Haley & Aldrich, Inc.
11020 King Street
Suite 450
Overland Park, KS 66210

Tel: 913.693.1905
Fax: 913.906.0931
HaleyAldrich.com

HALEY&
ALDRICH

TECHNICAL MEMORANDUM

27 September 2013
File No. 37294-018

TO: Missouri Department of Natural Resources
Hazardous Waste Program, Superfund Section
ATTN: Wane Roberts

C: RACER Trust
ATTN: Robert Hare

FROM: Haley & Aldrich, Inc.
Bruce Wilkinson and Mariruth Gruis

SUBJECT: Scope of Work Addendum for Supplemental Site Investigation Activities
Former Leeds Assembly Plant - Northern Parcel
South of 6817 Stadium Drive
Kansas City, Missouri

Haley & Aldrich, Inc. (Haley & Aldrich) has prepared this Scope of Work (SOW) Addendum for Supplemental Site Investigation Activities (the SOW Addendum) for the Former Leeds Assembly Plant - Northern Parcel (herein referred to as the Site or Northern Parcel) on behalf of the Revitalizing Auto Communities Environmental Response (RACER) Trust. This SOW Addendum specifically addresses supplemental investigation activities for the Northern Parcel that have been verbally discussed and agreed upon with the Missouri Department of Natural Resources (MDNR) but that were not initially planned or included in the MDNR-approved Revised Site Investigation Workplan, Revision No. 2, dated 15 September 2011 (the Workplan; Haley & Aldrich, 2011).

As proposed in the Workplan, initial soil and groundwater investigation activities were conducted between November 2011 and April 2012 to characterize the nature and extent of impacts from historic filling operations on the Site. Details and results for the initial investigation efforts were documented in the Site Investigation Data Report, dated 21 June 2012 (Haley & Aldrich, 2012).

Based on results from soil and groundwater sampling and test pit excavations completed in early-2012, supplemental investigation activities have been proposed and discussed with MDNR. This SOW Addendum provides the written plan for the proposed supplemental investigation efforts at the Site, including standard operating procedures (SOPs) and updated Quality Assurance Project Plan (QAPP) information as it pertains to the proposed activities.

OBJECTIVES

The data collected during supplemental investigation activities will be evaluated to attain the following objectives:

1. To further assess the source and extent of volatile organic compounds (VOCs) in shallow and deep groundwater and in soil vapor;
2. To evaluate the mineral spirit-like odor detected at two locations during test pit excavation activities;
3. To refine the understanding of groundwater flow across site; and
4. To gather sufficient data to develop a conceptual site model (CSM).

PROPOSED SUPPLEMENTAL INVESTIGATION ACTIVITIES

The proposed supplemental investigation will consist of the following activities designed to meet the project objectives stated above:

- Use Geoprobe® to evaluate the previously detected VOCs in deep groundwater and to further assess if VOCs in deep groundwater are present up-gradient and/or down-gradient of the Drum Discovery Area (shown on Figure 1).
- Use Geoprobe® to further assess the presence of VOCs in shallow groundwater on-site.
- Use Geoprobe® to evaluate the mineral spirit-like odor detected at two locations during test pit excavation activities and whether VOCs may be present in soil vapor in the shallow vadose zone near the Drum Discovery Area.
- Conduct a groundwater monitoring event for comparison against prior groundwater sampling results and to obtain baseline natural attenuation data.
- Conduct in-situ permeability tests (slug tests) to estimate the permeability of the aquifer(s) identified beneath the Site.
- Conduct a final horizontal and vertical survey for completed groundwater and soil vapor sampling locations.

The following subsections provide additional details for the proposed activities as a supplement to the Workplan and the QAPP (Haley & Aldrich, 2011). Where applicable, SOPs are referenced and provided as attachments to this SOW Addendum.

Pre-Field Activities

Prior to mobilizing for field activities, Haley & Aldrich will provide RACER and MDNR with a minimum two-week notice of the start date and anticipated schedule for field activities. This will allow interested parties to plan for oversight of work performed at the Site and sufficient time for MDNR to plan for collecting split samples, if desired.

A Site reconnaissance survey will be conducted to mark proposed groundwater and soil vapor sampling locations and to coordinate with the Leeds facility management for temporary relocation of vehicles and equipment that may interfere with planned site activities. Once the sampling locations have been marked, a utility location survey will be performed prior to mobilization through the use of the Missouri one-call utility locator service. Additionally, a survey using ground penetrating radar (GPR) equipment will be conducted to locate utilities within Site boundaries. If obstructions are observed based on the one-call and/or GPR surveys, the locations will be adjusted. If locations are moved by more than five feet from the initially proposed/marked location, the modified locations will be reviewed with RACER and MDNR to ensure they still meet project objectives.

Geoprobe® Groundwater Sampling

Shallow and deep grab groundwater samples will be collected at select locations using Geoprobe® before consideration is given to whether additional groundwater monitoring wells should be installed at the Site. This will allow a lower cost alternative to collecting shallow and deep groundwater samples without installing additional permanent monitoring wells. Groundwater results will be used to confirm previously detected concentrations in deep groundwater and to further assess the presence and extent of VOCs in both shallow and deep groundwater.

Four Geoprobe® locations will be advanced to monitor groundwater in the deep zone (i.e., atop bedrock at approximately 60 feet below ground surface [bgs]) and two Geoprobe® locations will be advanced to monitor groundwater in the shallow zone (i.e., water table at approximately 22 feet bgs). Figure 1 shows the proposed deep (GP-6D, -7D, -10D, and -11D) and shallow (GP-12A and -13A) Geoprobe® locations. The deep Geoprobe® locations are proposed along the site perimeters to the west, north, and south in an effort to better understand extent of VOC concentrations in groundwater and whether there is potential that VOCs may be coming onto the site from an upgradient location. The shallow Geoprobe® locations are proposed to obtain data in the shallow zone near wells where deep VOCs were detected during groundwater sampling in February 2012 (i.e., where shallow wells were installed but dry at time of sampling) and in an area where no prior shallow wells had been installed.

Geoprobe® advancement and groundwater sampling will be completed per the SOP provided by the Geoprobe® subcontractor, PSA Environmental (PSA); the SOP is provided as Attachment A to this SOW Addendum. A field logbook and/or field sampling forms will be used to document groundwater sampling information at each location. A grab groundwater sample will be collected at depth for each location using a Geoprobe® SP-16 sampler that is advanced within the Geoprobe® direct push rods (per the SOP), a peristaltic pump, and poly (or equivalent) tubing. Samples will be analyzed by TestAmerica Laboratories (Nashville, TN) for VOCs by EPA Method 8260B. Pending results of the grab groundwater sampling, the team can discuss whether additional Geoprobe® sampling or monitoring well installation should be conducted at the site.

Geoprobe® Soil Vapor Sampling

A limited soil vapor survey will be conducted in the immediate vicinity of the Drum Discovery Area (Figure 1) and other select locations where buried drum and debris were identified during test pit activities in April 2012. Soil vapor results will be used to further evaluate if VOCs may be present in

the vadose zone in these areas and to better define the mineral spirit-like odor that was detected at two locations during test pit excavation activities.

Soil vapor samples will be collected at ten locations on-site as shown on Figure 1 (SV-1 through SV-10). Two separate Geoprobe® boreholes will be advanced at each location with soil vapor samples collected at approximately five feet bgs from one borehole and at approximately ten feet bgs from the other borehole, unless subsurface conditions prevent sample collection at a particular location/hole.

Geoprobe® advancement and soil vapor sampling will be completed per the SOP provided by PSA; the SOP is provided as Attachment B to this SOW Addendum. A field logbook and/or field sampling forms will be used to document soil vapor sampling information at each location. Grab samples will be collected using the Post Run Tubing assembly (per the SOP) through Teflon® tubing and into 6L Summa® canisters. Each canister will be equipped with a flow regulator that restrict air flow to <200 milliliters per minute (mL/min), resulting in samples being collected over a 30 minute time span. Canisters and flow regulators will batch certified. All soil vapor samples will be analyzed by Air Toxics, Inc. (Folsom, CA) for VOCs by EPA Method TO-15. Additionally, two of the ten soil vapor sampling locations (SV-3 and SV-5) will have the 5- and 10-foot samples analyzed for hydrocarbons using the Massachusetts Department of Environmental Protection (MADEP) air-phase petroleum hydrocarbon (APH) Method. The Method for the Determination of APH (MADEP, dated December 2008) is provided as Attachment C. For the samples collected at SV-3 and SV-5, sufficient sample volume will be available in the 6L canister to run both the VOC and APH analysis; therefore, additional sample volume will not be collected at these locations.

Groundwater Sampling

A groundwater sampling event is proposed for fourth quarter 2013. Sampling will be conducted at the 13 groundwater monitoring wells existing at the Site (installed February 2012; Figure 1) to obtain data for comparison and evaluation purposes. If additional groundwater monitoring wells are installed based on results of the supplemental groundwater investigation effort described above, those wells would be added to subsequent sampling events as they are installed.

Prior to sampling, one round of static water levels will be collected from the installed monitoring wells to evaluate the groundwater flow across the Site. Water level measurements, measuring point locations, and time and date of collection will be entered in the field logbook and/or on field sampling forms.

Groundwater samples will be collected from each well by low-flow methodology using a submersible variable rate pump. This is the same method used during initial sampling in February 2012, following procedures identified in the QAPP (Haley & Aldrich, 2011). If low-flow cannot be used for location-specific reasons, bailers may be used to collect groundwater samples following the procedures identified in the QAPP. Field indicator parameters and sample information will be documented on a Low-Flow Groundwater Sampling Record (Haley & Aldrich, 2011).

Samples collected will be submitted to TestAmerica located in Nashville, Tennessee and analyzed for the same compounds that were analyzed for during the February 2012 event including: VOCs,

semi-volatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), ethylene glycol, and metals. In addition, we propose collecting natural attenuation parameters during the sampling event to better understand the subsurface conditions at the site. Parameters to be analyzed for will include the following, assuming sufficient water can be collected at each well to provide the laboratory-required sample volume: total and dissolved organic carbon (TOC and DOC), sulfate, sulfide, nitrate, nitrite, chloride, ethene, ethane, methane, carbon dioxide, total and dissolved manganese, and total iron. Samples collected from monitoring wells will follow the sample naming, collection, handling, and preservation methods provided in the QAPP.

In Situ Permeability Testing

Slug tests will be conducted at two shallow and two deep existing monitoring wells onsite to estimate the permeability of the aquifer(s) identified beneath the Site. Slug tests will be conducted as specified in the Workplan (Haley & Aldrich, 2011) and will be completed after samples have been collected during the proposed groundwater sampling event at existing monitoring wells.

Decontamination and Waste Handling

Decontamination for the Geoprobe® unit will follow the procedures identified in the SOPs for groundwater sampling (Attachment A) and soil vapor sampling (Attachment B). Decontamination for water level indicators and groundwater sampling equipment will follow the procedures outlined in the QAPP (Haley & Aldrich, 2011).

Soil cuttings generated from Geoprobe® advancement and water generated from sampling and decontamination activities will be collected, containerized, and stored in 55-gallon drums labeled with Non-Classified Waste labels. The drums will be placed on a secondary containment pallet, or equivalent device, in a secured area of the Site until transport and disposal can be coordinated with a MDNR-approved waste-handling facility. If any wastes are determined to be hazardous, Haley & Aldrich will coordinate with MDNR to obtain a hazardous waste generator number for the Site which would be required for transport and disposal of the hazardous waste offsite.

Disposable materials generated during field activities (i.e., bailers, disposable bladders, gloves, paper towels, etc.) will be collected and contained for proper disposal as municipal solid waste.

Site Restoration and Final Survey

It is expected that minimal surface disturbance will occur during the Geoprobe® groundwater and soil vapor sampling. Restoration will consist of removing any soil cuttings generated, and trash or debris. Ruts created will be smoothed.

Once the groundwater and soil vapor sampling is complete, a final horizontal and vertical survey will be conducted to document sampling locations. This survey will include ground surface measurement points for each Geoprobe® location, surveyed to the nearest 0.01 foot.

Data Quality and Evaluation

The measurement performance criteria (i.e., precision, accuracy, representativeness, comparability, completeness, and sensitivity) identified in the Workplan will be used to assess whether the generated data quality satisfies the project objectives. For the supplemental investigation activities, this will include field collection of:

- Field Blanks at a rate of one per twenty groundwater investigation samples to assess field accuracy and potential bias associated with water used for equipment blanks, air in contact with sample media during sample collection, and sample containers;
- Equipment Blanks at a rate of one per twenty groundwater investigation samples to assess potential bias associated with use of non-dedicated equipment following equipment decontamination;
- Trip Blanks submitted as one set of trip blank samples per cooler containing groundwater samples for VOC analysis to assess potential bias associated with sample transport and storage; and
- Field Duplicates at a rate of one per ten investigation samples for each matrix (groundwater and soil vapor) to evaluate sampling and analytical precision and representativeness.

In addition, the laboratory will use internal checks to verify data quality. At a minimum, this will include laboratory method blanks and laboratory control standard/laboratory control standard duplicates (LCS/LCSD) pairs. A laboratory method blank is used to demonstrate that target analytes are not present above reporting limits or may indicate potential sources of contamination from laboratory procedures. The LCS/LCSD pairs are used to document laboratory precision and accuracy.

As discussed in the Workplan, Site-specific health-based action levels have not been selected for the Northern Parcel. Similar to the evaluation process used for the initial investigation activities (Haley & Aldrich, 2011), the U.S. Environmental Protection Agency's (EPAs) Regional Screening Levels (RSLs) for Chemical Contaminants at Superfund Sites (EPA, 2011) will be used as a preliminary screening tool during the supplemental investigation activities. The future land use at the site is expected to remain industrial; therefore, the industrial RSLs for air will be used. Maximum contaminant levels (MCLs) will be used as conservative screening levels for groundwater. Laboratory reporting and detection limits will be identified at sufficiently low levels to enable effective screening using the RSLs.

COST AND SCHEDULE

In March 2013, RACER and MDNR approved the proposed 2013 budget prepared by Haley & Aldrich, which included costs to conduct supplemental investigation activities. Subsequent coordination efforts and updates to the supplemental investigation scope of work have resulted in slight modifications to the proposed 2013 budget. Table D-1 of Attachment D identifies the originally approved budget (March 2013), the currently scoped budget (September 2013), an explanation of the changes, and proposed modifications to the budget in terms of cost and allocation amongst the identified tasks. Table D-2 provides the modified Attachment 5 from the 2013 Annual Budget Authorization Request, identifying the associated changes to the following years budget projections.

An approximate schedule for the SOW Addendum task defined herein is included as Figure 2. This schedule is dependent upon MDNR review and approval of this SOW Addendum and approval of the budget by MDNR and RACER for conducting the proposed supplemental investigation work.

REPORTING

A Supplemental Investigation Data Report will be submitted within sixty days of receipt of validated analytical results from the groundwater sampling of existing monitoring wells. The report will summarize the findings from a groundwater use survey and seeps evaluation (conducted in Spring 2013) and will document the Geoprobe® groundwater and soil vapor sampling, the groundwater monitoring at existing wells, and in situ permeability testing activities. Field documentation will be provided and field and analytical data will be summarized in tables and presented in figures, as appropriate, to facilitate data review and evaluation.

A CSM will be developed for the Northern Parcel based on information gathered to date. Additionally, potential exposure pathways and receptors will be discussed. The report will summarize conclusions and recommendations for further assessment, if warranted, and/or recommended next steps for remediation activities.

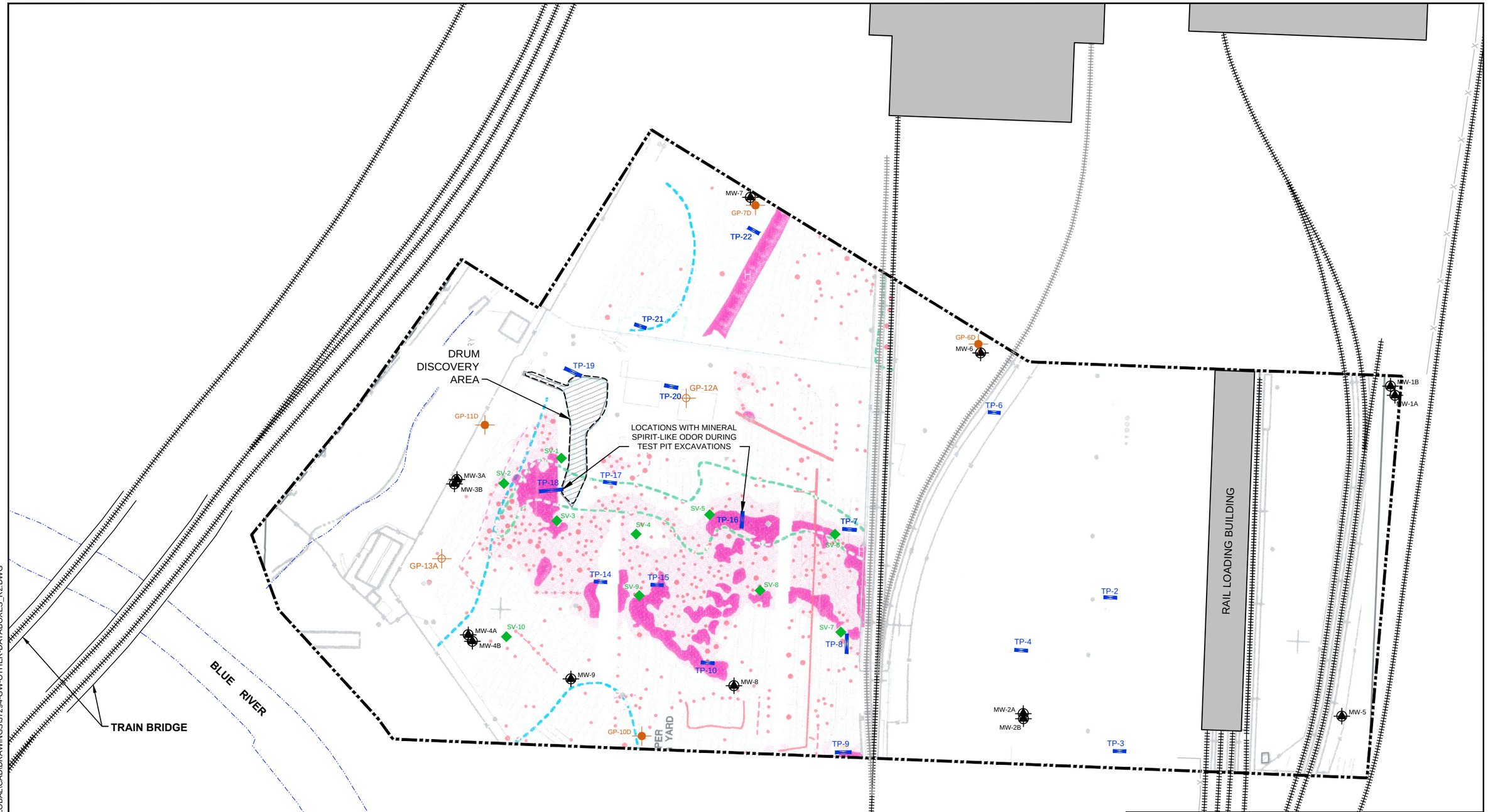
REFERENCES

Haley & Aldrich, Inc. (Haley & Aldrich), 2011. *Revised Site Investigation Workplan, Revision No. 2*, Former Leeds Assembly Plant – Northern Parcel, Kansas City, Missouri. Prepared for Revitalizing Auto Communities Environmental Response (RACER) Trust. 15 September 2011.

Haley & Aldrich, 2012. *Site Investigation Data Report*, Former Leeds Assembly Plant – Northern Parcel, Kansas City, Missouri. Prepared for RACER Trust. 21 June 2012.

U.S. Environmental Protection Agency (EPA), 2011. *Regional Screening Levels for Chemical Contaminants at Superfund Sites*; http://www.epa.gov/region09/superfund/prg/. June 2011 Update.

FIGURES



LEGEND:

- PROPERTY LINE
- RAIL ROAD TRACKS
- FORMER RAIL ROAD TRACKS
- RIVER / SWALE
- FENCE
- EXISTING STRUCTURE
- TEST PIT LOCATION
- GP-10D — PROPOSED DEEP GEOPROBE GW LOCATION
- GP-13A — PROPOSED SHALLOW GEOPROBE GW LOCATION
- SV-10 — PROPOSED GEOPROBE SOIL VAPOR LOCATION
- MW-04B — EXISITNG DEEP MONITORING WELL LOCATION
- MW-04A — EXISTING WATER TABLE MONITORING WELL LOCATION
- JANUARY 2000 GEOPHYSICAL SURVEY RESULTS AS ANOMALOUS ZONES OF POSSIBLE METALLIC OR OTHER MATERIAL BURIED OBJECTS

NOTES:

1. PROPERTY BOUNDARIES AND SITE FEATURES DEVELOPED FROM TOPOGRAPHIC SURVEY PROVIDED BY LOVELACE & ASSOCIATES PROJECT NUMBER 1130, DATED 11-14-2011.
2. EXPLORATION LOCATIONS, AND DRUM AREA WERE DIGITIZED FROM MAPS PROVIDED BY THE CLIENT.

N / W / E / S

0 120 240

APPROXIMATE SCALE IN FEET

HALEY & ALDRICH

REVITALIZING AUTO COMMUNITIES
ENVIRONMENTAL RESPONSE TRUST
FORMER LEEDS ASSEMBLY PLANT-NORTHERN PARCEL
SOUTH OF 6817 STADIUM DRIVE
KANSAS CITY, MISSOURI

2013 PROPOSED SUPPLEMENTAL INVESTIGATION LOCATIONS

SCALE: AS SHOWN
SEPTEMBER 2013

FIGURE 1

V:\PROJECTS\37294 - MLC LEEDS\GLOBAL\CAD\DRAWINGS\37294-GW-OTHER-DATABOXES_R2.DWG

FIGURE 2
2013 Project Schedule for Scope of Work Addendum
Leeds - Northern Parcel

Task ID	Project Tasks and Milestones	Dates		12-Sep-13	19-Sep-13	26-Sep-13	3-Oct-13	10-Oct-13	17-Oct-13	24-Oct-13	31-Oct-13	7-Nov-13	14-Nov-13	21-Nov-13	28-Nov-13	5-Dec-13	12-Dec-13	19-Dec-13	26-Dec-13	2-Jan-14	9-Jan-14	16-Jan-14	23-Jan-14	30-Jan-14	6-Feb-14	13-Feb-14	20-Feb-14	27-Feb-14	6-Mar-14	13-Mar-14	20-Mar-14
		Start	Finish	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	**Revised Site Investigation Work Plan**																														
2	**Site Investigation**																														
2.01	Draft Scope of Work Addendum Submittal	09/12/13 Thu	09/12/13 Thu																												
2.02	RACER Review	09/13/13 Fri	09/25/13 Wed																												
2.03	MDNR Review, Comment and Approval	09/27/13 Fri	10/07/13 Mon																												
2.04	Revise/Finalize SOW Addendum	10/08/13 Tue	10/11/13 Fri																												
2.05	Supplemental Investigation - Geoprobe Event	10/28/13 Mon	10/31/13 Thu																												
2.06	Geoprobe Laboratory Analysis (TestAmerica)	10/30/13 Wed	11/13/13 Wed																												
2.07	Geoprobe Laboratory Analysis (Air Toxics)	11/01/13 Fri	11/15/13 Fri																												
3	**Site Investigation Report**																														
3.01	Supplemental Investigation Data Report	11/19/13 Tue	01/13/14 Mon																												
3.02	Data Evaluation	11/19/13 Tue	11/27/13 Wed																												
3.03	RACER Review	12/20/13 Fri	01/03/14 Fri																												
3.04	Revise/Finalize Field Investigation Data Report	01/03/14 Fri	01/07/14 Tue																												
3.05	MDNR Review and Comment	01/08/14 Wed	03/10/14 Mon																												
4	**Deed Restriciton**																														
5	**Soil and Drum Removal**																														
6	**Project Management, Meetings with MoDNR**																														
7	**Cap Monitoring & Maintenance**																														
7.01	Test Pit Resurfacing - Completed July 2013																														
8	**Groundwater Monitoring and Reporting**																														
8.01	First Quarterly Groundwater Sampling and Reporting	10/31/13 Thu	01/13/14 Mon																												
8.02	Sampling	10/31/13 Thu	11/04/13 Mon																												
8.03	Lab Analysis (TestAmerica)	11/05/13 Tue	11/19/13 Tue																												
8.04	Draft Groundwater Report (combined with Supplemental Investigation Data Report)	11/19/13 Tue	12/20/13 Fri																												
8.05	RACER Review	12/20/13 Fri	01/03/14 Fri																												
8.06	Revise/Finalize Groundwater Report	01/03/14 Fri	01/07/14 Tue																												
9	**Agency Oversight and Fees**																														

ATTACHMENT A

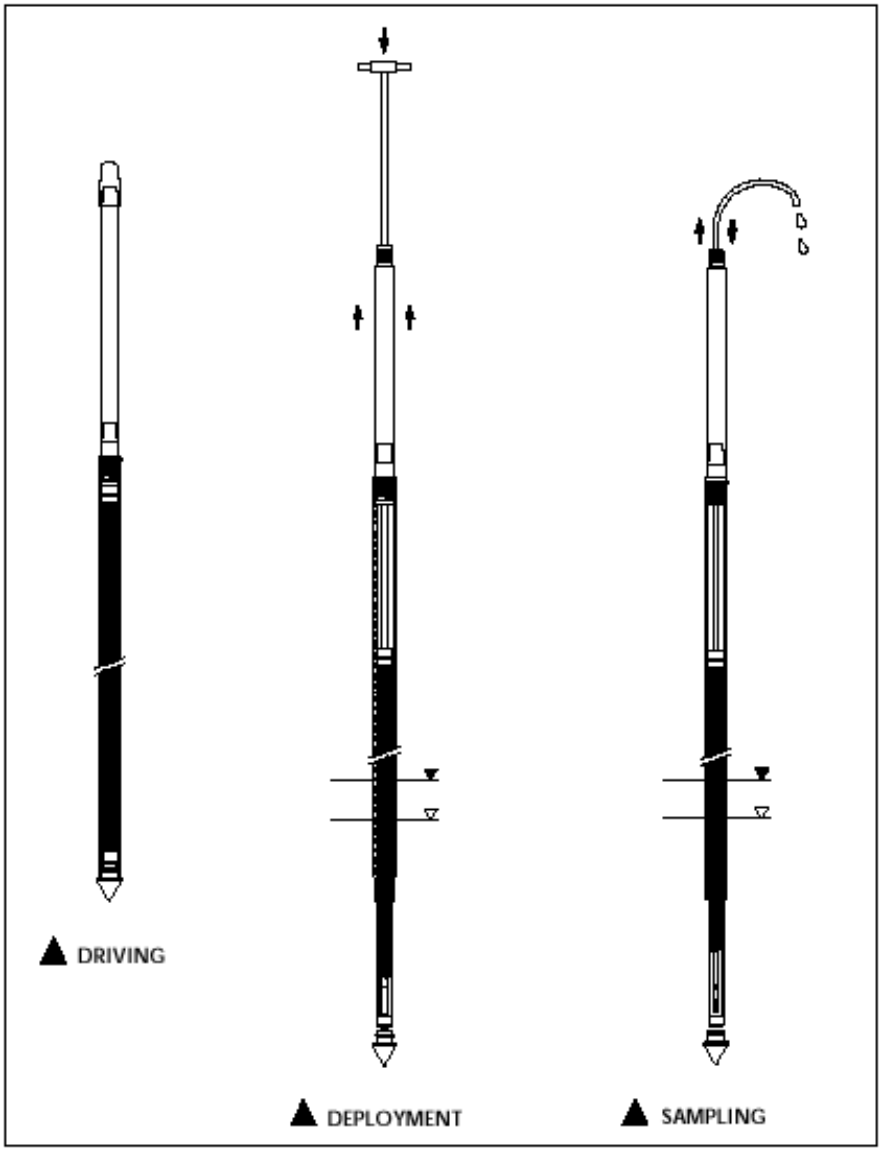
Supplemented Standard Operating Procedure
No. 2230.7A
Geoprobe® Operations for Groundwater Sampling

SUPPLEMENTED STANDARD OPERATING PROCEDURE

No. 2230.7A

Geoprobe® Operations for

Groundwater Sampling



12/09/98
Revised 11/03/02

1.0 OBJECTIVE

The objective of this procedure is to advance a sealed stainless steel or PVC screen to depth, deploy the screen and obtain a representative water sample from the screened interval.

1.1 Definitions

Geoprobe®: A brand name of hydraulically powered machines that utilize both static force and percussion to advance sampling and logging tools into the subsurface. The Geoprobe® brand name refers to both machines and tools manufactured by Geoprobe Systems®, Salina, Kansas. Geoprobe® tools are used to perform soil core and soil gas sampling, groundwater sampling and monitoring, soil conductivity and contaminant logging, grouting, and materials injection.

Screen Point 15 (SP-15) Groundwater Sampler (Fig. 1.1): A direct push device consisting of a PVC or stainless steel screen that is driven to depth within a sealed, steel sheath and then deployed for the collection of representative groundwater samples. The assembled SP-15 Sampler is approximately 50.5 inches (1283mm) long with an OD of 1.5 inches (38mm). Upon deployment, up to 41 inches (1041mm) of screen can be exposed to the formation. The Screen Point 15 Groundwater Sampler is used primarily with 1.25-inch probe rods and machines equipped with a GH40 Series (GH40, GH41, and GH42) Hydraulic Hammer.

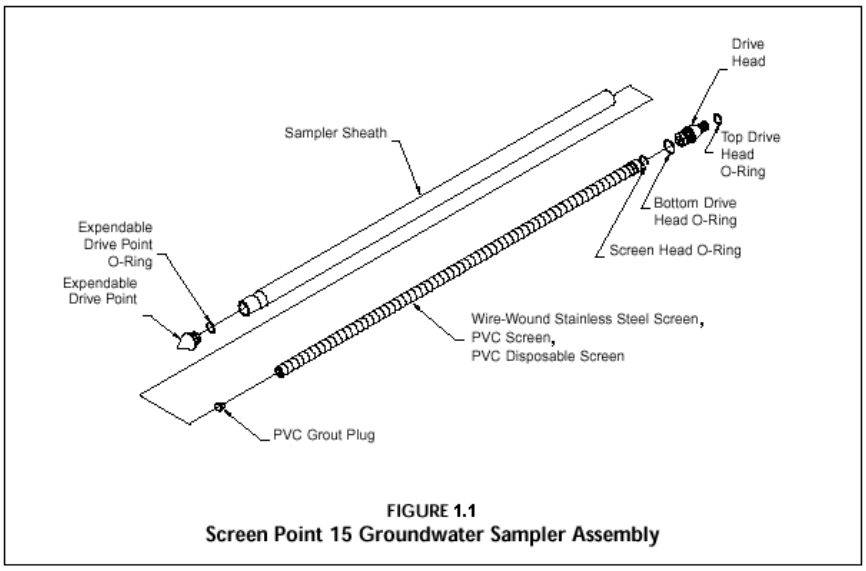


FIGURE 1.1
Screen Point 15 Groundwater Sampler Assembly

Screen Point 16 (SP-16) Groundwater Sampler (Fig. 1.2): A direct push device consisting of a PVC or stainless steel screen that is driven to depth within a sealed, steel sheath and then deployed for collection of representative groundwater samples. The assembled SP-16 Sampler is approximately 51.5 inches (1308mm) long with an OD of 1.625 inches (41mm). Upon deployment, up to 41 inches (1041mm) of screen can be exposed to the formation. The Screen Point 16 Groundwater ampler is designed for use with 1.5-inch probe rods and machines equipped with the more powerful GH60 Hydraulic hammer. Operators with GH40 Series hammers may chose to use this sampler in soils where driving is difficult.

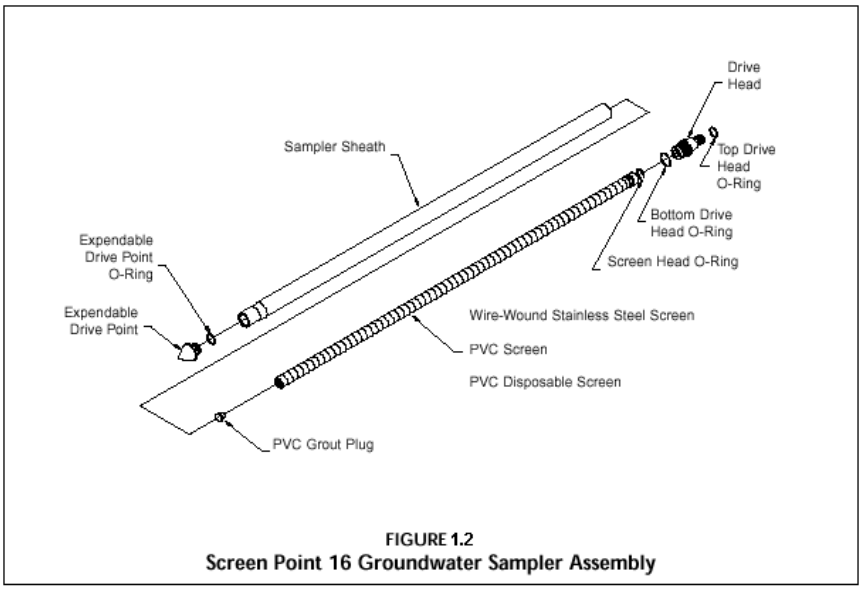


FIGURE 1.2
Screen Point 16 Groundwater Sampler Assembly

Rod Grip Pull System (Figures 1.3 & 1.4): An Attachment mounted on the hydraulic hammer of a direct push machine which makes it possible to retract tooling string with extension rods or flexible tubing protruding from the top of the probe rods. The Rod Grip Pull System includes a pull block with rod grip jaws and two support straps that are bolted directly to the machine. A removable handle assembly straddles the tool string while hooking onto the pull block to effectively grip the probe rods as the hammer is raised. A separate handle assembly is required for each probe rod diameter.

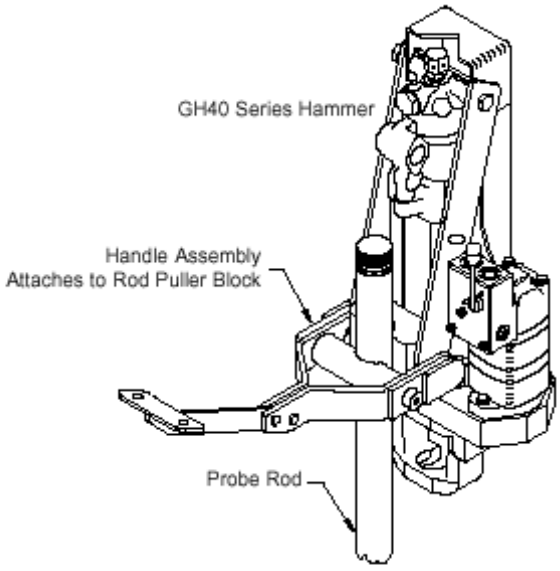


FIGURE 1.3
Rod Grip Pull System for Units Equipped With a GH40 Series Hammer

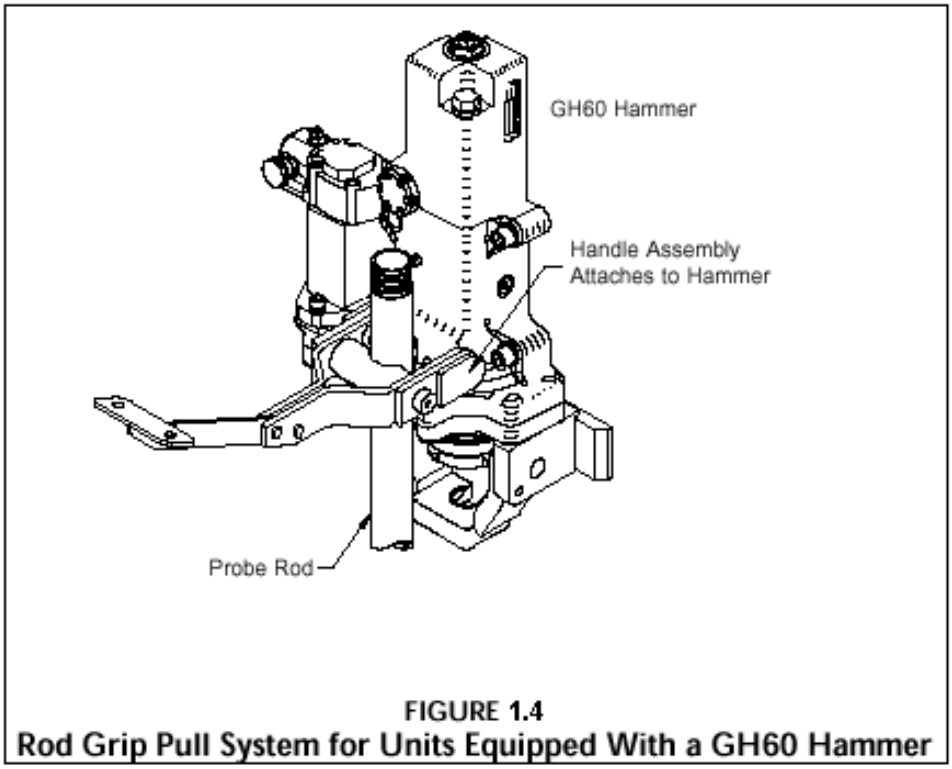


FIGURE 1.4
Rod Grip Pull System for Units Equipped With a GH60 Hammer

For the purpose of sampling groundwater both the SP-15 and SP-16 are identical in working form. The only distinction between the two is that of which percussion hammer they have been designed to work under.

1.2 Discussion

In this procedure, the assembled Screen Point 15/16 Groundwater Sampler is threaded onto the leading end of a Geoprobe® probe rod and advanced into the subsurface with a Geoprobe® probing machine. Additional probe rods are subsequently added and advanced until the desired sampling interval is reached. While the sampler is advanced to depth, O-ring seals at the drive head and expendable drive point provide a watertight system. This system eliminates the threat of formation fluids entering the screen before deployment and assures sample integrity.

The Screen Point 15/16 Sampler utilizes a stainless steel or PVC screen with a standard slot size of 0.004 inches (0.10 mm), stainless steel, and 0.010 inches (0.25mm) PVC. The screen will then have an exposed length of 41 inches (1041 mm). The screen is constructed such that a check valve, mini-bailer, or small bladder pump can be inserted into the screen cavity. This makes direct sampling possible from anywhere within the saturated zone (Fig. 1.5).

Groundwater samples can be obtained in a number of ways. The most common method utilizes polyethylene or Teflon® tubing and a Tubing Bottom Check Valve. The check valve (with check ball) is attached to one end of the tubing and inserted down the casing until it is immersed in groundwater. Water is pumped through the tubing and to the ground surface by oscillating the tubing up and down. If oscillating the tubing is undesirable, lower the check valve and tubing to the bottom of the sampler without the check ball. Then drop the check ball into the tubing from the ground surface. The ball will seat in the check valve and trap the sample in the tubing. Collect the sample by withdrawing and draining the tubing.

The alternative means of collecting groundwater samples is to attach a peristaltic or vacuum pump to the tubing. This method is limited in that water can be pumped to the surface from a maximum depth of approximately 26 feet (8m). Another technique for ground water sampling is to use a stainless steel Mini-Bailer Assembly. The mini-bailer is lowered down the inside of the probe rod string below the water level where it fills with water and is then retrieved. Most recently the innovation is Geoprobe's GW1400 Series Pneumatic Bladder Pump. This type of pump is preferred for low-flow sampling (EPA 1996). It provides minimal disturbance of sample because fluid is pushed, not drawn or vacuumed, to the surface. Turbidity is low and loss of volatile contaminants is negligible.

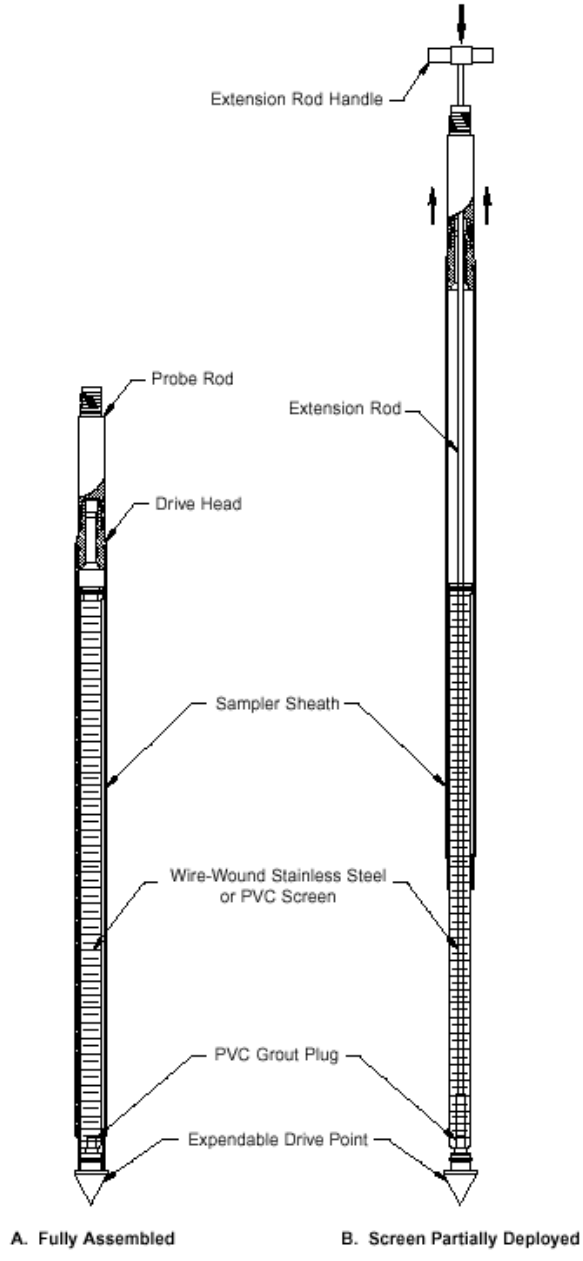


FIGURE 1.5
Screen Point 15 / Screen Point 16 Groundwater Sampler

2.0 BASIC OPERATION

The Screen Point 15/16 Groundwater Sampler utilizes a stainless steel or PVC screen, which is encased in an alloy steel sampler sheath. An expendable drive point is placed in the lower end of the sheath while a drive head is attached to the top. O-rings on the drive head and expendable point provide a watertight seal, which keeps contaminants out of the system as the sampler is advanced to depth. Once the desired sampling interval is reached, extension rods equipped with a screen push adapter are inserted down the inside diameter of the probe rod string to hold the screen in place. The tool string is then retracted approximately 44 inches (1118mm) while the screen is held in place with the extension rods. At this point the system is ready for groundwater sampling.

2.1 Sampler Assembly

1. Install an O-ring on a steel expendable drive point. Firmly seat the expendable point in the necked end of a sampler sheath.

2. Place a PVC plug in the lower end of the wire-wound steel screen. Install an O-ring in the groove on the upper end of the screen. Slide the screen inside of the sampler sheath with the PVC plug toward the bottom of the sampler. Ensure that the screen did not displace the expendable point.

3. Install a bottom O-ring on a drive head. Thread the drive head onto the sampler sheath. Attach a drive cap to the top of the drive head. Ensure that the threads engage completely. Tighten with an adjustable wrench if necessary.

4. Sampler assembly is complete.

2.2 Advancing the Screen Point 15/16 Samplers (Fig. 2.1)

To provide adequate room for screen deployment with the Rod Grip Pull System, the probe derrick should be extended a little over half way out of the carrier vehicle before advancing the Screen Point 15/16 Sampler.

1. Begin by placing the assembled sampler in the advancement position beneath the hammer on the extended probe derrick.

2. Advance the sampler with throttle control at slow speed for the first 1 or 2 feet to ensure that the sampler is advancing straight. Switch the throttle control to fast speed for the remainder of the probe stroke.

3. Completely raise the hammer assembly. Remove the drive cap and place an O-ring in the top groove of the drive head. Distilled water may be used to lubricate the O-ring if needed. Add a probe rod and reattach the drive cap to the rod string. Advance the sampler the entire length of the new rod with the throttle control at fast speed.

4. Repeat Step 3 until the desired sampling interval is reached. Approximately 12 inches (305 mm) of the last probe rod must extend above the ground surface to allow attachment of the puller assembly. An additional probe rod may be added if the tool string is over-advanced.

5. Remove the drive cap and retract the probe derrick away from the tool string.

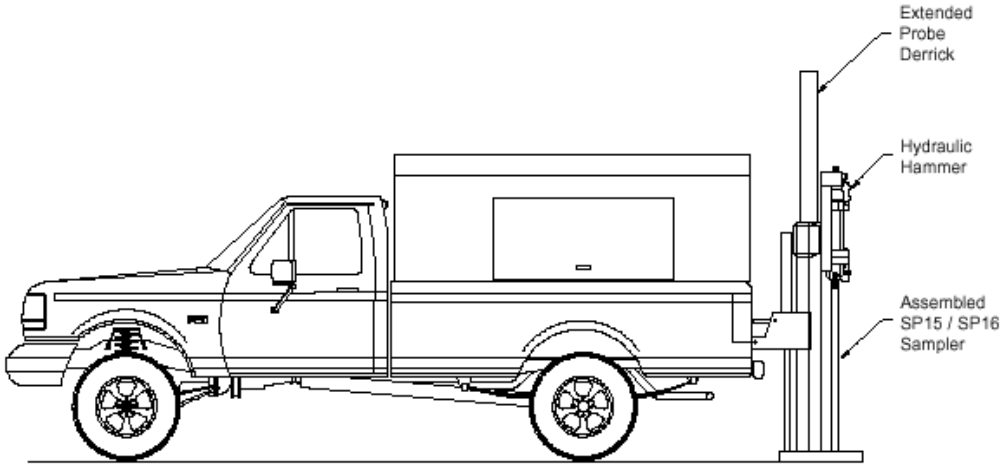


FIGURE 2.1
Screen Point 15 / Screen Point 16 Groundwater Sampler in Driving Position

2.3 Screen Deployment

1. Thread the screen push adapter on an extension rod. Attach a coupler to the other end of the extension rod. Lower the extension rod inside of the probe rod taking care not to drop it down the tool string. An extension rod jig may be used to hold the rods.

2. Add extensions until the adapter contacts the bottom of the screen. To speed up this step, extension rod Quick Links are recommended.

3. Maneuver the probe assembly into position for pulling.

Note: In this section, "Puller" refers to either Rod Grip Pull System.

4. Ensure that at least 48 inches (1219 mm) of extension rod protrudes from the probe rod. Thread an extension rod handle on the top extension.

5. Retract probe rods and sampler sheath while physically holding the screen in place with the extension rods. A slight knock with the extension rod string will help to dislodge the expendable point and start the screen moving inside the sheath. Raise the hammer and pull bracket assembly about 44 inches (1118 cm). At this point the screen head will rise with the probe rods. The screen is now deployed.

6. Lower the hammer assembly and retract the probe derrick. Remove the top extension rod and handle and top probe rod. Finally, extract all extension rods.

7. Groundwater samples can now be collected with a tubing bottom check valve assembly, mini-bailer, peristaltic pump, vacuum pump, small bladder pump, or other acceptable small diameter sampling device.

8. When inserting the tubing down the rod string to collect a sample, ensure that the tubing enters the screen interval. The tubing will sometimes catch on the edge of the funnel opening of the screen head. An up-and-down motion combined with rotation helps move the tubing past the lip and into the screen.

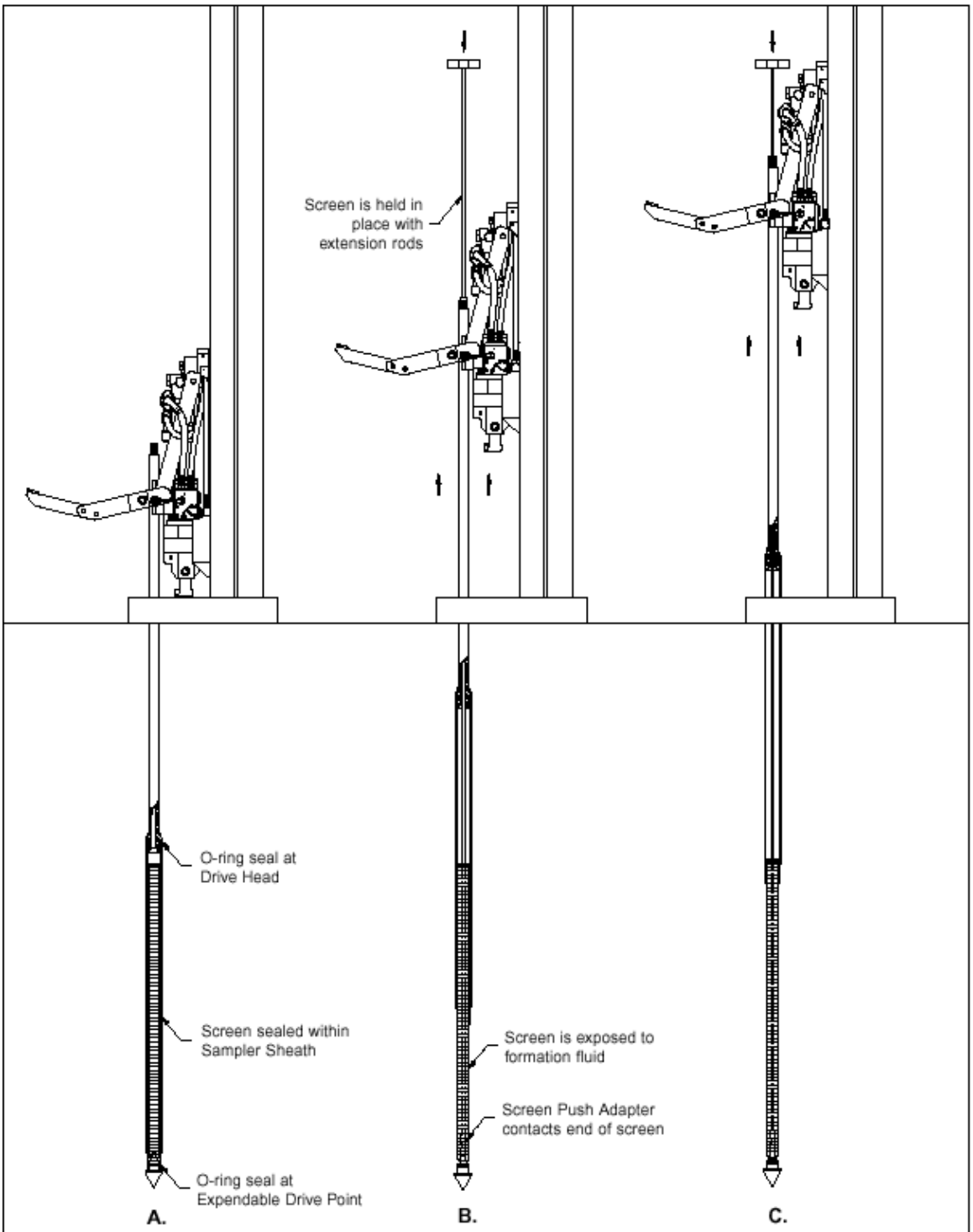


FIGURE 2.2
Screen Deployment for SP15 / SP16 Sampler

2.4 Retrieving the Screen Point 15/16 Samplers

The Rod Grip Pull System should be used for this process as it allows the operator to remove rods without releasing the tool string. This keeps rods from falling to the bottom of the probe hole. If a Rod Grip Pull System is not available, utilize a standard Pull Cap.

1. Position the probe derrick and hammer assembly to interface the splines on the Rod Grip Pull System with the outside surface of the protruding probe rod. Take care to align the splines parallel to the probe rod so not to cause a binding of the rod.

2. Lower the hammer to the bottom of the probe derrick.

3. Attach the Rod Grip Puller to the hammer assembly, encapsulating the probe rod.

4. Depress the handle on the Rod Grip Puller while raising the hammer assembly. The hammer assembly and the probe rod will rise together. Once the hammer assembly has reached the top of the derrick, release the probe rod by pushing up on the Rod Grip Puller handle. Lower the hammer assembly and remove the protruding probe rod from the sample string. Repeat this process until the SP-15/16 sampler drive head is at the grounds surface.

5. When all subsequent rods have been removed and the SP-15 sampler drive head is at ground surface lower the hammer assembly and pull the SP-15/16 sampler. Detach the SP-15/16 from the probe rod still encapsulated in the Rod Grip Puller. Slowly raise the probe foot and retract the derrick away from the SP-15/16 sampler. Manually retrieve the SP-15/16 sampler from the hole and disassemble it for decontamination.

3.0 DECONTAMINATION

After each sample location each portion of the sampler and its fittings are decontaminated. An Alconox detergent wash is used to remove all sources of possible cross contamination, i.e. loose or firmly attached soils or product. Upon completion of washing all surfaces of the sampler and fittings a potable water rinse is performed. A close visual inspection is conducted and the sampler and fittings are allowed to dry.

ATTACHMENT B

Supplemented Standard Operating Procedure
No. 2230.5A
Geoprobe® Operations for Soil Gas Sampling

SUPPLEMENTED STANDARD OPERATING PROCEDURES

No. 2230.5A

Geoprobe Operations for

Soil Gas Sampling

12/09/98

1.0 OBJECTIVE

The objective of this procedure is to retrieve a representative sample of soil gas at a desired depth.

1.1 DISCUSSION

Soil gas investigation is the process by which a vacuum system is applied to a sampling device that is deployed below the ground surface and the vapor retrieved from the soil is encapsulated within a sample container or syringe at the vacuums interface. This vapor sample can then be sent to a laboratory or analyzed on-site for subsequent volatile organic compounds.

2.0 POST RUN TUBING SYSTEM

2.1 Post Run Tubing Assembly

The initial Geoprobe® rod section is fitted with a Post Run Tubing (PRT) point holder in to which an expendable point is inserted (the expendable point remains in the hole). Successive probe rods are added and advanced into the ground until the desired sampling depth is achieved.

The probe rod sections are then raised four (4) to eight (8) inches to create a void to facilitate soil gas migration. A stainless steel PRT tubing adapter fitted with a neoprene "O" ring is secured into length polyethylene tubing. The tubing should have three (3) to four (4) feet sticking out of the sample string advanced into the ground. The tubing end with the adapter is inserted into the protruding probe rod and "fed" down the length of the sample string. Upon refusal, the tubing is turned clock wise to thread the adapter into the PRT point holder. This set-up is called the System Train.

1. Install an O-ring on the PRT expendable point holder. Thread the PRT expendable point holder in to the lead rod to seat the O-ring
2. Insert the expendable drive point into the PRT expendable point holder.
3. Install an O-ring on the PRT adapter and push the adapter into the Polyethylene tubing.

2.2 Advancing the Post Run Tubing System

1. Place the assembled PRT system in the advancing position beneath the hammer on the extended probe derrick.

2. Drive the system with throttle control at slow speed for the first 1 or 2 feet to ensure that the sampler is advancing straight. Switch the throttle to fast speed for the remainder of the probe stroke.

3. Completely raise the hammer assembly. Remove the drive cap, add a probe rod and reattach the drive cap to the rod string. Drive the sampler the entire length of the new rod with the throttle control at fast speed.

4. Repeat Step 3 until the desired sampling interval is reached.

5. Remove the drive cap and retract the probe derrick away from the tool string.

2.3 Connection of System Train to Vacuum/Volume System

A small length of Poly tubing is connected to the line valve on the vacuum/volume control panel. The sample train is then connected to a silicone septa tube. The system train septa is then attached to the Poly tube from the line valve on the Vacuum/Volume panel.

1. After the sample depth has been reached, disengage the expendable point by pulling up on the probe rods with the pull cap.

2. Remove the pull cap from the top probe rod and position the Geoprobe® unit to allow room to work.

3. Insert the adapter end of the tubing down the inside diameter of the rod bore until it hits bottom on the expendable point holder.

4. Allow at least 3 to 4 feet of tubing to extend out of the hole before cutting it.

5. Apply some downward pressure on the excess tubing while turning it clockwise to engage the adapter threads with the threads on the expendable point holder.

6. Pull up lightly on the tubing to test engagement of the threads.

2.4 Purge the System

A vacuum is applied to the system until five (5) to ten (10) times the sample volume is purged from the sample train. The gauges within the system measure vapor movement. The vacuum is applied for three (3) minutes. The vacuum draw is then shut off and the elapsed time it takes the system to reach ambient air pressure, or zero (0) on the gauges, is recorded.

2.5 Obtaining a Sample

Once draw is established and the system reaches equilibrium with ambient pressure a sample can be taken. One soil gas sample will be collected from each soil gas well. Soil gas samples will be collected in stainless steel Summa canisters (minimum volume of 400 mL) for laboratory submittal/analysis. A flow rate of <200 mL/min (calibrated orifice) will be maintained during sample collection. Flow and vacuum rates will be recorded during sampling activities. Please note that equipment and ambient air blanks should be collected during the sampling event.

3.0 QUALITY CONTROL

3.1 Vacuum/Volume System

Once daily the Vacuum/Volume tank should be tested for leaks. To test for leaks, pump down the system and then shut it off with line valve closed. Monitor the tank pressure for one half-hour. The pressure will remain constant if the system is free of leakage.

3.2 Testing of Integrity of Sample Train

Connect the sample train to the Vacuum/Volume system, plug the sampling end, and apply vacuum to the system. Shut off the line valve and monitor the sample line pressure gauge for three (3) minutes, look for decay of vacuum, as a sign of leakage.

4.0 DECONTAMINATION

The Poly tube will be disposed of after each use. All fittings, probe rods, adapters and subsequent sample train apparatus will be washed with an Alconox detergent and rinsed then allowed to dry.

ATTACHMENT C

Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH)

METHOD FOR THE DETERMINATION OF AIR-PHASE PETROLEUM HYDROCARBONS (APH)

Massachusetts Department of Environmental Protection

Office of Research and Standards

Bureau of Waste Site Cleanup

Commonwealth of Massachusetts

Executive Office of Energy & Environmental Affairs
Ian A. Bowles
Secretary

Department of Environmental Protection
Laurie Burt
Commissioner

December 2008
Final
Revision 0

METHOD FOR THE DETERMINATION OF AIR-PHASE PETROLEUM HYDROCARBONS (APH)

TABLE OF CONTENTS

	Topic		Page
1.0	Scope and Application		1
2.0	Summary of Method and Data Quality Objectives		2
3.0	Definitions and Units of Measure		3
4.0	Interferences and Method Limitations		5
5.0	Health and Safety Issues		5
6.0	Apparatus and Materials		5
7.0	Reagents and Standards		6
8.0	Sample Collection and Handling		8
9.0	Analytical Procedure		10
	9.1	Sample Preparation and Concentration	10
	9.2	GC/MS Conditions	10
	9.3	Retention Time Windows	11
	9.4	Calibration	11
	9.5	GC/MS Analysis of Samples	16
	9.6	Calculations	17
10.0	Quality Control		19
11.0	Data Production and Reporting		22
12.0	Reporting Limits		24
13.0	Method Performance		25
14.0	References		25
	Tables		26
Appendix 1	APH Method Detection Limit Studies		
Appendix 2	APH Method Chromatogram		
Appendix 3	Required APH Data Reporting Information		
Appendix 4	Recommended SOP For Cleaning, Certification, and Calibration of APH Air Sampling Equipment		
Appendix 5	APH Method Calculations		

LIST OF ACRONYMS

APH	Air-Phase Petroleum Hydrocarbons
BFB	4-Bromofluorobenzene
CAM	Compendium of Analytical Methods
%D	Percent Difference
GC/MS	Gas Chromatography / Mass Spectrometry
HPLC	High Pressure Liquid Chromatography
IDLC	Initial Demonstration of Laboratory Capability
IS	Internal Standard
LCS	Laboratory Control Sample
LMB	Laboratory Method Blank
MCP	Massachusetts Contingency Plan
MDL	Method Detection Limit
MtBE	Methyl tert-butylether
NIST	National Institute of Standards and Technology
QA/QC	Quality Assurance / Quality Control
RL	Reporting Limit
RPD	Relative Percent Difference
RRF	Relative Response Factor
RRT	Relative Retention Time
%RSD	Percent Relative Standard Deviation
Rt	Retention Time
SOP	Standard Operating Procedure
UHP	Ultra High Purity

NOTE: Abbreviations of units (e.g., amu, in. or mm Hg, m/e, $\mu g/m^3$, mL, min, ng, ppbV, psia, psig, etc.) are not included.

METHOD FOR THE DETERMINATION OF AIR-PHASE PETROLEUM HYDROCARBONS (APH)

MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION (MassDEP)

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the gaseous-phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in air and soil gas. Volatile aliphatic hydrocarbons are collectively quantified within two carbon number ranges: C5 through C8 and C9 through C12. Volatile aromatic hydrocarbons are collectively quantified within the C9 to C10 range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 28°C (isopentane) and 218°C (naphthalene).

1.2 This method is based on the collection of whole air samples in passivated stainless steel canisters, with subsequent analysis by gas chromatography/mass spectrometry (GC/MS). This method should be used by, or under the direct supervision of, analysts experienced in the use of GC/MS instrumentation for the identification and quantification of contaminant concentrations in air.

1.3 This method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MassDEP, 1994 and Updated Petroleum Hydrocarbon Fraction Toxicity Values For VPH/EPH/APH Methodology, November 2003). The method is intended to produce data in a format suitable for the characterization of risk at sites undergoing evaluation under the Massachusetts Contingency Plan (MCP, 310 CMR 40.0000) using the aforementioned toxicological approach.

1.4 This method may also be used to directly quantify the individual concentrations of the Target APH Analytes 1,3-butadiene, methyl-tert-butylether (MtBE), benzene, toluene, ethylbenzene, m- & p-xylenes, o-xylene and naphthalene in air and soil gas samples.

1.5 Petroleum products suitable for evaluation by this method include gasoline, as well as the volatile fractions of mineral spirits, kerosene, #2/diesel fuel oil, jet fuels, and certain petroleum naphthas. This method is not suitable for the identification and quantification of entrained aerosols, particulate-phase hydrocarbons, and petroleum products with a significant percentage of hydrocarbons with boiling points > 218°C.

1.6 The Reporting Limit (RL) of this method for each of the Target APH Analytes is determined by the lowest applicable Calibration Standard. The nominal RL for the individual target analytes is approximately 2 to 5 µg/m3. The RLs for the collective hydrocarbon ranges are empirically determined based on the number and lowest concentration of the component standards used in the calibration of the individual ranges. The nominal RLs for the aliphatic and aromatic ranges are 12 µg/m3 and 10 µg/m3, respectively.

1.7 This method includes a series of data adjustments steps to determine the concentrations of the collective aliphatic and aromatic hydrocarbon ranges of interest. These steps must be taken by the laboratory.

1.8 Data reports produced using this method must contain all of the information presented in Appendix 3. The format of these reports is left to the discretion of individual laboratories (but must include the same certification statement presented in the aforementioned Appendix and must be provided in a clear, concise, and succinct manner).

1.9 There may be better, more accurate, and/or less conservative ways to produce APH target and range data. MassDEP encourages methodological innovations that: (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes.

All significant modifications to this method, however, must be disclosed and described on the data report, as detailed in Section 11.1.2. Laboratories that make such modifications, and/or develop and utilize alternative approaches and methods, are further required to demonstrate that:

- Such modifications or methodologies adequately quantify the petroleum hydrocarbon target ranges, as defined in Sections 3.1.9 through 3.1.11 of this document, ensuring that any methodological uncertainties or biases are addressed in a manner that ensures protective (i.e., conservative) results and data (e.g., over, not under-quantification of the more toxic ranges);

- Such modifications and/or methodologies employ and document initial method demonstration and ongoing QA/QC procedures consistent with approaches detailed in the MassDEP CAM; and

- Such method and procedural modifications are fully documented in a detailed SOP.

1.10 This method is one way to quantify collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons within specified carbon number ranges. It has been designed in a manner that attempts to strike a reasonable balance between analytical method performance and utility. In this manner, assumptions and biases have been structured into the method to help ensure protective, though not overly conservative, data.

As an example, the Department recognizes that branched alkanes have lower boiling points than their n-alkane counterparts while many of the cycloalkane constituents of gasoline-range volatile organics have higher boiling points than their n-alkane counterpart. As a consequence:

(1) Depending upon the specific chromatographic column used, most branched C_9 alkanes are expected to elute before n-nonane, the beginning marker compound for the C_9 through C_{12} aliphatic hydrocarbon range, and will be conservatively counted in the more toxic C_5 through C_8 aliphatic hydrocarbon range;

(2) Depending upon the specific chromatographic column used, most branched C_5 alkanes will elute before n-pentane and before isopentane, the beginning marker compound for the C_5 through C_8 aliphatic hydrocarbon range, and will not be counted at all in the C_5 through C_8 aliphatic hydrocarbon range; and

(3) Depending upon the specific chromatographic column used, most cycloalkanes within the C_5 through C_8 and C_9 through C_{12} aliphatic hydrocarbon ranges will be counted within their proper range, with the exception of some C_{12} cycloalkanes which will elute after dodecane, the end marker compound for the C_9 through C_{12} aliphatic hydrocarbon range.

Based on the nature of petroleum releases encountered in the environment, the collective concentrations of the volatile aliphatic ranges as measured by the APH Method are considered to be suitable, along with concentrations of target analytes, for the evaluation of the risks posed by these releases, consistent with the toxicological approach developed by the Department to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MassDEP, 1994 and Updated Petroleum Hydrocarbon Fraction Toxicity Values For VPH/EPH/APH Methodology, November 2003).

1.11 This method should be used in conjunction with the current version of WSC-CAM-IVC, Quality Assurance and Quality Control Requirements for the Air-Phase Petroleum Hydrocarbons (APH) Method. WSC-CAM-IVC was developed by the Department to complement the MassDEP APH Method (MassDEP-APH-09) and to provide more detailed guidance regarding compliance with the quality control requirements and performance standards of the MassDEP APH Method. WSC-CAM-IVC is scheduled to be available on or before June 2009.

2.0 SUMMARY OF METHOD AND DATA QUALITY OBJECTIVES

2.1 Samples are collected in pre-cleaned, evacuated, passivated stainless steel canisters.

2.2 A concentrator system capable of the automated collection, trapping, focusing, and injection of measured aliquots removed from sample containers that employs a suitable mechanism for sample moisture control is recommended. Depending on the water retention properties of the packing, some or most of the water vapor contained in the sample completely passes through the concentrator during this process. Additional drying of the "trapped" sample aliquot, if required, is accomplished by forward purging the trap with clean, dry helium

(or other inert gas). Other water management approaches are also acceptable providing their use does not compromise the performance standards of the method (see Section 10.2).

2.3 Following preconcentration, the sample is transferred and cryogenically refocused onto the inlet of a capillary column on a gas chromatograph, further concentrating the sample.

2.4 The sample is then injected onto the gas chromatographic column, which separates the individual compounds and hydrocarbon ranges of interest. All compounds are detected using a mass spectrometer. Target APH Analytes are identified and quantified using characteristic ions. Collective concentrations of C_9-C_{10} aromatic hydrocarbons are quantified using extracted ions. Collective concentrations of aliphatic hydrocarbon ranges are quantified using the total ion chromatogram.

2.5 This method is based on USEPA Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-prepared Canisters And Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS).

2.6 Data Quality Objectives should be developed and applied for sampling and analytical efforts involving the use of this method. Key parameters of interest include: (a) the need for and extent of time-integrated air samples, (b) the acceptability of RLs achievable by the laboratory for the contaminants of interest, and (c) the identification and reporting of target and non-target analytes.

3.0 DEFINITIONS AND UNITS OF MEASURE

3.1 **Definitions**

3.1.1 **Absolute Pressure** is defined as the pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as, mm Hg, or psia.

3.1.2 **Air-Phase Petroleum Hydrocarbons** are defined as collective ranges of hydrocarbon compounds eluting from isopentane to n-dodecane, excluding Target APH Analytes. APH is comprised of C_5-C_8 aliphatic hydrocarbons, C_9-C_{12} aliphatic hydrocarbons, and C_9-C_{10} aromatic hydrocarbons.

3.1.3 **Aliphatic Hydrocarbon** is defined as acyclic or cyclic, saturated or unsaturated compounds, excluding aromatic compounds, that contain only carbon and hydrogen atoms.

3.1.4 **APH Calibration Check Standard** is defined as a gaseous-phase mixture of APH Components that is used to periodically check the calibration state of the GC/MS system. The APH Calibration Check Standard is prepared from the APH Working Standards and is generally one of the mid-level concentrations.

3.1.5 **APH Calibration Standard** is defined as a gaseous-phase mixture of APH Components that is used to calibrate the GC/MS system. The APH Calibration Standards are prepared from the APH Working Standards and are prepared at a minimum of five different concentrations.

3.1.6 **APH Components** are defined as the 26-component mixture of the aliphatic and aromatic compounds listed in Table 1. The APH Components are used to (a) define the individual retention times and chromatographic response factors for each of the Target APH Analytes, (b) define and establish the retention time windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average response factors which are used to calculate the collective concentrations of hydrocarbons within these ranges.

3.1.7 **APH Working Standards** are defined as gaseous-phase mixtures of all APH components which are used in the preparation of calibration standards (see Tables 3a and 3b). These standards are prepared with concentrations over the working range of the calibration curve by dynamic dilution of the gaseous Stock Standard with humidified ultra zero air or ultra high purity (UHP) nitrogen. The Stock Standard is delivered to a clean, passivated canister using a pump and mass flow controller.

3.1.8 **Aromatic Hydrocarbons** are defined as compounds whose structures include a cyclic structure and a closed conjugated system of double bonds containing only carbon and hydrogen atoms.

3.1.9 **C_5 through C_8 Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds that elute from isopentane to just before n-nonane (C_9).

3.1.10 **C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds that elute from just before n-nonane to just after n-dodecane.

3.1.11 **C_9 through C_{10} Aromatic Hydrocarbons** are defined as all aromatic petroleum hydrocarbon compounds that elute from just after o-xylene to just before naphthalene.

3.1.12 **Cryogen** is defined as the refrigerant used to obtain very low temperatures in the cryogenic trap of an analytical system. A typical cryogen is liquid nitrogen (boiling point = -196°C).

3.1.13 **Gauge Pressure** is defined as the pressure measured above atmospheric pressure (as opposed to absolute pressure). Zero gauge (0 psig) is equal to ambient atmospheric (barometric) pressure.

3.1.14 **Humidified Canister** is defined as a passivated stainless steel canister containing ultra zero air or UHP nitrogen pressurized to 30 psig with a relative humidity of 30 – 40% at 25°C to simulate moisture conditions in real-world samples. For example, a 6-liter humidified canister may be prepared by fortifying a certified-clean passivated canister with 130 µL of high pressure liquid chromatography (HPLC)-grade water and pressurizing to 30 psig. Alternatively, ultra zero air passed through HPLC-grade water contained in an in-line bubbler (humidifier) may be used to pressurize a certified-clean passivated canister to 30 psig.

3.1.15 **Laboratory Control Sample (LCS)** is defined as a Humidified Canister containing a separate source gaseous standard obtained from a different source than that used to prepare the APH Working Standards.

3.1.16 **Laboratory Method Blank (LMB)** is defined as a Humidified Canister pressurized with ultra zero air or UHP nitrogen to 30 psig.

3.1.17 **Nominal Sample Volume** is defined as the routine sample volume employed by the laboratory for APH Method sample analysis and calibration.

3.1.18 **Petroleum Hydrocarbon** is a generic term used to describe the complex mixture of chemical compounds derived from crude oil containing only carbon and hydrogen atoms.

3.1.19 **Stock Standard** is a gaseous cylinder containing the APH Components (all aliphatic and aromatic range calibration compounds and target analytes) and is used to prepare Working Standards.

3.1.20 **Target APH Analytes** are defined as 1,3-butadiene, MtBE, benzene, toluene, ethylbenzene, m- & p-xylene, o-xylene, and naphthalene.

3.2 Units of Measure

3.2.1 The units of measure referenced in this method for volume, concentration, and pressure are reflective of the conventions and standards that are commonly used by practitioners within this field, and/or the conventions and standards associated with commonly available instrumentation and equipment.

3.2.2 Concentrations of APH Target Analytes must be reported in $\mu g/m^3$. Collective aliphatic and aromatic hydrocarbon range data can only be reported in $\mu g/m^3$ (See Section 9.6.2).

3.2.3 Other physical measurements (pressure, volume, etc.) should only be reported in units specifically referenced in the APH Method.

4.0 INTERFERENCES AND METHOD LIMITATIONS

4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.2 System carryover can be a potential problem, particularly for heavier molecular weight hydrocarbons such as naphthalene. Carryover can occur after the analysis of high concentration standards or samples. Measures that must be taken to remove this system contamination can include the analysis of multiple blanks, the use of humidified air through the system, and occasional bake out or replacement of the concentrator system components.

4.3 High methane levels and/or carbon dioxide levels may interfere with the chromatography. Dilution may be performed on samples to minimize this effect; however, the RLs for diluted samples will be proportionately increased. It should be noted that although the concentrator systems must be designed to minimize elevated levels of carbon dioxide, the potential still exists to have interfering levels.

4.4 Certain organic compounds not associated with the release of petroleum products, including chlorinated solvents, ketones, and ethers may be detected by this method and may contribute to the collective response quantified within an aliphatic or aromatic hydrocarbon range. When requested by the data user, the identification of such non-APH compounds must be disclosed on the laboratory report form or case narrative. See Table 7 for a list of potential non-petroleum compounds which may contribute to hydrocarbon range concentrations.

5.0 HEALTH AND SAFETY ISSUES

5.1 The toxicity and carcinogenicity 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 file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 **Sample Canisters**

Certified clean, leak-free, stainless steel polished or silica lined passivated air sampling canisters, 1.0, 2.7, 3.0, and 6.0 liter capacity are most commonly used for the collection of APH Method samples depending on project requirements.

6.2 **Canister Sample Concentrator**

6.2.1 Two current systems include: Tekmar-Dohrmann AutoCan Autosampler & Cryogenic Concentrating Trap and Entech 7100A Preconcentrator/7016 Canister Autosampler. The mention of these canister sample concentrator systems by name does not preclude the use of other equivalent technologies for the APH Method.

6.2.2 Minimum Sample Concentrator Capabilities

- Concentrator system must have the ability to remove moisture.
- Internal standards must be added to all standards, field samples, and QC samples using the same technique.
- Concentrator system must have the ability to minimize elevated levels of carbon dioxide (can affect integration of C_5-C_8 aliphatic range).

6.3 **Gas Chromatograph System**

6.3.1 An analytical system complete with a temperature programmable gas chromatograph for use with a capillary column is required.

6.3.2 The required chromatographic column phase is 100% dimethyl polysiloxane (e.g., RTX-1, DB-1, etc.); required column dimensions are 60 meters, 0.25 mm ID, 1-micron film thickness, or column with demonstrated and documented equivalent chromatographic properties (i.e., same compound elution order).

> **NOTE: Based upon data obtained from the MassDEP VPH Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment and quantification of aliphatic and aromatic compounds within the collective hydrocarbon ranges specified in the method. Substitution of the required column is not allowed, unless it can be demonstrated that the selected column has equivalent chromatographic properties and elution order for the aliphatic and aromatic compounds and ranges of interest.**
>
> **To demonstrate equivalency of column chromatography,** a mid-range APH Calibration Standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C_5-C_8 and, C_9-C_{12} aliphatic hydrocarbons, C_9-C_{10} aromatic hydrocarbon ranges and target analytes must be determined for each column. The relative percent difference (RPD) between the concentrations of each hydrocarbon range and target analyte, excluding naphthalene, obtained from each column must be ≤25. The RPD for naphthalene must be ≤40. The elution order of APH Components on the proposed substitute column must be equivalent to the elution order on the required column.

6.4 **Mass Spectrometer System**

6.4.1 The mass spectrometer must be capable of scanning from 35 to 250 amu every three seconds or less, utilizing 70 eV in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when at least 50 *n*g of 4-bromofluorobenzene (BFB) is injected.

6.4.2 A data station is required that is capable of storing and reintegrating chromatographic data and capable of determining peak areas using a forced baseline projection.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 HPLC-grade water for canister humidification.

7.1.2 UHP helium for the GC/MS system.

7.1.3 Liquid nitrogen for the concentrator system and GC.

7.1.4 Ultra zero air or UHP nitrogen for the concentrator system and standard preparation.

7.2 **Stock Standard**

7.2.1 Gaseous cylinder containing all aliphatic and aromatic range calibration compounds and target analytes (see Table 1). Recommended concentration is 1 mg/m^3 for all components.

7.2.2 At the time this document was published, NIST-certified APH Stock Standards were commercially available from Air Liquide America Specialty Gases (formerly Scott Specialty Gases: Plumsteadville, Pa) and Spectra Gases, Inc. (Branchburg, NJ). The mention of any trade name, product or vendor in this document does not constitute an endorsement or recommendation by the MassDEP.

7.3 APH Working Standards

7.3.1 The preparation of gaseous Working Standards and Calibration Standards described in the following sections is based on the use of mass flow controllers to accurately measure and dispense volumes of the gaseous standards used in the preparation of intermediate (Working) and final (Calibration) Standards. Other gas metering or measuring devices may be used to prepare Working Standards and Calibration Standards for the APH Method so long as the accuracy and precision of standards prepared using these devices is documented and consistent with the overall quality objectives of the method.

> **NOTE:** It is unacceptable to use methanol-based stock standards for preparation of Working Standards due to fluctuations observed in the analytical system response when high levels of methanol are present in the canister. This option was acceptable in the prior version of the APH method but is no longer acceptable.

7.3.2 Prepare gaseous-phase APH Working Standards in pre-evacuated passivated canisters. The usual laboratory practice is to prepare Working Standards at two concentration levels (20 $\mu g/m^3$ and 500 $\mu g/m^3$, as shown in Tables 3a and 3b).

7.3.3 Using a mass flow controller, flow-inject a measured volume (flow rate x time) of the Stock Standard(s) into a pre-evacuated passivated canister using ultra zero air or UHP nitrogen for dilution/pressurization. For example, the Working Standard concentration to be used to establish the lower end of the calibration range (20 $\mu g/m^3$ nominal concentration) should allow for a flow-injection volume of at least 25 mL over a minimum of 10 seconds (150 mL/min x 10 seconds) for the lowest calibration point (the target RL). The Working Standard concentration to be used to establish the higher end of the calibration range (500 $\mu g/m^3$ nominal concentration) should allow for a flow-injection volume of at least 25 mL over 10 seconds (150 mL/min x 10 seconds) for the mid-range calibration point. In practice a known flow rate of ultra zero air or UHP nitrogen is added concurrently with the Stock Standard in most automated devices.

> **NOTE 1:** Other mass flow controllers may allow for lower volumes to be injected. At a minimum, the laboratory should not exceed the mass flow controller manufacturer's minimum flow rate or volume.

> **NOTE 2:** Gas-tight syringes can also be used in lieu of mass flow controllers in certain instances. Syringes may be more appropriate when preparing standards in low volume canisters (e.g., 1-liter canisters). In general, the use of the mass flow controllers is preferred for preparation of all Working Standards.

7.3.4 All Working Standards must be humidified to a minimum of 30% relative humidity. A ratio of 7.2 µL water/liter of gaseous standard is acceptable for humidification of Working Standards if the laboratory's calibration preparation system is not equipped with a humidification chamber (e.g., 6-liter canister = 18 liters when pressurized and therefore requires 7.2 µL x 18 L = 130 µL of water). After the addition of the stock standard, dilution gas, and humidification liquid (if required), the Working Standard canister must be pressurized (maximum 30 psig) with ultra zero air or UHP nitrogen. The internal pressure of the Working Standard canister should be accurately measured and documented.

7.3.5 It is recommended that all Working Standard canisters be allowed to equilibrate for at least 24 hours before use.

7.4 APH Calibration Standards

7.4.1 APH Calibration Standards consist of a series of measured flow-injected volumes of the APH Working Standards directly injected into the concentrator/GC/MS system.

7.4.2 For the individual APH Calibration Standards, a pre-designated concentration is directly flow-injected into the concentrator/GC/MS by varying the volumes of the Working Standards. At a minimum, five different concentrations are required for a valid calibration curve. The concentrations must be evenly dispersed over the full working range of the detector with the lowest calibration point corresponding to the target RL. Tables 3a and 3b provide recommended concentrations and preparation methods for each Calibration Standard used in the initial calibration of hydrocarbon ranges and Target Analytes, respectively.

7.4.3 The range of volumes used for the APH Calibration Standards must be inclusive of the minimum and maximum sample volumes that will be used during routine sample analysis (e.g., as shown in Tables 3a and 3b, the minimum volume is 25 mL and the maximum volume is 250 mL).. If sample volumes outside the range of calibration volumes are utilized, the laboratory must statistically demonstrate acceptable recovery of all target analytes over the full dynamic range of the calibration curve using the out-of-range injection volume. This statistical demonstration will be performed using the procedure described in Section 10.5, using the injection volume of interest with the higher concentration Working Standard. In any case, the minimum sample volume used should not be less than the manufacturer's recommendation for the concentrator (typically 20-25 mL).

7.5 Internal Standard and MS Tuning Standard

The recommended internal standards are Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5. The required MS tuning standard is BFB. Stock standards of these compounds should be prepared or purchased in a humidified canister at a concentration to accurately flow-inject a concentration of 10 ppbV or 10 $\mu g/m^3$ into the trap during the collection time for all calibration, blank, and sample analyses, whether through a mass flow controller or a sample loop injector. The volume of internal standard mixture added for each analysis must be the same from run to run. The concentrations of internal standards can be assigned a nominal value of 10 ppbV or 10 $\mu g/m^3$ for comparison and consistency with the laboratory's selected reporting units. This will vary among laboratories depending on which units are used during the calibration of the instrument.

8.0 SAMPLE COLLECTION AND HANDLING

8.1 Canister and Flow Controller Cleaning

All canisters must be leak tested and certified clean prior to being used for sampling. Associated canister sampling equipment (e.g., flow controllers, critical orifice assemblies) must also be deemed clean and appropriate for use prior to sampling. Cleaning techniques and acceptance criteria may vary between laboratories but, in general, procedures should include backflushing with humidified ultra zero air or UHP nitrogen. Flow controllers are calibrated with NIST-traceable flow meters. A detailed procedure for canister cleaning and maintenance is presented in Appendix 4.

8.2 Sample Collection

8.2.1 All samples must be accompanied by a chain-of-custody form, or equivalent, that documents the canister and flow controller serial numbers, date and time of sample collection, and all other pertinent sampling information.

8.2.2 Grab samples are collected by opening the sampling valve of a pre-evacuated canister (initial vacuum $\geq$ 28 in. Hg) and allowing the canister to fill to ambient pressure. Equalization to atmospheric pressure under these conditions may be completed in a minute or less.

8.2.3 Time-integrated samples require the use of a properly calibrated flow controller. The flow controller's calibration must be performed and verified (by the laboratory) prior to sample collection. Upon receipt at the laboratory, a post-sampling flow controller calibration verification must be performed. The RPD between the initial and post sampling calibration readings must be calculated. As long as the RPD is $\leq$ 20, the calibration and associated time interval are considered valid. If the RPD is >20, a notation must be provided in the data report form and case narrative disclosing the deficient RPD value. The flow controller RPD is one line of evidence in the proper

collection of samples for APH analysis. If the canister vacuum is acceptable after sampling and the flow controller RPD is outside of the acceptance criteria, data quality is not adversely affected.

Sampling Note:	Flow controllers will be calibrated such that a small amount of vacuum will remain in the canister at the end of sampling (approximately 5 in. Hg). The post-sampling canister vacuum will be measured by the laboratory using an annually calibrated, NIST-traceable vacuum/pressure gauge. The vacuum should be approximately 5 in. Hg to ensure a consistent flow rate throughout the measured time interval. However, due to temperature/pressure differences in the field, as well as site-specific conditions for various sampling applications (e.g., moisture levels, soil type, site access issues), the actual post-sampling canister pressure may be slightly different than 5 in. Hg.

8.2.4 Upon receipt at the laboratory, all samples must be assigned unique laboratory identification numbers.

8.2.5 The canister pressure of all grab and time-integrated samples must be measured and documented upon receipt at the laboratory. An annually calibrated NIST-traceable vacuum/pressure gauge is attached to the canister inlet, the sampling valve is briefly opened and the pressure is recorded. If the canister vacuum on receipt is > 15 in. Hg or if the canister vacuum measured on receipt at the laboratory differs from the final canister vacuum measured in the field by more than ±5 in. Hg, the client should be contacted to determine if analysis should proceed. If client indicates that the analysis should proceed, the noted anomalies should be documented on the data report form or the case narrative.

8.2.6 Samples may be pressurized to a maximum of 5 psig with humidified ultra zero air or UHP nitrogen after receipt in the laboratory. Refer to Section 9.5.1.3 for the calculation of dilution factors for pressurized samples.

8.2.7 **Documentation Requirements**

8.2.7.1 Pre-Sampling Information: Provided by the Laboratory

Canister Serial Number
Individual or Batch Certification Results
Canister Volume
Pre-sampling Canister vacuum
Flow controller serial number
Date Canister Released by the laboratory

8.2.7.2 Sampling Information: Provided by the Sampler

Site Location
Sampling Date
Sampling Location
Sample Identification (ID)
Canister Serial Number for each Sample ID
Canister Volume (liters) for each Sample ID
Sampling Duration
Flow Controller Identification Number (if utilized) for each Sample ID
Sampling Start and End Times
Initial and Final Ambient Temperatures and Atmospheric Pressures
Initial and Final Interior Temperatures
Initial and Final Canister Vacuums (in. Hg)
Date Shipped to Laboratory

8.2.7.3 Post Sampling Information: Provided by the Laboratory

Date Received
Laboratory ID
Vacuum of canister upon receipt at laboratory
Flow controller calibration RPD

8.3 **Holding Time**

Canisters should be used in the field in a timely manner (i.e., they should not be stockpiled at the site prior to use). The maximum holding time for the analysis of passivated canister samples for APH analyses is 30 days from the date of sample collection.

9.0 ANALYTICAL PROCEDURE

9.1 **Sample Preparation and Concentration**

9.1.1 Ensure the integrity of the canister sample as described in Section 8.0.

9.1.2 Connect the canister(s) valve to the concentrator autosampler or sample inlet line. The canister must remain closed.

9.1.3 Leak check all canister inlet connections. Analysis may not begin until the leak check has passed for each canister being tested. Refer to the concentrator manufacturer's specifications for leak check criteria. For example, the pressure change should not exceed 2.0 psia over a 30 second period for an Entech 7100A concentrator.

9.1.4 Open the canister valves.

9.1.5 For the analysis of low concentration samples, set up the concentrator system to withdraw the nominal sample volume (i.e., "1x" volume) of air from each canister. If high concentrations are expected, lower volumes may be used, but should be within the range of volumes used for the initial calibration standards (See Section 7.4.3). The nominal (1x) volume for typical analytical applications is 0.25 liters.

9.1.6 General description of the whole air sample concentration procedure: commercially available systems typically consist of a 2 to 3 stage trapping procedure that "freezes out" analytes of interest while simultaneously removing as much of the matrix (i.e., nitrogen, oxygen, carbon dioxide, methane, and moisture) as possible. Sample volume and flow rates are controlled via a mass flow controller which negates the effect of variations in the pressure and temperature of the samples and calibration standards. Sample is withdrawn from the canister by creating a pressure differential with a vacuum pump across the mass flow controller which is in line with the canister. An aliquot of sample is withdrawn at a constant flow rate onto a trap containing a sorbent material capable of adsorbing the analytes of interest. After equilibration, the target analytes are transferred to a cryofocusing unit, and when the GC is ready, the sample is injected by ballistic heating of the cryofocuser. The heating of the cryofocuser transfers the target analytes to the GC/MS system.

9.2 **GC/MS Conditions**

NOTE: Conditions described below are for an Agilent 6890/5973 GC/MS system.

9.2.1 **Gas Chromatograph**

9.2.1.1 Recommended oven program: initial temperature 25°C, hold for 5.0 min. Increase temperature to 100°C at 8.0°C/min, then increase temperature to 220°C at 25°C/minute. Hold for 4.0 min.

GC conditions may vary, but a minimum separation requirement of 50% (maximum peak height to valley height) must be met, particularly for hexane and bromochloromethane (IS) in a 20 µg/m^3 Calibration Standard.

9.2.1.2 Gas Flows: Helium carrier gas flow: 2 mL/min is the recommended flow rate.

9.2.1.3 Recommended Sample Injection

Injection mode: splitless.

Injection port temperature: 220°C.

Inlet pressure: 25.77 psi.

Purge flow: 36.3 mL/min at 0 minutes.

Gas saver flow: 20 mL/min.

9.2.2 **Recommended MS Conditions**

9.2.2.1 Temperature of MS transfer line: 240°C.

9.2.2.2 Temperature of MS Quad: 150°C.

9.2.2.3 Temperature of MS Source: 230°C.

9.2.2.4 Solvent Delay: 4.0 minutes.

9.2.2.5 Scanning Parameters: minimum range 35-250 amu.

9.2.2.6 MS must be tuned to pass BFB criteria listed in Table 2.

9.3 **Retention Time Windows**

The APH retention time (Rt) window for the C_5 - C_8 aliphatic hydrocarbons is defined as beginning 0.1 minutes before the elution of isopentane and ending 0.01 min before the elution of nonane. The C_9 - C_{12} aliphatic hydrocarbon range begins 0.01 min before the elution of nonane; therefore there is no overlap of the two ranges and the nonane peak is only included in the C_9 - C_{12} aliphatic hydrocarbon range. The C_9 - C_{12} aliphatic hydrocarbon range ends 0.1 min after the elution of dodecane.

The APH Rt window for the C_9 - C_{10} aromatic hydrocarbons is defined as beginning 0.1 minutes **after** the Rt of the beginning marker compound (o-xylene) and ending 0.1 before the Rt of the ending marker compound (naphthalene)

APH marker compounds and windows are summarized in Table 4.

9.4 **Calibration**

NOTE: Calibration and sample analysis calculations presented in this section are based on the GC/MS system response to multiple calibration standards expressed in units of "nominal" concentration (*u*g/m^3). Other quantitative approaches such as GC/MS system response to multiple calibration standards expressed in units of on-column mass (*u*g) are also acceptable.

9.4.1 The APH Working Standards are used to calibrate the GC/MS system. Two distinct calibration operations are necessary:

9.4.1.1 Target APH Analytes: Relative Response Factors (RRFs) are calculated for the Target APH Analytes, based upon a correlation between the concentration of analyte and area counts for the relevant quantitation ions. This allows for the individual identification and quantitation of these specific compounds. It is not necessary to develop response factors for any other individual APH Components.

9.4.1.2 Collective Aliphatic/Aromatic Hydrocarbon Ranges: RRFs are calculated for C_5-C_8 aliphatic hydrocarbons and C_9-C_{12} aliphatic hydrocarbons the TOTAL concentration of aliphatic APH Components eluting within the range of interest and the total ion area count. An RRF is calculated for C_9-C_{10} aromatic hydrocarbons based upon a correlation between the TOTAL concentration of aromatic APH Components eluting within this range and the total area count of extracted ions 120 and 134. Specified APH Components are designated marker compounds to define the beginning and end of the hydrocarbon ranges (see Table 4).

9.4.2 Primary (quantitation) and secondary extracted ions for all APH Components and the recommended internal standards are provided in Table 5. The recommended internal standards used for quantitation of each Target APH Analyte and hydrocarbon range are provided in Table 6. A listing of the hydrocarbon range compounds used to establish response factors for each hydrocarbon range of interest and their Individual Range Component Concentration ($\mu g/m^3$) are provided in Table 3a.

Initial Calibration

NOTE: A sample calculation demonstrating the proper application of the equations shown in the following sections is presented in Appendix 5, APH METHOD CALCULATIONS.

9.4.3 Perform the initial calibration at a minimum of five different concentrations prepared using various volumes of the APH Working Standards. Recommended range and target analyte calibration standard concentrations are provided in Tables 3a and 3b, respectively. The lowest calibration standard must be at or below the RL. If the response for a Target APH Analyte is not linear at the lowest level for the higher molecular weight compounds, this point should not be included in the calibration curve for the compound. As a result, the analysis of more than five concentrations may be required in order to ensure a minimum of five calibration points for each analyte.

9.4.4 Analyze each Calibration Standard according to the procedures specified in Sections 9.1 and 9.2.

9.4.5 Target APH Analytes - Tabulate the area response of the primary (or quantitation) ions against the concentration for each Target APH Analyte and internal standard and calculate an RRF for each compound using Equation 1. Perform this calculation for each Target APH Analyte.

Equation 1: Relative Response Factor for Target APH Analytes

$$RRF = [(A_{EC}) * (C_I)] / [(A_{EI}) * (C_c)]$$

where:

RRF = relative response factor
A_{EC} = area count of the primary (quantitation) ion for the analyte of interest
C_I = concentration of the associated internal standard ($\mu g/m^3$): See Section 7.5
A_{EI} = area count of the primary (quantitation) ion for the associated internal standard
C_C = concentration of analyte of interest ($\mu g/m^3$): refer to last column of Table 3b

9.4.6 Hydrocarbon Ranges - Establish retention time windows for the hydrocarbon ranges using the APH Component marker compounds shown in Table 4.

9.4.7 Calculate an RRF for the C_5-C_8 aliphatic hydrocarbon range using the following steps.

9.4.7.1 Using total ion integration, sum the individual peak areas of the six APH Components that are used to establish an average range RRF for C_5-C_8 aliphatic hydrocarbons, as designated in Table 3a. Do not include the peak areas of internal standards (all of the recommended internal standards elute in this range).

9.4.7.2 Using the total area generated in Section 9.4.7.1, calculate the C_5-C_8 aliphatic hydrocarbon range RRF using Equation 2.

Equation 2: Relative Response Factor for C_5-C_8 Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

where:

A_T = total ion area count of the six aliphatic APH Components which elute within this range (see Table 3a)

C_T = summation of the concentrations of the six aliphatic APH Components ($\mu g/m^3$) which elute within this range: refer to the last column of Table 3a

9.4.8 Calculate an RRF for the C_9-C_{12} aliphatic hydrocarbon range using the following steps.

9.4.8.1 Using total ion integration, sum the individual peak areas of the six APH Components that are used to establish an average range RRF for C_9-C_{12} aliphatic hydrocarbons, as designated in Table 3a. Do not include the peak area of BFB.

9.4.8.2 Using the total area generated in Section 9.4.8.1, calculate the C_9-C_{12} hydrocarbon range RRF using Equation 3.

Equation 3: Relative Response Factor for C_9-C_{12} Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

9.4.9 Calculate an RRF for the C_9-C_{10} aromatic hydrocarbon range using the following steps.

9.4.9.1 Using extracted ion m/e 120, sum the individual peak areas of the five APH Components that are used to establish an average range RRF for C_9-C_{10} aromatic hydrocarbons, as designated in Table 3a.

9.4.9.2 Using extracted ion m/e 134, sum the individual peak areas of the five APH Components that are used to establish an average range RRF for C_9-C_{10} aromatic hydrocarbons, as designated in Table 3a.

9.4.9.3 Sum the area counts from Sections 9.4.9.1 and 9.4.9.2.

9.4.9.4 Using the area count generated in 9.4.9.3, calculate the C_9-C_{10} aromatic range RRF using Equation 4.

Equation 4: Relative Response Factor for C_9-C_{10} Aromatic Hydrocarbons

$$\text{Range } RRF = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

where:

A_T = summation of area counts for extracted ions 120 and 134 for the five aromatic APH Components which elute within this range (see Table 3a)

C_T = summation of the concentrations of the five aromatic APH Components ($\mu g/m^3$) which elute within this range: refer to the last column of Table 3a

9.4.10 Calculate the average RRF for each of the Target APH Analytes and each hydrocarbon range.

9.4.11 Calculate the percent relative standard deviation (%RSD) of the RRFs over the working range of the curve for each of the Target APH Analytes and each hydrocarbon range using Equation 5.

Equation 5: Percent Relative Standard Deviation

$$\%RSD = [(SD_{n-1})/(AVG_X)]*100$$

where:

%RSD = percent relative standard deviation
SD_{n-1} = standard deviation (n-1 degrees of freedom)
AVG_x = average RRF from the initial calibration curve

9.4.11.1 If the %RSD is ≤30, linearity can be assumed for the associated Target APH Analyte or hydrocarbon range. For naphthalene, the %RSD can be ≤40.

NOTE: The use of linear or quadratic regression to evaluate the calibration curve is not allowed.

9.4.12 The initial calibration must be verified through the analysis of an LCS. This analysis must be performed every time an initial calibration is performed and prior to sample analyses on a daily basis.

9.4.12.1 The LCS must be prepared in a certified-clean canister from a different Stock Standard than that used to prepare the calibration standard. The LCS should be prepared at a mid-range calibration curve concentration.

9.4.12.2 At a minimum, the LCS must contain 1,3-butadiene, benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, and naphthalene and at least one compound from each hydrocarbon range (recommended representative range compounds: heptane for C_5-C_8 aliphatics, decane for C_9-C_{12} aliphatics, and 1,3,5-trimethylbenzene for C_9-C_{10} aromatics). The concentration of the representative range compounds must be greater than the lowest summed range concentration in Table 3a (e.g., suggest using 20-50 $\mu g/m^3$).

9.4.12.3 Calculate the percent recovery of each Target APH Analyte and hydrocarbon range using Equation 6. The percent recovery must be between 70% and 130%.

Equation 6: Percent Recovery

$$\%R = [(C_{found}) / (C_{true})]*100$$

where:

%R = Percent recovery
C_{found} = Concentration of the analyte or hydrocarbon range detected in the LCS ($\mu g/m^3$)

C_{true} = True concentration of the analyte or hydrocarbon range in the LCS ($\mu g/m^3$)

Continuing Calibration

9.4.13 A continuing calibration check must be performed daily prior to sample analysis.

9.4.14 The concentration of the APH Calibration Check Standard must be near the midpoint of the calibration curve.

9.4.15 Calculate the RRF for each APH Target Analyte and hydrocarbon range from the Calibration Check Standard using Equations 1 through 4.

9.4.15.1 Calculate the percent difference (%D) of the Calibration Check Standard RRF from the initial calibration average RRF using Equation 7.

Equation 7: Percent Difference

$$\%D = [(RRF_C) - (RRF_I)]/[(RRF_I)] * 100$$

where:

%D = percent difference
RRF_C = RRF from the APH Calibration Check Standard
RRF_I = average RRF from the initial calibration curve

9.4.16 The %Ds must be ≤30. If more than one compound fails to meet this criterion, or if the %D for any one compound is greater than 50, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

Retention Time Windows

9.4.17 The range retention time windows must be established daily based upon the retention time of the marker compounds in the APH Calibration Check Standard. The marker compounds used for each range are defined in Table 4.

Daily GC/MS Performance Check

9.4.18 A check of the GC/MS tuning must be performed daily prior to sample analyses. The GC/MS system is checked to confirm that acceptable performance criteria for mass spectral ion abundance ratios are met for BFB. These criteria must be met prior to analyzing any additional standards, blanks and samples.

9.4.19 Performance criteria for the required tuning standard, BFB, are provided in Table 2. If the tuning criteria are not met, the GC/MS must be retuned and the analysis repeated.

9.5 **GC/MS Analysis of Samples**

9.5.1 Pre-concentrate the pre-established nominal volume of sample (typically 0.25 liters) on the concentrator and inject it onto the GC column. When the nominal volume of the sample is analyzed, the dilution factor is 1.0.

Dilution Factors and Sub-Atmospheric Samples

9.5.1.1 For dilutions, sample volumes smaller than the nominal volume can be analyzed. The smallest volume used should not be less than that used for the initial calibration. See

Section 7.4.3 for further instructions on sample volumes. When volumes less than the nominal sample volume are analyzed, the dilution factor is calculated as follows:

DF = nominal sample volume/actual volume analyzed

9.5.1.2 For more concentrated samples where analysis of smaller volumes will not be adequate to ensure concentrations are within the calibration range, the canister must be pressurized and an aliquot of sample removed and injected into another canister. The dilution factor is calculated using the following steps:

1. Calculate the dilution factor (DF1) due to the pressurization of the sample using Equation 8 below.

2. Calculate the dilution factor (DF2) of the prepared sample:

DF(2) = DF(1) * volume sample removed from original canister/volume of new canister

3. Calculate the final dilution factor:

DF = DF(2)* (nominal sample volume/actual volume analyzed)

9.5.1.3 Samples which arrive at the laboratory with high vacuum levels (i.e., > 15 in. Hg) must be pressurized with ultra zero air or UHP nitrogen. The laboratory may also choose to pressurize all canisters upon receipt. This pressurization results in a dilution factor. The dilution factor is calculated using Equation 8.

Equation 8: Dilution Factor for Pressurization of Subatmospheric Samples

$$DF = (P_f + 14.7)/(Pi + 14.7)$$

where:

P_i = pressure reading of canister prior to pressurization (units = psig)
P_f = pressure reading of canister after pressurization (units = psig)
DF = dilution factor

Note: To convert from in. Hg to psig:

psig = in. Hg * 0491159

9.5.2 **Identification of APH Target Analytes**

The Target APH Analytes in field samples must be identified by a qualified mass spectrometrist competent in the interpretation of chromatograms and mass spectra.

9.5.2.1 The laboratory **must** report all APH Target Analytes that meet the following criteria:

(1) The relative retention time (RRT) of the target analyte in the sample agrees with the RRT of the target analyte in the associated Calibration Check Standard within $\pm$ 0.33 minutes; and
(2) The relative intensities of the primary (quantitation) and secondary ions (Table 5) for the target analyte in the sample agree within ± 20% of the relative intensities of the same ions in the Calibration Check Standard.

9.5.2.2 If co-elution of interfering components prohibits accurate identification of the sample component RRT from the total ion chromatogram, the RRT should be assigned using extracted ion current profiles for the ion unique to the component of interest.

9.5.2.3 If the above-referenced criteria are met but in the analyst's opinion, a false positive result is suspected, this must be reported and explained in the case narrative.

9.5.2.4 For comparison of the target analyte's mass spectra between samples and standards, mass spectra of standards obtained on the GC/MS under the same instrument conditions are required (e.g., from the calibrations). Once obtained, these standard spectra must be used for identification and reference purposes.

9.6 Calculations

9.6.1 **Individual Target APH Analytes:** The average response factor from the initial calibration is used to calculate the concentration of an analyte detected in the sample. Equation 9 is used to calculate the concentration of Target APH Analytes in µg/m^3. Equation 10 is used to convert µg/m^3 to ppbV.

Equation 9: Calculation of Sample Concentration (µg/m^3)

$$Cx = [(A_x) * (C_{IS})]/[(A_{IS}) * (RRF_{avg})] * DF$$

where:

Cx= concentration of target analyte, µg/m^3
Ax = area of primary (quantitation) ion for the Target APH Analyte (see Table 5)
C_{IS} = concentration of the associated internal standard, µg/m^3: See Section 7.5
A_{IS} = area of primary (quantitation) ion for the associated internal standard (see Table 5)
RRF_{avg} = average RRF for the Target APH analyte to be measured
DF = dilution factor (See Section 9.5.1)

Equation 10: Conversion of µg/m^3 to ppbV

$$ppbV = Cx * 24.45 / MW$$

where:

MW = molecular weight of the compound of interest, g/mol (see Table 1 for a list of the molecular weights of the Target APH Analytes)
24.45= molar gas constant; assumes R = 0.08206 L-atm/mole-K, T = 298K and P = 1 atm

9.6.1.1 The integration of Target APH Analytes and internal standards must be performed from valley to valley.

9.6.2 **Hydrocarbon Ranges**

When calculating the APH Method aliphatic and aromatic hydrocarbon range concentrations, the laboratory **must** include the area of **all** peaks eluting within the retention time windows specified for these ranges, excluding internal standards and target analytes, as described in Sections 9.6.2.1, 9.6.2.2, and 9.6.2.3 below.

The average hydrocarbon range RRF from the initial calibration is used to calculate the concentration (µg/m^3) of hydrocarbon ranges in samples**. Collective peak area integration for the hydrocarbon ranges must be from baseline (i.e., must include the unresolved complex mixture).**

NOTE: Hydrocarbon range concentrations can only be reported in µg/m^3.

At the discretion of the data user, the contribution of non-APH compounds (compounds not meeting the definitions in Sections 3.1.9, 3.1.10 and 3.1.11) that elute within the method-defined retention time windows for the aliphatic and aromatic ranges may be excluded from collective range concentration calculations. Specifically, the total ion area counts (aliphatic ranges) and the 120/134 m/e area counts (aromatic range) for these non-APH compounds may be excluded providing the compound is **positively identified** by GC/MS. However, if the non-APH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count cannot be subtracted from the range. In addition, in complex sample matrices (i.e., many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible. All data adjustments and the presence of these non-APH compounds must be disclosed on the laboratory report form and case narrative. A list of common non-APH compounds that elute within the aliphatic and aromatic ranges is presented in Table 7.

Detailed guidance regarding the identification criteria for these non-APH compounds is presented in Section 11.2.

9.6.2.1 **C_5-C_8 Aliphatic Hydrocarbons**

- Using total ion integration, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 4.

- From this sum, subtract the total ion area counts of all internal standards which elute in this range (all of the recommended internal standards elute in this range).

- Calculate a preliminary concentration in µg/m^3 using Equation 11.

Equation 11: Calculation of Preliminary Sample Concentration (µg/m^3)

$$Cx = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})]$$

where:

Cx= concentration of hydrocarbon range, µg/m^3
A_x = C_5-C_8 aliphatics: total ion area count of all peaks eluting within aliphatic hydrocarbon range window (excluding the internal standards)
C_{IS} = concentration of the associated internal standard (µg/m^3): See Section 7.5
A_{IS} = area count of the primary (quantitation) ion for the associated internal standard
RRF_{avg} = average RRF for the hydrocarbon range of interest

- From the preliminary concentration (µg/m^3), calculate an adjusted concentration of C_5-C_8 aliphatic hydrocarbons by subtracting the concentrations of Target APH Analytes which elute in this range (typically MtBE, benzene, toluene, ethylbenzene, and m-, p- & o- xylenes for the C_5-C_8 aliphatic hydrocarbons).

9.6.2.2 **C_9-C_{10} Aromatic Hydrocarbons**

- Using extracted ion 120, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 4.
- Using extracted ion 134, sum all peaks in the appropriate retention time window, as determined in Section 9.3 and Table 4.
- Sum the area counts of extracted ions 120 and 134 from the above two steps.
- Calculate the concentration in $\mu g/m^3$ using Equation 11, using the summed areas of extracted ions 120 and 134 for Ax.

9.6.2.3 **C_9-C_{12} Aliphatic Hydrocarbons**

- Using total ion integration, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 4.
- From this sum, subtract the total ion area count of the BFB peak.
- Calculate a preliminary concentration in $\mu g/m^3$ using Equation 11, using the area count generated from the previous step for Ax.
- From the preliminary concentration, calculate an adjusted concentration of C_9-C_{12} aliphatic hydrocarbons by subtracting the concentrations of Target APH Analytes which elute in this range (possibly naphthalene depending on GC conditions), and by subtracting out the concentration of C_9-C_{10} aromatic hydrocarbons.

10.0 QUALITY CONTROL

10.1 General Requirements and Recommendations

10.1.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an Initial Demonstration of Laboratory Capability (IDLC) and an ongoing analysis of prepared QC samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data produced. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method.

10.1.2 At a minimum, for each analytical batch (up to 20 samples), a beginning Initial Calibration or Calibration Check Standard, LMB, LCS, and a Sample Duplicate must be analyzed. However, it should be noted that the analysis of the Calibration Check Standard is required prior to sample analysis and every 24 hours, at a minimum. The LMB and LCS should be carried through the complete sample preparation and measurement processes.

10.1.3 The recommended sequence of analysis is as follows:

(1) Analytical batch calibration standards (initial) or mid-range Calibration Check Standard (daily check of initial calibration), either of which are used to evaluate BFB for GC/MS tuning. [**REQUIRED**]
(2) Analytical batch LCS. **[REQUIRED]**
(3) Analytical batch LMB. **[REQUIRED]**
(4) Batch samples (up to 20).
(5) Sample Duplicate. **[REQUIRED]**

All analytical sequences and data must be recorded in a daily run log.

10.2 **Minimum Instrument QC**

10.2.1 **Internal standards**

10.2.1.1 Internal standards must be adequately resolved from individual compounds in the APH Calibration Standard. A minimum separation requirement of 50% (maximum peak height to valley height) must be met, particularly for hexane and bromochloromethane (IS) in a 20 µg/m^3 Calibration Standard.

10.2.1.2 Internal standard recoveries must be evaluated with each field sample, blank, LCS and Sample Duplicate. The internal standard area counts in each field sample, blank, and LCS must be evaluated. The internal standard area counts must be within 50-200% of the internal standard area counts in the corresponding Calibration Check Standard. If the internal standard area counts fall outside of this range, check calculations to locate possible errors, check the sample introduction system for leaks or other malfunctions, and check for changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture).
(2) The internal standard exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in the sample.

If a sample with an internal standard recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the data report form and discussed in the case narrative.

Analysis of the sample on dilution may diminish matrix-related internal standard recovery problems. This approach can be used as long as RLs less than or equal to the applicable MCP standards will still be achieved with the dilution. If not, reanalysis without dilution must be performed, unless the concentrations of target analytes do not allow an undiluted run. Recoveries of internal standards outside of the acceptable range after reanalysis must also be noted on the data report form and discussed in the case narrative.

10.2.2 **Mass spectrometer tuning** must be performed daily (once every 24 hours) before any analyses are conducted. Acceptance criteria for the recommended tuning standard, BFB, are provided in Table 2.

10.2.3 **Laboratory Method Blanks** must be analyzed daily (once every 24 hours) prior to sample analyses and after samples which are highly contaminated (i.e., at concentrations above the highest calibration standard) to determine if sample carryover has occurred. If samples have been analyzed using an autosampler, data should be evaluated for potential carryover and reanalysis conducted, as appropriate. The Laboratory Method Blank must be free of Target APH Analyte and hydrocarbon range contamination at or above the RL. However, C_{12} hydrocarbons and naphthalene may be present at up to two times the RL.

10.2.4 **Relative Retention Times** must be established for each analyte and hydrocarbon range of interest each time a new GC column is installed and must be verified and/or adjusted on a daily basis. (See Section 9.3).

10.2.5 **Calibration**

10.2.5.1 **Initial Calibration:** RRFs must be generated for each APH Target Analyte and hydrocarbon range based upon the analysis of calibration standards prepared at a minimum of 5 concentrations. With the exception of naphthalene, the linearity of RRFs may be assumed if the %RSD over the working range of the curve is ≤30. (See Section 9.4). For naphthalene, the %RSD must be ≤40.

10.2.5.2 **Calibration Check Standard:** The Calibration Check Standard must be analyzed prior to sample analysis to verify the accuracy of the calibration of the instrument. For analytes of interest, the %D must be ≤30. If more than one compound fails to meet this criteria, or if the %D for any one compound is greater than 50 the instrument must be recalibrated. Otherwise, sample analysis may proceed.

10.2.6 **Laboratory Control Samples** must be analyzed daily (once every 24 hours) prior to sample analyses. Recoveries of APH target analytes and representative aliphatic and aromatic range compounds must be between 70 and 130%.

- If the recoveries are low and outside of the acceptance limits, reanalyze the LCS and associated samples. If still outside of the acceptance limits, recalibrate.
- If the recoveries are high and outside of the acceptance limits and the affected compound was detected in the associated samples, reanalyze the LCS and the associated samples. If still outside of the acceptance limits, recalibrate.
- If the recoveries are high and sample results were nondetect, data can be reported without qualification; however, the high recoveries should be noted in the case narrative.

10.2.7 **Sample Duplicate** - One sample duplicate must be analyzed with every batch of 20 samples or less per matrix. Sample duplicates are prepared by analyzing one sample in duplicate. The purpose of the sample duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. Equation 12 is used to calculate the RPD of the Target APH Analyte and hydrocarbon range concentrations. The RPD of detected results in the sample duplicate samples must not exceed 30 when the results are >5x the RL.

- If the RPD exceeds 30 and both results are >5x the RL, the sample analysis must be repeated.
- If an analyte is detected in one analysis at >5x the RL and not detected in the duplicate analysis, the analysis must be repeated.
- If an analyte is detected in one analysis at ≤5x the RL and not detected in the duplicate analysis, the RPD is not calculable and the analysis does not have to be repeated.
- If an analyte is not detected in both the original and duplicate analyses, the RPD is not calculable. No further action is required.

Equation 12. Relative Percent Difference Calculation:

$$RPD = (C_s - C_d)/[(C_s + C_d)/2]*100$$

where:

C_s = concentration in original sample analysis
C_d = concentration in duplicate sample analysis

10.3 If any of the performance standards specified in Section 10.2 are not met, the cause of the non-conformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the criteria and those that are fallen out must be rerun. These QC samples include the Calibration Check Standard, LMB and LCS. If this is not possible, that data must be reported as suspect.

10.4 **Initial and Periodic Method QC Demonstrations**

The procedure specified below must be conducted, successfully completed and documented as an IDLC prior to the analysis of any samples by the APH Method. Subsequent to this initial demonstration, additional

evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, training new analysts, and/or in response to confirmed or suspected systems, method, or operational problems.

The IDLC includes an initial demonstration of accuracy and precision. The following procedure must be used:

10.4.1 Analyze a minimum of 4 replicate samples of a Calibration Check Standard.

10.4.2 Calculate the measured concentrations of each analyte and hydrocarbon range in all replicates, the mean accuracy (as a percentage of the true value) for each analyte and hydrocarbon range, and the precision (as %RSD) of the measurements for each analyte and hydrocarbon range.

10.4.3 For each analyte and hydrocarbon range, the mean accuracy, expressed as a percentage of the true value (i.e., recovery), must be between 70% and 130%, and the replicate precision, expressed as %RSD, must be ≤25. The IDLC must meet these conditions for analysis to proceed.

11.0 DATA PRODUCTION AND REPORTING

11.1 General Reporting Requirements

11.1.1 The required data report content for the APH Method is presented in Appendix 3. While it is permissible to alter the form and presentation of the data, all of the information must be provided in a clear, concise, and succinct manner. This information provides data users with a succinct and complete summary of pertinent information and data, as well as a clear affirmation that the QC procedures and standards specified in this method were evaluated and achieved.

11.1.2 If a significant modification to the APH Method is utilized, an attachment to the analytical report must be included to demonstrate compliance with the method performance requirements of Section 1.9 on a matrix-specific and petroleum product-specific basis.

"Significant Modifications" to the APH Method shall include, but are not limited to, any of the following:

(1) The use of sample collection devices other than evacuated passivated stainless steel canisters (i.e., tedlar bags).
(2) The use of alternative detectors other than GC/MS to quantify Target APH Analytes and/or hydrocarbon range concentrations.
(3) The use of extracted ions other than 120 and 134 to quantify C_9-C_{10} aromatic hydrocarbons.
(4) The failure to provide all of the data and information required in the report form presented in Appendix 3.

Data produced using an analytical method incorporating any of the "Significant Modifications" described above may ***not*** be reported as APH data. APH range concentrations are method-defined parameters and as such may only be reported as APH data when produced using the method without "Significant Modifications."

11.1.3 Positive affirmation that all required QA/QC procedures and performance standards were followed and achieved means that all of the required steps and procedures detailed in Sections 9.0 and 10.0 have been followed, and that all data obtained from these steps and procedures were within the acceptance limits specified for these steps and procedures.

11.1.4 In addition to sample results, the APH data report must contain the following items:

- LMB results.
- LCS results.
- Sample duplicate results.
- Internal standard results (for all field samples and QC samples).

- Results of re-analyses or dilutions must be reported as follows:

  (1) If re-analysis due to internal standard issues yields similar non-conformances, the laboratory must report both results.

  (2) If re-analysis due to internal standard issues is performed outside of holding time and yields acceptable internal standard recoveries, the laboratory must report results of both analyses.

  (3) If sample is not re-analyzed for internal standard issues due to obvious interference, the laboratory must provide the chromatogram in the data report.

  (4) If diluted and undiluted analyses are performed, the laboratory must report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc) for each analysis must be reported. This may result in more than one analysis per sample being reported.

- If a significant modification to the analytical method is utilized, demonstration of compliance with analytical performance standards specified in Section 1.9 on a matrix-specific and petroleum product-specific basis must be included as an attachment to the analytical report. If the modification was not an analytical modification (i.e., use of tedlar bags), the demonstration of compliance is not required; however, the modification must be noted in the case narrative.

11.1.5 General laboratory reporting requirements are outlined in Section 2.4 of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data*.

11.2 Reporting Requirements for Non-APH Compounds

As described in Section 9.6.2, the contribution (i.e., area count) of compounds not meeting the regulatory definition of the aromatic and/or aliphatic hydrocarbons, defined in Sections 3.1.9, 3.1.10 and 3.1.11 that elute within the method-defined retention time windows for these hydrocarbon ranges, may be excluded from collective range concentrations **at the discretion of the data user** providing the compound meets the requirements for positive **GC/MS identification** as described in Section 11.2.1.

- If the non-APH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count may not be subtracted from the aliphatic range.
- In complex sample matrices (i.e., many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible.

All data adjustments and the presence of these positively identified non-APH compounds must be disclosed on the laboratory report form and case narrative. If this data adjustment is requested by the data user, the laboratory will be required to evaluate those peaks with a peak height ≥ ½ of the peak height of the closest internal standard. Refer to Table 7 for a list of common non-APH compounds that elute within the aliphatic and aromatic hydrocarbon ranges.

11.2.1 Requirements for Positive GC/MS Identification of Non-APH Compounds

- Spectral identification must be evaluated by a qualified mass spectrometrist.
- The spectral library match must be ≥ 85% for an identification to be made.
- The major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or for the presence of co-eluting compounds.

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.
- Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different chromatographic retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs (as a mixture of two isomers).

  NOTE: Analyst may use professional judgment for the identification of non-APH compounds. If non-APH compounds are identified using criteria different than the criteria listed above, this should be disclosed in the case narrative,
- If the data user determines that the presence of the non-APH compound reported by the laboratory may appreciably increase the overall risk posed by the site or the utility/cost of the potential remedial measures under consideration, additional analytical work is recommended to verify the identification and/or concentration of the reported non-APH compound either by reanalysis or resampling. This contingency will require additional coordination and communication between the laboratory and the data user.

12.0 REPORTING LIMITS

The RLs for Target APH Analytes and hydrocarbon ranges will be determined as follows.

Target APH Analyte RLs

The RLs for the Target APH Analytes shall be based upon the concentration of the lowest calibration standard for the analyte of interest. The RL must be greater than or equal to the concentration of the lowest calibration standard.

Example: Benzene:
- Lowest calibration standard concentration = 2 µg/m^3
- RL for benzene = 2 µg/m^3

C_9-C_{10} Aromatic Hydrocarbons

The RL for the C_9-C_{10} aromatic hydrocarbons range is determined empirically and is based upon the concentration of the lowest range calibration standard for the components which make up this range. The RL is calculated by multiplying the concentration of the lowest calibration standard by the number of APH range component compounds used in the calibration of the range.

Example: C_9-C_{10} aromatic hydrocarbons:
- Lowest calibration standard concentration = 2 µg/m3
- Number of APH components in this range = 5
- Total concentration of lowest calibration standard = 2 µg/m3 * 5 = 10 µg/m3
- RL for C_9-C_{10} aromatic hydrocarbons = 10 µg/m3

C_5-C_8 and C_9-C_{12} Aliphatic Hydrocarbons

The RLs for the C_5-C_8 aliphatic and C_9-C_{12} aliphatic hydrocarbons range are determined empirically and are based upon the concentration of the lowest range calibration standard for the components which make up these ranges. The RLs are calculated by multiplying the concentration of the lowest calibration standard by the number of APH range component compounds used in the calibration of these ranges.

Example: C_5-C_8 aliphatic hydrocarbons:
- Lowest calibration standard concentration = 2 µg/m3
- Number of APH components in this range = 6
- Total concentration of lowest calibration standard = 2 µg/m3 * 6 = 12 µg/m3
- RL for C_5-C_8 aliphatic hydrocarbons = 12 µg/m3

13.0 METHOD PERFORMANCE

Single laboratory accuracy and precision data for method analytes are provided in Appendix 1. An example chromatogram is provided in Appendix 2.

14.0 REFERENCES

(1) ENSR, 1999: *Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air*, ENSR Corporation, June 1999.

(2) EPA, 1987: *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* US EPA, EPA-600/4-84-041, 1987. Research Triangle Park, NC.

(3) MassDEP, 1994: *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*, Massachusetts Department of Environmental Protection, August 1994.

(4) MassDEP, 1998: *Report on Results of the Fall 1997 VPH/EPH Round Robin Testing Program*, Massachusetts Department of Environmental Protection, January 12, 1998.

(5) MassDEP, 2002a: *Indoor Air Sampling and Evaluation Guide*, Massachusetts Department of Environmental Protection, WSC Policy # 02-430, April 2002.

(6) MassDEP, 2002b: *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach*, Massachusetts Department of Environmental Protection, WSC Policy # 02-411, October 31, 2002

.

(7) MassDEP, 2003: *Updated Petroleum Hydrocarbon Fraction Toxicity Values For VPH/EPH/APH Methodology*, Massachusetts Department of Environmental Protection, November 2003.

(8) MassDEP, 2004: *Method for the Determination of Volatile Petroleum Hydrocarbons (VPH),* Massachusetts Department of Environmental Protection, May 2004.

(9) MassDEP, 2007: *Standard Operating Procedure for Indoor Air Contamination*, Massachusetts Department of Environmental Protection, SOP BWSC-07-01, August 2007.

TABLES

Table 1. APH Components

Compound	CAS Number	Boiling Point (°C)	Mol. Wt. g/mol	APH Analysis Function	Retention Time (minutes)[1]	Concentration Conversion[2] (ppbV →µg/m³)
1,3-Butadiene	106990	- 4.4	54.09	TA	5.76	2.21
Isopentane	78784	28	72.15	RC/RM	7.27	2.95
Methyl-tert-butylether	1634044	55	88.15	TA	9.64	3.61
n-Hexane	110543	69	86.17	RC	10.71	3.53
Benzene	71432	80	78.11	TA	12.37	3.19
Cyclohexane	110827	81	84.16	RC	12.66	3.44
2,3-Dimethylpentane	565593	90	100.20	RC	12.91	4.10
n-Heptane	142825	98	100.20	RC	13.81	4.10
Toluene	108883	111	92.14	TA	15.44	3.77
n-Octane	111659	126	114.23	RC	16.29	4.67
Ethylbenzene	100414	136	106.17	TA	17.28	4.34
2,3-Dimethylheptane	3074713	141	128.26	RC	17.32	5.25
m-Xylene	108383	139	106.17	TA	17.42	4.34
p-Xylene	106423	138	106.17	TA	17.42	4.34
o-Xylene	95476	144	106.17	TA/RM	17.78	4.34
n-Nonane	111842	151	128.26	RC/RM	17.91	5.25
Isopropylbenzene	98828	152	120.20	RC	18.21	4.92
1-Methyl-3-ethylbenzene	620144	161	120.20	RC	18.65	4.92
1,3,5-Trimethylbenzene	108678	165	120.20	RC	18.74	4.92
n-Decane	124185	174	142.28	RC	19.08	5.83
1,2,3-Trimethylbenzene	526738	176	120.20	RC	19.36	4.92
p-Isopropyltoluene	99876	177	134.22	RC	19.35	5.49
Butylcyclohexane	1678939	181	140.27	RC	19.54	5.74
n-Undecane	1120214	196	156.32	RC	20.03	6.39
Naphthalene	91203	218	128.17	TA/RM	21.04[3]	5.24
n-Dodecane	112403	216	170.33	RC/RM	20.92[3]	6.97

[1]Results obtained using an RTX-1 column and chromatographic conditions described in Sections 6.3 and 9.2, respectively.
[2]Conversion factors assume standard temperature and pressure (R = 0.08026 L-atm/mole-K; T = 298K; P = 1 atm).
[3]The elution order of naphthalene and dodecane may be reversed, depending on the exact chromatographic conditions.

TA- Target Analyte	**RC - Range Calibration Aliphatic**
RM - Range Marker	**RC - Range Calibration Aromatic**

Table 2. BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40.0 percent of m/e 95
75	30.0 to 66.0 percent of m/e 95
95	Base peak, 100 percent relative abundance
96	5.0 – 9.0 percent of m/e 95
173	Less than 2.0 percent of m/e 174
174	50.0 to 120.0 percent of m/e 95
175	4.0 to 9.0 percent of m/e 174
176	93.0 to 101.0 percent of m/e 174
177	5.0 – 9.0 percent of m/e 176

Table 3a. Initial Calibration of APH Hydrocarbon Range Components

Hydrocarbon Range	Hydrocarbon Range Compounds used to Establish Range Response Factor	Calib. Level	Calibration Standard Preparation		Component Standard Calibration Concentration (based on a 0.25 liter "nominal" sample volume)	
			Working Standard Concentration ($\mu g/m^3$)	Injection Volume (mL)*	Individual Range Component Concentration ($\mu g/m^3$)	Hydrocarbon Range Total Concentration ($\mu g/m^3$)
C_5-C_8 Aliphatic	Isopentane	1	20	25	2.0	12
	n-Hexane	2	20	50	4.0	24
	Cyclohexane	3	20	250	20.0	120
	2,3-Dimethylpentane	4	500	25	50.0	300
	n-Heptane	5	500	125	250	1500
	n-Octane	6	500	250	500	3000
C_9-C_{12} Aliphatic	2,3-Dimethylheptane	1	20	25	2.0	12
	n-Nonane	2	20	50	4.0	24
	n-Undecane	3	20	250	20.0	120
	n-Dodecane	4	500	25	50.0	300
	Butylcyclohexane	5	500	125	250	1500
	n-Decane	6	500	250	500	3000
C_9-C_{10} Aromatic	Isopropylbenzene	1	20	25	2.0	10
	1-Methyl-3-ethylbenzene	2	20	50	4.0	20
	1,3,5-Trimethylbenzene	3	20	250	20.0	100
	1,2,3-Trimethylbenzene	4	500	25	50.0	250
	p-Isopropyltoluene	5	500	125	250	1250

* nominal sample volume for purposes of this calibration is 250 mL
** concentration of the individual hydrocarbon range compound multiplied by the total # of hydrocarbon range compounds used to generate the range response factor

Table 3b. Initial Calibration of APH Target Analytes

APH Target Analytes	Level	Working Standard		Calibration Standard
		Concentration ($\mu g/m^3$)	Volume (mL)*	Concentration ($\mu g/m^3$)
1,3-Butadiene	1	20	25	2.0
Methyl-tert-butylether Benzene	2	20	50	4.0
Toluene Ethylbenzene	3	20	250	20
m-Xylene	4	500	25	50
p-Xylene o-Xylene	5	500	125	250
Naphthalene	6	500	250	500

* nominal sample volume for purposes of this calibration is 250 mL

Table 4. APH Range Marker Compounds and Range Retention Time Windows

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons	0.1 min. before isopentane	0.01 min. before n-nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min. before n-nonane	0.1 min. after dodecane
C_9-C_{10} Aromatic Hydrocarbons	0.1 min. after o-xylene	0.1 min. before naphthalene

Table 5. Primary (Quantitation) & Secondary Ions for APH Components/Internal Standards

APH Components	CAS Number	Target APH Analyte	Primary (Quantitation) Ion	Secondary Ion(s)
Bromochloromethane (IS1)	74975		128	49, 130
1,3-Butadiene	106990	✓	54	53, 50
Isopentane	78784		43	42, 41, 57
Methyl-tert-butyl ether	1634044	✓	73	45
n-Hexane	110543		57	41, 43, 56
Cyclohexane	110827		56	84, 41
1,4-Difluorobenzene (IS2)	540363		114	63
2,3-Dimethylpentane	565593		56	43, 57, 41
Benzene	71432	✓	78	52, 51
n-Heptane	142825		43	71, 57, 100
Toluene	108883	✓	91	92
Chlorobenzene-d5 (IS3)	3114554		117	119, 82
n-Octane	111659		43	85, 57, 71
2,3-Dimethylheptane	3074713		43	84, 85
Ethylbenzene	100414	✓	91	106
m & p-Xylene	1330207	✓	91	106, 105
n-Nonane	111842		43	57, 85
o-Xylene	95476	✓	91	106, 105
Isopropylbenzene	98828		105	120
1-Methyl-3-ethylbenzene	620144		105	120
1,3,5-Trimethylbenzene	108678		105	120
n-Decane	124185		57	43, 71, 85
Butylcyclohexane	1678939		83	55, 82
p-Isopropyltoluene	99876		119	105, 134
1,2,3-Trimethylbenzene	526738		105	120
n-Undecane	1120214		57	43, 71, 85
n-Dodecane	112403		57	43, 71, 85
Naphthalene	91203	✓	128	

NOTE: All APH Components are listed in Table 5 for reference purposes. Only the RRFs for Target APH Analytes need to be determined on a compound-specific basis

Table 6. Internal Standards and Associated Target APH Analytes and Hydrocarbon Ranges

Bromochloromethane (IS #1)	**1,4-Difluorobenzene (IS #2)**	**Chlorobenzene-d5 (IS #3)**
1,3-Butadiene Methyl-tert-butylether	Benzene C_5-C_8 Aliphatics	Toluene Ethylbenzene m&p-Xylenes o-Xylene Naphthalene C_9-C_{12} Aliphatics C_9-C_{10} Aromatics

Table 7. List of Common Non-APH Compounds That Elute Within the APH Method Ranges

Hydrocarbon Range	Potential Non-APH Compounds
C_5-C_8 Aliphatic Hydrocarbons	Acetone may co-elute/interfere with isopentane. Isopropyl alcohol, methyl ethyl ketone, trichloroethene, tetrachloroethene, tetrahydrofuran, hexanal, 1-butanol, hexamethylsiloxane
C_9-C_{12} Aliphatic Hydrocarbons	Terpenes (e.g., a-Pinene, d-Limonene), phenol, benzaldehyde, n-chain aldehydes, 2-ethyl-1-hexanol, siloxanes, dichlorobenzenes.
C_9-C_{10} Aromatic Hydrocarbons	Siloxanes, a-pinene, and d-limonene may slightly interfere if present at high concentrations (contribute to the area of ions 120/134).

APPENDIX 1
APH METHOD DETECTION LIMIT STUDIES
Results from 5 Laboratories

	MDL C_5-C_8 Aliphatics (ug/m^3)	MDL C_9-C_{12} Aliphatics (ug/m^3)	MDL C_9-C_{10} Aromatics (ug/m^3)
Lab 1	1.8	1.0	0.67
Lab 2	3.7	1.0	0.29
Lab 3	5.7	5.0	1.9
Lab 4	4.6	6.3	1
Lab 5	4.1	4.7	5.9

	MDL C_5-C_8 Aliphatics (ug/m^3)	Calculated RL C_5-C_8 Aliphatics (ug/m^3)	MDL C_9-C_{12} Aliphatics (ug/m^3)	Calculated RL C_9-C_{12} Aliphatics (ug/m^3)	MDL C_9-C_{10} Aromatics (ug/m^3)	Calculated RL C_9-C_{10} Aromatics (ug/m^3)
Lab 1	1.8	5.4	1.0	3	0.67	2.01
Lab 2	3.7	11.1	1.0	3	0.29	0.87
Lab 3	5.7	17.1	5.0	15	1.9	5.7
Lab 4	4.6	13.8	6.3	18.9	1	3
Lab 5	4.1	12.3	4.7	14.1	5.9	17.7

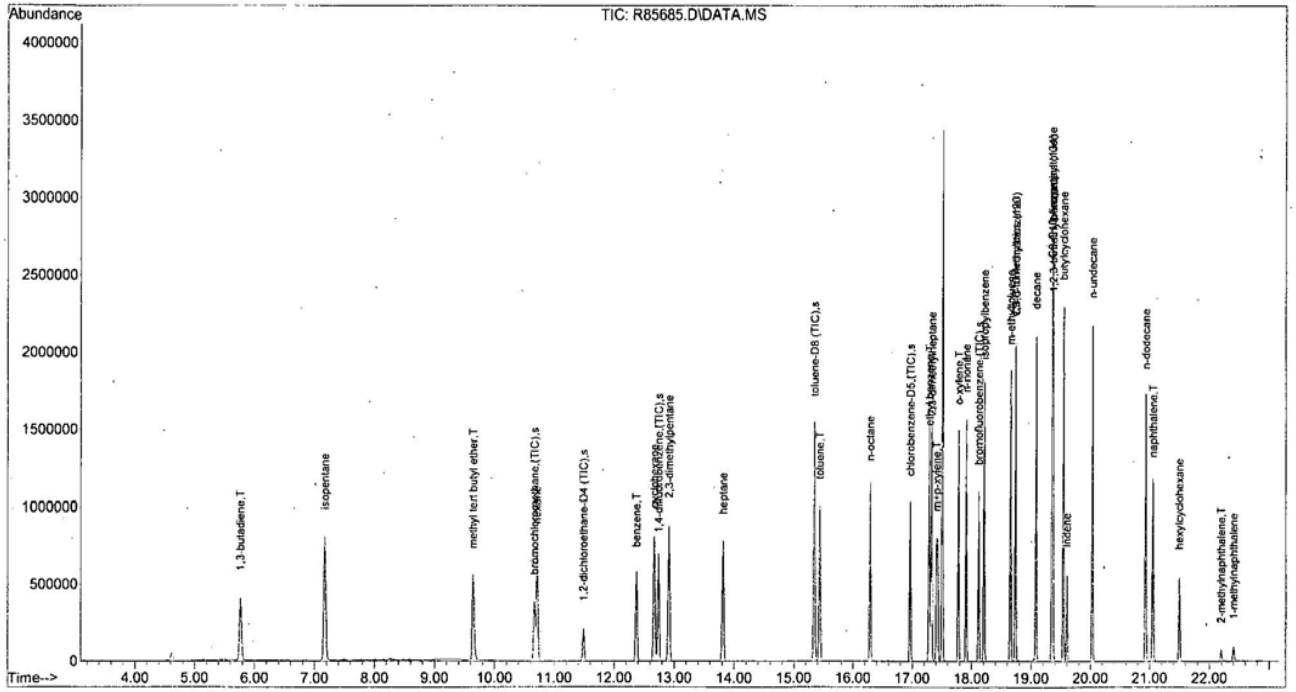
Calculated RL = 3xMDL
MDL = Method detection limit
MDL studies performed in Fall 2008.

APPENDIX 2
APH METHOD CHROMATOGRAM

Quantitation Report (QT Reviewed)

Data Path : O:\Forensics\Data\Airlab8\081002aph\
Data File : R85685.D
Acq On : 3 Oct 2008 6:28 am
Operator : AIRLAB8:RY
Sample : iaphstd20
Misc : wg338743
ALS Vial : 3 Sample Multiplier: 1

Quant Time: Oct 03 10:50:35 2008
Quant Method : O:\Forensics\Data\Airlab8\081002aph\APH1003.M
Quant Title : APH Analysis
QLast Update : Fri Oct 03 11:46:09 2008
Response via : Initial Calibration



APH1003.M Thu Dec 04 14:02:25 2008 Page: 3

APPENDIX 3
REQUIRED APH DATA REPORTING INFORMATION

SAMPLE INFORMATION (check all that apply)

Sample Type(s)	θ Grab θ Time-integrated: □ 2 hour □ 4 hour □ 8 hour □ 24 hour □ Other:
Sample Container(s)	θ Canister(s) size: θ Other:
Sampling Flow Controller(s)	θ Mechanical θ Fixed-Orifice θ Electronic θ Other:
Sampling Flow Meter(s)	RPD of pre & post-sampling calibration check(s): θ ≤ 20% θ > 20%

APH ANALYTICAL RESULTS

Internal Standards:	Client ID		
	Lab ID		
	Date Collected		
	Date Received		
	Date Analyzed		
	Pre-sample vacuum (field)	**in. Hg**	**in. Hg**
MS Tuning Standard:	**Post-sample vacuum (field)**	**in. Hg**	**in. Hg**
	Lab Receipt vacuum	**in. Hg**	**in. Hg**
	Dilution Factor		

Target APH Analytes & Hydrocarbon Ranges	**Reporting Limit**		**Sample Results**		**Sample Results**	
	µg/m³	**ppb v/v**	**µg/m³**	**ppb v/v**	**µg/m³**	**ppb v/v**
1,3-Butadiene						
Methyl-tert-butylether						
Benzene						
Toluene						
Ethylbenzene						
m- & p- Xylenes						
o-Xylene						
Naphthalene						
C_5-C_8 Aliphatic Hydrocarbons[1,2]		**N/A**		**N/A**		**N/A**
C_9-C_{12} Aliphatic Hydrocarbons[1,3]		**N/A**		**N/A**		**N/A**
C_9-C_{10} Aromatic Hydrocarbons		**N/A**		**N/A**		**N/A**

[1]Hydrocarbon range data from total ion chromatogram excluding any internal/tuning standards eluting in that range
[2]C_5-C_8 aliphatic hydrocarbons exclude the concentration of Target APH Analytes eluting in that range
[3]C_9-C_{12} aliphatic hydrocarbons exclude concentration of Target APH Analytes eluting in that range AND concentration of C_9-C_{10} aromatic hydrocarbons

CERTIFICATION

Were all QA/QC procedures REQUIRED by the APH Method followed? ☐ **Yes** ☐ **No - Details Attached**
Were all performance/acceptance standards for required QA/QC procedures achieved? ☐ **Yes** ☐ **No - Details Attached**
Were any significant modifications made to the APH method, as specified in Sect 11.1.2? ☐ **No** ☐ **Yes - Details Attached**

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE: _____ **POSITION:** _____
PRINTED NAME: _____ **DATE:** _____

APPENDIX 4

RECOMMENDED SOP FOR CLEANING, CERTIFICATION, AND CALIBRATION OF APH AIR SAMPLING EQUIPMENT

1.0 Canister Cleaning

All canisters must be certified clean and verified as leak free prior to being used for sampling.

1.1 Recommended Equipment and Supplies

- Flow Manifold – For attaching canisters and conveying flow during evacuation and flushing.
- Flushing Gas Source – Ultra zero air or UHP Nitrogen (compressed cylinder or on-site source) with appropriate cleaning media in line to ensure gas cleanliness.
- Roughing Pump – For initial evacuation stage.
- High Vacuum Pump – For final evacuation. Alcatel or equivalent molecular drag recommended. Alternatively, a non-oil equivalent pump may be used.
- Controls/Gauges
    - ♦ Control valves or solenoids for enacting cycles.
    - ♦ Electronic gauges for measuring rough pressures (in psia or mm Hg) and fine pressure values (millitorrs).
    - ♦ Rough vacuum/pressure gauges used for field pressure and vacuum measurements.
- Humidification Device – Fixture or device to add humidity to canisters and flushing gas during cleaning and batch certification. Water should be deionized double distilled or HPLC grade.
- Canister Heaters – Heating belts or ovens for heating canisters to 100 degrees C to enhance removal of organic compounds.
- Laboratory Notebook/Log Book – Used to record dates and canister conditioning actions and certifications. Canisters last use must be tracked.

1.2 Recommended Procedures

- Empty all canisters to ambient pressure and attach to the manifold. Make sure that there are no leaks. This can be performed in one of two ways.
    - ♦Pressurize canisters with ultra zero air or UHP nitrogen to 30 psig. The canister pressure cannot vary by more than ±2 psig over a 24 hour period.
    - ♦Apply vacuum pimp to the manifold to reduce manifold pressure. The system is leak free if the vacuum prior to cleaning is less than 500 mtorr.
- Evacuate canisters to at least 1 torr (1 mm Hg).
- Pressurize with humidified UHP nitrogen or ultra zero air up to 30 psig. Activate heating source during cleaning cycle.
- Repeat above two steps (evacuating and pressurizing). Note cycle numbers and ensure that a minimum of three cleaning cycles are completed. On the final cycle, turn off heating source and pump down with high vacuum pump to a maximum of 0.05 mm Hg (50 mtorr). This vacuum would correspond to 30 in. Hg.

Close canister sampling valve prior to turning off high vacuum pump or placing the system in a standby mode.

- Remove treated canisters from the manifold. A properly evacuated canister should have a canister pressure of ≤ 0.05 mm Hg (50 mtorr; vacuum of 30 in. Hg).

2.0 Associated canister sampling equipment (e.g., flow controllers, critical orifice assemblies) should also be deemed clean and appropriate for use prior to sampling. Cleaning techniques may vary between laboratories but all procedures will include backflushing with humidified ultra zero air or UHP nitrogen. All flow controllers will be calibrated by the laboratory such that a small amount of vacuum (approximately 5 in. Hg) will remain in the canister at the end of sampling.

3.0 Recommended Equipment Certification Procedures

Batch or individual canister certification may be required depending on the requirements of the testing program.

3.1 Batch Canister Certification

- After the cleaning process is completed, a minimum of one canister per batch must be tested. A batch size of up to 20 canisters is allowed.

- Remove the canister from the manifold that exhibited the highest levels of contamination prior to cleaning (according to the analytical results). Pressurize the canister to a maximum of 30 psig with humidified ultra zero air or UHP nitrogen and analyze as a Laboratory Method Blank. Record in a laboratory notebook the serial number of this canister used for batch certification. If any of the APH Target Analytes or hydrocarbon range concentrations are detected at a concentration greater than one-half of their respective RLs, the entire batch of canisters must be rejected and recleaned. If three consecutive certifications fail, system maintenance is required.

- If the batch certification canister passes certification, batch canisters should be held for 24 hours uncapped prior to issue for field use. The vacuum in each canister should be rechecked prior to release for field use. The acceptance criterion for the "stored" canister vacuum is ≥ 28 in. Hg. Canisters not meeting this criterion must be retained for leak repair and not released for field use.

- At a minimum, the following information regarding canister certification should be permanently recorded and retained for a minimum of 5 years.

  Processing Date
  Canister Serial Number
  Canister Volume (liters)
  Serial Number for Canister used for Batch Certification
  Post-cleaning Vacuum (in. Hg)
  Results of the Certification Analysis

3.2 Individual Canister Certification

- After the cleaning process is completed, each canister from the batch must be tested.

- Remove each canister from the manifold. Pressurize the canister to a maximum of 30 psig with humidified ultra zero air or UHP nitrogen and analyze as a Laboratory Method Blank. Record in a laboratory notebook the serial number of the canisters being certified. If any of the APH Target Analytes or hydrocarbon range concentrations are detected at a concentration greater than one-half of their respective RLs, the individual canister must be recleaned and re-certified.

- If the individual canister passes certification, it must be reevacuated and held for 24 hours uncapped prior to issue for field use. The vacuum in each canister should be re-checked prior to release for field

use. The acceptance criterion for the "stored" canister vacuum is ≥ 28 in. Hg. Canisters not meeting this criterion must be retained for leak repair and not released for field use.

- At a minimum, the same information listed above for Batch Canister Certification should be permanently recorded and retained for a minimum of 5 years.

3.3 Certification procedures associated with canister sampling equipment (e.g., flow controllers, critical orifice assemblies) will vary between laboratories. If certification is required, the data user must request this from the laboratory when ordering the sampling equipment.

4.0 Flow Controller Calibration

Flow controllers may be calibrated by either simulating a vacuum on the outlet side of the flow controller (the end that attaches to the canister) or by applying positive pressure to the inlet side of the flow controller. Using a NIST-traceable primary standard flow calibrator (e.g., BIOS Dry-Cal), the flow rate of air passing through the flow controller is measured. The flow rate may be adjusted by changing the size of the critical orifice used and/or performing coarse/fine adjustments on the flow controller itself. Specific procedures will vary depending on the model flow controller that is used.

The NIST-traceable primary standard flow calibrator is a mass flow meter used to accurately measure flow rates of 0 to 200 cubic centimeters per minute. This device must be constructed of inert materials. These flow calibrators must be calibrated at least annually using a certified volumetric measuring device (soap film or equivalent) and an accurate stopwatch.

The flow controller's calibration must be verified prior to sample collection by the laboratory. Upon receipt of the canister and associated flow controller back at the laboratory, a post-sampling calibration verification must be performed and the relative percent difference (RPD) between the initial and post sampling calibration calculated.

$$RPD = \frac{|F_f - F_i|}{(F_i + F_f)/2} \times 100$$

F_i = Pre-sampling Flow Rate

F_f = Post-Sampling Flow Rate

The flow calibration and associated sample collection interval are considered valid if the RPD is $\leq$20. If the RPD is >20, re-sampling may be required to achieve data quality objectives. If the "elevated RPD" sample is analyzed, a notation must be provided in the case narrative documenting the "compromised RPD" flow rate value. The flow controller RPD is one line of evidence in the proper collection of samples for APH analysis. If the canister vacuum is acceptable after sampling and the flow controller RPD is outside of the acceptance criteria, data quality is not adversely affected.

APPENDIX 5
APH METHOD CALCULATIONS

This Appendix provides (1) example RRF calculations for APH aliphatic and aromatic ranges and the target analyte Benzene, based on multi-point calibration data and (2) example calculations of sample concentrations for APH aliphatic and aromatic ranges and the target analyte Benzene, based on the calculated RRFs, simulated area counts and other sample-specific data. The APH Method Analytical Flow Chart is shown in Figure 5-1.

Example Calculations
Refer to information found on Tables 5-1 through 5-4. An APH Method Calculation Worksheet in Microsoft Excel format using the analytical data presented in Tables 5-1 through 5-4 is available on the APH Method web page.

Equation 1: Relative Response Factor for Target APH Analytes
RRFs are calculated for each APH Target analyte using the area response of the analyte's characteristic ion, its true concentration, the area response of the associated internal standard's characteristic ion and its concentration using Equation 1.

RRF calculated for Benzene, Calibration Level 1 using data found in Tables 5-2 and 5-3:

$$RRF_{Benzene} = [(A_{EC}) * (C_I)] / [(A_{EI}) * (C_C)]$$

$A_{EC} = 3556$ area count of the primary quantitation ion for Benzene (m/e 78)
$C_I = 37$ ug/m^3 concentration of internal standard (IS2)
$A_{EI} = 143419$ area count of the primary quantitation ion for the associated internal standard (m/e 114)
$C_C = 2$ ug/m^3 concentration of Benzene, Calibration Level 1

$$RRF_{Benzene} = [(3556) * (37)] / [(143419) * (2)]$$
$$RRF_{Benzene} = 0.4587$$

Equation 2: Relative Response Factor for C_5-C_8 Aliphatic Hydrocarbons
The RRF for the C_5-C_8 Aliphatic range is based on a correlation between the total concentration of aliphatic components eluting within this range and their total ion area counts.

RRF calculated for C_5-C_8 Aliphatic Hydrocarbons, Calibration Level 1 using data found in Tables 5-2 and 5-3:

$$RRF_{Range_x} = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

$A_T = 18097$ total ion area count of C_5-C_8 Aliphatic range (6 aliphatic components)
$C_I = 37$ ug/m^3 concentration of internal standard (IS2)
$A_{EI} = 143419$ area count of the primary ion for the associated internal standard (m/e 114)
$C_T = 12$ ug/m^3 total concentration of C_5-C_8 Aliphatic range, Calibration Level 1 (6 aliphatic components)

$$RRF_{Range} = [(18097) * (37)] / [(143419) * (12)]$$
$$RRF_{Range} = 0.3891$$

Equation 3: Relative Response Factor for C_9-C_{12} Aliphatic Hydrocarbons
The RRF for the C_9-C_{12} Aliphatic range is based on a correlation between the total concentration of aliphatic components eluting within this range and their total ion area counts.

RRF calculated for C_9-C_{12} Aliphatic Hydrocarbons, Calibration Level 1 using data found in Tables 5-2 and 5-3:

$$RRF_{Range_x} = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

A_T = 32296 total ion area count of C_9-C_{12} Aliphatic range (6 aliphatic components)
C_I = 38 ug/m^3 concentration of internal standard (IS3)
A_{EI} = 316020 area count of the primary ion for the associated internal standard (m/e 117)
C_T = 12 ug/m^3 total concentration of C_9-C_{12} Aliphatic range, Calibration Level 1 (6 aliphatic components)

$$RRF_{Range} = [(32296) * (38)]/[(316020) * (12)]$$
$$RRF_{Range} = 0.3236$$

Equation 4: Relative Response Factor for C_9-C_{10} Aromatic Hydrocarbons

The RRF for the C_9-C_{10} Aromatic range is calculated using a summation of the m/e 120 and m/e 134 extracted ion area counts for the APH aromatic components eluting within this range (see Table 3a of method).

RRF calculated for C_9-C_{10} Aromatic Hydrocarbons, Calibration Level 1 using data found in Tables 5-2 and 5-3:

$$RRF_{Range_x} = [(A_T) * (C_I)]/[(A_{EI}) * (C_T)]$$

A_T = 54343 summation of extracted ion area counts (m/e 120 + m/e 134: 5 aromatic components)
C_I = 38 ug/m^3 concentration of internal standard (IS3)
A_{EI} = 316020 area count of the primary ion for the associated internal standard (m/e 117)
C_T = 10 ug/m^3 total concentration of C_9-C_{10} Aromatic range, Calibration Level 1 (5 aromatic components)

$$RRF_{Range} = [(54343) * (38)]/[(316020) * (10)]$$
$$RRF_{Range} = 0.6535$$

Equation 5: Percent Relative Standard Deviation

For each target compound and range a percent relative standard deviation (%RSD) is calculated from the RRFs generated for each point of the curve using equation 5 below.

Example: Benzene from Table 5-1:

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Mean	SD
Benzene	0.4587	0.5119	0.5167	0.4679	0.5540	0.5083	0.5029	0.03490

$$\%RSD_{Benzene} = [(SD_{n-1})/(AVG_X)] * 100]$$

%RSD = percent relative standard deviation
SD_{n-1} = 0.03490 standard deviation (n-1 degrees of freedom)
AVG_x = 0.5029 mean response factor from the initial calibration

$$\%RSD_{Benzene} = (0.03490 / 0.5029) * 100$$
$$\%RSD_{Benzene} = 6.9$$

Equation 7: Percent Difference

Calculate a percent difference for Benzene in a continuing calibration standard having a calculated RRF of 0.4769:

$$\%D_{Benzene} = [(RRF_C) - (RRF_I)]/[(RRF_I)] * 100$$

%D = percent difference
RF_C = 0.4769 response factor from the continuing calibration
RF_I = 0.5029 mean response factor from the initial calibration

$$\%D_{Benzene} = [(0.4769) - (0.5029)]/[(0.5029)] * 100$$
$$\%D_{Benzene} = -5.2$$

Equation 8: Dilution Factor for Pressurization of Subatmospheric Samples

$$DF = (P_f + 14.7)/(Pi + 14.7)$$

P_I = pressure reading of canister prior to pressurization (units – psig)
P_F = pressure reading of canister after pressurization (units – psig)
DF = dilution factor

Note: To convert from in. Hg to psig: psig = in. Hg * 0.491159

Example Canister Dilution Calculation Final Pressure >0

P_I = -2.5 in. Hg = -1.28 psig
P_F = 10 psig

$$DF = (10 + 14.7)/(-1.28 + 14.7)$$
$$DF = 1.84$$

Example Canister Dilution Calculation Final Pressure <0

P_I = -2.5 in. Hg = -1.28 psig
P_F= -0.5 in. Hg = -0.246 psig

$$DF = (-0.246 + 14.7)/(-1.28 + 14.7)$$
$$DF = 1.08$$

Equation 9: Calculation of Sample Results in µg/m^3: Target Analyte (Benzene)
Calculate a final µg/m^3 concentration for Benzene using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250L):

$$ug/m3_{Benzene} = [(A_x) * (C_{IS})]/[(A_{IS}) * (RRF_{avg})] * DF$$

A_x = 60285 area count of the primary ion for Benzene (m/e78)
C_{IS} = 37 µg/m^3 concentration of internal standard (IS2)
A_x = 115082 area count of the primary ion for the associated internal standard (m/e 114)
RRF_{avg} = 0.5029 average RRF for benzene
DF = 1.0 dilution factor

$$ug/m3_{Benzene} = [(60285) * (37)]/[115082) * (0.5029)] * 1.0$$
$$ug/m3_{Benzene} = 38.5$$

Equation 11: Calculation of Sample Results in µg/m^3: C_5-C_8 Aliphatic Range

A. Calculate a preliminary µg/m^3 concentration for C_5-C_8 Aliphatic range using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250L):

$$ug/m3_{Aliphatic} = [(A_x) * (C_{IS})]/[(A_{IS}) * (RRF_{avg})] * DF$$

A_x =	823563	total ion area count of all peaks eluting within this range (excluding internal standard areas)
C_{IS} =	37 µg/m^3	concentration of internal standard (IS2)
A_{IS} =	115082	area count of the primary ion for the associated internal standard (m/e 114)
RRF_{avg} =	0.4177	average RRF for C_5-C_8 Aliphatic range
DF=	1.0	dilution factor

$$ug/m3_{Aliphatic} = [(823563)*(37)]/[(115082)*(0.4177)]*1.0$$
$$ug/m3_{Aliphatic} = 634$$

B. Calculate a final µg/m^3 concentration for C_5-C_8 Aliphatic range using data found in the Sample Data Table 5-4:

Final C_5-C_8 Aliphatic range µg/m^3 concentration = (Preliminary µg/m^3 concentration) – (concentrations of target analytes which elute within the C_5-C_8 Aliphatic range)

Final C_5-C_8 Aliphatic range µg/m^3 concentration = (634 µg/m^3) – (concentrations of MTBE, benzene, toluene, ethylbenzene, xylenes)

Final C_5-C_8 Aliphatic range µg/m^3 concentration = (634 µg/m^3) – (44.5 + 38.5 + 37.7 + 41.0 + 78.0 + 37.9 µg/m^3)

Final C_5-C_8 Aliphatic range µg/m^3 concentration = 356 µg/m^3

Equation 11: Calculation of Sample Results in µg/m^3: C_9-C_{10} Aromatic Range

Calculate a final µg/m3 concentration for C_9-C_{10} Aromatic range using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250L):

$$ug/m3_{Aromatic} = [(A_x)*(C_{IS})]/[(A_{IS})*(RRF_{avg})]*DF$$

A_x =	3217570	summation of extracted ion area counts (m/e 120 + m/e 134) eluting within range
C_{IS} =	38 µg/m^3	concentration of internal standard (IS3)
A_{IS} =	289465	area count of the primary ion for the associated internal standard (m/e 117)
RRF_{avg} =	0.8187	average RRF for C_9-C_{10} Aromatic range
DF=	1.0	dilution factor

$$ug/m3_{Aromatic} = [(3217570)*(38)]/[(289465)*(0.8187)]*1.0$$
$$ug/m3_{Aromatic} = 516$$

Equation 11: Calculation of Samples Results in µg/m^3: C_9-C_{12} Aliphatic Range

A. Calculate a preliminary µg/m^3 concentration for C_9-C_{12} Aliphatic range using data found in the Sample Data Table 5-4 (Note: sample aliquot volumes are assumed to be 0.250L):

$$ug/m3_{Aliphatic} = [(A_x)*(C_{IS})]/[(A_{IS})*(RRF_{avg})]*DF$$

A_x =	1971741	total ion area count of all peaks eluting within this range (excluding BFB)
C_{IS} =	38 µg/m^3	concentration of internal standard (IS3)
A_{IS} =	289465	area count of the primary ion for the associated internal standard (m/e 117)
RRF_{avg} =	0.3677	average RRF for C_9-C_{12} Aliphatic range
DF=	1.0	dilution factor

$$ug/m3_{Aliphatic} = [(1971741)*(38)]/[(289465)*(0.3677)]*1.0$$
$$ug/m3_{Aliphatic} = 704$$

B. Calculate a final µg/m^3 concentration for C_9-C_{12} Aliphatic range using data found in the Sample Data Table 5-4:

Final C_9-C_{12} Aliphatic range µg/m^3 concentration = (Preliminary µg/m^3 concentration) – (concentrations of naphthalene and C_9-C_{10} Aromatics)

Final C_9-C_{12} Aliphatic range µg/m^3 concentration = (704 µg/m^3) – (38 + 516 µg/m^3)

Final C_9-C_{12} Aliphatic range µg/m^3 concentration = 150 µg/m^3

Equation 6: Percent Recovery

From information found in Table 5-4 (Sample Data Table), calculate a percent recovery for Benzene having a true, or spiked concentration of 40 µg/m3.

$$\%R_{Benzene} = [(C_{found})/(C_{true})]*100$$

%R =		percent recovery
C_{found} =	38.5	concentration of the analyte or range (µg/m^3)
C_{true} =	40	true concentration of the analyte or range (µg/m^3)

$$\%R_{Benzene} = [(38.5)/(40)]*100$$
$$\%R_{Benzene} = 96$$

Equation 10: Conversion of µg/m^3 to ppbV

To convert target analyte results from µg/m3 into ppbv, use the flowing equation. NOTE: this equation is not applicable to the hydrocarbon ranges.

$$ppbV_{Benzene} = (\mu g/m3)_{Benzene} * 24.45/MW_{Benzene}$$

$\mu g/m3_{Benzene}$=	38.5
$MW_{Benzene}$=	78.1

$$ppbV_{Benzene} = 38.5*24.45/78.1$$
$$ppbV_{Benzene} = 12.05$$

TABLE 5-1: RELATIVE RESPONSE FACTORS

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Mean	%RSD
1,3-Butadiene	3.7454	4.2517	3.8698	3.7343	4.0661	2.5931	3.7101	15.7
Methyl-t-Butyl Ether	3.9877	5.0958	4.6380	4.4756	5.9072	5.0969	4.8669	13.5
Bromochloromethane (IS1)								
Benzene	0.4587	0.5119	0.5167	0.4679	0.5540	0.5083	0.5029	6.9
1,4-Difluorobenzene (IS2)								
Toluene	0.3663	0.3700	0.3991	0.3792	0.4910	0.4887	0.4157	14.1
Chlorobenzene-d5 (IS3)								
Ethylbenzene	0.9927	1.0447	1.1267	1.0705	1.0902	0.9343	1.0432	6.7
Xylene (m,p)	0.7869	0.8913	0.9613	0.9133	0.9041	0.7809	0.8730	8.4
Xylene (o)	0.7809	0.8473	0.9138	0.8682	0.9504	0.8417	0.8671	6.8
4-Bromofluorobenzene (BFB)								
Naphthalene	0.4234	0.2969	0.3203	0.3043	0.3681	0.3530	0.3443	13.8
C_5-C_8 Aliphatic Hydrocarbons	0.3891	0.4618	0.4662	0.4221	0.4073	0.3594	0.4177	10.0
C_9-C_{12} Aliphatic Hydrocarbons	0.3236	0.3598	0.3881	0.3687	0.4018	0.3640	0.3677	7.3
C_9-C_{10} Aromatics (m/e 120)	0.5452	0.6602	0.7121	0.6765	0.7895	0.6795	0.6772	11.7
C_9-C_{10} Aromatics (m/e 134)	0.1082	0.1330	0.1435	0.1363	0.1668	0.1612	0.1415	14.9
C_9-C_{10} Aromatic Hydrocarbons	0.6535	0.7932	0.8555	0.8128	0.9563	0.8406	0.8187	12.1

TABLE 5-2: CALIBRATION CURVE AREA COUNTS

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6
1,3-Butadiene	6337	14664	36660	183300	980573	1854649
Isopentane	2223	7456	18640	93200	459196	1031595
Methyl-t-Butyl Ether	6747	17575	43937	219688	1424596	3645385
n-Hexane	1391	3384	8460	42300	255744	761077
Bromochloromethane (IS1)	35531	36214	39788	41232	40515	60078
Benzene	3556	8201	20502	102512	647506	1691722
1,4-Difluorobenzene (IS2)	143419	148189	146799	162114	172980	246302
Cyclohexane	1788	5250	13125	65625	374747	967332
2,3-Dimethylpentane	2999	6325	15812	79062	471028	1248544
n-Heptane	1827	6002	15005	75025	489349	1288707
Toluene	6092	12494	31235	156175	1086109	2437046
n-Octane	7869	15973	39932	199662	806445	1881104
Chlorobenzene-d5 (IS3)	316020	320770	297404	313031	336207	378992
Ethylbenzene	16511	35273	88182	440912	2411322	4659148
2,3-Dimethylheptane	9786	21985	54962	274812	1301031	2402318
Xylene (m,p)	26176	60190	150475	752375	3999652	7788338
Xylene (o)	12988	28608	71520	357600	2102284	4197368
n-Nonane	6763	14581	36452	182262	1060313	2016617
4-Bromofluorobenzene (BFB)	342161	346944	362579	373001	397666	422781
Isopropylbenzene	12267	29472	73680	368400	2221982	3497442
1-Methyl-3-ethylbenzene	10155	24432	61080	305400	2021310	4120625
1,3,5-Trimethylbenzene	9935	25420	63550	317750	1965146	4005654
n-Decane	4417	10654	26635	133175	821407	1690516
1,2,3-Trimethylbenzene	9383	23154	57885	289425	1785313	3709878
4-Isopropyltoluene	9002	22455	56137	280687	1844647	4019022
Butylcyclohexane	4510	11261	28152	140762	841313	1747933
n-Undecane	3083	7327	18317	91587	641647	1558980
Naphthalene	7042	10026	25065	125325	814108	1760433
n-Dodecane	3737	7084	17710	88550	666786	1473457
C_5-C_8 Aliphatic Hydrocarbons	18097	44390	110974	554874	2856509	7178359
C_9-C_{12} Aliphatic Hydrocarbons	32296	72892	182228	911148	5332497	10889821
C_9-C_{10} Aromatics (m/e 120)	45341	111460	278650	1393250	8731610	16941208
C_9-C_{10} Aromatics (m/e 134)	9002	22455	56137	280687	1844647	4019022
C_9-C_{10} Aromatic Hydrocarbons	54343	133915	334787	1673937	10576257	20960230

TABLE 5-3: CALIBRATION STANDARD CONCENTRATIONS (µg/m^3)

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6
1,3-Butadiene	2	4	10	50	250	500
Isopentane	2	4	10	50	250	500
Methyl-t-Butyl Ether	2	4	10	50	250	500
n-Hexane	2	4	10	50	250	500
Bromochloromethane (IS1)	42	42	42	42	42	42
Benzene	2	4	10	50	250	500
1,4-Difluorobenzene (IS2)	37	37	37	37	37	37
Cyclohexane	2	4	10	50	250	500
2,3-Dimethylpentane	2	4	10	50	250	500
n-Heptane	2	4	10	50	250	500
Toluene	2	4	10	50	250	500
n-Octane	2	4	10	50	250	500
Chlorobenzene-d5 (IS3)	38	38	38	38	38	38
Ethylbenzene	2	4	10	50	250	500
2,3-Dimethylheptane	2	4	10	50	250	500
Xylene (m,p)	4	8	20	100	500	1000
Xylene (o)	2	4	10	50	250	500
n-Nonane	2	4	10	50	250	500
4-Bromofluorobenzene (BFB)	57	57	57	57	57	57
Isopropylbenzene	2	4	10	50	250	500
1-Methyl-3-ethylbenzene	2	4	10	50	250	500
1,3,5-Trimethylbenzene	2	4	10	50	250	500
n-Decane	2	4	10	50	250	500
1,2,3-Trimethylbenzene	2	4	10	50	250	500
4-Isopropyltoluene	2	4	10	50	250	500
Butylcyclohexane	2	4	10	50	250	500
n-Undecane	2	4	10	50	250	500
Naphthalene	2	4	10	50	250	500
n-Dodecane	2	4	10	50	250	500
C_5-C_8 Aliphatic Hydrocarbons	12	24	60	300	1500	3000
C_9-C_{12} Aliphatic Hydrocarbons	12	24	60	300	1500	3000
C_9-C_{10} Aromatics (m/e 120)	10	20	50	250	1250	2500
C_9-C_{10} Aromatics (m/e 134)	10	20	50	250	1250	2500
C_9-C_{10} Aromatic Hydrocarbons	10	20	50	250	1250	2500

TABLE 5-4: SAMPLE ANALYSIS DATA

Compound	RT	Area	ISTD µg/m^3	Concentration µg/m^3*
1,3-Butadiene	5.262	100452		36.1
Methyl-t-Butyl Ether	7.572	162682		44.5
Bromochloromethane (IS1)	8.332	31534	42	
Benzene	9.654	60285		38.5
1,4-Difluorobenzene (IS2)	9.852	115082	37	
Toluene	12.724	119314		37.7
Chlorobenzene-d5 (IS3)	15.399	289465	38	
Ethylbenzene	16.098	325648		41.0
Xylene (m,p)	16.447	518803		78.0
Xylene (o)	17.374	250488		37.9
4-Bromofluorobenzene (BFB)	18.317	425176	57	
Naphthalene	29.274	99759		38.0
C_5-C_8 Aliphatic Hydrocarbons		823563		634
C_9-C_{12} Aliphatic Hydrocarbons		1971741		704
C_9-C_{10} Aromatics (m/e 120)		2256810		
C_9-C_{10} Aromatics (m/e 134)		960760		
C_9-C_{10} Aromatic Hydrocarbons		3217570		516

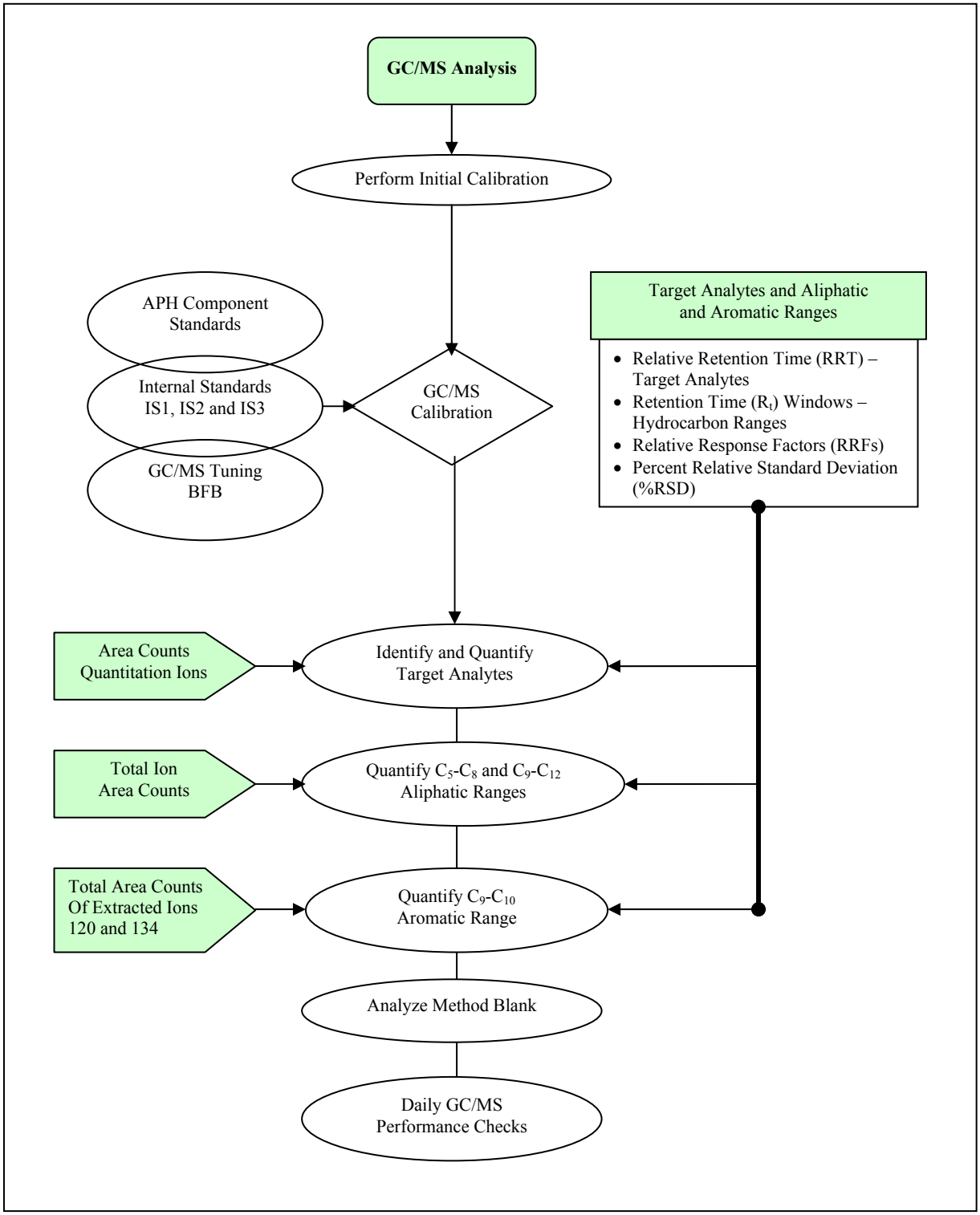
*Sample aliquot volume = 0.250 L

From Table 4 of Method. APH Range Marker Compounds and Range Retention Times

C_5-C_8 Aliphatic Hydrocarbons	0.1 min. before isopentane	0.01 min. before n-Nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min. before n-Nonane	0.1 min. after dodecane
C_9-C_{10} Aromatic Hydrocarbons	0.1 min. after o-xylene	0.1 min. before naphthalene

Ranges for Sample Data	Range Start RT	Range End RT
C_5-C_8 Aliphatic Hydrocarbons	6.028	17.744
C_9-C_{12} Aliphatic Hydrocarbons	17.744	29.724
C_9-C_{10} Aromatic Hydrocarbons	17.474	29.174

Figure 5-1: Air-Phase Hydrocarbons (APH) Method Analytical Flow Chart



ATTACHMENT D

Proposed Budget Modification

Table D-1
Proposed Budget Modification
Leeds - Northern Parcel

	TASK DESCRIPTION	Approved Jan-Jun 2013 Budget (March)	Revised Jan-Dec 2013 Budget (September)	Notes RE changes to budget as of Sep 2013	Delta from March to September	Proposed Shift Among Tasks
1	Site Investigation Work Plan	$0	$0		$0	-
2	Site Investigation	$30,000	$34,100	Adjusted costs for scope and includes efforts spent to date on teleconferences, SOW adjustments, and SOW Addendum based on comments from MDNR. Assumes may have minor response to address from MDNR on SOW Addendum.	$4,100	Shift/Add $4,100 from Task 8
3	Site Investigation Report	$8,000	$8,000	same	$0	-
4	Deed Restriction	$0	$0	same	$0	-
5	Soil and Drum Removal	$0	$0	same	$0	-
6	Project Management, Meetings with MoDNR	$4,000	$9,000	Adjusted based on recent level of effort; extend costs through Dec (prior through Jun only)	$5,000	Shift/Add $5,000 from Task 8
7	Cap Monitoring & Maintenance	$6,600	$5,400	Reduced; client requested only 4 trenches be repaved (prior quote for 6)	-$1,200	Reduce by $1,200
8	Groundwater Monitoring and Reporting	$40,000	$25,200	Reduced. Includes adjustment for slug testing/analysis not included in prior estimate	-$14,800	Reduce/Shift $9,100 to Tasks 2 and 6 Reduce by $5,700
9	Agency Oversight and Fees	$10,000	$10,000	same (pending further input from Agency if additional funds are needed)	$10,000	-
		$98,600	**$91,700**		**-$6,900**	

Table D-2
Modification to Attachment 5 of the 2013 Annual Budget Authorization Request
Following Years Budget Projections

Former Leeds Assembly Plant - Northern Parcel - 1007

Year	Expected Cost	Task 1 Site Investigation Work Plan	Task 2 Site Investigation	Task 3 Site Investigation Report	Task 4 Deed Restriction	Task 5 Soil and Drum Removal	Task 6 Project Management, Meetings with MoDNR	Task 7 Cap Monitoring & Maintenance	Task 8 Groundwater Monitoring and Reporting	Task 9 Agency Oversight and Fees
2009	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
2010 (1)	$ 21,305	$ 21,305	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
2011 (2)	$ 80,541	$ 8,690	$ 32,101	$ -	$ -	$ -	$ 14,762	$ -	$ -	$ 24,988
2012 (3)	$ 185,440	$ -	$ 138,430	$ 21,567	$ -	$ -	$ 4,939	$ -	$ -	$ 20,504
2013	$ 91,700	$ -	$ 34,100	$ 8,000	$ -	$ -	$ 9,000	$ 5,400	$ 25,200	$ 10,000
2014	$ 378,346	$ -	$ -	$ -	$ 25,000	$ 233,160	$ -	$ 26,836	$ 80,000	$ 13,350
2015	$ 70,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 11,800	$ 55,570	$ 3,155
2016	$ 60,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 3,155
2017	$ 60,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 3,155
2018	$ 62,225	$ -	$ -	$ -	$ -	$ -	$ -	$ 3,500	$ 55,570	$ 3,155
2019	$ 60,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 3,155
Subtotal	$ 1,071,658	$ 29,995	$ 204,631	$ 29,567	$ 25,000	$ 233,160	$ 28,701	$ 52,936	$ 383,050	$ 84,618
Subtotal from Original Cost Breakdown (4)	$ 1,220,021	$ 30,000	$ 138,000	$ 80,000	$ 25,000	$ 233,160	$ 26,000	$ 66,400	$ 555,700	$ 65,761
Variance	$ 148,363	$ 5	$ (66,631)	$ 50,433	$ -	$ -	$ (2,701)	$ 13,464	$ 172,650	$ (18,857)
2020	$ 92,725	$ -	$ -	$ -	$ -	$ -	$ -	$ 34,000	$ 55,570	$ 3,155
2021	$ 60,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 3,155
2022	$ 60,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 3,155
2023	$ 62,225	$ -	$ -	$ -	$ -	$ -	$ -	$ 3,500	$ 55,570	$ 3,155
2024	$ 60,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 3,155
2025	$ 59,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 2,155
2026	$ 59,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 2,155
2027	$ 59,525	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ 55,570	$ 2,155
2028	$ 3,693	$ -	$ -	$ -	$ -	$ -	$ -	$ 3,500	$ -	$ 193
2029	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2030	$ 33,320	$ -	$ -	$ -	$ -	$ -	$ -	$ 31,392	$ -	$ 1,928
2031	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2032	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2033	$ 3,693	$ -	$ -	$ -	$ -	$ -	$ -	$ 3,500	$ -	$ 193
2034	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2035	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2036	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2037	$ 1,899	$ -	$ -	$ -	$ -	$ -	$ -	$ 1,800	$ -	$ 99
2038	$ 3,693	$ -	$ -	$ -	$ -	$ -	$ -	$ 3,500	$ -	$ 193
Totals	$ 1,644,450	$ 29,995	$ 204,631	$ 29,567	$ 25,000	$ 233,160	$ 28,701	$ 155,728	$ 827,610	$ 110,058
Subtotal from Original Cost Breakdown (4)	$ 1,644,450	$ 30,000	$ 138,000	$ 80,000	$ 25,000	$ 233,160	$ 26,000	$ 190,800	$ 833,550	$ 87,940
Variance	$ (0)	$ (5)	$ 66,631	$ (50,433)	$ -	$ -	$ 2,701	$ (35,072)	$ (5,940)	$ 22,118

Notes
(value in parenthesis denotes cost is greater than in original cost breakdown)
Identifies cells/amounts that were revised from the original cost breakdown
(1) July 2010 through December 2010
(2) January 2011 through December 2011
(3) 2012 Estimated reflects actual spent from January through December 2012, except for Agency oversight costs estimated for December 2012
(4) The original cost breakdown and schedule of cash flow as established by MLC pursuant to the May 2010 RCES