UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

February 13, 2012

Ronald Zelt
USGS
5231 South 19th
Lincoln, NE 68512-1271

Gregory Douglas
NewFields Environmental Forensics
100 Ledgewood Place
Rockland, MA 02370

Re: Analytical Plan Prepared by the Scientific Support Coordination Group (SSCG), for the Enbridge Line 6B MP608 Release, Marshall, MI

Dear Ron and Gregg:

I have reviewed the above-referenced Analytical Plan and accompanying memo that were prepared in response to Charge 1 submitted to the SCCG:

a) Provide an evaluation of viable analytical approaches, including benefits and draw backs for each, to quantify the amount of submerged oil in the Kalamazoo River sediments attributable to the Enbridge Oil pipeline Release.
b) Provide a recommendation for the best analytical approach to accomplish this goal.

I hereby accept all of the group's recommendations on this issue. Our Environmental Unit and Enbridge have initiated its implementation.

I want to extend my sincere appreciation to both of you for leading the SSCG subgroup in producing a clear and unambiguous response in a timely manner. Please extend my regards to all members of the subgroup for the time and effort expended in bringing their experience and expertise to bear on this issue (including: A. Bejarano, M. Boufadel, I. Cozzarelli, S. Hamilton, B. Hollebone, J. Michel, S. Millsap, M. Sprenger, R. Steede, A.Uhler, and E. Wessling).

I appreciate the ability of the SSCG to demonstrate its value to the project, and respond in an expedited fashion.

Sincerely,

Ralph Dollhopf
Federal On-Scene Coordinator and Incident Commander
U.S. EPA, Region 5

cc: L. Kirby-Miles, U.S. EPA, ORC
Sonia Vega, U.S. EPA, Deputy Incident Commander
John Sobojinski, Enbridge
Isaac Aboulafia, START
Mike Alexander, MDEQ
Adriana Bejarano, RPI
Michel Boufadel, Temple University
Jim Chapman, U.S. EPA
Isabelle Cozzarelli, USGS
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Jacqui Michel, RPI
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Greg Powell, U.S. EPA – ERT
David Soong, USGS
Mark Sprenger, U.S. EPA – ERT
Bob Steede, Enbridge
Al Uhler, NewFields
Albert Venosa, U.S. EPA
Lisa Williams, USFWS

February 10, 2012

Mr. Ralph Dollhopf
Federal OSC and Incident Commander
U.S. EPA, Region 5
Emergency Response Branch
801 Garfield Avenue, #229
Traverse City, MI 49686

Subject: Analytical Plan - Enbridge Line 6B MP 608, Marshall, Mich., Pipeline Release

Dear Mr. Dollhopf,

With this memorandum, the Chemistry, Fingerprinting, and Biodegradation Subgroup of the SSCG transmits its response to the FOSC's charge (1) to the Science Support Coordination Group:

a) Provide an evaluation of viable analytical approaches, including benefits and draw backs for each, to quantify the amount of submerged oil in the Kalamazoo River sediments attributable to the Enbridge Oil pipeline Release.

b) Provide a recommendation for the best analytical approach to accomplish this goal.

Specifically, this memo summarizes the rationale for selecting the chemical analytes and analytical protocols outlined in the recommended Analytical Plan (AP) for the above-referenced oil spill response, and how the methods described within that plan will be used to support a variety of spill-related environmental studies. The methods recommended in the AP are heavily vetted in the scientific literature, published in the Federal Register, and represent the industry standard for oil spill analytical chemistry. The analytical methods and QA/QC program defined in the AP are used exclusively on most large oil spill responses in the United States. For example, this AP is patterned after that used by NOAA for the BP MC-252 (*Deepwater Horizon*) oil spill in the Gulf of Mexico; this approach also was applied for the 1991 Gulf War, *Selendang Ayu*, *Cosco Busan*, and *Exxon Valdez* incidents.

Reliable, petroleum-specific analytical chemistry data are a cornerstone of a defensible oil spill response program, and the selection of the appropriate analytical methodologies is critical for producing useful and meaningful data to support a host of different spill-focused environmental investigations. The data requirements and data quality objectives for oil spill investigations are almost always different from those of standard regulatory investigations, e.g., Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) or Resource Conservation and Recovery Act of 1976 (RCRA) -type investigations. Such regulatory investigations typically focus on *a limited number of parameters and chemicals of concern.* Target compounds that are the focus of standard EPA methods of analysis are overwhelmingly non-petroleum industrial chemicals, or only simple (gross) measures of petroleum. Examples of these measurements include total petroleum hydrocarbons (TPH), concentrations of water-soluble

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benzene, toluene, ethyl-benzene, and *o*-, *m*-, and *p*-xylenes (BTEX), and the 16 Priority Pollutant polycyclic aromatic hydrocarbons (PAH). These compliance-driven measurements—while adequate for gross descriptions of the types of contaminants found at a site (e.g., frequency distribution relative to regulatory action limit)—are largely insufficient to address fundamental concerns in an oil spill response (e.g., the FOSC's charge [1]a).

Almost always, the principal analytical chemistry needs for an oil spill investigation include 1) a detailed chemical compositional signature for the spilled oil(s), 2) reliable chemical metrics to identify the presence or absence of the spilled oil in complex environments such as river sediments, ground- or pore-water, or soils, 3) a chemical basis to assist in quantifying amount of the oil in the environment and to estimate exposure of oil to aquatic organisms, and 4) a reliable, long-term basis to monitor intrinsic weathering and/or facilitated biodegradation of the oil in the environment.

Achieving these technical objectives requires that petroleum-specific chemical measurement data of only the highest quality be generated by an experienced petroleum fingerprinting laboratory. The AP recommended for this spill response provides evaluations and sound guidance to the FOSC for communication to Enbridge Energy and its laboratory your expectations for how these goals are to be met by identifying the appropriate analytical methods, target analyte lists, quality control (QC) and quality assurance requirements, and overall data quality objectives (DQO).

These methods as described in the AP are primarily derived from standard EPA methods that, over the last two decades, have been modified to achieve the forensic chemistry goals necessary for oil spill investigations. The features of these methods that distinguish them from standard EPA methods of analysis fall into several categories:

- Target analytes that are petroleum-specific, to ensure adequate characterization of important constituents that comprise petroleum. Target compounds include chemicals that are subject to weathering, others that are recalcitrant and stable, and others that are of importance to ecological and human health risk assessors.
- Low detection limits, to achieve environmentally meaningful reporting limits for petroleum-derived chemicals of concern in environmental samples
- Dynamic detection limits, to assure accurate measurement of chemicals of concern that can co-occur at high- and low concentrations in oil (or oiled samples)
- Rigorous quality control criteria, to ensure the highest precision and accuracy.

Briefly, the AP describes how petroleum residues are isolated from the environmental samples (extracted with a solvent), processed in the laboratory to remove naturally occurring matrix interferences (sample extract cleanup), concentrated to improve analytical sensitivity (the solvent is carefully evaporated leaving the petroleum compounds in a more concentrated extract), and analyzed using gas chromatography techniques to separate and measure the compounds of interest.[1] Finally, the AP describes how the results are reported and the quality-control measures recommended to ensure that the chemical data are both accurate and precise.

The recommended techniques are proven to provide data that can help answer the following questions with a high degree of reliability:

[1]The compounds of interest include petroleum specific polycyclic aromatic hydrocarbons (including their associated alkylated homologs), and sulfur heterocyclic compounds, saturated hydrocarbons, and weathering resistant and oil source specific biomarker compounds.

1. What is the chemical composition of the spilled oil?
2. What chemicals of concern present a risk to the aquatic wildlife and what potential levels of environmental exposure may be present?
3. Is the oil in the environmental sample (e.g., water, sediment, soil) from the oil spill or from a secondary source?
4. What is the spatial extent of the spill? How far did the spilled oil spread?
5. If other oils are present in the samples, what percentage is related to the spill?
6. What is the weathering pathway of the oil in the environment?[2]
7. What is the degree of oil weathering and biodegradation in the oiled samples?

Based on subgroup members' experience working on oil spill related issues for the past 20 years, we strongly recommend the adoption of this technical approach in completing the response to the Enbridge Line 6B MP 608 Marshall, Michigan, Pipeline Release.

On behalf of the SSCG sub-group, very sincerely yours,

Gregory Douglas, Ph.D.
Senior Consultant

[2] How the oil degrades under different environmental conditions, and which chemical indicators enable classifying the degree of oil degradation in a sample.

DRAFT

ANALYTICAL QUALITY ASSURANCE PLAN

ENBRIDGE LINE 6B MP 608

MARSHALL, MICHIGAN, PIPELINE RELEASE

Version 2.1

Prepared for:

U.S. Environmental Protection Agency

February 10, 2012

TABLE OF CONTENTS

Acronyms and Abbreviations

%D	Percent difference
%R	Percent recovery
ASTM	American Society for Testing and Materials
LCS/LCSD	Blank spike/blank spike duplicate
CCV	Continuing calibration verification
CRM	Certified reference material
DQO	Data quality objectives
EDD	Electronic data deliverable
EIP	Extracted ion Profile
EPA	U.S. Environmental Protection Agency
GC/MS-SIM	Gas chromatography with low resolution mass spectrometry using selected ion monitoring
GC-FID	Gas chromatography with flame ionization detection
MDL	Method detection limit
MQO	Measurement quality objectives
MS/MSD	Matrix spike/matrix spike duplicate
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
PAH	Polycyclic aromatic hydrocarbons
QA	Quality assurance
QAP	Quality assurance plan
QC	Quality control
QL	Quantitation Limit
RM	Reference material
RPD	Relative percent difference
RSD	Relative standard deviation
SHC	Saturated hydrocarbons
SOP	Standard Operating Procedures
TEH	Total extractable hydrocarbons
TEM	Total extractable matter
TEO	Total extractable organics
GS	Grain Size
PIANO	Paraffins, isoparafins, aromatics, napthenes, olefins
TOC	Total organic carbon
AVS-SEM	Acid Volatile Sulfide and Simultaneously Extracted Metals
EICP	Extracted Ion Chromatographic Profile

INTRODUCTION

This Analytical Quality Assurance (QA) Plan describes the minimum requirements for the chemical analysis of the environmental samples that are collected in areas along the channel, banks, and floodplains of the Kalamazoo River including the Morrow Lake Delta and Morrow Lake. This will improve the understanding of submerged oil transport, source identification (e.g., fingerprinting), degree of environmental weathering (evaporation and water washing) and oil biodegradation, containment of oil, and temporal recovery of oil-containing soil/sediment related to the Enbridge Line 6B Incident Marshall, Michigan, Pipeline Release.

This plan does not address the actual field collection or generation of these samples. This information is provided in the Field Sampling Plans (FSP). The scope of the laboratory work is twofold: (1) generate concentrations for key chemicals related to crude oil releases, (2) produce more extensive chemical data to use in fingerprinting for source identification in both fresh and weathered samples, and (3) provide a means to monitor the natural attenuation of the oil in the environment. The applicable chemicals, need and frequency of environmental sample analyses, quality control requirements, and data usage vary for these three purposes, although implementation of this plan enables both to be achieved. In recognition of these differences, sampling plans may reference the Analytical QA Plan and cite the specific tables of chemical analyses that are appropriate to the needs of the particular sampling effort.

The requirements specified in this plan are designed to: (1) monitor the performance of the measurement systems to maintain statistical control over the reported concentrations of target analytes and provide rapid feedback so that corrective measures can be taken before data quality is compromised; and (2) verify that reported data are sufficiently complete, comparable, representative, unbiased and precise so as to be suitable for their intended use.

The analytes of concern addressed in this QA Plan are polycyclic aromatic hydrocarbons (PAHs) including alkyl homologues, saturated hydrocarbons (SHC), total extractable hydrocarbons (TEH)[1], volatile organic compounds (VOCs), petroleum biomarkers, and metals. A variety of matrices may be analyzed including water, sediment/soil, tissue, absorbent materials (e.g. Teflon nets, etc.), oils and oil debris. In addition to the primary analytes of concern, ancillary tests may include: percent moisture, total organic carbon (TOC) and grain size for sediment samples. The methods and associate QA criteria proposed in this plan represent standard oil spill analytical protocols that have been extensively vetted in the peer reviewed literature, defended in US and international courts, and applied on most major oil spill events over the past two decades.

The work plans and associated QA plans under which these samples were generated or collected are independent documents and not included or considered herein. This Analytical QA Plan describes the minimum requirements to be taken to provide for the chemical analyses (and associated physical normalizing parameters) of the previously generated or collected samples in a technically sound and legally defensible manner.

This Analytical QA Plan satisfies the requirements listed in the relevant EPA guidance for QA plans (USEPA 2002 and USEPA 2001) as far as the documents relate to analytical testing services. This QA plan will be revised as appropriate.

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[1] TEH is the total aromatic and aliphatic content as determined by GC-FID. If the sample extract is not "cleaned up" to remove biogenic material prior to the GC-FID analysis, then the result from the GC-FID analysis is termed Total Extractable Matter (TEM).

1.0 PROJECT DESCRIPTION

The intent of this plan is to present the minimum requirements for the performance criteria for the laboratories providing data in support of this investigation. The analytes of specific interest and brief descriptions of the analytical methods are as follows:

- Polycyclic Aromatic Hydrocarbons and Sulfur Heterocyclic Compounds (PAHs) including alkyl homologues by gas chromatography with low resolution mass spectrometry using selected ion monitoring (GC/MS-SIM). The concentration and distribution (e.g., Fingerprint) of these petroleum diagnostic compounds are defined by the geological source of the oil and mixing with other products (e.g., diluents) at the refinery or in the environment (environmental background). The chemical fingerprint generated by this analysis provides a means to reliably identify the presence of the source oil(s) in environmental samples. In addition, the parent PAH compounds and their associated homologues follow a predictable degradation pathway which is used as one measure of intrinsic oil degradation. This analysis is the foundation for most defensible oil spill studies performed during the past two decades, from the *Exxon Valdez* to the MS-252 oil spills. They are routinely used by NOAA, USEPA, Environment Canada, European Union and the oil industry and have been extensively vetted in the peer reviewed scientific oil spill literature for use in oil spill investigations.

  The analytical procedure is based on EPA Method 8270D with the GC and MS operating conditions optimized for separation and sensitivity of the target analytes. Alkyl PAH homologues are quantified using a response factor assigned from the parent PAH compound. Analytes, associated response factors and target detection limits are listed in **Table 1.1a.** Due to the potential high organic carbon content of the sediment/soils (and lipid in tissues), sample extracts will at a minimum be processed through a sufficiently sized silica gel or alumina column designed to remove polar interferences. Further clean up techniques may need to be employed such as silica gel fractionation (aromatic fraction) or HPLC GPC (tissues) depending on the level of interferences. The following references discuss the method options in further detail:

Federal Register 40CFR300, Subchapter J, Part 300, Appendix C, 4-6-3 to 4-6-5, pp. 234-237.

Murphy, Brian L., and Robert D. Morrison (Editors). 2007. *Introduction to Environmental Forensics*, 2nd Edition. Chapter 9, p. 389 – 402.

Page, D.S., P.D. Boehm, G.S. Douglas, and A.E. Bence. 1995. Identification of hydrocarbon sources in the benthic sediments of Prince William Sound and the Gulf of Alaska following the *Exxon Valdez* oil spill. *In*: *Exxon Valdez Oil Spill: Fate and Effects in Alaskan Waters, ASTM STP 1219*, P.G. Wells, J.N. Bulter, and J.S. Hughes, Eds., American Society for Testing and Materials, Philadelphia, pp. 44-83.

Douglas, G.S., Bence, A.E., Prince, R.C., McMillen, S.J. and Butler, E.L. 1996. Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environ. Sci. Technology*, 30(7):2332-2339.

Kimbrough, K.L., G.G. Lauenstein, and W.E. Johnson (Editors). 2006. *Organic Contaminant Analytical methods of the National Status and Trends Program: Update 2000-2006*. NOAA Technical Memorandum NOS NCCOS 30, p. 25- 37.

Sauer, T.C., and P.D. Boehm. 1995. *Hydrocarbon Chemistry Analytical Methods for Oil Spill Assessments*. MSRC Technical Report Series 95-032, Marine Spill Response Corporation, Washington, D.C., 114 p.

Douglas, G.S., Stout, S.A., Uhler, A.D., McCarthy, K.J., Emsbo-Mattingly, S.D. 2006. Advantages of quantitative chemical fingerprinting in oil spill source identification. *In:* Spill Oil Environmental Forensics: Fingerprinting and Source Identification. Z. Wang and S.A. Stout, Eds. Elsevier Publishing Co., Boston, MA.

USEPA. 2008. *Test Methods for Evaluating Solid Waste, Physical/Chemical Method* (SW846).

Wang, Z., and S.A. Stout. 2007. Chemical fingerprinting of spilled or discharged petroleum – methods and factors affecting petroleum fingerprints in the environment. In: *Oil Spill Environmental Forensics: Fingerprinting and Source Identification*. Z. Wang, and S.A. Stout, Eds., Elsevier Publishing Co., Boston, MA, pp. 1-53.

Douglas, G.S., Burns, W.A., Bence, A.E., Page, D.S. and Boehm, P.B. 2004. Optimizing detection limits for the analysis of petroleum hydrocarbons in complex samples. *Environ. Sci. Technol.* 38(14):3958-3964.

- Saturate hydrocarbons by gas chromatography with flame ionization detection (GC/FID) based on U.S. EPA Method 8015. Analytes and target detection limits are listed in **Table 1.1b**.

  GC/FID fingerprint provides a means to identify mild to moderate oil biodegradation and to quantify the GC detectable (*n*-C_9 through *n*-C_{44}) amount of oil in the sample. The GC/FID chromatogram provides a chemical fingerprint of the sample that is used by the analyst to assist in the identification of the oil and determine the presence of other types of oil and background hydrocarbons (e.g., alkanes derived from plant waxes). This analysis is a key component for most defensible oil spill studies performed during the past two decades, from the *Exxon Valdez* to the MS-252 oil spills. They are routinely used by NOAA, USEPA, Environment Canada, European Union and the oil industry and have been extensively vetted in the peer reviewed scientific oil spill literature for use in oil spill investigations.

- Total Extractable Hydrocarbons (TEH[2]) representing the total aromatic and aliphatic hydrocarbon content of sample extracts after silica gel clean-up and analysis by GC/FID (**Table 1.1b**). Note: Due to the potential high organic carbon content of the sediment/soils, sample extracts will at a minimum be processed thru a sufficient size silica gel or alumina column designed to remove polar interferences. The result is reported based on integration of the FID signal over the entire hydrocarbon range from *n*-C9 to n-C44 and calibrated against the average alkane hydrocarbon response factor.

  If the sample extract does not receive any clean-up (samples of water, oil and oily debris) then the result will be reported as Total Extractable Matter (TEM) because the extract may contain non-hydrocarbon compounds. Either TEH or TEM may be reported by the laboratory depending on the handling of the extract.

  The results may also be used to normalize the hopane concentration in the sediment sample on an oil weight basis to provide estimates of total oil degradation. Gravimetric analysis of these extracts for non-volatile oils can provide a more accurate concentration of sediment oil mass for biomarker normalization.[3]

- The distribution of biomarker compounds in petroleum is a function of geological source, refinery practices, and mixing (e.g., condensate) and provides a *stable, source specific fingerprint of the oil(s)* for source identification. Because they are highly resistant to environmental degradation, they are routinely used to estimate the percent degradation of the petroleum components in the sample. As the

[2] Note that the term TEH is being used for the total hydrocarbon analysis. The term "Total Petroleum Hydrocarbon" (TPH) may be used to refer to TEH, in some instances. For this QAP, the term TEH is used to avoid confusion with state-regulated gasoline or diesel determinations, rather TEH is used to refer to the sum of hydrocarbons from C_9 to C_{44}.

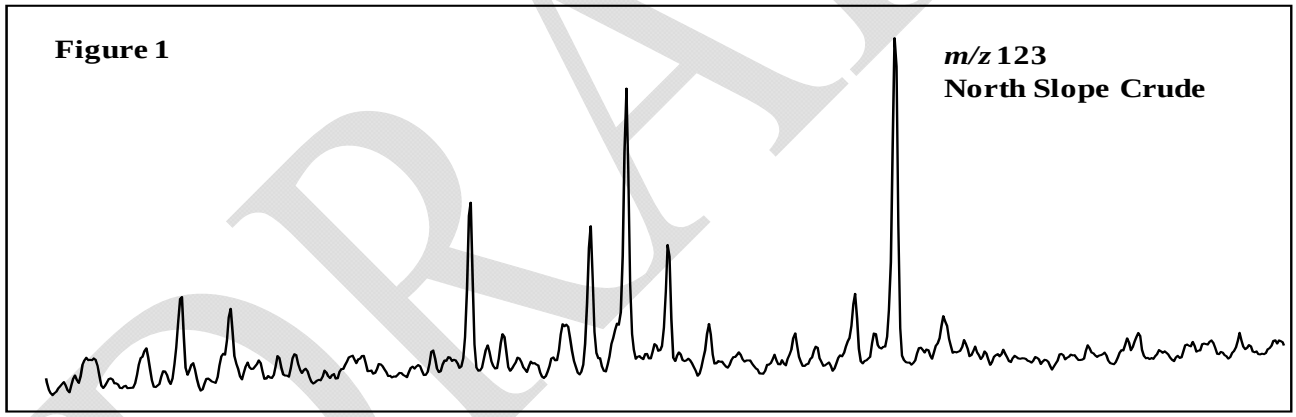
[3] Note: Gravimetric analysis of cleaned up extracts include the extractable C_{10} through C_{44+} fraction of the oil.

petroleum degrades, biomarker compounds (e.g., hopane) becomes enriched in the sample *on an oil weight basis*. The degree of enrichment relative to the source oil is a measure of percent oil degradation. This approach can also be used to calculate the percentage of individual and total PAH degradation in the field samples. This analysis is the foundation for most defensible oil spill studies performed during the past two decades, from the *Exxon Valdez* to the MS-252 oil spills. They are routinely used by NOAA, USEPA, Environment Canada, European Union and the oil industry and have been extensively vetted in the peer reviewed scientific oil spill literature for use in oil spill investigations.

Petroleum biomarkers by GC/MS-SIM. The analysis of petroleum biomarkers are carried out as part of the EPA 8270D PAH analysis discussed above. Should further clean-up be necessary, extracts will be fractionated using silica gel into a aliphatic fraction prior to analysis. The proposed target analyte list for quantitative biomarkers is provided in **Table 1.1c.** This list may be expanded if warranted. In addition, the *m/z* 123 sesquiterpane extracted ion chromatographic profile (EICP) will be printed out for each sample and included in the data package (Figure 1). This method is discussed in further detail in:

Douglas, G.S., S.D. Emsbo-Mattingly, S.A. Stout, A.D. Uhler, and K.L. McCarthy, 2007. Chemical fingerprinting methods, Chap. 9 *in* Murphy, B.L., and R.D. Morrison (eds), *Introduction to Environmental Forensics*, 2nd ed. Elsevier Academic Press, London, p. 389 – 402.

Wang, Z., Stout, S.A., and Fingas, M., 2006. Forensic fingerprinting of biomarkers for oil spill characterization and source identification (Review). *Environ. Forensics* 7(2): 105-146.



- Metals by ICP/MS based on EPA Method 6020. The proposed target analyte list is provided in **Table 1.1d.** A multilevel calibration and independent calibration check standard will be analyzed prior to sample analysis.

- Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM) in sediment following published procedure (Boothman et al. 1992 or equivalent)[4]. Sulfide is volatilized in sediment after the addition of acid. The acid extraction produced in this step is also analyzed for simultaneously extractable metals (SEM) that became soluble during the acidification step. As a precipitant with heavy metals, sulfide is fundamental in the determination of the bioavailability of metals in anoxic sediment.

[4] "Determination of acid-volatile sulfide and simultaneously-extracted metals in sediments using sulfide-specific electrode detection," Warren S. Boothman, USEPA Environmental Research Laboratory, Narragansett, RI, and Andrea Helmstetter, Science International Corp., Narragansett, RI. September 4, 1992. AVSSEM SOP v2.0

When the molar ratio of SEM to AVS exceeds one, the metals are potentially bioavailable to aquatic organisms. The proposed target analyte list is provided in **Table 1.1d.**

- Extended list of volatile organic compounds (VOC) by GC/MS based on EPA Method 8260B. The list of hydrocarbons are contained in five compound classes of paraffins, isoparaffins, aromatics, napthenes, and olefins (PIANO) in the gasoline range ($C_5 - C_{13}$). Analytes and target detection limits are provided in **Table 1.1e**.

  This method is provided to characterize the volatile hydrocarbons that may be present in the field samples. Given that condensate was used as a diluent in the Enbridge oil, it is important to 1) characterize these toxic compounds in the spilled oil, and 2) verify in selected samples that at this stage of the oil spill, these volatile hydrocarbons are no longer present in the sediment or water field samples. An understanding of the concentrations of these compounds in the spilled oil will provide the environmental risk assessment team a means to estimate environmental exposure during the early phase of the spill. It is expected that this analysis would only be performed on selected samples based on field observation (e.g., odor) and other factors as defined by the ecological risk group.

Analyses may include a number of different sample matrices. Matrices that will be analyzed will be determined in sampling plans and may not include all analyses for each matrix. The following table provides a summary of which analyses may be applicable to each matrix (analyses may be added or deleted as warranted over time).

Matrix	PAH	SHC/TEH	BIOMARK	PIANO[2]	Metals	AVS-SEM	TOC	Grain Size
Water[1]	X	X	X	X	X		X	
Sediment/Soil	X	X	X	X	X	X	X	X
Tissues[1]	X		X					
Inert Sorbent Materials	X	X	X					
Oil/Oily Debris	X	X	X	X				

[1]Selected water and tissues may be analyzed for petroleum biomarkers depending on PAH concentrations.

[2]Selected samples may be analyzed from areas being sampled for the Toxicity testing.

TABLE1.1a
Extended PAH (Parent and Alkyl Homologues) and Related Compounds

	Compound	RF Source[5]
D0	cis/trans-Decalin	
D1	C1-Decalins	D0 or tD0[6]
D2	C2-Decalins	D0 or tD0
D3	C3-Decalins	D0 or tD0
D4	C4-Decalins	D0 or tD0
BT0	Benzothiophene	
BT1	C1-Benzo(b)thiophenes	BT0
BT2	C2-Benzo(b)thiophenes	BT0
BT3	C3-Benzo(b)thiophenes	BT0
BT4	C4-Benzo(b)thiophenes	BT0
N0	Naphthalene	
N1	C1-Naphthalenes	N0
N2	C2-Naphthalenes	N0
N3	C3-Naphthalenes	N0
N4	C4-Naphthalenes	N0
B	Biphenyl	
DF	Dibenzofuran	
AY	Acenaphthylene	
AE	Acenaphthene	
F0	Fluorene	
F1	C1-Fluorenes	F0
F2	C2-Fluorenes	F0
F3	C3-Fluorenes	F0
A0	Anthracene	
P0	Phenanthrene	
PA1	C1-Phenanthrenes/Anthracenes	P0
PA2	C2-Phenanthrenes/Anthracenes	P0
PA3	C3-Phenanthrenes/Anthracenes	P0

	Compound	RF Source
PA4	C4-Phenanthrenes/Anthracenes	P0
RET	Retene	RET or P0
DBT0	Dibenzothiophene	
DBT1	C1-Dibenzothiophenes	DBT0
DBT2	C2-Dibenzothiophenes	DBT0
DBT3	C3-Dibenzothiophenes	DBT0
DBT4	C4-Dibenzothiophenes	DBT0
BF	Benzo(b)fluorene	BF or FL0
FL0	Fluoranthene	
PY0	Pyrene	
FP1	C1-Fluoranthenes/Pyrenes	FL0 or PY0
FP2	C2-Fluoranthenes/Pyrenes	FL0 or PY0
FP3	C3-Fluoranthenes/Pyrenes	FL0 or PY0
FP4	C4-Fluoranthenes/Pyrenes	FL0 or PY0
NBT0	Naphthobenzothiophenes	
NBT1	C1-Naphthobenzothiophenes	NBT0
NBT2	C2-Naphthobenzothiophenes	NBT0
NBT3	C3-Naphthobenzothiophenes	NBT0
NBT4	C4-Naphthobenzothiophenes	NBT0
BA0	Benz[a]anthracene	
C0	Chrysene/Triphenylene	
BC1	C1-Chrysenes	C0
BC2	C2-Chrysenes	C0
BC3	C3-Chrysenes	C0
BC4	C4-Chrysenes	C0
BBF	Benzo[b]fluoranthene	
BJKF	Benzo[j,k]fluoranthene	BKF[7]
BAF	Benzo[a]fluoranthene	BKF or BAF

	Compound	RF Source
BEP	Benzo[e]pyrene	
BAP	Benzo[a]pyrene	
PER	Perylene	
IND	Indeno[1,2,3-cd]pyrene	
DA	Dibenz[a,h]anthracene	
GHI	Benzo[g,h,i]perylene	
4MDT	4-Methyldibenzothiophene	DBT0
2MDT	2/3-Methyldibenzothiophene	DBT0
1MDT	1-Methyldibenzothiophene	DBT0
3MP	3-Methylphenanthrene	P0
2MP	2/4-Methylphenanthrene*	P0
2MA	2-Methylanthracene	P0
9MP	9-Methylphenanthrene*	P0
1MP	1-Methylphenanthrene	P0
	2-Methylnaphthalene	
	1-Methylnaphthalene	
	2,6-Dimethylnaphthalene	
	1,6,7-Trimethylnaphthalene	
	Other	
	Carbazole	

*Possible coelution issue.

Target Method Detection Limit Range

Sediment/Soil =	0.1 – 0.5 ng/g dry weight
Tissue =	0.2 – 1.0 ng/g wet weight
Water =	1 – 5 ng/L

Target Reporting Limit

Oil =	2.0 mg/kg

[5] Response factor (RF) to be used for quantitation. If blank, compound is included in the calibration mix

[6] tD0 = transD0 (used if cis/trans in separate standards)

[7] BKF = Benzo(k)fluoranthene. Benzo(j)fluoranthene and Benzo(k)fluoranthene coelute and will be reported as Benzo(j,k)fluoranthene (BJKF)

TABLE 1.1b
Saturated Hydrocarbons (Alkanes/Isoprenoids Compounds)
and Total Extractable Hydrocarbons

Abbr.	Analyte
nC9	n-Nonane
nC10	n-Decane
nC11	n-Undecane
nC12	n-Dodecane
nC13	n-Tridecane
1380	2,6,10 Trimethyldodecane
nC14	n-Tetradecane
1470	2,6,10 Trimethyltridecane
nC15	n-Pentadecane
nC16	n-Hexadecane
nPr	Norpristane
nC17	n-Heptadecane
Pr	Pristane
nC18	n-Octadecane
Ph	Phytane
nC19	n-Nonadecane
nC20	n-Eicosane
nC21	n-Heneicosane
nC22	n-Docosane

Abbr.	Analyte
nC23	n-Tricosane
nC24	n-Tetracosane
nC25	n-Pentacosane
nC26	n-Hexacosane
nC27	n-Heptacosane
nC28	n-Octacosane
nC29	n-Nonacosane
nC30	n-Triacontane
nC31	n-Hentriacontane
nC32	n-Dotriacontane
nC33	n-Tritriacontane
nC34	n-Tetratriacontane
nC35	n-Pentatriacontane
nC36	n-Hexatriacontane
nC37	n-Heptatriacontane
nC38	n-Octatriacontane
nC39	n-Nonatriacontane
nC40	n-Tetracontane

TEH	$\Sigma(C_9\text{-}C_{44})$ Integration of the FID signal over the entire hydrocarbon range from n-C9 to n-C44 after silica gel cleanup.
TEM	$\Sigma(C_9\text{-}C_{44})$ Integration of the FID signal over the entire hydrocarbon range from n-C9 to n-C44 no silica gel cleanup.

	Target Method Detection Limit
Sediment (Alkanes) =	0.01 µg/g dry weight
Sediment (TEH) =	1 µg/g dry weight
Water (Alkanes) =	0.8 µg/L
	Target Reporting Limit
Oil (Alkanes) =	200 mg/kg
Oil (TEH) =	200 mg/kg
Water (TEH/TEM) =	200 µg/L

TEH = Total Extractable Hydrocarbons with silica gel "clean-up"
TEM = Total Extractable Matter with no extract "clean-up"

TABLE 1.1c
Petroleum Biomarkers for Quantitative Analysis

Compound *	Quant Ion m/z
C23 Tricyclic Terpane (T4)	191
C24 Tricyclic Terpane (T5)	191
C25 Tricyclic Terpane (T6)	191
C24 Tetracyclic Terpane (T6a)	191
C26 Tricyclic Terpane-22S (T6b)	191
C26 Tricyclic Terpane-22R (T6c)	191
C28 Tricyclic Terpane-22S (T7)	191
C28 Tricyclic Terpane-22R (T8)	191
C29 Tricyclic Terpane-22S (T9)	191
C29 Tricyclic Terpane-22R (T10)	191
18a-22,29,30-Trisnorneohopane-Ts (T11)	191
C30 Tricyclic Terpane-22S (T11a)	191
C30 Tricyclic Terpane-22R (T11b)	191
17a(H)-22,29,30-Trisnorhopane-Tm (T12)	191
17a/b,21b/a 28,30-Bisnorhopane (T14a)	191
17a(H),21b(H)-25-Norhopane (T14b)	191
30-Norhopane (T15)	191
18a(H)-30-Norneohopane-C29Ts (T16)	191
17a(H)-Diahopane (X)	191
30-Normoretane (T17)	191
18a(H)&18b(H)-Oleananes (T18)	191
Hopane (T19)	191
Moretane (T20)	191
30-Homohopane-22S (T21)	191
30-Homohopane-22R (T22)	191
T22a-Gammacerane/C32-diahopane	191
30,31-Bishomohopane-22S (T26)	191
30,31-Bishomohopane-22R (T27)	191
30,31-Trishomohopane-22S (T30)	191

Compound	Quant ion m/z
30,31-Trishomohopane-22R (T31)	191
Tetrakishomohopane-22S (T32)	191
Tetrakishomohopane-22R (T33)e	191
Pentakishomohopane-22S (T34)	191
Pentakishomohopane-22R (T35)	191
13b(H),17a(H)-20S-Diacholestane (S4)	217
13b(H),17a(H)-20R-Diacholestane (S5)	217
13b,17a-20S-Methyldiacholestane (S8)	217
14a(H),17a(H)-20S-Cholestane/ 13b(H).17a(H)-20S-Ethyldiacholestane (S12)	217
14a(H),17a(H)-20R-Cholestane 13b(H),17a(H)-20R-Ethyldiacholestane (S17)	217
Unknown sterane(S18)	217
13a,17b-20S-Ethyldiacholestane (S19)	217
14a,17a-20S-Methylcholestane (S20)	217
14a,17a-20R-Methylcholestane (S24)	217
14a(H),17a(H)-20S-Ethylcholestane (S25)	217
14a(H),17a(H)-20R-Ethylcholestane (S28)	217
14b(H),17b(H)-20R-Cholestane (S14)	218
14b(H),17b(H)-20S-Cholestane (S15)	218
14b,17b-20R-Methylcholestane (S22)	218
14b,17b-20S-Methylcholestane (S23)	218
14b(H),17b(H)-20R-Ethylcholestane (S26)	218
14b(H),17b(H)-20S-Ethylcholestane (S27)	218
C26,20R- +C27,20S- triaromatic steroid	231
C28,20S-triaromatic steroid	231
C27,20R-triaromatic steroid	231
C28,20R-triaromatic steroid	231
Sesquiterpane EICPs	123

* Peak identification provided in parentheses.

	Target Reporting Limit
Sediments/Soil =	2 ug/Kg dry weight
Waters =	10 ng/L

	Target Reporting Limit
Oil =	2 mg/Kg

TABLE 1.1d
Standard Trace Metal Compounds

Analyte
Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)
Cadmium (Cd)*
Calcium (Ca)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)*
Iron (Fe)
Lead (Pb)*
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg) = CVAA
Nickel (Ni)*
Potassium (K)
Selenium (Se)
Silver (Ag)
Sodium (Na)
Thallium (Tl)
Vanadium (V)
Zinc (Zn)*

*AVS-SEM metals

Target Method Detection Limit Range
(TAL Metals)

Sediment/Soil = 0.0005 – 6.1 mg/kg
Water = 0.0002 – 19 µg/L

AVS-SEM Metals Reporting Limit Range

Sediment/Soil = 0.0009 – .04 µmol/g

AVS Reporting Limit

Sediment/Soil = 0.7 µmol/g

TABLE 1.1e
C5-C13 Volatile Compounds for PIANO Forensic Assessment

Abbrev.	Analyte
IP	Isopentane
1P	1-Pentene
2M1B	2-Methyl-1-butene
C5	Pentane
T2P	2-Pentene (trans)
C2P	2-Pentene (cis)
TBA	Tertiary butanol
CYP	Cyclopentane
23DMB	2,3-Dimethylbutane
2MP	2-Methylpentane
MTBE	MTBE
3MP	3-Methylpentane
1HEX	1-Hexene
C6	Hexane
DIPE	Diisopropyl Ether (DIPE)
ETBE	Ethyl Tertiary Butyl Ether (ETBE)
22DMP	2,2-Dimethylpentane
MCYP	Methylcyclopentane
24DMP	2,4-Dimethylpentane
12DCA	1,2-Dichloroethane
CH	Cyclohexane
2MH	2-Methylhexane
B	Benzene
23DMP	2,3-Dimethylpentane
THIO	Thiophene
3MH	3-Methylhexane
TAME	TAME
1H	1-Heptene/1,2-DMCP (trans)
ISO	Isooctane
C7	Heptane

Abbrev.	Analyte
MCYH	Methylcyclohexane
25DMH	2,5-Dimethylhexane
24DMH	2,4-Dimethylhexane
223TMP	2,2,3-Trimethylpentane
234TMP	2,3,4-Trimethylpentane
233TMP	2,3,3-Trimethylpentane
23DMH	2,3-Dimethylhexane
3EH	3-Ethylhexane
2MHEP	2-Methylheptane
3MHEP	3-Methylheptane
T	Toluene
2MTHIO	2-Methylthiophene
3MTHIO	3-Methylthiophene
1O	1-Octene
C8	Octane
12DBE	1,2-Dibromoethane
EB	Ethylbenzene
2ETHIO	2-Ethylthiophene
MPX	p/m-Xylene
1N	1-Nonene
C9	Nonane8
STY	Styrene
OX	o-Xylene
IPB	Isopropylbenzene
PROPB	n-Propylbenzene
1M3EB	1-Methyl-3-ethylbenzene
1M4EB	1-Methyl-4-ethylbenzene
135TMB	1,3,5-Trimethylbenzene
1D	1-Decene
1M2EB	1-Methyl-2-ethylylbenzene

Abbrev.	Analyte
C10	Decane[8]
124TMB	1,2,4-Trimethylbenzene
SECBUT	sec-Butylbenzene
1M3IPB	1-Methyl-3-isopropylbenzene
1M4IPB	1-Methyl-4-isopropylbenzene
1M2IPB	1-Methyl-2-isopropylbenzene
IN	Indan
1M3PB	1-Methyl-3-propylbenzene
1M4PB	1-Methyl-4-propylbenzene
BUTB	n-Butylbenzene
12DM4EB	1,2-Dimethyl-4-ethylbenzene
12DEB	1,2-Diethylbenzene
1M2PB	1-Methyl-2-propylbenzene
14DM2EB	1,4-Dimethyl-2-ethylbenzene
C11	Undecane8
13DM4EB	1,3-Dimethyl-4-ethylbenzene
13DM5EB	1,3-Dimethyl-5-ethylbenzene
13DM2EB	1,3-Dimethyl-2-ethylbenzene
12DM3EB	1,2-Dimethyl-3-ethylbenzene
1245TMP	1,2,4,5-Tetramethylbenzene
PENTB	Pentylbenzene
C12	Dodecane8
N0	Naphthalene[9]
BT0	Benzothiophene9
MMT	MMT
C13	Tridecane8
2MN	2-Methylnaphthalene9
1MN	1-Methylnaphthalene9

Target Method Detection Limit Range
Sediment/Soil = 0.1 – 10 ng/g
Water = 0.2 - 2.0 µg/L
Target Reporting Limit
Oil = 2 mg/kg

[8] These compounds are also included on the **Table 1.1b** target analyte list of saturate hydrocarbons. Because of the extraction technique, the GC-FID method for hydrocarbons is the preferred method, rather than this volatile method. Thus, if a sample location is analyzed for both saturate hydrocarbons by GC-FID and VOC the result from the GC-FID analysis will be noted in the database as the preferred result.

[9] These compounds are also included on the **Table 1.1a** target analyte list of PAH compounds. Because of the extraction technique, the PAH analysis is the preferred method, rather than this volatile method. Thus, if a sample location is analyzed for both PAH and VOC the result from the PAH analysis will be noted in the database as the preferred result.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

2.1 Assessment Manager

The Assessment Manager is the designated U.S. EPA representative who is responsible for the review and acceptance of specific work plans and associated QA plans.

2.2 Environmental Chemistry Project Coordinator

The Environmental Chemistry Project Coordinator is responsible for administration of the contracts with the laboratory(ies). The Environmental Chemistry Project Coordinator will oversee the proper scheduling and transmittal of the data from the time of sampling to data reporting.

2.3 Quality Assurance Coordinator

The QA Coordinator is responsible for the implementation of this Analytical QA Plan. The QA Coordinator will work closely with laboratory representatives and the project team to assure that project and data quality objectives are met.

2.4 Analytical Laboratories

The laboratories to be contracted for analytical work in support of and compliance with U.S. EPA directives must show **proficiency and experience** in individual alkane, PAH homologue, and biomarker analysis in the proposed matrices. **Copies of established SOPs and example data will be submitted to the QA Coordinator for review prior to analysis of any field samples.** The laboratory will assign a project manager responsible for assuring that all analyses performed meet project and measurement quality objectives. Precision and reproducibility are key components to a successful analytical program because the data will be critically interpreted using source ratio analysis, principal component analysis, cluster analysis, mixing model analysis, and possibly other interpretive methods. Due to the complexity of the methods, the river sediment matrix (high TOC), and training required to perform these analyses, inter-laboratory variability generally reduces the interpretive power of the data.

3.0 SAMPLE HANDLING AND CHAIN OF CUSTODY PROCEDURES

Chain of custody procedures will be used for all samples throughout the analytical process and for all data and data documentation, whether in hard copy or electronic format. Sampling procedures, including sample collection and documentation, are part of the work plans of the individual projects and as such, are not considered here.

3.1 Sample Preservation and Holding Times

Sample preservation and field treatment of samples for analyses should be described in relevant field sampling plans. Based on U.S. EPA guidance, "advisory" sample holding times prior to analysis and holding times for the extracts are presented below. These holding times may be extended or preservation guidance changed, as options are assessed.

Matrix	Storage for Samples	Holding Time to Extraction	Holding Time to Analysis
VOC Analyses			
Water	Refrigeration 4ºC ±2º with no headspace; Optional: Preserved with HCl in the field in VOA vial.	Not applicable	7 days if not acid preserved; 14 days if acid preserved
Sediment for VOC	Refrigeration 4ºC ±2º	Not applicable	14 days
Oil/Oily Debris	Refrigeration <6ºC	Not applicable	No holding time
PAH, SHC/TEH, Biomarker Analyses			
Water	Refrigeration 4ºC ±2º;	7 days	40 days from extraction[10]; except biomarkers no holding time
Sediment/Soil (also grain size and TOC	Frozen, except Grain Size should not be frozen – store at 4ºC ±2º	1 Year, except not applicable for Grain Size, and TOC	40 days from extraction[9] except biomarkers grain size and TOC no holding time.
Tissue, Total Extractable Organics (TEO, aka Lipids)	Frozen	1 Year	40 days from extraction[9]; except biomarkers and TEO no holding time.
Inert Sorbent Material (Teflon Nets)	Frozen	1 Year	40 days from extraction[9]; except biomarkers no holding time
Oil/Oily Debris	Refrigeration <6ºC	No holding time	40 days from extraction[9]; except biomarkers no holding time
Metal Analyses			
Water for Metals	Refrigeration 4ºC ±2º; Preserved with 1:1 Nitric Acid to pH<2	180 days from time of collection	180 days from time of collection
Sediment	Frozen (-20ºC ±10ºC) AVS-SEM Frozen or refrigeration 4ºC ±2º, zero headspace	TAL Not applicable AVS-SEM – 14 days	TAL Metals: 2 years except Mercury: 1 year[11] AVS-SEM – 14 days

[10] 40 days is an advisory extraction holding time. Extracts should be held at -20ºC in the dark, and may be analyzed past 40 days and results not qualified if surrogates are within criteria.

[11] Holding time for metals, except mercury, is based on *Puget Sound Dredged Disposal Analysis Data Quality Guidance Manual* (PTI July 1988). Holding time for mercury is based on *Appendix to Method 1631 Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation* (EPA-821-R-01-013, January 2001)

3.2 Chain of Custody

Chain of custody records will be completed in ink.

A sample is considered in "custody" if:

- it is in the custodian's actual possession or view, or
- it is retained in a secured place (under lock) with restricted access, or
- it is placed in a container and secured with an official seal(s) such that the sample cannot be reached without breaking the seal(s).

Samples are kept in the custody of designated sampling and/or field personnel until shipment.

3.3 Sample Shipping

Any transfer or movement of samples will use chain of custody procedures. The original signed and dated chain of custody record accompanies the sample(s); a copy is retained by the sample shipper. All shipments will comply with DOT regulations (*49CFR, Parts 172 and 173*).

3.4 Sample Receipt

Immediately upon receipt of samples, the recipient will review the shipment for consistency with the accompanying chain of custody record and sample condition, before signing and dating the chain of custody record. Sample condition(s) will be noted on the laboratory's sample receipt form and maintained with the chain of custody records. If there are any discrepancies between the chain of custody record and the sample shipment, the recipient will contact the sample shipper immediately in an attempt to reconcile these differences. Reconciliation of sample receipt differences will be maintained with the chain of custody records and discussed in the laboratory narrative which accompanies the data report.

3.5 Intra-Laboratory Sample Transfer

The laboratory sample custodian or designee will maintain a laboratory sample-tracking record, similar to the chain of custody record that will follow each sample through all stages of laboratory processing. The sample-tracking record will show the name or initials of responsible individuals, date of sample extraction or preparation, and sample analysis.

3.6 Inter-Laboratory Sample Transfer

Transfer of samples from one analytical laboratory to another, e.g. for grain size or TOC analysis, will follow chain of custody, sample shipping and receipt procedures described above. Transfer of samples between laboratories will be noted in the laboratory case narrative which accompanies the data report.

3.7 Sample Archival

All remaining sample archives will be stored frozen at -20°C (waters < 6°C) and unutilized sample extracts will be topped with the appropriate solvent (to prevent extracts from evaporating to

dryness) and stored frozen at -20°C in glass vials with Teflon lined screw caps and Teflon tape. All samples and extracts will be held by the laboratory in a manner to preserve sample integrity at a secure location with chain of custody procedures for one (1) year after the data package has been validated for that particular set of samples. All archived materials will be accessible for review upon request. At the end of the archival period, the laboratory shall contact the Project Coordinator to obtain directions for handling remaining samples. The samples will not be disposed of by the laboratory unless provided with written approval from the Assessment Manager.

3.8 Data and Data Documentation

The laboratories will provide electronic and hardcopy data tables, QC documentation, and instrument printouts suitable for QA assessment/data validation. In addition, laboratories will provide raw integrated instrument files for all field samples, dilutions, QC samples, calibration standards and quantification methods for GC/MS and GC/FID. Required laboratory deliverables are listed in **Table 7.1**. Data packages will include all related instrument print-outs ("raw data") and bench sheets. A copy of the data and data documentation developed by the laboratory for a given data package will be kept by the laboratory in a secure location using chain of custody procedures for five (5) years after data packages have been validated. All archived data and documentation will be accessible for review upon request. These materials will become the responsibility of the Assessment Manager upon termination of the archival period.

4.0 LABORATORY OPERATIONS

All laboratories providing analytical support must have the appropriate facilities to store and prepare samples, and appropriate instrumentation and staff to provide data of the required quality within the time period dictated. Laboratories are expected to conduct operations using good laboratory practices, including:

- Training and appropriate certification of personnel.
- A program of scheduled maintenance of analytical balances, laboratory equipment and instrumentation.
- Routine checking of analytical balances using a set of standard reference weights (ASTM class, NIST Class S-1, or equivalents).
- Recording all analytical data in secure electronic system with date and associated analyst identification, and/or logbooks with each entry signed and dated by the analyst.
- Monitoring and documenting the temperatures of cold storage areas and freezer units.

Personnel in any laboratory performing analyses should be well versed in good laboratory practices, including standard safety procedures. It is the responsibility of the laboratory manager and /or supervisor to ensure that safety training is mandatory for all laboratory personnel. The laboratory is responsible for maintaining a current safety manual in compliance with the Occupational Safety and Health Administration (OSHA) or equivalent state or local regulations. Proper procedures for safe storage, handling and disposal of chemicals should be followed at all times; each chemical should be treated as a potential health hazard and/or physical hazard, and good laboratory practices should be implemented accordingly.

4.1 Quality Assurance Documentation

All laboratories must have the following documents and information must be current and available to all laboratory personnel:

- Laboratory Quality Assurance Management Plan
- Laboratory Standard Operating Procedures (SOPs) – Detailed instructions for performing routine laboratory procedures.

5.0 ASSESSMENT OF DATA QUALITY

The purpose of this Analytical QA Plan is to develop and document analytical data of known, acceptable, and defensible quality. The quality of the data is presented as a set of statements that describe in precise quantitative terms the level of uncertainty that can be associated with the data without compromising their intended use. These statements are referred to as Data Quality Objectives (DQOs) and are usually expressed in terms of precision, bias, sensitivity, completeness, and comparability.

5.1 Precision

Precision is the degree of mutual agreement among individual measurements of the same property under prescribed similar conditions, such as replicate measurements of the same sample. Precision is concerned with the "closeness" of the results. Where suitable reference materials (RMs) are available, precision will be expressed as the relative standard deviation (RSD) for the repeated measurements. This use of RMs allows for the long-term measurement of precision but does not include homogenization as a source of analytical variability.

In addition to tracking the precision of replicate RM analyses, precision will be expressed as the relative percent difference (RPD) between a pair of replicate data from environmental samples prepared and analyzed in duplicate.

5.2 Bias

Bias is the degree of agreement of a measurement with an accepted reference value and may be expressed as the difference between the two measured values or as a percentage of the reference value.

The primary evaluation of bias will be through the use of RMs. RMs with certified values (from NIST or a similar source) will be used if they are available. Spiked matrix samples will also be analyzed to assess bias for those analytes that are not available in suitable reference materials.

5.3 Comparability

Comparability expresses the confidence with which one data set can be evaluated in relationship to another data set. Comparability of the chemical analytical data is established through the use of:

- Program-defined general analytical methodology (e.g., low resolution MS), detection limits, bias and precision requirements and reporting formats;

- Traceable calibration materials;
- Reference material with each sample batch;
- Analysis of a North Slope Crude "reference oil;"
- Analysis of two site-specific oils representative of the spilled material.

5.4 Completeness

Completeness is a measure of the proportion of data specified in the sampling plan which is determined to be valid. Completeness will be assessed by comparing the number of valid sample results to the total number of potential results planned to be generated. The DQO for completeness is 95%, i.e. no more than 5% of the analytical data missing or qualified as unreliable (rejected).

6.0 QUALITY CONTROL PROCEDURES

No particular analytical methods are specified for this project, but the QA/QC requirements will provide a common foundation for each laboratory's protocols. This "common foundation" includes: (1) the specification of the analytes to be identified and quantified and the minimum sensitivity of the analytical methods, and (2) the use of NIST reference materials, and (3) **the use of a North Slope Crude Reference Oil, and 4) the use of two site-specific oils representative of the spilled material.**

Prior to the analysis of samples, each laboratory must provide written protocols for the analytical methods to be used; calculate detection limits for each analyte in each matrix of interest and establish an initial calibration curve in the appropriate concentration range for each analyte. The laboratory must demonstrate its continued proficiency by repeated analyses of reference materials, calibration checks, and laboratory method blanks. Laboratories will be expected to take corrective actions promptly if measurement quality objectives described in this plan are not met.

A laboratory may be audited at any time to determine and document that they have the capability to analyze the samples and can perform the analyses in compliance with the QA plan. Independent data validation will be undertaken promptly after analyses of each sample batch to verify that measurement quality objectives are met. The data validator will discuss any unacceptable findings with the laboratory as soon as possible, and assist the laboratory in developing a satisfactory solution to the problem.

6.1 Standard Operating Procedures for Analytical Methods

Prior to the analysis of field samples, each laboratory is required to have written Standard Operating Procedures (SOPs) detailing the procedures used in sample receipt and handling, sample preparation and analysis, data reduction and reporting.

6.2 Determination of Method Detection Limit, Quantitation Range, and Reporting Limits

The analytical laboratory will establish and report a method detection limit (MDL) for each analyte of interest in each matrix, with the exception of oil for which MDLs cannot be accurately

determined. The target detection ranges or limits are specified in **Tables 1.1a – 1.1e**. The actual MDLs will be established by following the method in *40CFR part 136*. The reporting limit (RL) will be based on the low calibration standard analyzed as part of the initial calibration. Results that are less than 5X the MDL or less than the lowest calibration standard will not be required to meet the measurement quality objectives (MQOs) for precision and bias, because these results may be outside the "quantitation range". Thus, these results may be flagged by the laboratory with a J, to indicate the results are possibly an estimate and have not been required to meet the MQOs. If the analyte is not detected in a sample, the result will be reported as non-detected at the MDL (or reporting limit) and flagged with a "U".

Target detection limits, as shown at the bottom of **Tables 1.1a through 1.1e**, may not be met due to required dilutions, interferences, and/or limited sample size. If a laboratory MDL does not meet the target detection limit, the reason for the elevated detection limits should be discussed in the laboratory case narrative.

At the discretion of the analytical laboratory, detected analytes at concentrations less than the MDL may be reported, provided that the compound meets the established identification criteria and the peak height is greater than or equal to three times the background noise level. These results will be "J" flagged by the laboratory.

6.3 Quality Control Criteria

MQOs and required minimum frequency of analysis for each QC element or sample type are summarized in **Tables 6.1a – 6.1f**. The analytical laboratory will determine when MQOs have not been met, and perform appropriate corrective actions before continuing the analyses or reporting of the data. If the "Corrective Action" in the Method Performance Criteria table states "Resolve before proceeding", the laboratory must perform an adjustment to the analytical process and subsequently demonstrate the criteria will be met before proceeding with analysis for project samples. In addition, if results associated with a non-compliant QC element have been obtained, the laboratory must repeat those analyses until acceptable QC results are obtained. If the laboratory determines the non-compliance does not affect the quality of the data, the laboratory will discuss the non-compliance and the rationale, used to conclude the data are not affected, in the case narrative which accompanies the data report. If the laboratory determines the non-compliance is due to interferences or circumstances outside the laboratory's control, the laboratory will discuss the reason for the non-compliance in the case narrative and the results reported.

TABLE 6.1a
Method Performance Criteria for Extended PAH (Parent and Alkyl Homologues) and Related Compounds

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Tuning	Prior to every sequence	Tune as specified in laboratory SOP	Resolve before proceeding.
Initial Calibration (All parent PAH and selected alkyl homologue PAH)	Prior to every sequence, or as needed based on continuing calibration/verification check.	5-point calibration curve over two orders of magnitude %RSD ≤ 20. Linearity check, r2>0.999	Resolve before proceeding.
Continuing Calibration (CCAL)	Every 12 field samples not to exceed 24 hrs	%D ≤ 25 for 90% of analytes %D ≤ 35 for 10% of analytes	Perform instrument maintenance. Re-analyze affected samples.
Initial Calibration Verification (Second Source or can be met if CCAL is second source)	Per initial calibration	%R target analytes 80-120%	Resolve before proceeding.
Matrix SRM 1941b for sediment; SRM 1974b for tissue	One per batch/every 20 field samples	Within ±30% of NIST 95% uncertainty range for analytes within the quantitation range. 2 analytes may be greater than 30% outside, however average %D must be <35%[12]	Resolve before proceeding.
North Slope Crude Reference Oil	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Two site specific oils (to be determined).	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Matrix Spike/Matrix Spike Duplicate (Sediments, Soils, Tissues only)	One per batch/every 20 field samples	%R 50% - 125% for target analytes detected at >5X the spiked amount; RPD ≤30%, except biphenyl (40%-140%) and decalin (25%-125%)	Evaluate impact to data, discuss with manager, determine if corrective action is needed.
LCS/LCSD	One per batch/every 20 field samples	%R 50% - 125% for target analytes, RPD ≤30%, except biphenyl (40%-140%) and decalin (25%-125%)	Resolve before proceeding.
Procedural Blank	One per batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration >5x blank value	Resolve before proceeding. QA coordinator may be contacted to resolve issues surrounding 'minor exceedance'.
Sample Duplicate (not required for water matrix)	One per batch/every 20 field samples	RPD ≤ 30% if analyte concentration is greater than QL	Evaluate impact to data, discuss with manager, and determine if corrective action is needed.
Mass Discrimination	Initial calibration and CCVs (mid-level)	Ratio for the concentration of Benzo[g,h,i]perylene to phenanthrene ≥0.70. Also benzo(b)fluoranthene and benzo(k)fluoranthene must be at least 50% resolved	Resolve before proceeding.
Internal Standard (IS)	Every sample	50% - 200% of the area of the IS in the associated calibration standard	Resolve before proceeding.
Surrogates	Every sample	%R 40-120%	Re-extract affected samples. Evaluate impact to data, discuss with manager, if corrective action is needed.

[12] Except for fluorene in SRM 1941b extend the low end to 40%.

TABLE 6.1b
Method Performance Criteria for Alkanes/Isoprenoids Compounds and Total Extractable Hydrocarbons

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Initial Calibration (Standard solution - all target analytes, except phytane, and C_{31}, C_{33}, C_{35}, and C_{39} n-alkanes)	Prior to every sequence, or as needed based on continuing calibration/verification check.	5-point calibration curve %RSD ≤ 20. Linearity check, r2>0.999	Resolve before proceeding.
Continuing Calibration (CCAL)	Every 12 field samples not to exceed 24 hrs	%D ≤ 15 for 90% of analytes %D ≤ 20 for 10% of analytes	Perform Instrument Maintenance. Re-analyze affected samples.
Initial Calibration Verification (Second Source or can be met if CCAL is second source)	Per initial calibration	%R target analytes 80-120%	Resolve before proceeding.
SRMs - no SRMs for SHC or TPH are available at this time			
North Slope Crude Reference Oil	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Two site specific oils (to be determined).	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Matrix Spike/Matrix Spike Duplicate (Sediments, Soils only)	One per batch/every 20 field samples	%R 50% - 125% for target analytes detected at >5X the spiked amount; RPD ≤30%.	Evaluate impact to data, discuss with manager, determine if corrective action is needed.
LCS/LCSD	One per batch/every 20 field samples	%R 50% - 125% for target analytes, RPD ≤30%.	Resolve before proceeding.
Procedural Blank	One per batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration >5x blank value	Resolve before proceeding. QA coordinator may be contacted to resolve issues surrounding 'minor exceedances'.
Duplicate Sample Analysis (not required for water matrix)	One per batch/every 20 field samples	RPD ≤ 30% if analyte concentration is greater than QL	Evaluate impact to data, discuss with manager, determine if corrective action is needed.
Mass Discrimination	Initial calibration and CCVs (mid-level)	Ratio for the raw areas of n-C36 / n-C20 ≥0.70	Resolve before proceeding.
Surrogates	Every sample	%R 40-125%	Re-extract affected samples. Evaluate impact to data, discuss with manager, determine if corrective action is needed.

TABLE 6.1c
Method Performance Criteria for Quantitative Biomarkers

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Tuning	Prior to every sequence	Tune as specified in laboratory SOP	Resolve before proceeding.
Initial Calibration	Prior to every sequence, or as needed based on continuing calibration/verification check.	5-point calibration curve over two orders of magnitude %RSD ≤ 20	Resolve before proceeding.
Continuing Calibration (CCAL)	Every 12 hours or every 12 field samples	%D ≤ 25 for 90% of analytes %D ≤ 35 for 10% of analytes	Perform instrument maintenance. Re-analyze affected samples.
Oil SRM 1582 (Oil and Water only)	One per batch of oil/every 20 field samples	Biomarker concentrations are not certified; Peak resolution (*m/z* 191) of: (a) oleanane (T18) from hopane (T19); (b) C26 Tricyclic Terpane stereoisomers 22R (T6b) from 22S (T6c) and from C24 Tetracyclic Terpane (T6a)	Resolve before proceeding.
North Slope Crude Reference Oil	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Two site specific oils (to be determined).	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Method Blank	One per batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration >5x blank value	Resolve before proceeding. QA coordinator may be contacted to resolve issues surrounding 'minor exceedance'.
Sample Duplicate	One per batch/every 20 field samples	RPD ≤ 30% if analyte concentration is greater than QL	Evaluate impact to data, discuss with manager, and determine if corrective action is needed.
Internal Standard (IS)	Every sample	50% - 200% of the area of the IS in the associated calibration standard	Resolve before proceeding.
Surrogate	Every sample	%R 50-130%	Evaluate impact to data, discuss with manager, if corrective action is needed.

TABLE 6.1d
Method Performance Criteria for TAL Metals and AVS-SEM

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Tuning Solution	Once Daily	$\leq$ 5% RSD	Perform Instrument Maintenance. Re-tune
Mass Calibration	Once Daily	Must not differ by more than 0.1 amu from true value	Perform Instrument Maintenance. Re-calibrate
Resolution Checks	Once Daily	Less than 0.9 amu at full width at 10% peak height	Perform Instrument Maintenance. Re-check
Initial Calibration Curve	Prior to every sequence, or as needed based on continuing calibration/verification check.	$r^2 \geq 0.995$	Perform Instrument Maintenance. Re-calibrate
Method Blank	One per batch of every 20 field sample	< reporting limit	Notify project manager. Re-extract samples. Evaluate impact to data, discuss with manager, determine if corrective action is necessary
Laboratory Control Sample	One per batch of every 20 field sample	80-120%R for aqueous 80-120% for soils	Evaluate impact to data, discuss with manager, determine if corrective action is necessary
Matrix Duplicate	One per batch of every 20 field sample	20%RPD for results <5x reporting limit	Evaluate impact to data, discuss with manager, determine if corrective action is necessary
Matrix Spike	One per batch of every 20 field sample	75-125%R for solid and aqueous	Evaluate impact to data, discuss with manager, determine if corrective action is necessary
Initial and Continuing Calibration Verification	One per every 10 Samples	90-110%R	Perform Instrument Maintenance. Re-analyze affected samples. Notify project manager and justify.
Initial and Continuing Calibration Blank	One per every 10 Samples	< reporting limit	Perform Instrument Maintenance. Re-analyze affected samples. Notify project manager and justify.
ICSA and ICSAB Solution	Prior to every sequence	80-120%R for spiked analytes	Evaluate impact to data, discuss with manager, determine if corrective action is necessary
Internal Standard	Every Sample	80-120%R for instrument QC samples and 30-120%R for field samples	Evaluate impact to data, discuss with manager, determine if corrective action is necessary
Serial Dilution Sample	One per batch of every 20 field sample	<10% D	Evaluate impact to data, discuss with manager, determine if corrective action is necessary

TABLE 6.1e
Method Performance Criteria for VOCs

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Tuning	Prior to every sequence	Per SW846 8260B	Resolve before proceeding
Initial Calibration (ICAL)	Prior to every sequence, or as needed based on continuing calibration/verification check.	Minimum of 5 concentration levels %RSD ≤ 25% for 90% of analytes %RSD ≤ 35% for all analytes >C6	Resolve before proceeding.
Continuing Calibration (CCAL)	Every 24 hours or every 12 field samples	%D ≤ 25% for 90% of analytes %D ≤ 35% for all analytes >C6 Except t-butanol <50%	Perform Instrument Maintenance. Re-analyze affected samples.
Initial Calibration Verification (Second Source or can be met if CCAL is second source)	Per initial calibration	%R target analytes 80-120%. Except 2 analytes can be at 60 - 140%	Resolve before proceeding.
SRMs – No SRMs are available at this time			
Reference Oil	Prior to every sequence, reported per analytical batch	± 35% difference from established laboratory mean	Resolve before proceeding.
Matrix Spike/Matrix Spike Duplicate (Sediments, Soils)	One per batch/every 20 field samples	%R 50% - 130% for target analytes detected at >5X the spiked amount; RPD ≤30%.	Evaluate impact to data, discuss with manager, determine if corrective action is needed.
LCS/LCSD	One per batch/every 20 field samples	%R 50% - 130% for target analytes, RPD ≤30%.	Resolve before proceeding.
Procedural Blank	One per batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration >10x blank value	Resolve before proceeding. QA coordinator may be contacted to resolve issues surrounding 'minor exceedances'.
Sample Duplicate	One per batch/every 20 field samples	RPD ≤ 30% if analyte concentration is greater than QL	Evaluate impact to data, discuss with manager, determine if corrective action is needed.
Internal Standard (IS)	Every sample	50% - 200% of the area of the IS in the associated calibration standard	Resolve before proceeding.
Surrogates	Every sample	%R 70-130%	Re-extract or re-analyze affected samples. Evaluate impact to data, discuss with manager, determine if corrective action is needed.

TABLE 6.1f
Method Performance Criteria for General/Conventional Chemistry

Conventional Sediment Parameters: Total Organic Carbon (TOC), Grain Size
Tissues: Total Extractable Organics (TEO)

QC Element or Sample Type	Minimum Frequency	Acceptance Criteria	Relevant Parameter(s) Reference Methods*
Initial Calibration	Prior to analysis (method and instrument specific procedures & number of standards)	For multipoint calibration, Correlation coefficient (r) >0.995	TOC
Continuing Calibration	Must start and end analytical sequence and every 10 samples	%R 90%-110%	TOC
Method Blanks	One per batch/every 20 field samples	Not to exceed QL	TOC, TEO
Laboratory Control Samples	One per batch/every 20 field samples	%R 75% - 125%	TOC
Matrix Spike Samples	One per batch/every 20 field samples	%R 75% - 125% If MS/MSD analyzed, RPD ≤ 25%	TOC
Replicate Analyses[13]	Each sample must be analyzed at least in duplicate. The average of the replicates shall be reported.	RPD or %RSD < 20% for concentrations > QL	TOC
Sample Duplicates[14]	One per batch/every 20 field samples	RPD ≤ 25% for analyte concentrations greater than QL	TOC, Grain Size, TEO
Reference Materials TOC NIST 1941B TEO NIST 1974B	One per batch/every 20 field samples	Values must be within ±20% of NIST uncertainty range	TOC, TEO

* Reference Methods

TOC	Plumb 1981/SW 846 Method 9060A
Grain Size	ASTM D422. If using sieve analysis only, report as percent gravel, coarse sand, medium sand, fine sand, very fine sand, and silt/clay. If using sieve and hydrometer, report as percent gravel, coarse sand, medium sand, fine sand, very fine sand, silt, and clay.

Method 9000 series - analytical methods from SW-846 (U.S. EPA 1986) and updates.
The SW-846 and updates are available from the web site at: *http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm*

Plumb, R.H., Jr., 1981. Procedures for Handling and Chemical Analysis of Sediment and Water Samples. Technical Report EPA/CE-81-1, U.S. Army Corps of Engineers, Vicksburg; available at:
http://yosemite.epa.gov/r10/CLEANUP.NSF/ph/T4+Technical+Documents/$FILE/Plumb.pdf

[13] Method SW9060 requires quadruplicate analyses, however duplicate or triplicate analyses are acceptable.

[14] Method SW9060 requires a duplicate spike. A matrix spike and sample duplicate are acceptable in lieu of matrix spike/matrix spike duplicates. For grain size, RPD criteria only applied if fraction is greater than 5%.

6.3.1 Initial Calibration

Acceptable calibration (initial and continuing) must be established and documented before sample analyses may begin. NIST-traceable calibration materials must be used where available in establishing calibration. Initial calibrations will be established according to the criteria in **Tables 6.1a – 6.1f**. A specific requirement for this project is to use methodology (and tune instrumentation) for low detection limits, therefore, samples with analytes above the calibration range will be diluted and reanalyzed. If samples require a dilution, results from the initial analytical run that were within the calibration range should be reported. Results from the diluted analyses should be reported for only those analytes which exceeded the calibration.

6.3.2 Continuing Calibration Verification

Continuing calibration verification (CCV) standards will be run at the beginning (opening) and end (closing) of each analytical sequence, and at the frequencies indicated in **Tables 6.1a – 6.1f**. If CCV results do not meet the specified criteria, then the instrument must be re-calibrated and all samples analyzed since the last acceptable CCV must be re-analyzed.

6.3.3 Reference Materials

Reference materials of a matrix appropriate to the samples being analyzed, will be analyzed every 20 samples throughout the analytical program, if available. The data resulting from the analysis of these samples will be reported in the same manner as that from the field samples. These data will be the prime materials used to determine and document the accuracy and precision of the associated field sample data. The reference materials to be used are listed in the criteria tables.

Accuracy is computed by comparing the laboratory's value for each analyte against either end of the range of values reported by the certifying agency. The laboratory's value must be within 30% of either the upper or lower end of NIST's 95% uncertainty range for SRM 1941b and SRM 1974b except the low end for fluorine for 1941b is extended to 40%. For oil, water, filters, and inert sorbent materials analyses, a North Slope Crude and two site-specific oils that contain homologue patterns as well as reported biomarker compounds will be run with each instrumental sequence. For PIANO analysis, a gasoline reference material will be used. Values will be ± 35% from the established laboratory mean for that oil determined over the course of at least 20 replicate analyses.

6.3.4 Method Blanks

Method blanks are laboratory derived samples which have been subjected to the same preparation or extraction procedures and analytical protocols as project samples and measures contaminants in solvents, reagents, glassware or other laboratory hardware that lead to false analyte concentrations and or elevated baselines in chromatograms and ion profiles. A method blank will be analyzed with every 20 field samples analyzed. Acceptance criteria are provided in **Tables 6.1a – 6.1f**. Failure to meet acceptance criteria requires definitive corrective action to identify and eliminate the source(s) of contamination before the subsequent reanalysis and re-extraction of the blank and affected samples. Sample results will not be blank corrected.

6.3.5 Sample Duplicates

A duplicate sample aliquot from a representative matrix will be prepared and analyzed with every 20 field samples, except for water samples, filters, and inert sorbent materials for SHC/TEH and

PAH. Water samples, filters and inert sorbent materials for SHC/TEH and PAH will not be analyzed in duplicate because of the difficulty in sub-sampling representative aliquots. Acceptance criteria for the other matrices are provided in **Tables 6.1a – 6.1f**.

6.3.6 Matrix Spike/Matrix Spike Duplicates or Laboratory Control/Laboratory Control Duplicate

Matrix spike/matrix spike duplicates (MS/MSDs) will be analyzed every 20 samples, except for water samples, filters and inert sorbent materials. MS/MSDs will not be analyzed with the water sample batches because of the difficulty in sub-sampling representative aliquots from a sample container. Instead, laboratory control/laboratory control duplicates (LCS/LCSDs) will be analyzed with each batch of water samples. Samples will be spiked prior to extraction. Spike solution concentrations for the MS must be appropriate to the matrix and anticipated range of contaminants in the sample; that is 2 to 10 times analyte concentration. However, because it is not possible to know the concentration of contaminants prior to analysis, professional judgment may be exercised in choosing concentrations that are reasonable under the circumstances.

6.3.7 Internal Standards

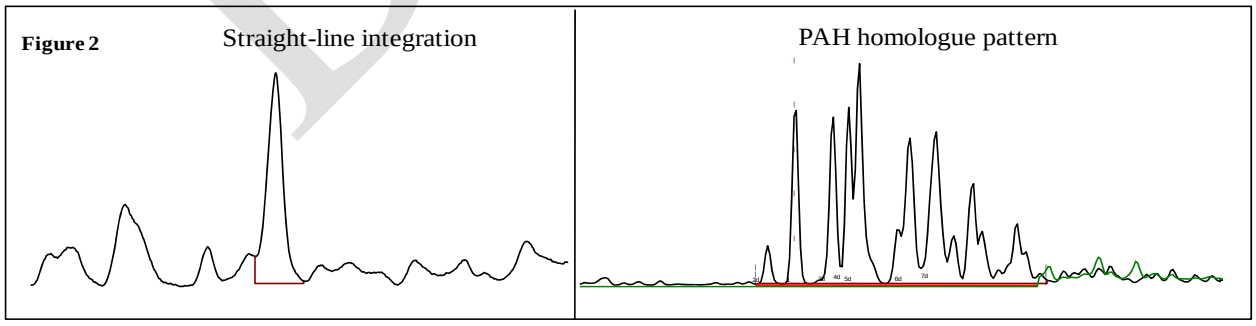
All samples will be spiked with internal standards prior to analysis, when required by the analytical method. Control criteria for internal standard recovery are listed in **Tables 6.1a – 6.1f**.

6.3.8 Surrogates

All field and QC samples will be spiked with surrogates prior to extraction, as required by the analytical methods. Control criteria for the surrogate recovery are listed in Tables 6.1a – 6.1e. **Sample data will NOT be corrected for surrogate recovery.** However SRM 1941b and 1974b data will be surrogate corrected as the certified values were based on surrogate corrected data.

6.3.9 Manual Integrations

Due to the nature of these samples (high organic content) and the nature of PAH homologue pattern recognition (multiple peaks rather than a single peak) the majority of these samples will require manual integrations. Manual integrations will be made using a straight-line integration relative to the baseline taking into account background noise (Figure 2). Manual integration is not to be used solely to meet QC criteria or as a substitute for corrective action related to the instrument (i.e., instrument maintenance). Peaks will be integrated down to three (3) times signal-to-noise, provided the peak has the correct ion profile (GC/MS), retention time and symmetry.



7.0 DATA REDUCTION, VALIDATION AND REPORTING

7.1 Data Reduction

Data reduction is the process whereby raw data (analytical measurements) are converted or reduced into meaningful results (analyte concentrations). This process may be either manual or electronic. Primary data reduction requires accounting for specific sample preparations, sample volume (or weight) analyzed, and any concentrations or dilutions required.

Primary data reduction is the responsibility of the analyst conducting the analytical measurement and is subject to further review by laboratory staff, the Laboratory Project Manager and finally, independent reviewers. All data reduction procedures will be described in the laboratory SOPs. Any deviations from the laboratory SOPs will be discussed in the laboratory case narratives.

- Concentrations will be reported as if three figures were significant.
- Data generated from the analysis of blank samples will not be utilized for correction of analyte data.
- Surrogate compounds, matrix spikes, and spike blanks will be evaluated as %R.
- Reference materials will be reported in units indicated on the certificate of analysis.
- Continuing calibration factors will be presented as %D
- Duplicate sample results will be expressed as RPD.

7.2 Data Review and Validation

Data review is an internal review process where data are reviewed and evaluated by personnel within the laboratory. Data validation is an independent review process conducted by personnel not associated with data collection and generation activities.

Data review is initiated at the bench level by the analyst, who is responsible for ensuring that the analytical data are correct and complete, the appropriate SOPs have been followed, and the QC results are within the acceptable limits. The Laboratory Project Manager has final review authority. It is the Laboratory Project Manager's responsibility to ensure that all analyses performed by that laboratory are correct, complete, and meet project data quality objectives.

External and independent data validation will be performed for all samples by the QA Coordinator using a full data package containing sufficient information to allow the independent validation of the sample identity and integrity, the laboratory measurement system, and resulting quantitative and qualitative data. The required information with associated instrument print-outs are listed in **Table 7.1**.

TABLE 7.1 Laboratory Data Deliverables Per Sample Batch

Chain-of-Custody:	COC, Sample Receipt Checklist and list of discrepancies and resolution
Sample Data:	Result summaries including surrogate recoveries, percent total solids, dilutions, etc
Standards Data:	Target MDL data based on the method in *40 CFR, 136* Calibration summaries: Initial calibration data, standard curve equation, correlation coefficient or %RSD, continuing calibration %D.
Quality Control Data (Method Blanks, CRMs, Duplicates, Matrix Spikes, Spike Blanks):	Results summaries including surrogate recoveries, plus %R and RPD, as applicable.
Case Narrative:	Special handling or analysis conditions. Any circumstance that requires special explanation such as an exception to QA/QC conditions or control criteria, dilutions, reanalysis, etc. Corrective actions/procedure alterations
Electronic Instrument Data:	All sample, QC, calibration and method instrument files in ChemStation .d format.
Chromatograms and Extracted Ion Profiles:	Appropriately scaled (1) GC/FID chromatograms for samples and associated QC analyzed for extractable hydrocarbons; (2) GC/MS EIPs for samples and associated QC analyzed for qualitative biomarkers
Electronic Data Deliverable:	Excel format.

Full validation will consist of a review of the entire data package for compliance with documentation and quality-control criteria for all the following items, plus recalculations of instrument calibration curves, sample and QC results:

- Package completeness
- Holding times from extraction to analysis
- Instrument calibration, initial and continuing
- Blank results
- Instrument performance
- Spike recoveries
- Standard reference material results
- Laboratory duplicate results
- Reported detection limits
- Compound quantitation
- Compound identification
- Verification of electronic data deliverable (EDD) against hardcopy (10% verification)

8.0 CORRECTIVE ACTION AND PROCEDURE ALTERATION

When the data from the analyses of any quality control sample exceeds the project specified control limits or indicates that the analytical method is drifting out of control, it is the immediate responsibility of the analyst to identify and correct the situation before continuing with sample analysis.

A narrative describing the problem noted, the steps taken to identify and correct the problem and the treatment of the relevant sample batches must be prepared and submitted with the relevant data package. If the action indicates a revision to the current SOP is warranted, the laboratory will revise the SOP and submit the SOP to the U.S. EPA Assessment Manager within 30 working days after the problem was noted. Until the revised SOP is approved, any data sets reported with the revised method will have the any changes to the method noted in the laboratory's case narrative.

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