult Oxygen Solubility at Indicated Pressure chart attached to the SOP for conversion at selected pressures].

6. The instrument should indicate that the calibration is in progress. After calibration, the instrument should display percent saturated DO.

7. Select measurement mode and set the display to read DO mg/L and temperature. Compare the DO mg/L reading to the Oxygen Solubility at Indicated Pressure chart attached to the SOP. The numbers should agree. If they do not agree within the accuracy of the instrument (usually ± 0.2 mg/L), repeat calibration. If this does not work, change the membrane and electrolyte solution.

8. Remove the probe from the container and place it into a 0.0 mg/L DO solution (see footnote). Check temperature readings. They must stabilize before continuing.

9. Wait until the "mg/L DO" readings have stabilized. The instrument should read less than 0.5 mg/L (assuming an accuracy of ± 0.2 mg/L). If the instrument reads above 0.5 mg/L or reads negative, it will be necessary to clean the probe, and change the membrane and electrolyte solution. If this does not work, try a new 0.0 mg/L DO solution. If these changes do not work, contact the manufacturer. Note: some projects and instruments may have different accuracy requirements. The 0.5 mg/L

value may need to be adjusted based on the accuracy requirements of the project or instrument.

10. After the calibration has been completed, rinse the probe with tap or deionized water and store the probe according to manufacturer's instructions. It is important that all of the 0.0 mg/L DO solution be rinsed off the probe so as not to effect the measurement of environmental samples.

11. Record calibration information on Table 1.

Note: You can either purchase the 0.0 mg/L DO solution from a vendor or prepare the solution yourself. To prepare a 0.0 mg/L DO solution, follow the procedure stated in Standard Methods (Method 4500-O G). The method basically states to add excess sodium sulfite (until no more dissolves) and a trace amount of cobalt chloride (read warning on the label before use) to water. This solution is prepared prior to the sampling event. Note: this solution can be made without cobalt chloride, but the probe will take longer to respond to the low DO concentration.

5.4 SPECIFIC CONDUCTANCE

Conductivity is used to measure the ability of an aqueous solution to carry an electrical current. Specific conductance is the conductivity value corrected to 25°C.

Most instruments are calibrated against a single standard which is near the specific conductance of the environmental samples. The standard can be either below or above the specific conductance of the environmental samples. A second standard is used to check the linearity of the instrument in the range of measurements.

When performing specific conductance measurement on groundwater or surface water and the measurement is outside the initial calibration range defined by the two standards, the instrument will need to be re-calibrated using the appropriate standards.

<u>Specific Conductance Calibration Procedure</u>

1. Allow the calibration standards to equilibrate to the ambient temperature.

2. Fill calibration containers with the standards so each standard will cover the probe and temperature sensor. Remove probe from its storage container, rinse the probe with deionized water or a small amount of the standard (discard the rinsate), and place the

probe into the standard.

3. Select measurement mode. Wait until the probe temperature has stabilized.

4. Select calibration mode, then specific conductance. Enter the specific conductance standard value. Make sure that the units on the standard are the same as the units used by the instrument. If not, convert the units on the standard to the units used by the instrument.

5. Select measurement mode. The reading should remain within manufacturer's specifications. If it does not, re-calibrate. If readings continue to change after re-calibration, consult manufacturer or replace calibration solution.

6. Remove probe from the standard, rinse the probe with deionized water or a small amount of the second standard (discard the rinsate), and place the probe into the second standard. The second standard will serve to verify the linearity of the instrument. Read the specific conductance value from the instrument and compare the value to the specific conductance on the standard. The two values should agree within the specifications of the instrument. If they do not agree, re-calibrate. If readings do not compare, then the second standard may be outside the linear range of the instrument. Use a standard that is closer to the first standard and repeat the verification. If values still do not compare, try cleaning the probe or consult the manufacturer.

7. After the calibration has been completed, rinse the probe with deionized water and store the probe according to manufacturer's instructions.

8. Record the calibration information on Table 1.

Note: for projects where specific conductance is not a critical measurement it may be possible to calibrate with one standard in the range of the expected measurement.

5.5 OXIDATION/REDUCTION POTENTIAL (ORP)

The oxidation/reduction potential is the electrometric difference measured in a solution between an inert indicator electrode and a suitable reference electrode. The electrometric difference is measured in millivolts and is temperature dependent.

Calibration or Verification Procedure

1. Allow the calibration standard (a Zobell solution: read the warning on the label before use) to equilibrate to ambient temperature.

2. Remove the probe from its storage container and place it into the standard.

3. Select measurement mode.

4. Wait for the probe temperature to stabilize, and then read the temperature.

5. If the instrument is to be calibrated, do Steps 6 and 7. If the instrument calibration is to be verified, then go to Step 8.

6. Look up the millivolt (mv) value at this temperature from the millivolt versus temperature correction table usually found on the standard bottle or on the standard instruction sheet. You may need to interpolate millivolt value between temperatures. Select "calibration mode", then "ORP". Enter the temperature-corrected ORP value into the instrument.

7. Select measurement mode. The readings should remain unchanged within manufacturer's specifications. If they change, re-calibrate. If readings continue to change after re-calibration, try a new Zobell solution or consult manufacturer. Go to Step 9.

8. If the instrument instruction manual states that the instrument is factory calibrated, then verify the factory calibration against the Zobell solution. If they do not agree within the specifications of the instrument, try a new Zobell solution. If it does not agree, the instrument will need to be re-calibrated by the manufacturer.

9. After the calibration has been completed, rinse the probe with deionized water and store the probe according to manufacturer's instructions.

10. Record the calibration information on Table 1.

5.6 TURBIDITY

The turbidity method is based upon a comparison of intensity of light scattered by a sample under defined conditions with the intensity of light scattered by a standard reference suspension. A

turbidimeter is a nephelometer with a visible light source for illuminating the sample and one or more photo-electric detectors placed ninety degrees to the path of the light source. Note: the below calibration procedure is for a turbidimeter which the sample is placed into a cuvette.

Some instruments will only accept one standard. For those instruments, the second, third, etc., standards will serve as check points.

Calibration Procedures

1. Allow the calibration standards to equilibrate at the ambient temperature. The use of commercially available polymer primary standards (AMCO-AEPA-1) is preferred; however, the standards can be prepared using Formazin (read the warning on the label before use) according to the EPA analytical Method 180.1. Other standards may be used if they can be shown that they are equivalent to the previously mentioned standards.

2. If the standard cuvette is not sealed, rinse a cuvette with deionized water. Shake the cuvette to remove as much water as possible. Do not wipe dry the inside of the cuvette because lint from the wipe may remain in the cuvette. Add the standard to the cuvette.

3. Before performing the calibration procedure, make sure the cuvettes are not scratched and the outside surfaces are dry and free from fingerprints and dust. If the cuvette is scratched or dirty, discard or clean the cuvette respectively. Note: some manufacturers require the cuvette to be orientated in the instrument in a particular direction for accurate reading.

4. Select a low value standard such as a zero or 0.02 NTU and calibrate according to manufacturer's instructions. Note: a zero standard (approximately 0 NTU) can be prepared by passing distilled water through a 0.45 micron pore size membrane filter.

5. Select a high standard and calibrate according to manufacturer's instructions or verify the calibration if instrument will not accept a second standard. In verifying, the instrument should read the standard value to within the specifications of the instrument. If the instrument has range of scales, check each range that will be used during the sampling event with a standard that falls within that range.

6. Record the calibration information on Table 1.

6.0 POST CALIBRATION CHECK

After the initial calibration is performed, the instrument's calibration may drift during the measurement period. As a result, you need to determine the amount of drift that occurred after collecting the measurements. This is performed by placing the instrument in measurement mode (not calibration mode) and placing the probe in one or more of the standards used during the initial calibration; for turbidity place the standard in a cuvette and then into the turbidimeter. Wait for the instrument to stabilize and record the measurement (Table 1). Compare the measurement value to the initial calibration value. This difference in value is then compared to the drift criteria or post calibration criteria described in the quality assurance project plan or the sampling and analysis plan for the project. If the check value is outside the criteria, then the measurement data will need to be qualified.

For the dissolved oxygen calibration check, follow the calibration instructions steps one through three while the instrument is in measurement mode. Record dissolved oxygen value (mg/L), temperature, and barometric pressure. Compare the measurement value to the Oxygen Solubility at Indicated Pressure chart attached to this SOP. The value should be within the criteria specified for the project. If measurement value drifted outside the criteria, the data will need to be qualified.

If the quality assurance project plan or the sampling and analysis plan do not list the drift criteria or the post-calibration criteria, use the criteria below.

Measurement	**Post Calibration Criteria**
Dissolved Oxygen	± 0.5 mg/L of sat. value* < 0.5 mg/L for the 0 mg/L solution, but not a negative value
Specific Conductance	±5% of standard or ± 10 μS/cm (whichever is greater)
pH	± 0.3 pH unit with pH 7 buffer*
Turbidity	± 5% of standard
ORP	± 10 mv*

Note: * Table 8.1, USEPA Region 1 *YSI 6-Series Sondes and Data Logger SOP*, January 30, 2007, revision 9.

7.0 DATA MANAGEMENT AND RECORDS MANAGEMENT

All calibration records must be documented in the project's log book or on a calibration log sheet. At a minimum, include the instrument manufacturer, model number, instrument identification number (when more than one instrument of the same model is used), the standards used to calibrate the instruments (including source), the calibration date, the instrument readings, the post calibration check, and the name of the person(s) who performed the calibration. An example of a calibration log sheet is shown in Table 1.

8.0 References

Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998.

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983.

Turbidity - Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100, August 1993.

USEPA Region 1 YSI 6-Series Sondes and Data Logger SOP, January 30, 2007, revision 9.

USGS Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting, Techniques and Methods 1-D3.

TABLE 1
INSTRUMENT CALIBRATION LOG

Project Name_____ Date_____
Weather_____

Calibrated by_____ Instrument_____
Serial Number_____

Parameters	Morning Calibration	Morning Temperature	End of Day Calibration Check*	End of Day Temperature
Specific Conductance Standard #1				
Specific Conductance Standard #2				
pH (7)				
pH (4)				
pH (10)				
ORP Zobel solution				
Dissolved Oxygen 100% water saturated air mg/L				
Dissolved Oxygen Zero Dissolved Oxygen Solution mg/L				
Barometric Pressure mm Hg		NA		NA
Turbidity Standard #1				
Turbidity Standard #2				
Turbidity Standard #3				

* For each Parameter, chose one standard as your check standard. If possible, choose the one that is closest to the ambient measurement value.

Oxygen Solubility at Indicated Pressure

Temp.	Pressure (Hg)							
	760	755	750	745	740	735	730	mm
°C	29.92	29.72	29.53	29.33	29.13	28.94	28.74	in
0	14.57	14.47	14.38	14.28	14.18	14.09	13.99	mg/l
1	14.17	14.08	13.98	13.89	13.79	13.70	13.61	
2	13.79	13.70	13.61	13.52	13.42	13.33	13.24	
3	13.43	13.34	13.25	13.16	13.07	12-98	12.90	
4	13.08	12.99	12.91	12.82	12.73	12.65	12.56	
5	12.74	12.66	12.57	12.49	12.40	12.32	12.23	
6	12.42	12.34	12.26	12.17	12.09	12.01	11.93	
7	12.11	12.03	11.95	11.87	11.79	11.71	11.63	
8	11.81	11.73	11.65	11.57	11.50	11.42	11.34	
9	11.53	11.45	11.38	11.30	11.22	11.15	11.07	
10	11.28	11.19	11.11	11.04	10.96	10.89	10.81	
11	10.99	10.92	10.84	10.77	10.70	10.62	10.55	
12	10.74	10.67	10.60	10.53	10.45	10.38	10.31	
13	10.50	10.43	10.36	10.29	10.22	10.15	10.08	
14	10.27	10.20	10.13	10.06	10.00	9.93	9.86	
15	10.05	9.98	9.92	9.85	9.78	9.71	9.65	
16	9.83	9.76	9.70	9.63	9.57	9.50	9.43	
17	9.63	9.57	9.50	9.44	9.37	9.31	9.24	
18	9.43	9.37	9.30	9.24	9.18	9.11	9.05	
19	9.24	9.18	9.12	9.05	8.99	8.93	8.87	
20	9.06	9.00	8.94	8.88	8.82	8.75	8.69	
21	8.88	8.82	8.76	8.70	8.64	8.58	8.52	
22	8.71	8.65	8.59	8.53	8.47	8.42	8.36	
23	8.55	8.49	8.43	8.38	8.32	8.26	8.20	
24	8.39	8.33	8.28	8.22	8.16	8.11	8.05	
25	8.24	8.18	8.13	8.07	8.02	7.96	7.90	
26	8.09	8.03	7.98	7.92	7.87	7.81	7.76	
27	7.95	7.90	7.84	7.79	7.73	7.68	7.62	
28	7.81	7.76	7.70	7.65	7.60	7.54	7.49	
29	7.68	7.63	7.57	7.52	7.47	7.42	7.36	
30	7.55	7.50	7.45	7.39	7.34	7.29	7.24	
31	7.42	7.37	7.32	7.27	7.22	7.16	7.11	
32	7.30	7.25	7.20	7.15	7.10	7.05	7.00	
33	7.08	7.13	7.08	7.03	6.98	6.93	6.88	
34	7.07	7.02	6.97	6.92	6.87	6.82	6.78	
35	6.95	6.90	6.85	6.80	6.76	6.71	6.66	
36	6.84	6.79	6.76	6.70	6.65	6.60	6.55	
37	6.73	6.68	6.64	6.59	6.54	6.49	6.45	
38	6.63	6.58	6.54	6.49	6.44	6.40	6.35	
39	6.52	6.47	6.43	6.38	6.35	6.29	6.24	
40	6.42	6.37	6.33	6.28	6.24	6.19	6.15	
41	6.32	6.27	6.23	6.18	6.14	6.09	6.05	
42	6.22	6.18	6.13	6.09	6.04	6.00	5.95	
43	6.13	6.09	6.04	6.00	5.95	5.91	5.87	
44	6.03	5.99	5.94	5.90	5.86	5.81	5.77	
45	5.94	5.90	5.85	5.81	5.77	5.72	5.68	

(Continued)

Source: Draft EPA Handbook of Methods for Acid Deposition Studies, Field Operations for Surface Water Chemistry, EPA/600/4-89/020, August 1989.

Oxygen Solubility at Indicated Pressure (continued)

Temp.	Pressure (Hg)								
	725	720	715	710	705	700	695	690	mm
°C	28.54	28.35	28.15	27.95	27.76	27.56	27.36	27.17	in
0	13.89	13.80	13.70	13.61	13.51	13.41	13.32	13.22	mg/l
1	13.51	13.42	13.33	13.23	13.14	13.04	12.95	12.86	
2	13.15	13.06	12.07	12.88	12.79	12.69	12.60	12.51	
3	12.81	12.72	12.63	12.54	12.45	12.36	12.27	12.18	
4	12.47	12.39	12.30	12.21	12.13	12.04	11.95	11.87	
5	12.15	12.06	11.98	11.89	11.81	11.73	11.64	11.56	
6	11.84	11.73	11.68	11.60	11.51	11.43	11.35	11.27	
7	11.55	11.47	11.39	11.31	11.22	11.14	11.06	10.98	
8	11.26	11.18	11.10	11.02	10.95	10.87	10.79	10.71	
9	10.99	10.92	10.84	10.76	10.69	10.61	10.53	10.46	
10	10.74	10.66	10.59	10.51	10.44	10.36	10.29	10.21	
11	10.48	10.40	10.33	10.28	10.18	10.11	10.04	9.96	
12	10.24	10.17	10.10	10.02	9.95	9.88	9.81	9.46	
13	10.01	9.94	9.87	9.80	9.73	9.66	9.59	9.52	
14	9.79	9.72	9.65	9.68	9.51	9.45	9.38	9.31	
15	9.58	9.51	9.44	9.58	9.31	9.24	9.18	9.11	
16	9.37	9.30	9.24	9.17	9.11	9.04	8.97	8.91	
17	9.18	9.11	9.05	8.98	8.92	8.85	8.79	8.73	
18	8.99	8.92	8.86	8.80	8.73	8.67	8.61	8.54	
19	8.81	8.74	8.68	8.62	8.56	8.49	8.43	8.37	
20	8.63	8.57	8.51	8.45	8.39	8.33	8.27	8.21	
21	8.46	8.40	8.34	8.28	8.22	8.16	8.10	8.04	
22	8.30	8.24	8.18	8.12	8.06	8.00	7.95	7.89	
23	8.15	8.09	8.03	7.97	7.91	7.86	7.80	7.74	
24	7.99	7.94	7.88	7.82	7.76	7.71	7.65	7.59	
25	7.85	7.79	7.74	7.68	7.60	7.57	7.51	7.46	
26	7.70	7.65	7.59	7.54	7.48	7.43	7.37	7.32	
27	7.57	7.52	7.46	7.41	7.35	7.30	7.25	7.19	
28	7.44	7.38	7.33	7.28	7.22	7.17	7.12	7.06	
29	7.31	7.26	7.21	7.15	7.10	7.05	7.00	6.94	
30	7.19	7.14	7.08	7.03	6.98	6.93	6.88	6.82	
31	7.06	7.01	6.96	6.91	6.86	6.81	6.76	6.70	
32	6.95	6.90	6.85	6.80	6.70	6.70	6.64	6.59	
33	6.83	6.78	6.73	6.68	6.83	6.58	6.53	6.48	
34	6.73	6.68	6.63	6.58	6.53	6.48	6.43	6.38	
35	6.61	6.56	6.51	6.47	6.42	6.37	6.36	6.27	
36	6.51	6.46	6.41	6.36	6.31	6.27	6.22	6.17	
37	6.40	6.35	6.31	6.26	6.21	6.16	6.12	6.07	
38	6.30	6.26	6.21	6.16	6.12	6.07	6.02	5.98	
39	6.26	6.15	6.11	6.06	6.01	5.97	5.92	5.87	
40	6.10	6.06	6.01	5.96	5.92	5.86	5.83	5.78	
41	6.00	5.96	5.91	5.87	5.82	5.78	5.73	5.69	
42	5.91	5.86	5.82	5.77	5.73	5.69	5.64	5.60	
43	5.82	5.78	5.73	5.69	5.65	5.60	5.56	5.51	
44	5.72	5.68	5.64	5.59	5.55	5.51	5.46	5.42	
45	5.64	5.59	5.55	5.51	5.47	5.42	5.38	5.34	

Source: Draft EPA Handbook of Methods for Acid Deposition Studies, Field Operations for Surface Water Chemistry, EPA/600/4-89/020, August 1989.

Title: **Calibration of Field Instruments for Water Quality Parameters**	Procedure Number: **024**
Supersedes:	Revision Number: **0**
Reason for Revision:	Effective Date: **December 2003**

Authorization Signatures

Author	Date	Technical Review	Date	Quality Assurance Review	Date
Sandy Weymouth	12/8/03	Adam Balogh	12/8/03	Elizabeth Denly	12/8/03

TABLE OF CONTENTS

Page No.

1.0 INTRODUCTION 3
- 1.1 *Scope & Applicability* 3
- 1.2 *Summary of Method* 3
- 1.3 *Equipment* 3
- 1.4 *Definitions* 4
- 1.5 *Health & Safety Warnings* 5
- 1.6 *Cautions & Potential Problems* 5
- 1.7 *Personnel Qualifications* 5

2.0 PROCEDURES 6
- 2.1 *Temperature* 6
- 2.2 *Dissolved Oxygen* 7
- 2.3 *pH (electrometric)* 8
- 2.4 *Specific Conductance* 9
- 2.5 *Oxidation-Reduction Potential (ORP)* 10
- 2.6 *Turbidity* 10

3.0 DATA MANAGEMENT AND RECORDS MANAGEMENT 11

4.0 REFERENCES 11

LIST OF ATTACHMENTS

Attachment A Dissolved Oxygen Calibration Values for Various Atmospheric Pressures and Altitudes 13
Attachment B Oxygen Solubility at Indicated Pressure 14
Attachment C Zobell Temperature Correction Chart 16
Attachment D TRC Field Instrument Calibration Log 17

1.0 INTRODUCTION

1.1 Scope & Applicability

The purpose of this standard operating procedure (SOP) is to provide a framework for calibrating field instruments used to measure water quality parameters for ground water and surface water. Water quality instruments addressed in this SOP include those that measure temperature, pH, dissolved oxygen (DO), conductivity/specific conductance, oxidation-reduction potential (ORP), and turbidity.

This SOP is written for instruments that utilize multiple probes for temperature, pH, DO, conductivity/specific conductance, ORP, and turbidity. This SOP refers to instrumentation and outlines calibration procedures consistent with those discussed in USEPA Region I Standard Operating Procedure, *Draft Calibration of Field Instruments*, dated June 3, 1998.

For ground water monitoring during well development and/or purging prior to sample collection, the multiple probe instrument must be equipped with a flow-through cell, and the display/logger or computer display screen should be large enough to simultaneously display the readouts of each probe in the instrument. Turbidity is measured using a separate instrument because turbidity cannot be measured accurately in a flow-through cell.

1.2 Summary of Method

All monitoring instruments must be calibrated before they are used to measure environmental samples.

Most instruments will require at least two standards to bracket the expected measurement range, one standard less than the expected value and one higher. At a minimum, calibration must be performed at the beginning of each sampling day prior to sample collection. Site-specific plans should be consulted for required calibration frequency. Note: Part of the instrument preparation and initial calibration is performed prior to the field event.

This SOP requires that the manufacturer's instruction manual (including the instrument specifications) accompany the instrument into the field.

1.3 Equipment

The following equipment should be used when calibrating water quality parameter measuring equipment. Site-specific conditions may warrant the use of additional items or deletion of items from this list.

- Appropriate level of personal protection
- Water quality meter capable of measuring pH, temperature, dissolved oxygen, specific conductivity, and oxidation-reduction potential (e.g., YSI 600XL, or equivalent)
- Turbidity Meter (e.g., LaMotte 2020, or equivalent)
- Distilled water
- Deionized water

- Flow-through cell
- Ring stand with clamp
- Paper towels
- Soft tissue (e.g., Kimwipes)
- Cuvette
- pH buffer solutions (4,7,10 SU)
- Conductivity solution (100, 1000 µmhos)
- Zobell solution
- Turbidity standards (0,5,20 NTU)
- Zero DO solution (0.0 mg/L)
- DO membrane kit (electrolyte solution, membranes)
- NIST thermometer (0.01°C accuracy)
- Small glass or polyethylene jars to hold the calibration standards (4-8 oz.)
- Calibration Logbook
- Field Instrument Calibration Logs
- Cup or spray bottle for the distilled water

1.4 Definitions

SOP	Standard Operating Procedure
pH	Potential of Hydrogen
ORP	Oxidation-Reduction Potential
NIST	National Institute of Standards and Technology
C	Celsius
mg	Milligram
L	Liter
DO	Dissolved Oxygen
mm	Millimeter
NTU	Nephelometric Turbidity Unit
PPE	Personal Protective Equipment
Sonde	Device that holds the measuring probes
SU	Standard Units
µg	Microgram

1.5 Health & Safety Warnings

TRC employees will be on site when implementing this SOP. Therefore, TRC personnel shall follow the site-specific Health & Safety Plan. TRC personnel will use the appropriate level of PPE, which includes (at a minimum) the following: 1) hardhat; 2) safety boots (steel toe/steel shank); 3) safety glasses; and 4) chemical-resistant gloves.

Implementing this SOP will require the use of calibration solutions. The following health and safety precautions must be taken with the pH, conductivity, and ORP solutions: Avoid inhalation, skin and eye contact to ingestion.

Maintenance of the instruments will require the use of liquid cleaners. Although these substances are not hazardous materials, TRC will appropriately handle and store them at all times in accordance with manufacturer's instructions.

1.6 Cautions & Potential Problems

- Prior to calibration, all instrument probes must be cleaned according to the manufacturer's instructions. Failure to perform this step (proper maintenance) can lead to erroneous measurements.
- Prior to using calibration standards, check all expiration dates.
- Use a ring stand and clamp to secure the sonde in an upright position. This will prevent the sonde from falling over and damaging the probes.
- The volume of the calibration solutions must be sufficient to cover both the probe being calibrated and the temperature sensor (see manufacturer's instructions for additional information).
- While calibrating or performing sample measurements, make sure there are no air bubbles lodged between the probe and the probe guard.
- DO content in water is measured using a membrane electrode. The DO probe's membrane and electrolyte solution should be replaced prior to the sampling period. Failure to perform this step may lead to erratic and or erroneous measurements. If the probe reading shows the error message, "value out of range", the instrument probe must be recalibrated.

1.7 Personnel Qualifications

Since this SOP will be implemented at sites or in work areas that entail potential exposure to toxic chemicals or hazardous environments, all TRC personnel must be adequately trained. Before implementing this SOP alone, TRC personnel must be trained in these procedures by a senior staff member with experience operating the equipment. In addition, all personnel utilizing this SOP must have completed the following:

- 40-hour OSHA training
- 8-hour annual refresher training
- On-site training

In addition to the 40-hour initial OSHA training (and annual 8-hour refresher training), all TRC field staff will complete 24 hours of supervised field experience that contribute toward the 24-hour field supervised requirement in compliance with OSHA regulation: 29 CFR 1910.120(e)(4).

2.0 PROCEDURES

The probe readings for pH, dissolved oxygen, and specific conductance are automatically corrected for temperature by the instrument. Communications to the instrument (programming and displaying the measurement files) are performed using a display/logger or a computer. Information sent to the instrument is entered through the keypad on the display/logger or computer. It is desirable that the display/logger or computer have data storage capabilities. If the instrument does not have a keypad, follow the manufacturer's instructions for entering information into the instrument.

- Program the multi-probe instrument so that the following parameters to be measured will be displayed: temperature, pH, percent dissolved oxygen, mg/L dissolved oxygen, conductivity, specific conductance, and ORP. Refer to Attachment D for correct units.

For instrument probes that rely on the temperature sensor (pH, DO, conductivity/specific conductance, and ORP), each temperature sensor needs to be checked for accuracy against a thermometer that is traceable to the National Institute of Standards and Technology (NIST). Before any instrument is calibrated or used to perform environmental measurements, the instrument must stabilize (warm-up) according to manufacturer's instructions.

2.1 *Temperature*

Most instrument manuals state that calibration of the temperature sensor is not required, but this SOP requires that the temperature sensor be checked to verify its accuracy. This accuracy check is performed at least once per year and the accuracy check date/information is kept with the instrument. If the accuracy check date/information is not included with the instrument or the last check was performed over a year prior to the date of use, it is recommended that the temperature sensor accuracy be checked at the beginning of the sampling event. If the instrument contains multiple temperature sensors, each sensor must be checked.

VERIFICATION PROCEDURE

1. Allow a container filled with water to equilibrate to ambient temperature.

2. Place a NIST-traceable thermometer and the instrument's temperature sensor into the water and wait approximately five minutes for both temperature readings to stabilize.

3. Compare the two measurements. The instrument's temperature sensor must agree with the NIST-traceable thermometer measurement within the accuracy of the sensor (usually $\pm$0.15°C). If the measurements do not agree, the instrument may not be working properly and the manufacturer needs to be consulted.

2.2 *Dissolved Oxygen*

DO is the volume of oxygen that is dissolved in water and is measured using a membrane electrode. The DO probe's membrane and electrolyte solution should be replaced prior to the sampling period. Failure to perform this step may lead to erratic or erroneous measurements.

CALIBRATION PROCEDURE

1. Gently dry the temperature sensor according to manufacturer's instructions.

2. Place a wet sponge or a wet paper towel on the bottom of the DO calibration container that comes with the instrument.

3. Place the DO probe in the container without the probe coming in contact with the wet sponge or paper towel. The probe must fit loosely in the container to ensure it is vented to the atmosphere.

4. Allow the confined air to become saturated with water vapor (saturation occurs in approximately 10 to 15 minutes). During this time, turn-on the instrument to allow the DO probe to warm-up. Select monitoring/run mode. Check temperature readings. Readings must stabilize before continuing to the next step.

5. Select calibration mode; then select "DO%".

6. Enter the local barometric pressure (usually in mm of mercury) for the sampling location into the instrument. This measurement can be determined from an on-site barometer. Do not use barometric pressure obtained from the local weather services unless the pressure is corrected for the elevation of the sampling location and unless this is the only source of barometric data. [**Note:** inches of mercury times 25.4 mm/inch mercury equals mm of mercury].

7. The instrument should indicate that the calibration is in progress. After calibration, the instrument should display percent saturated DO. Check the reading against the Temperature/Atmospheric Pressure table in Attachment A. For example, if the barometric pressure is 752 mm Hg at an elevation of 278 feet, the percent saturation value after calibration should be 99%.

8. While the probe is still in the calibration cup, select monitoring/run mode. Compare the DO mg/L reading to the Oxygen Solubility at Indicated Pressure chart in Attachment B. For example, if the barometric pressure is 750 mm Hg and the temperature inside the calibration cup is 20°C, the DO mg/L reading should be 8.94 mg/L. If they do not agree to the accuracy of the instrument (usually $\pm$ 0.2 mg/L), repeat calibration. If this does not work, change the membrane and electrolyte solution and repeat calibration.

9. Remove the probe from the container, rinse it with distilled water, pat it dry with a towel, and place it into a 0.0 mg/L DO Standard. The standard must be filled to the top of its container and the DO probe must fit tightly into the standard's container (no headspace). Check temperature readings. They must stabilize before continuing.

10. Wait until the "mg/L DO" readings have stabilized. The instrument should read < 0.5 mg/L or to the accuracy of the instrument (usually $\pm$ 0.2 mg/L) within 30 seconds. If the

instrument cannot reach this value, it will be necessary to clean the probe, and change the membrane and electrolyte solution. If this does not work, prepare a new 0.0 mg/L standard. If these measures do not work, contact the manufacturer.

2.3 *pH (electrometric)*

The pH is the measure of the degree of the acidity or alkalinity of a solution as measured on a scale of 0 to 14. The pH of a sample is determined electrometrically using a glass electrode. All pH measurements are in standard units (SU).

Choose the appropriate buffered standards that will bracket the expected values at the sampling locations. For ground water, the pH will usually be close to seven. Three standards are needed for the calibration: one close to seven, one at least two pH units below seven and the other at least two pH units above seven. For those instruments that will not accept three standards, the instrument will need to be re-calibrated if the water sample's pH is outside the range defined by the two standards used in the initial calibration.

CALIBRATION PROCEDURE

1. Allow the buffered standards to equilibrate to the ambient temperature.

2. Fill calibration containers with the buffered standards so each standard will cover the pH probe and temperature sensor.

3. Remove the cover of the probe, rinse in a cup filled with distilled water or use a spray bottle, and blot dry with soft tissue.

4. Select monitoring/run mode. Immerse probe in the initial buffered standard (e.g., pH 7) and allow at least 1 minute for temperature equilibration before proceeding.

5. Enter the buffered standard value (7) into the pH calibration menu of the instrument. Allow the pH reading to stabilize for approximately 30 seconds and if the reading does not change, finish the calibration. The reading should remain within the manufacturer's specifications; if it changes, recalibrate. If readings continue to fluctuate or readings do not stabilize after recalibration, consult the manufacturer.

6. Remove probe from the initial buffered standard, rinse in a cup filled with distilled water or use a spray bottle, and blot dry with soft tissue.

7. Immerse probe into the second buffered standard (e.g., pH 4). Repeat step 5, substituting "4" into the pH calibration menu instead of "7".

8. Remove probe from the second buffered standard, rinse in a cup filled with distilled water or use a spray bottle, and blot dry with soft tissue. If the instrument only accepts two standards the calibration is complete. Proceed to step 11. Otherwise continue with step 9.

9. Immerse probe in third buffered standard (e.g., pH 10). Repeat step 5, substituting "10" into the pH calibration menu instead of "7".

10. Remove probe from the third buffered standard, rinse in a cup filled with distilled water or use a spray bottle, and blot dry with soft tissue.

11. Select monitoring/run mode, if not already selected. To ensure that the initial buffered calibration standard (e.g., pH 7) has not changed, immerse the probe into the initial standard. Wait for the reading to stabilize. The reading should read the initial standard value (e.g., 7) within the manufacturer's specifications. If not, re-calibrate the instrument. If re-calibration does not help, the calibration range may be too great. Reduce calibration range by using standards that are closer together.

2.4 *Specific Conductance*

Conductivity is used to measure the ability of an aqueous solution to conduct an electrical current. Specific conductance is the conductivity value corrected to 25°C. Calibrating an instrument for specific conductance automatically calibrates the instrument for conductivity, and vice-versa.

Most instruments are calibrated against a single standard which is near, but below the specific conductance of the environmental samples. A second standard which is above the environmental sample specific conductance is used to check the linearity of the instrument in the range of measurements.

CALIBRATION PROCEDURE

1. Allow the calibration standard to equilibrate to the ambient temperature.

2. Remove probe from its storage container, rinse the probe with a small amount of the conductivity/specific conductance standard (discard the rinsate), and place the probe into the conductivity/specific conductance standard. Gently move the probe up and down in the solution to remove any air bubbles from the sensor. Allow the probe to sit in the solution for at least 1 minute for temperature equilibration before proceeding.

3. Select calibration mode.

4. Select Specific Conductance from the Calibration menu. Enter the calibration value of the solution (mS/cm at 25°C) and continue. Allow the Specific Conductance reading to stabilize for approximately 30 seconds and finish the calibration. The reading should remain within manufacturer's specifications. If it does not, recalibrate. If readings continue to change after recalibration, consult the manufacturer.

5. Remove probe from the standard, rinse the probe with a small amount of the second conductivity/specific conductance standard (discard the rinsate), and place the probe into the second conductivity/specific conductance standard. The second standard will serve to verify the linearity of the instrument. Read the specific conductance value from the instrument and compare the value to the specific conductance on the standard. The two values should agree within the specifications of the instrument. If they do not agree, re-calibrate. If readings do not compare, then the second standard may be outside the linear range of the instrument. Use a standard that is closer, but above the first standard and repeat the verification. If values still do not compare, try cleaning the probe or consult the manufacturer.

NOTE: These procedures should only be used for instruments that are capable of automatically correcting specific conductance for temperature (to 25°C). For instruments that cannot calibrate for specific conductance, follow the procedures in the instrument's manual for conductivity calibration. If calibrating for conductivity instead of specific conductance, the solutions conductivity value must be corrected for the temperature that the sensor is reading.

2.5 *Oxidation-Reduction Potential (ORP)*

The oxidation-reduction potential is the electrometric difference measured in a solution between an inert indicator electrode and a suitable reference electrode. The electrometric difference is measured in millivolts and is temperature dependent.

CALIBRATION OR VERIFICATION PROCEDURE

1. Allow the calibration standard (a Zobell Solution) to equilibrate to ambient temperature.
2. Remove the cover of the probe and place it into the standard.
3. Select monitoring/run mode.
4. While stirring the standard, wait for the probe temperature to stabilize, and then read the temperature.
5. Look up the millivolt (mV) value at this temperature from the millivolt versus temperature correction table found in Attachment C. It may be necessary to interpolate millivolt values between temperatures. Select "calibration mode", then "ORP". Enter the temperature-corrected ORP value and calibrate the instrument.
6. Select monitoring/run mode. The reading should remain unchanged within manufacturer's specifications. If it changes, re-calibrate. If readings continue to change after calibration, consult manufacturer.
7. If the instrument instruction manual states the instrument is factory calibrated, then verify the factory calibration against the standard. If reading does not agree within the specification of the instrument, the instrument will need to be re-calibrated by the manufacturer.

2.6 *Turbidity*

Turbidity refers to how clear the water is and is a measure of relative sample clarity. The greater the amount of total suspended solids in the water, the higher the measured turbidity. The turbidity method is based upon a comparison of intensity of light scattered by a sample under defined conditions with the intensity of light scattered by a standard reference suspension. A turbidity meter is a nephelometer with a visible light source for illuminating the sample and one or more photo-electric detectors placed ninety degrees to the path of the light source.

Some instruments will only accept one standard. For these instruments, the standards will serve as check points.

CALIBRATION PROCEDURES

1. If the standard cuvette is not sealed, rinse a cuvette with deionized water. Shake the cuvette to remove as much water as possible. Do not wipe the inside of the cuvette because lint from the wipe may remain in the cuvette. Add the standard to the cuvette.

2. Before performing the calibration procedure, make sure the cuvettes are not scratched and the outside surfaces are dry, free from fingerprints and dust. If the cuvette is scratched or dirty, discard or clean the cuvette, respectively.

3. Zero the instrument by using either a zero or 0.02 NTU standard. A zero standard (approximately 0 NTU) can be prepared by passing distilled water through a 0.45 micron pore size membrane filter.

4. Using a standard at 1 NTU, calibrate according to manufacturer's instructions or verify calibration if instrument will not accept a second standard. If verifying, the instrument should read the standard value to within the specifications of the instrument. If the instrument has a range of scales, check each range that will be used during the sampling event with a standard that falls within that range.

5. Using a standard at 10 NTU, calibrate according to manufacturer's instruction or verify calibration if instrument does not accept a third standard. If verifying, the instrument should read the standard value to within the specifications of the instrument.

Note: If only performing a two-point calibration (depending on project requirements), the 0.02 NTU and 10 NTU standard should be used.

3.0 DATA MANAGEMENT AND RECORDS MANAGEMENT

Prior to calibrating, the field equipment and calibration standard information should be recorded in a field logbook or separate Field Instrument Calibration Log. For field equipment, the information recorded should include the make, model number and the serial number of the instrument. Each instrument can be assigned an identification number which can be referenced in future field notes or when filling out the Field Instrument Calibration Log. For calibration standards, the information recorded should include the manufacturer, expiration date, true value, and any other description such as lot number. Each calibration standard can also be assigned an identification number which can be referenced in future field notes or when filling out the Field Instrument Calibration Log. All standards should be initialed and dated when opened.

All calibration measurements must be documented in a field logbook or separate Field Instrument Calibration Log. An example calibration log is presented in Attachment D. At a minimum, the log must include the instrument information described above, calibration standard information described above, calibration date, and the instrument calibration results.

4.0 REFERENCES

USEPA Region I. *Standard Operating Procedure, Draft Calibration of Field Instruments,* June 3, 1998.

USEPA Region I. *Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples for Monitoring Wells,* July 30, 1996.

Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

ATTACHMENT A
DISSOLVED OXYGEN CALIBRATION VALUES FOR VARIOUS ATMOSPHERIC PRESSURES AND ALTITUDES

PRESSURE			ALTITUDE		CALIBRATION VALUE
Inches Hg	mm Hg	Millibars	Feet	Meters	Percent Saturation
30.23	768	1023	-276	-84	101
29.92	760	1013	0	0	100
29.61	752	1003	278	85	99
29.33	745	993	558	170	98
29.02	737	983	841	256	97
28.74	730	973	1126	343	96
28.43	722	963	1413	431	95
28.11	714	952	1703	519	94
27.83	707	942	1995	608	93
27.54	699	932	2290	698	92
27.24	692	922	2587	789	91
26.93	684	912	2887	880	90
26.61	676	902	3190	972	89
26.34	669	892	3496	1066	88
26.02	661	882	3804	1160	87
25.75	654	871	4115	1254	86
25.43	646	861	4430	1350	85
25.12	638	851	4747	1447	84
24.84	631	841	5067	1544	83
24.53	623	831	5391	1643	82
24.25	616	821	5717	1743	81
23.94	608	811	6047	1843	80
23.62	600	800	6381	1945	79
23.35	593	790	6717	2047	78
23.03	585	780	7058	2151	77
22.76	578	770	7401	2256	76
22.44	570	760	7749	2362	75
22.13	562	750	8100	2469	74
21.85	555	740	8455	2577	73
21.54	547	730	8815	2687	72
21.26	540	719	9178	2797	71
20.94	532	709	9545	2909	70
20.63	524	699	9917	3023	69
20.35	517	689	10293	3137	68
20.04	509	679	10673	3253	67
19.76	502	669	11058	3371	66

Table taken from EPA Region I SOP, Draft Calibration of Field Instruments, June 3, 1998.

ATTACHMENT B
OXYGEN SOLUBILITY AT INDICATED PRESSURE
(Page 1 of 2)

Oxygen Solubility at Indicated Pressure

Temp.	Pressure (Hg)							
	760	755	750	745	740	735	730	mm
°C	29.92	29.72	29.53	29.33	29.13	28.94	28.74	in
0	14.57	14.47	14.38	14.28	14.18	14.09	13.99	mg/l
1	14.17	14.08	13.98	13.89	13.79	13.70	13.61	
2	13.79	13.70	13.61	13.52	13.42	13.33	13.24	
3	13.43	13.34	13.25	13.16	13.07	12.98	12.90	
4	13.08	12.99	12.91	12.82	12.73	12.65	12.56	
5	12.74	12.66	12.57	12.49	12.40	12.32	12.23	
6	12.42	12.34	12.26	12.17	12.09	12.01	11.93	
7	12.11	12.03	11.95	11.87	11.79	11.71	[illegible]	
8	11.81	11.73	11.65	11.57	11.50	11.42	11.34	
9	11.53	11.45	11.38	11.30	11.22	[illegible]	11.07	
10	11.28	11.19	11.11	11.04	10.96	[illegible]	10.81	
11	10.99	10.92	10.84	10.77	10.70	[illegible]	[illegible]	
12	10.74	10.67	10.60	10.53	10.45	[illegible]	[illegible]	
13	10.50	10.43	10.36	10.29	10.22	[illegible]	[illegible]	
14	10.27	10.20	10.13	10.06	10.00	[illegible]	[illegible]	
15	10.05	9.98	9.92	9.85	9.78	[illegible]	9.65	
16	9.83	9.76	9.70	9.63	9.57	[illegible]	9.43	
17	9.63	9.57	9.50	9.44	[illegible]	[illegible]	9.24	
18	9.43	9.37	9.30	9.24	[illegible]	[illegible]	9.05	
19	9.24	9.18	9.12	9.05	8.99	[illegible]	[illegible]	
20	9.06	9.00	8.94	[illegible]	8.82	8.75	[illegible]	
21	8.88	8.82	8.76	[illegible]	8.64	8.58	[illegible]	
22	8.71	8.65	8.59	[illegible]	[illegible]	8.42	8.36	
23	8.55	8.49	8.43	[illegible]	[illegible]	8.26	8.20	
24	8.39	8.33	[illegible]	8.22	[illegible]	8.11	8.05	
25	8.24	8.18	[illegible]	8.07	[illegible]	[illegible]	7.90	
26	8.09	[illegible]	[illegible]	7.92	[illegible]	7.81	7.76	
27	[illegible]	[illegible]	[illegible]	7.78	[illegible]	7.68	7.62	
28	[illegible]	7.76	[illegible]	7.65	7.60	7.54	7.49	
29	[illegible]	7.63	[illegible]	[illegible]	7.47	7.42	7.36	
30	[illegible]	[illegible]	[illegible]	[illegible]	7.34	7.29	7.24	
31	[illegible]	[illegible]	7.32	[illegible]	7.22	7.16	7.11	
32	[illegible]	[illegible]	7.20	7.15	7.10	7.05	7.00	
[illegible]	7.08	[illegible]	[illegible]	7.04	6.98	6.93	6.88	
34	7.07	[illegible]	[illegible]	6.91	6.87	6.82	6.78	
35	6.95	[illegible]	6.85	6.80	6.76	6.71	6.66	
36	6.84	[illegible]	6.76	6.70	6.65	6.60	6.55	
37	6.73	[illegible]	6.64	6.59	6.54	6.49	6.45	
38	6.63	6.58	6.54	6.49	6.44	6.40	6.35	
39	6.53	6.47	6.43	6.38	6.35	6.29	6.24	
[illegible]	[illegible]	6.37	6.33	6.28	6.24	6.19	6.15	
[illegible]	6.32	6.27	6.23	6.18	6.14	6.09	6.05	
[illegible]	6.22	6.18	6.13	6.09	6.04	6.00	5.95	
43	6.13	6.09	6.04	6.00	5.95	5.91	5.87	
44	6.03	5.99	5.94	5.90	5.86	5.81	5.77	
45	5.94	5.90	5.85	5.81	5.77	5.72	5.68	

Table taken from EPA Region I SOP, Draft Calibration of Field Instruments, June 3, 1998.

ATTACHMENT B
OXYGEN SOLUBILITY AT INDICATED PRESSURE
(Page 2 of 2)

Oxygen Solubility at Indicated Pressure (continued)

Temp:	Pressure (Hg)								
	725	720	715	710	705	700	695	690	mm
°C	28.54	28.35	28.15	27.95	27.76	27.56	27.36	27.17	in
0	13.89	13.80	13.70	13.61	13.51	13.41	13.32	13.22	mg/l
1	13.51	13.42	13.33	13.23	13.14	13.04	12.95	12.86	
2	13.15	13.06	12.97	12.88	12.79	12.69	12.60	12.51	
3	12.81	12.72	12.63	12.54	12.45	12.36	12.27	12.18	
4	12.47	12.39	12.30	12.21	12.13	12.04	11.95	11.87	
5	12.15	12.06	11.98	11.89	11.81	11.73	11.64	11.56	
6	11.84	11.73	11.68	11.60	11.51	11.43	11.35	[illegible]	
7	11.55	11.47	11.39	11.31	11.22	11.14	[illegible]	[illegible]	
8	11.26	11.18	11.10	11.02	10.95	10.87	[illegible]	[illegible]	
9	10.99	10.92	10.84	10.76	10.69	10.61	10.53	[illegible]	
10	10.74	10.66	10.59	10.51	10.44	[illegible]	10.29	10.21	
11	10.48	10.40	10.33	10.28	10.18	[illegible]	10.04	9.96	
12	10.24	10.17	10.10	10.02	9.95	[illegible]	[illegible]	9.46	
13	10.01	9.94	9.87	9.80	9.73	9.66	[illegible]	9.52	
14	9.79	9.72	9.65	9.68	9.51	9.45	[illegible]	9.31	
15	9.58	9.51	9.45	9.58	9.31	9.24	[illegible]	[illegible]	
16	9.37	9.30	9.24	9.17	9.11	9.04	[illegible]	[illegible]	
17	9.18	9.11	9.05	8.98	8.92	[illegible]	8.79	[illegible]	
18	8.99	8.92	8.86	8.80	8.74	[illegible]	8.61	[illegible]	
19	8.81	8.74	8.68	8.62	[illegible]	[illegible]	8.43	[illegible]	
20	8.63	8.57	8.51	8.45	8.39	[illegible]	[illegible]	[illegible]	
21	8.46	8.40	8.34	8.28	8.22	8.16	[illegible]	8.04	
22	8.30	8.24	8.18	[illegible]	8.06	8.00	[illegible]	7.89	
23	8.15	8.09	8.03	7.97	[illegible]	7.86	7.80	7.74	
24	7.99	7.94	7.88	7.82	[illegible]	7.71	7.65	7.59	
25	7.85	7.79	[illegible]	7.68	[illegible]	[illegible]	7.51	7.46	
26	7.70	7.65	[illegible]	7.54	[illegible]	[illegible]	7.37	7.32	
27	7.57	7.52	[illegible]	7.41	[illegible]	7.30	7.25	7.19	
28	[illegible]	[illegible]	[illegible]	7.28	[illegible]	7.12	7.12	7.06	
29	[illegible]	7.26	[illegible]	7.15	7.10	7.05	7.00	6.94	
30	[illegible]	7.14	[illegible]	7.03	6.98	6.93	6.88	6.82	
31	[illegible]	[illegible]	6.9[illegible]	[illegible]	6.86	6.81	6.76	6.70	
32	[illegible]	[illegible]	6.85	[illegible]	6.70	6.70	6.64	6.59	
33	[illegible]	[illegible]	6.73	6.68	6.63	6.58	6.53	6.48	
34	6.73	[illegible]	[illegible]	6.58	6.53	6.48	6.43	6.38	
35	6.64	[illegible]	[illegible]	6.47	6.42	6.37	6.36	6.27	
36	6.51	[illegible]	6.41	6.36	6.31	6.27	6.22	6.17	
37	6.40	[illegible]	6.31	6.26	6.21	6.16	6.12	6.07	
38	6.30	[illegible]	6.21	6.16	6.12	6.01	6.02	5.98	
39	6.26	[illegible]	6.11	6.06	6.01	5.97	5.92	5.87	
40	6.10	6.06	6.01	5.96	5.92	5.86	5.83	5.78	
[illegible]	[illegible]	5.96	5.91	5.87	5.82	5.78	5.73	5.69	
[illegible]	5.91	5.86	5.82	5.27	5.73	5.69	5.64	5.60	
[illegible]	5.82	5.78	5.73	5.69	5.65	5.60	5.56	5.51	
44	5.72	5.68	5.64	5.59	5.55	5.51	5.46	5.42	
45	5.64	5.59	5.55	5.51	5.47	5.42	5.38	5.34	

Draft

Table taken from EPA Region I SOP, Draft Calibration of Field Instruments, June 3, 1998.

ATTACHMENT C
ZOBELL TEMPERATURE CORRECTION CHART
(ORP Calibration)

Zobell Temperature Correction Chart

Temperature (Celcius)	Corrected Zobell Reading (mV)
-5	270.0
-4	268.7
-3	267.4
-2	266.1
-1	264.8
0	263.5
1	262.2
2	260.9
3	259.6
4	258.3
5	257.0
6	255.7
7	254.4
8	253.1
9	251.8
10	250.5
11	249.2
12	247.9
13	246.6
14	245.3
15	244.0
16	242.7
17	241.4
18	240.1
19	238.8
20	237.5
21	236.2
22	234.9
23	233.6
24	232.3
25	231.0
26	229.7
27	228.4
28	227.1
29	225.8
30	224.5
31	223.2
32	221.9
33	220.6
34	219.3
35	218.0
36	216.7
37	215.4
38	214.1
39	212.8
40	211.5

Table taken from EPA Region I SOP, Draft Calibration of Field Instruments, June 3, 1998.

ATTACHMENT D
TRC FIELD INSTRUMENT CALIBRATION LOG

Water Quality Instrument ID _____
Turbidity Instrument ID _____
Date of Last Temperature Probe Check _____

Date _____

Site Name _____

Dissolved Oxygen (DO)

Time	Barometric Pressure (mmHg)	100% Saturation Calibration	Actual 100% Saturation Calibration (refer to table)	Oxygen Solubility at Indicated Pressure (mg/L)	Actual Oxygen Solubility at Indicated Pressure (mg/L) (refer to table)	Zero DO Check (mg/L)	Comments	Initials

pH

Time	pH 4	pH 7	pH 10	pH 4 Check	Comments	Initials

Specific Conductance

Time	Sp. Conductance Reading (umhos)	Comments	Initials

Oxidation Reduction Potential (ORP)

Time	Solution Temp (mV)	ORP Reading (mV)	Actual Reading (mV) (refer to table)	Comments	Initials

Turbidity

Time	Zero Standard	Standard #1 (___NTUs)	Standard #2 (___NTUs)	Comments	Initials

Calibration Fluid ID (refer to Calibration Logbook)
zero DO_____ Sp. Conductance_____ pH 4_____ pH 7_____ pH 10_____
ORP_____ Zero Turbidity_____ Turb. Standard #1_____ Turb. Standard #2_____

APPENDIX F:

MCP GROUNDWATER STANDARDS

Comparison Standards for Groundwater Samples -- 2010
Keith Middle School
New Bedford, Massachusetts

Analysis	CAS #	Analyte	MassDEP Method 1		
			GW-1	GW-2	GW-3
VOCs					
(ug/L)	67-64-1	Acetone	6,300	50,000	50,000
	994-05-8	tert-Amyl Methyl Ether (TAME)	NS	NS	NS
	71-43-2	Benzene	5	2,000	10,000
	108-86-1	Bromobenzene	NS	NS	NS
	74-97-5	Bromochloromethane	NS	NS	NS
	75-27-4	Bromodichloromethane	3	6	50,000
	75-25-2	Bromoform	4	700	50,000
	74-83-9	Bromomethane	10	7	800
	78-93-3	2-Butanone (MEK)	4,000	50,000	50,000
	104-51-8	n-Butylbenzene	200(1)	7,000(1)	50,000(1)
	135-98-8	sec-Butylbenzene	200(1)	7,000(1)	50,000(1)
	98-06-6	tert-Butylbenzene	200(1)	7,000(1)	50,000(1)
	637-92-3	tert-Butyl Ethyl Ether (TBEE)	NS	NS	NS
	75-15-0	Carbon Disulfide	NS	NS	NS
	56-23-5	Carbon Tetrachloride	5	2	5,000
	108-90-7	Chlorobenzene	100	200	1,000
	124-48-1	Chlorodibromomethane	2	20	50,000
	75-00-3	Chloroethane	NS	NS	NS
	67-66-3	Chloroform		50	20,000
	74-87-3	Chloromethane	NS	NS	NS
	95-49-8	2-Chlorotoluene	NS	NS	NS
	106-43-4	4-Chlorotoluene	NS	NS	NS
	96-12-8	1,2-Dibromo-3-chloropropane (DBCP)	NS	NS	NS
	106-93-4	1,2-Dibromoethane (EDB)	0.02	2	50,000
	74-95-3	Dibromomethane	NS	NS	NS
	95-50-1	1,2-Dichlorobenzene	600	2,000	2,000
	541-73-1	1,3-Dichlorobenzene	40	2,000	50,000
	106-46-7	1,4-Dichlorobenzene	5	200	8,000
	75-71-8	Dichlorodifluoromethane (Freon 12)	NS	NS	NS
	75-34-3	1,1-Dichloroethane	70	1,000	20,000
	107-06-2	1,2-Dichloroethane	5	5	20,000
	75-35-4	1,1-Dichloroethylene	7	80	30,000
	156-59-2	cis-1,2-Dichloroethylene	70	100	50,000
	156-60-5	trans-1,2-Dichloroethylene	100	90	50,000
	78-87-5	1,2-Dichloropropane	5	3	50,000
	142-28-9	1,3-Dichloropropane	NS	NS	NS
	594-20-7	2,2-Dichloropropane	NS	NS	NS
	563-58-6	1,1-Dichloropropene	NS	NS	NS
	10061-01-5	cis-1,3-Dichloropropene	0.4(2)	10(2)	200(2)
	10061-02-6	trans-1,3-Dichloropropene	0.4(2)	10(2)	200(2)
	60-29-7	Diethyl Ether	NS	NS	NS
	108-20-3	Diisopropyl Ether (DIPE)	NS	NS	NS
	123-91-1	1,4-Dioxane	3	6,000	50,000
	100-41-4	Ethylbenzene	700	20,000	5,000
	87-68-3	Hexachlorobutadiene	1	1	3,000
	591-78-6	2-Hexanone (MBK)	NS	NS	NS
	98-82-8	Isopropylbenzene (Cumene)	200(1)	7,000(1)	50,000(1)
	99-87-6	p-Isopropyltoluene (p-Cymene)	200(1)	7,000(1)	50,000(1)
	1634-04-4	Methyl tert-Butyl Ether (MTBE)	70	50,000	50,000
	75-09-2	Methylene Chloride	5	10,000	50,000
	108-10-1	4-Methyl-2-pentanone (MIBK)	350	50,000	50,000
	91-20-3	Naphthalene	140	1,000	20,000
	103-65-1	n-Propylbenzene	200(1)	7,000(1)	50,000(1)
	100-42-5	Styrene	100	100	6,000
	630-20-6	1,1,1,2-Tetrachloroethane	5	10	50,000
	79-34-5	1,1,2,2-Tetrachloroethane	2	9	50,000
	127-18-4	Tetrachloroethylene	5	50	30,000
	109-99-9	Tetrahydrofuran	NS	NS	NS

Comparison Standards for Groundwater Samples -- 2010
Keith Middle School
New Bedford, Massachusetts

Analysis	CAS #	Analyte	MassDEP Method 1		
			GW-1	GW-2	GW-3
	108-88-3	Toluene	1,000	50,000	40,000
	87-61-6	1,2,3-Trichlorobenzene	NS	NS	NS
	120-82-1	1,2,4-Trichlorobenzene	70	2,000	50,000
	71-55-6	1,1,1-Trichloroethane	200	4,000	20,000
	79-00-5	1,1,2-Trichloroethane	5	900	50,000
	79-01-6	Trichloroethylene	5	30	5,000
	75-69-4	Trichlorofluoromethane (Freon 11)	NS	NS	NS
	96-18-4	1,2,3-Trichloropropane	NS	NS	NS
	95-63-6	1,2,4-Trimethylbenzene	200(1)	7,000(1)	50,000(1)
	108-67-8	1,3,5-Trimethylbenzene	200(1)	7,000(1)	50,000(1)
	75-01-4	Vinyl Chloride	2	2	50,000
	106-42-3	m+p Xylene	10,000	9,000	5,000
	95-47-6	o-Xylene	10,000	9,000	5,000
PCBs					
(ug/L)	12674-11-2	Aroclor 1016	0.5	5	10
	11104-28-2	Aroclor 1221	0.5	5	10
	11141-16-5	Aroclor 1232	0.5	5	10
	53469-21-9	Aroclor 1242	0.5	5	10
	12672-29-6	Aroclor 1248	0.5	5	10
	11097-69-1	Aroclor 1254	0.5	5	10
	11096-82-5	Aroclor 1260	0.5	5	10
	1336-36-3	Total PCBs	0.5	5	10
Metals, dissolved					
(ug/L)	7440-36-0	Antimony	6	NS	8,000
	7440-38-2	Arsenic	10	NS	900
	7440-39-3	Barium	2,000	NS	50,000
	7440-41-7	Beryllium	4	NS	200
	7440-43-9	Cadmium	5	NS	4
	7440-47-3	Chromium	100	NS	300
	7439-92-1	Lead	15	NS	10
	7439-97-6	Mercury	2	NS	20
	7440-02-0	Nickel	100	NS	200
	7782-49-2	Selenium	50	NS	100
	7440-22-4	Silver	100	NS	7
	7440-28-0	Thallium	2	NS	3,000
	7440-62-2	Vanadium	30	NS	4,000
	7440-66-6	Zinc	5,000	NS	900
Metals, total					
(ug/L)	7440-36-0	Antimony	6	NS	8,000
	7440-38-2	Arsenic	10	NS	900
	7440-39-3	Barium	2,000	NS	50,000
	7440-41-7	Beryllium	4	NS	200
	7440-43-9	Cadmium	5	NS	4
	7440-47-3	Chromium	100	NS	300
	7439-92-1	Lead	15	NS	10
	7439-97-6	Mercury	2	NS	20
	7440-02-0	Nickel	100	NS	200
	7782-49-2	Selenium	50	NS	100
	7440-22-4	Silver	100	NS	7
	7440-28-0	Thallium	2	NS	3,000
	7440-62-2	Vanadium	30	NS	4,000
	7440-66-6	Zinc	5,000	NS	900

Notes:

ug/L - micrograms per liter.

VOCs - Volatile Organic Compounds.

(1) - MassDEP Method 1 standards for C9-C10 aromatic hydrocarbons used.

(2) - MassDEP Method 1 standards for 1,3-Dichloropropene used.

APPENDIX G:

INSPECTION FORMS

CAP INSPECTION FORM
KEITH MIDDLE SCHOOL

Use this inspection form to document cap inspections. If unacceptable conditions are observed, complete an additional form immediately after repairs are completed.

Inspection Date: Inspection by:

A. ASPHALT AND CONCRETE PAVING – observe asphalt and concrete paving for cracking, holes, asphalt removed during construction, other damage.

All Asphalt and concrete paving acceptable? ☐ YES ☐ NO

If no, attach photograph ☐

If no, describe unacceptable condition:

Location

Condition

Describe any repairs to asphalt and/or concrete paving conducted since previous inspection

All repairs adequate ☐ YES ☐ NO Photograph of repair attached ☐

B. INTERIOR CONCRETE FLOORS – observe concrete for cracking, holes, concrete removed during construction, other damage.

All interior concrete floors acceptable? ☐ YES ☐ NO

If no, attach photograph ☐

If no, describe unacceptable condition:

Location

Condition

Describe any repairs to interior concrete floors conducted since previous inspection

All repairs adequate ☐ YES ☐ NO Photograph of repair attached ☐

C. LANDSCAPING – observe landscaping for erosion animal holes, excavation, erosion control vegetation health.

All landscaped areas acceptable? ☐ YES ☐ NO

If no, attach photograph ☐

If no, describe unacceptable condition:

Location:

Condition:

Describe any repairs to landscaping since previous inspection:

All repairs adequate ☐ YES ☐ NO Photograph of repair attached ☐

D. Areas Not Inspected:

Reason:

Additional Notes: None

APPENDIX H:

SEDIMENT SAMPLING PROTOCOL

SEDIMENT SAMPLING PLAN
Keith Middle School

Samples will be collected from a depth of 0-6 inches below grade.

Sampling Analyses:

- PCB – Method 8082 (and 680 – if required)

Sample Jars required per location:

- 1 (8 oz.) **Packed Full** – Decant All Standing Water

Method Detection Limits (MDL): **These Must be Written on each Chain of Custody**

- PCB MDL = 10 ppb per Aroclor

Sample Analysis Turnaround Time (TT):

- For analyses – 5 to 7 day turnaround time (Write This on the Chain of Custody)
- Specify a **Due Date and Time** on the Chain of Custody

Tools required:

- Sampling barrel (2 foot lengths)
- Sample sleeves (2 foot lengths)
- Plastic end caps for sleeves
- Rods
- Slam bar
- Sledge hammer
- Back out cap (to use at top of rod upon completion of sample advancement)
- Needle nose pliers

Other Materials Required:

- Sampling Plan – multiple copies in case one gets wet
- Hip waders
- Sampling jars
- Chains-of-Custody (COC) – Filling out the "TESTS" header and "Remarks" sections ahead of time is recommended
- Sample Labels

Sampling Procedure:

- Remove leaf litter

- Next, use the hand tools and collect sediment from 0-6 inches below grade. Collect enough material to fill one (1) 8-oz jar.
- Use a new sampling sleeve per location
- **DO NOT REUSE ANY SLEEVE** (in the case of a refusal at location "A", do not use the sleeve at any other location than "A".
- Advance the barrel **from 0-6 inches** into the sediment
- Cap both ends of the sample sleeve
- Using permanent ink (Sharpie), write the sample ID on the sleeve (prior to collecting sample)
- Let sampling sleeves stand in an upright position for a period of time to aid in decanting
- Take sample sleeves back to the site
- ID all sample jars prior to filling of each sample
- Write ID on COC and specify particular analyses
- Fill sample jars with as much material as possible and place in a cooler with ice
- Use a new pair of sampling gloves for each sample.

APPENDIX I:

LETTER TO EPA RECOMMENDING CHANGES TO THE LTMMIP

Wannalancit Mills
650 Suffolk Street
Lowell, MA 01854

978.970.5600 PHONE
978.453.1995 FAX

www.TRCsolutions.com

TRC Project No. 115058

March 24, 2009

Kimberly N. Tisa
United States Environmental Protection Agency
One Congress Street
Suite 1100 – CPT
Boston, Massachusetts 02114-2023

RE: Recommended Changes
Long-Term Monitoring and Maintenance Implementation Plan (LTMMIP)
Keith Middle School (KMS) Site, New Bedford, Massachusetts

Dear Ms. Tisa:

TRC has prepared this letter to summarize recommended changes to the Long-Term Monitoring and Maintenance Implementation Plan (LTMMIP) for the above-referenced Keith Middle School (KMS) site. The LTMMIP sets forth requirements for the long-term monitoring and maintenance of the exposure management barrier, groundwater, wetland sediment, vent gas and indoor air quality of the KMS site. The LTMMIP also provides a description of the maintenance activities to be performed at the KMS site and related precautions to prevent exposure to the impacted fill layer located beneath the exposure management barrier.

TRC's use of the LTMMIP for monitoring and maintenance activities thus far through 2007 and 2008 has revealed a number of inconsistencies and technical errors that should be corrected to facilitate implementation of an effective LTMMIP. In addition, TRC has identified some activities that could be modified, reduced, or eliminated to decrease operation and maintenance costs for the KMS site and streamline monitoring and maintenance procedures while still providing useful data and effectively monitoring the protectiveness of the remedy. This letter and associated table summarize the recommended changes to the LTMMIP. Following your review and concurrence, TRC will prepare a revised LTMMIP for your review/approval.

INTRODUCTION

TRC assembled a panel of in-house technical specialists (e.g., chemists, air monitoring specialists, cap engineers, and risk assessor) to perform a comprehensive review of the LTMMIP. Members of the panel have also worked under the LTMMIP requirements. Our specialists have identified

areas in the LTMMIP where technical correction is warranted and have also identified suggested modifications to help streamline implementation and reduce monitoring costs.

RECOMMENDED CHANGES TO THE LTMMIP

The findings of the comprehensive technical review and the recommendations of the technical specialists are presented in Table 1, which summarizes the current LTMMIP element recommended to be changed or modified, the recommended change, and rationale/benefit of the change. The recommendations address technical deficiencies or suggest technical improvements, and where appropriate, potential cost savings. The recommended changes affect indoor air monitoring, groundwater monitoring, foundation vent air monitoring, wetland inspection and monitoring, and long-term cap monitoring.

With regard to cost savings, those recommended changes in Table 1 that have a significant cost impact are also summarized below. Please see Table 1 for additional details regarding the rationale/benefit of the recommended changes.

<u>LTMMIP Section 2 – Indoor Air Monitoring</u>

- **Indoor air sampling frequency for Volatile Organic Compounds (VOCs) –** Stop sampling of VOCs in indoor air at KMS. VOCs are not the principal contaminants of the soil/fill underlying the cap posing potential risk to building occupants. Eliminating VOC sampling for indoor air will save approximately $4,300 in annual laboratory expenses.

- **Indoor air sampling frequency for PCBs –** Reduce the frequency of sampling of PCBs to two events per year. Based on the eight rounds of indoor air monitoring conducted by TRC and six rounds conducted by the prior consultant, the remedy implemented for the KMS site has been shown to be protective of potential airborne PCB exposures associated with the capped PCB contamination. Reducing PCB indoor air sampling to two rounds per year will save approximately $34,000 in contractor labor and expense annually (assuming VOC and vent stack sampling is also reduced to the same frequency).

- **Analytical parameters –** Specify PCB air analysis by the homologue method (EPA Method 680) rather than congeners and Aroclors since it provides reliable total PCB quantification (upon which the site-specific risk-based comparison criteria are based) and the data are comparable to the air data gathered at New Bedford High School (NBHS), facilitating public communication. In addition, the Aroclor approach to the analysis of PCBs in air is not a suitable characterization methodology since PCBs do not vaporize as pure technical mixtures, whereas the homologue measurement approach is not impacted by this potentially significant source of measurement error. This change in PCB sampling for indoor air saves approximately $4,500 in annual laboratory expenses (based on the three rounds of sampling currently specified in the LTMMIP).

- **PCB sample media analysis –** Extract the quartz pre-filter and adsorbent (PUF) together per Method TO-4A, rather than separately as currently required by the LTMMIP. Separate analysis of the filter and PUF does not yield useful information about the physical state of the PCBs at the time of sampling due to evaporative losses of the analyte from the filter during sampling (as stated in the method). Eliminating this requirement would reduce analytical

laboratory costs for PCB indoor air monitoring by nearly $10,200 per year (based on the three rounds of sampling currently specified in the LTMMIP).

LTMMIP Section 3 – Groundwater Monitoring

- **Groundwater monitoring analytes –** Eliminate the requirement for VOC sampling and analysis for KMS groundwater, which is not a contaminant of concern. Limit monitoring to PCBs and metals. Eliminating the VOC analysis from the groundwater monitoring program saves approximately $1,000 in annual laboratory expenses (based on the two rounds of sampling currently specified in the LTMMIP).

LTMMIP Section 4 – Foundation Vent Stack Air Monitoring

- **Vent stack air sampling frequency for VOCs and PCBs –** Reduce the frequency of sampling of PCBs to two events per year and eliminate VOC sampling. Based on the eight rounds of vent stack air monitoring conducted by TRC and six rounds conducted by the prior consultant, the subslab venting system installed for the KMS building has been shown to effectively mitigate the migration of subsurface VOCs and PCBs into indoor air. This change will save approximately $34,000 in contractor labor and expense annually (assuming indoor air sampling is also reduced to the same frequency).

- **Background sampling –** Using the indoor air background sample (flag pole location) as a background sample for both indoor air and vent stack air sampling (VOCs and PCBs) saves approximately $2,100 of annual laboratory expenses (based on three rounds of sampling).

- **Analytical parameters –** Specify PCB air analysis by the homologue method (EPA Method 680) rather than congeners and Aroclors since it provides reliable total PCB quantification (upon which the site-specific risk-based comparison criteria are based) and the data are comparable to the air data gathered at NBHS, facilitating public communication. In addition, the Aroclor approach to the analysis of PCBs in air is not a suitable characterization methodology since PCBs do not vaporize as pure technical mixtures. The change in PCB sampling for vent stack air monitoring saves approximately $5,200 in annual laboratory expenses (based on three rounds of sampling).

LTMMIP Section 7 – Long-Term Cap Monitoring Plan

- **Cap inspections** – Schedule cap inspections for twice per year (spring and early fall). The change in inspection frequency saves approximately $3,000 in consultant labor and expense (assuming no need for follow-up inspections per the LTMMIP).

CONCLUSIONS

Once the recommended revisions to the LTMMIP described above and summarized in Table 1 have been agreed upon, a draft LTMMIP revision will be prepared for your regulatory review and approval. The revision will reflect the agreed-upon changes to the LTMMIP and will also provide more appropriate response actions and response action schedules that reflect the current comprehensive understanding of human health risk, sources, and air measurement data collected to

date. The draft revised LTMMIP will be provided to EPA for review and comment before implementation. Comments received by EPA will be incorporated, as warranted, into the revised LTMMIP.

Please call or write if you have any questions or comments.

Sincerely,

David M. Sullivan, LSP, CHMM
Sr. Project Manager

Attachment (Table 1)

cc: D. Fredette, S. Alfonse – City of New Bedford

Table 1 – Recommended Changes to LTMMIP
Keith Middle School Site, New Bedford, Massachusetts

Comment Number	Current LTMMIP Element	Recommended Change*	Rationale/Benefit
Section 2 – Indoor Air Monitoring			
1.	**Indoor air sampling frequency for VOCs –** The LTMMIP (Section 2.1) currently calls for sampling of indoor air with a minimum frequency of three times per year for VOCs. However, the LTMMIP also states that, after the collection of one complete year of data, a request may be submitted to EPA to reduce the indoor air sampling frequency.	Eliminate the VOC sampling requirement.	VOCs are not the principal contaminant of the soil/fill underlying the cap. In addition, the indoor air and vent stack air monitoring events conducted to date have demonstrated the protectiveness and functionality of the passive ventilation system. VOCs detected to date in indoor air at KMS are associated with off-gassing from building materials, shown to be trending downward over time, or are associated with cleaning materials, solvents, paints, and equipment used in the day-to-day maintenance of the building. ***Eliminating VOC sampling for indoor air will save approximately $4,300 in annual laboratory expenses.***
2.	**Indoor air sampling frequency for PCBs –** The LTMMIP (Section 2.1) currently calls for sampling of indoor air with a minimum frequency of three times per year for PCBs. However, the LTMMIP also states that, after the collection of one complete year of data, a request may be submitted to EPA to reduce the indoor air sampling frequency.	Reduce the frequency of sampling of PCBs to twice per year. Review frequency of monitoring again after 2 years.	Based on the eight rounds of indoor air monitoring conducted by TRC and six rounds conducted by the prior consultant, the remedy implemented for the KMS site has been shown to be protective of potential airborne PCB exposures associated with the capped PCB contamination. The proposed reduced frequency to twice per year will be sufficient to demonstrate protectiveness in the foreseeable future. Sampling would be conducted during July/August and December. Sampling during the July/August period will help evaluate PCB indoor air concentrations during warm weather conditions, when the school is experiencing lower than normal air exchanges and at temperatures favorable to increased PCB volatilization to demonstrate protectiveness based on site-specific "worst-case" conditions prior to the start of the new school year. (Based on 14 rounds of indoor air sampling at KMS, the highest concentration PCB detections in indoor air have been observed from June to September.) Sampling in December would monitor potential "worst-case" vapor intrusion conditions per MassDEP guidance. ***Reducing PCB sampling for indoor air to two events per year will save approximately $34000 in contractor labor and expense annually (assuming vent stack air sampling is also reduced to the same frequency).***
3.	**Indoor air sampling locations –** The LTMMIP (Section 2.2) currently states that one indoor air sample will be collected from the ground floor of each of the three school building sections (Sections A, B and C).	Allow the selection of the indoor air sample locations to be made at the discretion of the City.	This will allow the flexibility to sample particular areas of interest and the most appropriate exposure locations to provide information suitable for the risk evaluation without additional expense.

Table 1 – Recommended Changes to LTMMIP
Keith Middle School Site, New Bedford, Massachusetts

Comment Number	Current LTMMIP Element	Recommended Change*	Rationale/Benefit
4.	**Analytical parameters –** The LTMMIP (Section 2.3) calls for the analysis of air samples for PCBs according to EPA Method TO-4A for Aroclors (-1016, -1221, -1232, -1242, -1254, -1260, -1262, and -1268) and the 209 PCB congeners.	Specify PCB air analysis by the homologue method (EPA Method 680).	The homologue analytical method is a reliable analytical method to quantify total PCBs, which are also the basis for the risk-based Action Level (AL) and Acceptable Long-Term Average Exposure Concentration (ALTAEC) used to evaluate potential risk. In addition, by quantifying PCB homologues, total PCB air data gathered at the KMS are directly comparable to total PCB air data gathered at New Bedford High School (NBHS), greatly facilitating data comparison and risk communication to local citizens during Public Involvement Plan (PIP) meetings and related public communication regarding air monitoring. The bulk of PCBs detected in air at KMS and NBHS are associated with the vapor phase and PCBs do not vaporize as pure technical mixtures (i.e., they do not vaporize as Aroclor mixtures). Consequently, the Aroclor approach to analysis of PCBs in air is not a suitable characterization methodology at KMS. The homologue measurement approach is not impacted by this potentially significant source of error. ***This change in PCB sampling for indoor air saves approximately $4,500 in annual laboratory expenses (based on three rounds of sampling).***
5.	**PCB sample media analysis –** The LTMMIP (Section 2.3) currently requires analysis of the PUF cartridge and quartz pre-filter from high-volume sampling separately to differentiate between airborne particulate contamination captured on the pre-filter and vapor-phase contamination absorbed by the PUF.	Extract the quartz pre-filter and adsorbent (PUF) together per Method TO-4A, rather than separately as currently required by the LTMMIP.	EPA Method TO-4A notes that the filter and adsorbent are extracted together in order to reach detection limits and minimize cost, and to prevent misinterpretation of data. Separate analysis of the filter and PUF does not yield useful information about the physical state of the PCBs at the time of sampling due to evaporative losses of the analyte from the filter during sampling (Method TO-4A, Section 10.3.2 – Note). In addition, sufficient data have been collected and enough analysis of the data has been performed to evaluate any differentiation, however questionable, considering the above-stated EPA method stipulations. Eliminating this requirement would significantly reduce analytical laboratory costs for PCB indoor air monitoring. ***Eliminating the requirement to analyze the pre-filter separately would reduce analytical laboratory costs for PCB indoor air monitoring by nearly $10,200 per year (based on three rounds of PCB air sampling).***
6.	**PCB Action Levels –** Section 2.5.1 of the LTMMIP refers to an Action Level of 0.05 ug/m^3 and a Maximum Acceptable Level of 0.3 ug/m^3.	Replace the term "Maximum Acceptable Level" with the term "Acceptable Long-Term Average Exposure Concentration."	The term "Maximum Acceptable Level" is a misnomer; the concentration 0.3 $\mu g/m^3$ represents a long-term average concentration that corresponds to risk benchmarks established by the Massachusetts Department of Environmental Protection (MassDEP), assuming 25 years of daily work place exposure. TRC used BETA's "Maximum Acceptable Level" term during TRC's first PIP meeting (August 31, 2006) for consistency with prior presentations by BETA, but now refers to this concentration as the Acceptable Long-Term Average Exposure Concentration (ALTAEC). Short-term exposures at this concentration do not represent an immediate threat to health.

Table 1 – Recommended Changes to LTMMIP
Keith Middle School Site, New Bedford, Massachusetts

Comment Number	Current LTMMIP Element	Recommended Change*	Rationale/Benefit
7.	**Comparison Criteria for Indoor Air VOC Sample Results –** The LTMMIP (Section 2.5.2) currently requires that VOC results for each indoor air sample be evaluated by comparison to a combination of the contemporary outdoor air sample results and the 1995 MassDEP Threshold Effects Limits (TELs) and Allowable Ambient Limits (AALs) for ambient air. For VOCs lacking either a TEL or AAL, the LTMMIP charges the LSP-of-record with individual evaluation of the VOCs for human health risk to demonstrate a condition of No Significant Risk as defined in 310 CMR 40.0006.	Replace the use of TEL and AALs with a flexible approach to the selection and use of comparison criteria, given that changes do periodically occur in consensus standards/criteria as new technical data emerge meriting re-evaluation. For example, MassDEP recently solicited review comments on draft indoor air upper percentile values (UPVs), representative of air concentrations of VOCs in the absence of a site source, and indoor air threshold values which consider both typical VOC concentrations found indoors as well as risk-based air concentrations. In addition, EPA has developed risk-based screening values for indoor air in both residential and non-residential settings for a wide variety of VOCs.	The directives specified in the LTMMIP concerning VOC comparisons are not technically sound because TELs and AALs are toxicologically outdated (last updated in 1995) and comparison to ambient air criteria does not recognize the many and varied indoor sources of VOCs including paints, cleaning products, off-gassing from furniture and building materials, and indoor storage of VOC-containing products. There are more suitable and defensible values to use as comparison criteria for VOCs in indoor air. TRC recommends that the LTMMIP be revised to provide flexibility in the selection of the most appropriate manner in which to evaluate the indoor air VOC concentrations as long as VOC sampling and analysis is part of the KMS monitoring program. ***Note that eliminating VOC analysis as suggested under Comment Number 1 would eliminate the need for this change.***
8.	**Triggers for further analysis/evaluation of indoor air quality results –** The LTMMIP (Sections 2.5.1.1 and 2.5.2.1) currently specifies that if any indoor air sample result for PCBs or VOCs exceeds the PCB action level, TELs/AALs, or the VOC outdoor sample result by greater than 50-percent, follow-up assessment will be initiated including visual inspection of the sampling location, interviews with site personnel to identify activities that may have occurred during sample collection, consultation with the analytical laboratory to confirm the validity of the result, re-sampling of the location within seven days, supplemental assessment activities, submission of the laboratory data to a toxicologist/risk assessor for further evaluation, and/or additional monitoring or corrective actions.	Re-evaluate and re-state triggers for follow-up actions based on the degree of risk posed. This will result in a more rationale, cost-effective, yet health-protective, mechanism to address the detection of PCBs or VOCs in excess of a comparison criterion. Once the comparison criteria are updated and technically representative of specific risk levels (i.e., cancer risk of 1 x 10^{-6} or hazard quotient of 0.2), triggers for follow-up actions can be based on pre-specified risk levels (e.g., cancer risk of 1 x 10^{-5} or hazard quotient of 1) and/or exceedances of upper percentile indoor air levels. The follow-up actions can then be tailored to the degree of risk posed by the exceedance and the probability that the exceedance is associated with a source, not from a background condition.	Based on 12 monthly rounds of monitoring, and several rounds of tri-annual monitoring, TRC has had an opportunity to evaluate both the risks posed, the trends in the data, and the potential causes of exceedances (e.g., use and storage of cleaners and solvents at the school, off-gassing from building components). The LTMMIP specified follow-up actions are costly and time-consuming and can be triggered even when detected concentrations exceed comparison criteria and background concentrations to a minor degree. ***Note that eliminating VOC analysis as suggested under Comment Number 1 would eliminate the need for this change.***
9.	**Reporting/Timeframes –** The LTMMIP (Section 2.6) requires that all air monitoring analytical results be provided verbally to school officials within 72 hours of receipt of results from the laboratory. In addition, the LTMMIP calls for the City to contact EPA within 24 hours if a PCB or VOC action level is exceeded. Section 2.6 also calls for preparation of a written summary report within 10 days of receipt of results, with validated data to be provided separately within 21 days of receipt of results.	Modify the reporting timeframe requirements to allow for the following: ▪ Eliminate the need to contact the EPA within 24 hours if a VOC action level is exceeded. ▪ Retain the requirement to contact EPA within 24-hours if a PCB action level is exceeded. ▪ Provide the results to the City and school officials in a written report so that the results can be evaluated and explained in context. ▪ Prepare the written report only with validated data to eliminate the potential for reporting erroneous results.	Based on 12 monthly rounds of monitoring, and several rounds of tri-annual monitoring, TRC has had an opportunity to evaluate both the risks posed, the trends in the data, and the potential causes of exceedances (e.g., use and storage of cleansers and solvents at the school, off-gassing from building components). At this point, the conceptual model for detections and sources of VOCs and PCBs are well understood at KMS and do not present a significant risk to building occupants, even though as has been shown for VOCs, some detected levels exceed current reporting triggers. In the context of the conceptual model that has developed for the KMS, expediting reporting at the expense of rationale data review and reporting and risk analysis could be counterproductive.

Table 1 – Recommended Changes to LTMMIP			
Comment Number	**Current LTMMIP Element**	**Recommended Change***	**Rationale/Benefit**
Section 3 – Groundwater Monitoring			
10.	**Groundwater monitoring analytes –** The current LTMMIP (Section 3.3) calls for the analysis of groundwater samples for VOCs, PCBs, and select heavy metals.	Eliminate the requirement for VOC sampling and analysis. Limit monitoring to PCBs and metals.	PCBs, heavy metals and PAHs are the principal contaminants of concern in KMS fill/soil. VOCs were not present in significant quantities at the KMS site, nor are there significant sources of VOCs on-site warranting regular monitoring of groundwater. The added expense of VOC analysis is not justifiable. ***Eliminating the VOC analysis from the groundwater monitoring program saves approximately $1,000 in annual laboratory expenses (based on two rounds of sampling).***
11.	**Chromatography evaluation –** The LTMMIP (Section 3.4) currently requires a qualitative evaluation of gas chromatograms for PCB analysis to evaluate the potential presence of unidentified compounds.	Eliminate the requirement for a qualitative evaluation of GC chromatograms for unidentified compounds from the PCB analysis.	The qualitative screening requirement is technically erroneous given the "cleanup" procedures employed by the laboratory for the specified method. The laboratory currently performs acid cleanup on PCB extracts. The acid cleanup removes most of the organic chemicals with the exception of PCBs. Therefore, review of the resulting chromatograms for the presence of unidentified compounds is not a useful exercise.
12.	**Action level reporting triggers for groundwater –** Section 3.5 of the LTMMIP currently requires that laboratory results of the initial groundwater sampling be verbally reported to the School Department in 24 hours and in writing within 7 days of receipt, but in Section 3.6, the LTMMIP requires verbal transmission of results within 72 hours.	Reporting timeframes should be made consistent and lengthened to allow a reasonable timeframe for evaluation of results. In addition, laboratory errors have already been encountered that were eventually resolved, but not before LTMMIP reporting requirements were fulfilled. The reporting trigger timeframes do not allow sufficient time for resolution of such issues before triggering a reporting requirement.	Contradictory reporting timeframes only contribute to confusion. Also, as a practical matter, additional time should be allowed for technical evaluation and verification of results so that the City can be more fully informed of the situation, especially any potential regulatory reporting obligations.
13.	**Groundwater standards used for comparison –** The LTMMIP (Section 3.5) specifies comparison to GW-2 and GW-3 standards.	The KMS monitoring well results should be compared to the following MCP Method 1 groundwater standards: ▪ MW-1 – GW-3 ▪ MW-2 – GW-1, GW-2 and GW-3 ▪ MW-3 – GW-1, GW-2 and GW-3	The comparison recommendations are due to the proximity of a private drinking water supply well on Summit Street and the actual distance of the wells from occupied structures as per the Massachusetts Contingency Plan (MCP; 310 CMR 40.0000). **Note:** To achieve GW-1 standards for metals, the analytical method may need to be Method 6020A instead of Method 6010B as currently set forth in the LTMMIP, which is a negligible cost impact.
14.	**Follow-up verification for groundwater exceedance –** Section 3.5 of the LTMMIP requires at least one of the following activities: 1) a Phase I Initial Site Investigation; 2) a Method 3 risk assessment; or 3) other response actions determined by EPA and the LSP-of-Record if groundwater contamination in excess of GW-2 and GW-3 standards is confirmed.	The follow-up response actions should be determined on a case-by-case basis in consultation with an LSP.	The follow-up for the discovery of a condition of groundwater contamination in excess of MCP groundwater standards should be evaluated by the LSP. The EPA does not have jurisdiction relative to MCP cleanup standards; therefore, EPA does not need to be part of the decision process. However, EPA can be party to communication on these matters as a courtesy.

Table 1 – Recommended Changes to LTMMIP			
Comment Number	**Current LTMMIP Element**	**Recommended Change***	**Rationale/Benefit**
Section 4 – Foundation Vent Air Monitoring			
15.	**Vent Stack Sealing –** Section 4.1 of the LTMMIP calls for sealing all vent stacks with temporary covers for the 24 hours immediately preceding sampling. After 24 hours have elapsed, the sample will be collected from one of the vent stacks through a sample port in the vent stack cover, with one other vent stack cover removed to allow the inflow of air.	Just prior to sampling, remove covers from all vent stacks that are not being sampled to allow for the inflow of air.	This approach is a modification to the procedure outlined in the LTMMIP to improve representativeness by allowing sample air to be drawn from the entire vent stack zone without potential stagnation of flow caused by capped vent stacks.
16.	**Vent stack air sampling frequency for VOCs and PCBs –** The LTMMIP (Section 4.1) currently calls for sampling of vent stack air with a frequency of three times per year.	Reduce the frequency of sampling of PCBs to once per year in July/August and in December to be re-evaluated in two years. Eliminate the requirement for VOC sampling of the stacks.	The vent stack air monitoring events conducted to date have demonstrated the protectiveness and functionality of the passive ventilation system. The proposed reduced sampling frequency of twice per year will be sufficient to monitor PCBs emitted by the subsurface, if any, and evaluate temporal trends going forward. Sampling during the July/August period will help evaluate PCB concentrations during warm weather conditions when volatilization from the subsurface is expected to be greatest and when access to the steeper sections of the roof is safest. Sampling during December would monitor what MassDEP considers to be worst-case conditions for vapor intrusion. ***Reducing sampling for vent stack air to two events per year will save approximately $34,000 in contractor labor and expense annually (assuming VOC vent and indoor air PCB/VOC sampling is also reduced to the same frequency).***
17.	**Background sampling –** The LTMMIP (Section 4.2) specifies that one VOC and one PCB sample be collected from one upwind location to provide comparative background results for the vent stack sampling. In addition, Section 2.2 of the LTMMP specifies that at least one VOC and one PCB sample will be collected from immediately outside the building to provide comparative background results for the indoor air sampling.	Use the indoor air background sample (flag pole location) as a background sample for both indoor air and vent stack sampling.	The rationale for this change is follows: ▪ Provides equivalent data since the indoor air and vent stack sampling events occur concurrently. ▪ Eliminates unnecessarily duplicative sample collection since this sample can be used as a background sample for both indoor air and vent sampling. ***Using the indoor air background sample (flag pole location) as a background sample for both indoor air and vent stack sampling (VOCs and PCBs) saves approximately $2,100 of annual laboratory expenses (based on three rounds of sampling).***
18.	**Field screening –** Section 4.2 of the LTMMIP specifies that, to aid in the selection of sample collection locations, ambient air screening of each of the 16 rooftop foundation vent stacks be performed for VOCs with a PID prior to sampling. The rotation of monitoring for vent stacks should be established with emphasis on those stacks at which the highest PID reading is recorded.	Eliminate the field screening requirement.	Field screening of the vent stacks for VOCs has not aided in the selection of vent stack sampling locations due to the low levels of VOCs present in vent stack air and the uniform distribution of the low level VOCs. The KMS foundation venting system is comprised of six sub-slab vapor collection zones, each vented by two or four vent stacks penetrating the roof. The stacks sampled during each round of monitoring include VS-1 and VS-4, which vent from the two collection zones located under building Section A (classrooms), and one of two other vent stacks that are rotated to cover the remaining collection zones. Going forward, in lieu of field screening, TRC recommends either randomly selecting the third vent monitoring location or selecting a fixed third location to obtain comparative information over time from a third location.

Table 1 – Recommended Changes to LTMMIP			
Comment Number	**Current LTMMIP Element**	**Recommended Change***	**Rationale/Benefit**
19.	**Analytical parameters –** The LTMMIP (Section 4.3) calls for the analysis of air samples for PCBs according to EPA Method TO-4A for Aroclors (-1016, -1221, -1232, -1242, -1254, -1260, -1262, and -1268) and the 209 PCB congeners.	Specify PCB air analysis by the homologue method (EPA Method 680).	The homologue analytical method is a reliable analytical method to quantify total PCBs, which are also the basis for the risk-based AL and ALTAEC used to evaluate potential risk. In addition, by quantifying PCB homologues, total PCB air data gathered at the KMS are directly comparable to total PCB air data gathered at NBHS, greatly facilitating data comparison and risk communication to local citizens during PIP meetings and related public communication regarding air monitoring. The bulk of PCBs detected in air at KMS and NBHS are associated with the vapor phase and PCBs do not vaporize as pure technical mixtures (i.e., they do not vaporize as Aroclor mixtures). Consequently, the Aroclor approach to analysis of PCBs in air is not a suitable characterization methodology. ***The change in PCB sampling for vent monitoring saves approximately $5,200 in annual laboratory expenses (based on three rounds of sampling).***
20.	**Vent Stack Data Comparisons –** The LTMMIP (Sections 4.51 and 4.5.2) currently mandates that PCB and VOC results for each vent stack air sample be evaluated by comparison to site-specific PCB action levels and, for VOCs, the 1995 MassDEP TELs and AALs for ambient air.	Recommend eliminating the comparison of the vent stack sampling results to risk-based criteria. Instead provide a qualitative evaluation and trend analysis of the vent stack sampling results.	The City and School Department decided to install a vapor barrier on top of the soil beneath the school building concrete floor as an added layer of protection against intrusion of any gases that may accumulate under the building. Passive ventilation has been installed to allow any sub-slab soil gases to migrate from beneath the vapor barrier to the vent stacks installed through the school building roof. Sampling of vent stack air is conducted to confirm the proper functioning of the passive ventilation system, not to determine whether there is a risk or hazard associated with the inhalation of air from the passive ventilation system. The comparison of vent stack air sampling results to the criteria currently set forth in the LTMMIP is inappropriate because the inhalation of vent stack air is an incomplete human exposure pathway. The lack of a complete pathway renders the comparison to such criteria conceptually irrelevant. TRC recommends the vent stack air sampling for VOCs (if continued) and PCBs no longer be compared to risk-based criteria. Instead, TRC recommends evaluating the data over time to monitor concentration trends and comparing the data to historical soil gas sampling results to monitor system performance/functionality.
21.	**PCB Action Levels –** Section 4.5.1 of the LTMMIP refers to an Action Level of 0.05 ug/m^3 and a Maximum Acceptable Level of 0.3 ug/m^3.	Eliminate any reference to PCB Action Levels for vent stack sampling.	Because the comparison of vent stack air sampling results to the criteria currently set forth in the LTMMIP is inappropriate due to the lack of a complete human exposure pathway, TRC recommends the vent stack air sampling for PCBs no longer be compared to risk-based criteria.
22.	**Triggers for further analysis/evaluation of vent stack air results –** The LTMMIP (Sections 4.5.1 and 4.5.2) currently specifies that if any foundation vent stack sample result for PCBs or VOCs exceeds the PCB action level or TELs/AALs, follow-up assessment will be initiated including resampling of the location within seven days, supplemental assessment activities, submission of the laboratory data to a toxicologist/risk assessor for further evaluation, and/or additional monitoring or corrective actions.	Eliminate triggers for follow-up actions because of the recommendation for no comparison of vent stack air data to comparison criteria. Instead provide a qualitative evaluation and trend analysis of the vent stack sampling results. This will result in a more rationale and cost-effective mechanism to evaluate the vent stack air data since human exposure to vent stack air is not occurring.	These LTMMIP requirements are costly and time-consuming follow-up actions to be implemented when even minor exceedances of comparison criteria and background concentrations occur. Based on 12 monthly rounds of monitoring, and several rounds of tri-annual monitoring, TRC has had an opportunity to evaluate the trends in the data and the potential causes of exceedances (e.g., off-gassing from vent system components, evidence of proper functioning of the vent system that is designed to convey soil gases to the atmosphere). Due to a lack of human exposure to vent stack air, no risk-based evaluation is required and no triggers for follow-up actions are necessary.

Table 1 – Recommended Changes to LTMMIP			
Comment Number	**Current LTMMIP Element**	**Recommended Change***	**Rationale/Benefit**
23.	**Reporting/Timeframes –** The LTMMIP (Section 4.6) requires that all vent stack air monitoring analytical results be provided verbally to school officials within 72 hours of receipt of results from the laboratory. In addition, the LTMMIP calls for the City to contact EPA within 24 hours if a PCB or VOC action level is exceeded. Section 4.6 also calls for preparation of a written summary report within 10 days of receipt of results, with validated data to be provided separately within 21 days of receipt of results.	Modify the reporting timeframe requirements to allow for the following: ▪ Eliminate the need to contact the EPA within 24 hours if a VOC or PCB action level is exceeded since no comparison to VOC or PCB action levels will be recommended in the revised LTMMIP. ▪ Provide the results to the City and school officials in a written report so that the results can be evaluated and explained in context. ▪ Prepare the written report only with validated data to eliminate the potential for reporting erroneous results.	Based on 12 monthly rounds of monitoring, and several rounds of tri-annual monitoring, TRC has had an opportunity to evaluate both the trends in the data and the potential causes of exceedances (e.g., off-gassing from vent system components, evidence of proper functioning of vent system which is designed to convey soil gases to the atmosphere). At this point, the conceptual model for detections and sources of VOCs and PCBs are well understood at KMS. In the context of the conceptual model that has developed for the KMS, expediting reporting at the expense of rationale data review and reporting could be counterproductive especially for vent stack air for which no complete human exposure pathway has been identified.
Section 5 – Wetland Sediment Inspection and Monitoring			
24.	**Reporting/Timeframes –** The LTMMIP (Section 5.7) requires that all analytical results be provided verbally to school officials within 10 days of sample collection. Section 5.7 also calls for preparation of a written summary report within 10 days of receipt of results, with validated data to be provided separately within 21 days of receipt of results.	Modify the reporting timeframe requirements to allow for the following: ▪ Provide draft data to project monitors in the City's Department of Environmental Stewardship as soon as possible after data are reported from the laboratory, conference with the project monitors to discuss the results and evaluate appropriate response actions. ▪ Provide the results to the City and school officials in a written report so that the results can be evaluated and explained in context. ▪ Prepare the written report only with validated data to eliminate the potential for reporting erroneous results.	TRC's recommendation is to provide draft data to project monitors in the City's Department of Environmental Stewardship as soon as possible after data are reported from the laboratory and conferencing with the project monitors to discuss the results and evaluate appropriate response actions. This reporting paradigm allows for case-by-case evaluation/assessment.
Section 6 – Laboratory QC & Data Useability			
25.	**Data Validation and Usability –** The LTMMIP (Section 6.4) calls for Tier II data validation to be performed in accordance with EPA New England guidelines for all analyses.	Continue validation of PCB analyses, but perform MassDEP data usability assessments for VOCs and metals instead. Also, perform data usability assessments for PCBs.	Mass DEP requires data usability assessments. Data validation per EPA guidelines is not consistent with this MCP requirement. Retain data validation for PCB analysis given EPA's over-sight role and jurisdiction regarding PCBs at this Site.
Section 7 – Long-Term Cap Monitoring Plan			
26.	**Cap Inspections –** The LTMMIP (Section 7.3) requires cap inspections three times per year: April 1 through 15, August 1 through 15 and November 1 through 15.	Schedule cap inspections for twice per year (spring and late summer/early fall).	TRC's recommendation to perform KMS site cap inspections twice per year (spring and late summer/early fall) is consistent with typical EPA Superfund landfill cap inspection protocols. In addition, the timing of the two inspections allows sufficient time for repairing areas of damaged vegetative growth that would be difficult to accomplish following a November inspection. ***Scheduling cap inspections for twice per year (spring and late summer/early fall) saves approximately $3,000 in consultant labor and expense (assuming no need for follow-up inspections per the LTMMIP).***

Notes:

*** -** Appendices will be revised to be consistent with the proposed changes to the revised LTMMIP text.