ANALYTICAL QUALITY ASSURANCE PLAN

MISSISSIPPI CANYON 252 (DEEPWATER HORIZON) NATURAL RESOURCE DAMAGE ASSESSMENT

Version 3.0

Prepared for:

U.S. Department of Commerce
National Oceanic and Atmospheric Administration

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TABLE OF CONTENTS

VERSION 3.0 CHANGES FROM VERSION 2.2:

Version 2.2 Page No.	Change
Cover	Update version # & date
Acronyms	Insert QL (Quantitation Limit) and update format to keep all acronyms and abbreviations on one page.
5	Added a brief description of the analytical methods for metals as the last bulleted item and added a column for metals in the table at the end of the section.
9 (Table 1.1d)	Changed 'Target Detection Limit' to 'Target Method Detection Limit Range'
9 (Table 1.1d)	Changed analyte name from 1-methyl-3-isopropylbenzene to 1-methyl-2-ethylbenzene (center column, bottom cell)
10 (Table 1.1e)	Based on new analytical data, two target analyte names have been revised to indicate that the data refer to a co-elution, and not single target analytes. See the attached revised Table 1.1e
10	Based on new analytical data, one target analyte name was revised to indicate that the peak is an unknown sterane rather than an identified compound. See the attached revised Table 1.1e
10	The quantitation ion was corrected for six analytes (from 217 to 218). See the attached revised Table 1.1e.
None (Table 1.1h)	Added Table 1.1h Metals Target Analyte List
13	Deleted Mark Curry as Project Coordinator and added Dennis Beckmann and Tony Penn as Project Coordinators.
14	Changed company name from ENTRIX to Cardno ENTRIX and changed email address for Cheryl Randle to cheryl.randle@cardno.com from crandle@entrix.com.
14	Changed the contact person for Alpha Analytical from Liz Porta to Susan O'Neil and updated Susan's contact information.
14	Added Battelle Duxbury and NOAA NW Fisheries Science Center with contact information as laboratories contracted for analytical work in support of the NRDA.
15	Reorganized the holding time table. Increased holding time to 2 yrs for sediment and tissue if frozen. Added metals holding time. Separated Oil and Oily Debris as individual line items for each matrix type and adjusted holding times.
21	Section 6.2 - Add as the fourth sentence (after "40CFR part 136."): The quantitation limit (QL) will be defined as the concentration that is equivalent to five times the MDL result, or equivalent to the lowest concentration standard analyzed as part of the initial calibration.
21	Section 6.2 – Second paragraph. Delete grain size from the first sentence. Add "Reporting limit for grain size will be 0.1% or lower."
21	Section 6.2 - Add as the second paragraph: Note that for the Query Manager electronic data deliverable (EDD), there are two fields: detection limit and reporting limit. The detection limit field is equivalent to the MDL, except for those cases where no MDL value exists (for example, oils). If no MDL value exists, the detection limit field is populated with the quantitation limit (QL). The reporting limit field is always populated with the QL value.
21	Section 6.2 - Add the following paragraph to the end of this section: 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. During validation, these results will be qualified as "F" (found) to indicate that the value is less than the MDL (see Table 7.2).
21, 29 & 30	Updated references to the table numbers in Sections 6.3 and 6.3.1 through 6.3.8.
22 (Table 6.1a)	For Matrix SRM 1941b for sediment and SRM 1974b for tissue change MQO from 20% to 30% of the NIST uncertainty range, except for fluorene in SRM 1941b extend the low end to 40%.
24 (Table 6.1c)	Added indication that analysis of MC252 Reference Oil is optional.
27 (Table 6.1f)	Added two additional methods for TOC: Standard Methods 5310C and ASTM D4129-82M and one additional method for Grain Size: PSEP 1986 Particle Size plus footnote describing reference document name.
27 (Table 6.1f)	Grain Size footnote – Added reference to use of pipettes for PSEP Particle Size method in the second sentence.

Version 2.2 Page No.	Change
	Added as the last sentence: Additionally, grain size must be reported as "True" for sediment treated with hydrogen peroxide prior to analysis or "Apparent" for sediment not treated with hydrogen peroxide.
27 (Table 6.1f)	Added as the second sentence in footnote 15: Standard Method 5310C requires that injections be repeated until consecutive measurements within 10% are obtained for a water matrix, however, duplicate analyses < 20% RPD are acceptable based on a sediment matrix.
28 (Table 6.1g)	Corrected Continuing Calibration (CCAL) minimum frequency to read: Every 12 hours or every 12 field samples and added that analysis of the MC252 Reference Oil is optional
None (Table 6.1h)	Added Table 6.1h Measurement Quality Objectives for Metals by ICP-AES and & ICP-MS and Mercury by CVAA/CVAFS.
29	For Section 6.3.2, the first sentence is revised to read: 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 - 6.1d, and 6.1f - 6.1h.
29	For Section 6.3.3, second paragraph, change second and third sentence to read: 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. For oil, water, filters, and inert sorbent materials analyses, SRM 1582 is not extracted, but only diluted and analyzed on the instrument thus the laboratory's value must be within 20% of the NIST uncertainty range.
30	Include the following as Section 6.3.8: 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 - 6.1d, and 6.1g. For the PAH and saturated hydrocarbon analyses, the target analyte concentrations will be corrected for surrogate recovery as specified in the laboratory SOPs.
33 (Table 7.2)	The definition of a "J" qualifier is replaced with the following: Reported concentration is an estimate with potentially more bias or less precision than an unqualified result, as determined by the associated quality control results.

Acronyms and Abbreviations

%D	Percent difference
%R	Percent recovery
ASTM	American Society for Testing and Materials
BS/BSD	Blank spike/blank spike duplicate
CCV	Continuing calibration verification
CRM	Certified reference material
DISP	Dispersant
DOSS	Dioctylsulfosuccinate salt
DOT	U.S. Department of Transportation
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
LC	Liquid chromatography
MC 252	Mississippi Canyon 252 (Deepwater Horizon)
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
NRDA	Natural resource damage assessment
OPA	Oil Pollution Act
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbons
PIANO	Paraffins, isoparafins, aromatics, napthenes, olefins
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
TOC	Total organic carbon
USEPA	U.S. Environmental Protection Agency
VOC	Volatile organic compounds

INTRODUCTION

On April 20, 2010, a fatal explosion struck the Deepwater Horizon offshore oil platform approximately 50 miles off the Louisiana coast in the Gulf of Mexico, ultimately leading to the destruction of the platform and the connecting riser pipe to the seafloor a mile below the water surface, and the ongoing release of thousands of barrels of crude oil from the seafloor per day. The incident has been declared a Spill of National Significance by the U.S. Secretary of Homeland Security and a major spill response effort is in progress. The spill threatens a broad expanse of the U.S. Gulf Coast in addition to the natural resources in the path of the oil slick which has spread across thousands of square miles at sea. Federal and state natural resource trustees have begun collecting ephemeral data to support a natural resource damage assessment (NRDA). Currently, NOAA is the lead administrative trustee. Although a formal agreement has not yet been reached, BP America has indicated an interest in cooperating with the natural resource trustees in the damage assessment.

This Analytical Quality Assurance (QA) Plan describes the minimum requirements for the chemical analysis of the environmental samples that are collected in support of this NRDA. This plan does not address the actual field collection or generation of these samples. The scope of the laboratory work is twofold: (1) generate concentrations for key chemicals used in injury determinations for crude oil releases, and (2) produce more extensive chemical data to use in fingerprinting for source identification. The applicable chemicals, need and frequency of environmental sample analyses, quality control requirements, and data usage vary for these two 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 to 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], and volatile organic compounds (VOCs) and petroleum biomarkers. Additional analytes of concern are potentially toxic polar and non-polar components found within or formed from the dispersant agents utilized during the response to the incident, although the appropriate target analytes and methods are not yet established. A variety of matrices may be analyzed including water, filters, sediment/soil, tissues, vegetation, 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

[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).

organic carbon (TOC) and grain size for sediment samples, and total extractable organics (TEO) for tissues. Additional tests not currently addressed in the QAP but may be of interest are: SARA (%Saturate, %Aromatic, %Resin, % Asphaltene) content in oil[2]; carbon, hydrogen, and nitrogen (CHN)[3] for sediments and particulate material in water. Performance criteria will be added to the QAP for additional tests when requested under the NRDA program.

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 is consistent with the intent of NRDA regulations under OPA (33 U.S.C. §§ 2701 *et seq.)* and 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, as changes are made to the NRDA and the QA program.

[2] SARA according to method published by Zumberge et al (2005) or equivalent. [Zumberge, J., J.A. Russell, and S.A. Reid . 2005. Charging of Elk Hills reservoirs as determined by oil geochemistry AAPG Bull. v. 89, pp. 1347-1371]

[3] CHN by micro elemental analyzer using the Dumas method of complete and instantaneous oxidation (flash dynamic combustion) at >1,000 °C following exposure of the sample to HCl fumes to remove inorganic carbon.

1.0 PROJECT DESCRIPTION

A number of laboratories will be analyzing samples associated with this NRDA. 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:

- PAHs including alkyl homologues by gas chromatography with low resolution mass spectrometry using selected ion monitoring (GC/MS-SIM). 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.** 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.

  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.

  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.

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

- Total Extractable Hydrocarbons (TEH[4]) representing the total aromatic and aliphatic hydrocarbon content of sample extracts after silica gel clean-up and analysis by GC/FID (**Table 1.1b**). 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 then the result will be reported as Total Extractable Matter (TEM) because the extract may contain non-hydrocarbon compounds. Either TEH or TEM may reported by the laboratory depending on the handling of the extract.

- Standard volatile organic compounds (VOC) by GC/MS based on EPA Method 8260B but for aromatics hydrocarbons only. Analytes and target detection limits are listed in **Table 1.1c.**

- Extended list of VOCs for a specialized fingerprinting analysis of paraffins, isoparaffins, aromatics, napthenes, and olefins (PIANO) by GC/MS. Analytes and target detection limits are provided in **Table 1.1d** for this source identification list.

- Petroleum biomarkers by GC/MS-SIM. Two methods for the analysis of petroleum biomarkers are contained herein, viz., quantitative and qualitative. The difference between these two analyses is that quantitative analysis produces absolute concentrations of target analytes whereas qualitative analysis produced pattern, or fingerprints, only. The proposed target analyte list for quantitative biomarkers is provided in **Table 1.1e.** This list may be expanded if warranted. This method is discussed in further detail in:

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

- Qualitative biomarker patterns may also be acquired using GC/MS-SIM with monitoring of selected ions (m/z) as provided in **Table 1.1f**. Since no concentration data are generated by qualitative analysis the results are reported as hardcopy PDF files of each ion over the appropriate retention time(s) and scale and included in the hardcopy data package produced by the laboratory.

- Corexit indicator compounds can be identified and (semi-) quantified by conventional GC/MS-SIM. The indicator compounds presently identified include: 2-butoxyethanol, three closely-eluting glycol ether isomers (reported together as a single analyte), and

[4] 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}.

bis-(2-ethylhexyl)fumarate (the latter of which is a thermal degradation product of DOSS formed in the GC injection port). These indicator compounds can be identified in samples prepared for alkylated PAH analysis using conventional solvent extraction and preparation. These indicator compounds can be analyzed for concurrently with the alkylated PAHs during the same GC/MS acquisition by adding appropriate ions to the file. Suggested ions for monitoring are listed in **Table 1.1.g**. Indicator compound identifications are confirmed by analyzing a Corexit standard (i.e., a mixture of Corexit 9500 and 9527) under the same conditions as used for samples by comparing ion patterns and GC retention times. Semi-quantitative results for these indicator compounds can be based on a normalized response factor of 1 (without surrogate correction), and then the concentrations reported flagged by the laboratory as semi-quantitative.

- Corexit 9500/9527 dispersant (DISP) by liquid chromatography (LC)/MS for quantitative assessment, particularly dioctylsulfosuccinate sodium salt (DOSS). Proposed measurement performance criteria are presented in **Table 6.1g**. Because the method is under development the laboratory may develop appropriate performance criteria based on past method performance.

- GC/MS may have use for qualitative assessments of solvent package components (e.g. glycol ethers) or primary degradation products of DOSS (alkyl diesters), pending further method development. Standard methods are not available for either technique but provisional analytical criteria and detection limits are under development.

- Total metals in sediments and tissues by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) and total mercury in sediments and tissues by cold vapor atomic absorption (CVAA) or cold vapor atomic fluorescence spectrometry (CVAFS). The analytical procedures are based on EPA SW-846 Methods 6010C, 6020A, 7470A, 7471A, 7471B, 7474, and 7742. The target analyte list and target MRLs for each matrix are included in **Table 1.1h**. In order to meet the target MRLs, if may be necessary to use an increased sample size to account for the high moisture content in marine sediments.

Analyses will 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	DISP	VOC	Metals
Water	X	X	X	X	X	
Filters	X	X	X			
Sediment/Soil	X	X	X	X	X	X
Tissue	X		X	X		X
Vegetation	X	X	X	X		
Inert Sorbent Materials	X	X	X	X	X	
Oil/Oily Debris	X	X	X	X	X	

TABLE 1.1a
Extended PAH (Parent and Alkyl Homologs) 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[8]
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	
	C30-Hopane[7]	

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] Quantitative concentrations of C29-hopane and 18α-oleanane may be provided if laboratories are calibrated to do so; the C30-hopane is a minimum requirement.

[8] 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
Standard Volatile Organic Compounds

Analyte
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
4-Isopropyltoluene
Benzene
Ethylbenzene
Isopropylbenzene
m,p-Xylenes
Naphthalene[9]
n-Butylbenzene
n-Propylbenzene
o-Xylene
sec-Butylbenzene
Styrene
tert-Butylbenzene
Toluene

Target Method Detection Limit Range

Sediment/Soil = 0.1 – 1 ng/g

Water = 0.05 – 0.5 µg/L

Target Reporting Limit

Oil = 2 mg/kg

[9] Naphthalene is also included on the **Table 1.1a** target analyte list of PAH compounds. 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.

TABLE 1.1d
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	Nonane[10]
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[10]
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	Undecane[10]
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	Dodecane[10]
N0	Naphthalene[11]
BT0	Benzothiophene[11]
MMT	MMT
C13	Tridecane[10]
2MN	2-Methylnaphthalene[11]
1MN	1-Methylnaphthalene[11]

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

[10] 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.

[11] 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.

TABLE 1.1e
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

* 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 1.1f
Suggested Hydrocarbon Groups and Petroleum Biomarkers for Qualitative Analysis

n-Alkycyclohexanes (m/z 83)
n-Alkanes (m/z 85)
Diamondoids (m/z 135, 187)
Sesquiterpanes (m/z 109, 123)
Isoprenoids (m/z 183)
Triterpanes (m/z 191)
Regular Steranes (m/z 217)
Rearranged β,β-steranes (m/z 218)
Methyl steranes (m/z 232, 245)
Methyl and triaromatic steroids (m/z 231)
Monoaromatic steroids (m/z 253)
Diasteranes (m/z 259)

TABLE 1.1g
Corexit Indicator Compounds for Qualitative Analysis in Water Only
(monitoring mass/charge ion)

2-Butoxyethanol (m/z 87, 75)
Glycol ether Isomers (m/z 59, 103)
Bis-(2-ethylhexyl) fumarate (m/z 112, 211)

TABLE 1.1h
Metals Target Analyte List

Analyte	Method	Target Reporting Limits (RL)	
		Sediment (mg/Kg) dry weight	Tissues (mg/Kg) wet weight
Aluminum	ICP/ICP-MS	10	5
Antimony	ICP/ICP-MS	0.05	NA
Arsenic	ICP-MS	0.5	0.5
Barium	ICP/ICP-MS	0.1	0.05
Beryllium	ICP/ICP-MS	0.05	NA
Cadmium	ICP/ICP-MS	0.05	0.02
Calcium	ICP/ICP-MS	100	NA
Chromium	ICP/ICP-MS	0.2	0.2
Cobalt	ICP/ICP-MS	0.05	0.05
Copper	ICP/ICP-MS	0.1	0.1
Iron	ICP/ICP-MS	10	2
Lead	ICP/ICP-MS	0.05	0.02
Magnesium	ICP/ICP-MS	50	NA
Manganese	ICP/ICP-MS	0.2	0.2
Mercury	CVAA/CVAFS	0.01	0.01
Nickel	ICP/ICP-MS	0.5	0.5
Potassium	ICP/ICP-MS	100	NA
Selenium	ICP/ICP-MS	0.1	0.1
Silver	ICP/ICP-MS	0.05	0.05
Sodium	ICP/ICP-MS	100	NA
Strontium	ICP/ICP-MS	2.00	NA
Thallium	ICP/ICP-MS	0.1	NA
Vanadium	ICP/ICP-MS	0.5	0.5
Zinc	ICP/ICP-MS	1	0.5

Method detection limits (MDL) should be at least 3 times lower than the target reporting limits.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

2.1 Assessment Manager

Greg Baker
Office of Response and Restoration
NOAA
345 Middlefield Road, MS-999
Menlo Park, CA 94025
(650)329-5048 FAX (650)329-5198
greg.baker@noaa.gov

The Assessment Manager is the designated natural resource trustee representative who is responsible for the review and acceptance of specific work plans and associated QA plans.

2.2 Project Coordinators

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

Project Coordinator for Battelle:

Dennis Beckmann
Data and QA Manager
Gulf Coast Restoration
BP America, Inc.
501 Westlake Park Boulevard
Houston, TX 77079
dennis.beckmann@noaa.gov

Project Coordinator for Alpha Analytical, Columbia Analytical Services, and NOAA NW Fisheries Science Center:

Tony Penn
Deputy Division Chief
NOAA Assessment and Restoration Division
1305 East West Highway
Building SSMC4
Silver Spring, MD 20910
tony.penn@noaa.gov

2.3 Quality Assurance

Ann Bailey is the QA Coordinator reporting directly to the Assessment Manager. Ms. Bailey is responsible for the implementation of this Analytical QA Plan. She will receive assistance in the coordination and performance of laboratory technical audits and independent data validation from the QA Contractor (EcoChem). The QA Coordinator has the authority and responsibility to cease or temporarily halt activities not in keeping with this 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. The QA Coordinator may be reached at:

Ann Bailey
EcoChem, Inc.
710 Second Avenue, Suite 660
Seattle, WA 98104
(206)233-9332 x106 FAX (206)233-0114
abailey@ecochem.net

Cheryl Randle is a QA Reviewer conducting data validation on behalf of BP America. Ms. Randle is responsible for working closely with the Assessment Manager's QA Coordinator to assure the validity of the final data in accordance with this Analytical QA Plan. The QA Reviewer will conduct spot validation of up to 25 percent of the reported data, unless substantial problems are discovered in which case up to 100 percent validation may be performed. The QA Reviewer may be reached at:

Cheryl Randle
Cardno ENTRIX, Inc.
1000 Hart Road, Suite 130
Barrington, IL 60010
(847)277-2865 FAX (847)381-6679
cheryl.randle@cardno.com

2.4 Analytical Laboratories

The laboratories planned to be contracted at this time for analytical work in support of the NRDA are TDI-Brooks B&B Laboratories (B&B), Newfields/Alpha Analytical (Alpha), and Columbia Analytical Services (CAS). The laboratory project managers are responsible for assuring that all analyses performed meet project and measurement quality objectives. The Laboratory Project Managers are:

Juan Ramirez
TDI-Brooks B&B Laboratories
1902 Pinon
College Station, TX 77845-5816
(979)693-3446 FAX: (979)693-6389
juanramirez@TDI-BI.com

Jonathan Thorn
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Susan O'Neil
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Gina Ylitalo
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Seattle, WA 98112
206-860-3325
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Greg Salata, PhD.
Columbia Analytical Services (CAS)
1317 S. 13th Ave.
Kelso, WA 98626
(360)577-7222
gsalata@caslab.com

As additional analytical laboratories are brought under contract, this QAP will be updated to include their names and project managers.

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 work plans. Based on EPA guidance, "advisory" sample holding times prior to analysis and holding times for the extracts are presented in **Table 3-1**. These holding times may be extended or preservation guidance amended, as options are assessed.

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*).

TABLE 3-1
Sample Holding Times

Matrix/Analysis	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	Refrigeration 4ºC ±2º For preservation requirements, see SW-846 Method 5035A.	Not applicable	14 days
Oil	Above freezing to 30ºC	Not applicable	No holding time
Oily Debris	Refrigeration <6ºC	Not applicable	No holding time
PAH, SHC/TEH, Biomarker Analyses			
Water	Refrigeration 4ºC ±2º; Optional: Preserved with 1:1 HCl to pH<2	7 days if not acid preserved; 14 days if acid preserved	40 days from extraction[12]; except biomarkers no holding time
Filters	Frozen (-20ºC ±10ºC)	2 Years	40 days from extraction[12]; except biomarkers no holding time
Sediment/Soil (also total solids, grain size and TOC)	Frozen (-20ºC ±10ºC), except Grain Size should not be frozen – store at 4ºC ±2º	2 Years, except not applicable for Grain Size, Total Solids, and TOC	40 days from extraction[12]; except biomarkers grain size, total solids and TOC no holding time.
Tissue (Total Extractable Organics aka Lipids)	Frozen (-20ºC ±10ºC)	2 Years	40 days from extraction[12]; except biomarkers and TEO no holding time.
Vegetation	Frozen (-20ºC ±10ºC)	2 Years	40 days from extraction[12]; except biomarkers no holding time
Inert Sorbent Material	Frozen (-20ºC ±10ºC)	2 Years	40 days from extraction[12]; except biomarkers no holding time
Oil	Above freezing to 30ºC	No holding time	40 days from extraction[12]; except biomarkers no holding time
Oily Debris	Refrigeration <6ºC	No holding time	40 days from extraction[12]; except biomarkers no holding time
Dispersants (DOSS) Analyses			
Water	Frozen (-20º ±10ºC), 15mL plastic centrifuge tubes	Not established	Not established
Sediment and Tissue	Frozen (-20º ±10ºC), glass jars	Not established	Not established
Metals Analyses			
Water	Preserve with HNO_3 to pH <2	Not applicable	6 months except Mercury: 28 days
Sediment and Tissue	Frozen (-20°C ±10°C)	Not applicable	2 years except Mercury: 1 year[13]

[12] 40 days is an advisory extraction holding time. Extracts should be held at -20C in the dark, and may be analyzed past 40 days and results not qualified if surrogates are within criteria.

[13] 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)

3.4 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 unanalyzed samples and unutilized sample aliquots or 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 QA Contractor has validated the data package 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 QA 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 the QA Contractor with hardcopy data tables, QC documentation and instrument printouts suitable for QA assessment/data validation. 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 the QA Contractor has validated that data package. 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.

The original data will be transferred from the laboratory to the QA Contractor by means such that a signature is required at the time of document delivery. The QA Contractor will document receipt of packages and maintain a record of the method and date of data submittal with the complete data package. The QA Contractor will maintain the copy of the data packages and related validation documentation in a secure location for a period of one (1) year from the date of validation. 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 for the MC252 Damage Assessment 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.

Laboratory operations may be evaluated by the QA Coordinator through technical systems audits, performance evaluation studies, and performance in a NIST-managed intercomparison program. Personnel in any laboratory performing analyses for this damage assessment 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 good laboratory practices should be implemented accordingly.

4.1 Quality Assurance Documentation

All laboratories must have the latest revision of the MC 252 NRDA Analytical QA Plan. In addition, the following documents and information must be current and available to all laboratory personnel participating in the processing of MC 252 samples:

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

- Control charts or data tables – These must be developed and maintained throughout the project for appropriate analyses and measurements, including:
  - Alkyl PAH pattern book for MC252 reference oil.

4.2 Laboratory Systems Audits

Prior to or during sample analysis, QA systems audits will be performed. The laboratory audits will be conducted by the QA Coordinator or designee. The checklists used for the laboratory audits are based on requirements outlined in "Good Laboratory Practice Standards" (*40 CFR Part 792*) and audit procedures of the EPA National Enforcement Investigations Center, "NEIC Procedures Manual for the Contract Evidence Audit and Litigation Support for EPA Enforcement Case Development" (*EPA 330/9-89-002*). The Laboratory Project Managers will be informed of the findings and recommendations of the audit before the auditors leave the facility. A written report discussing the audits will be submitted to the Assessment Manager.

Additional laboratory audits may be performed at any time throughout the duration of the NRDA.

4.3 Participation in Intercomparison Exercises

Each analytical laboratory performing analysis will be required to participate in potential intercomparison exercises that may be organized by NS&T and/ or NIST during the duration of the laboratory's participation in this NRDA analytical program. A variety of samples including sample extracts and representative matrices (e.g., sediment or tissue samples) may be utilized in these exercises. Laboratories are required to analyze only those matrices or analytes that they are providing in like manner for the NRDA analytical program. When participating in the intercomparison exercise, the laboratory should analyze the sample(s) in the same manner as routinely performed for this NRDA and as specified in this Analytical QA Plan. Laboratories which fail to achieve acceptable performance will be required to provide an explanation to the QA Coordinator and/or undertake appropriate corrective actions.

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 the tracking 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. The laboratory will maintain control charts to track the RM performance. 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;
- NIST-traceable calibration materials;
- Reference material with each sample batch;
- Analysis of a common “reference oil”.

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 common MC252 Reference Oil.

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 participation in refereed intercomparison exercises (as available) and 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 submit to the QA Coordinator for review and approval, written Standard Operating Procedures (SOPs) detailing the procedures used in sample receipt and handling, sample preparation and analysis, data reduction and reporting. Once approved, the SOPs for each analytical method and from each analytical laboratory will be archived with this plan as part of the QA documentation.

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 and 1.1h**. The actual MDLs will be established by following the method in *40CFR part 136*. The quantitation limit (QL) will be defined as the concentration that is equivalent to five times the MDL result, or equivalent to the lowest concentration 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 and flagged with a "U".

Note that for the Query Manager electronic data deliverable (EDD), there are two fields: detection limit and reporting limit. The detection limit field is equivalent to the MDL, except for those cases where no MDL value exists (for example, oils). If no MDL value exists, the detection limit field is populated with the quantitation limit (QL). The reporting limit field is always populated with the QL value.

Reporting limits for the supporting analyses (percent moisture, percent total extractable organics [TEO], and total organic carbon) will be 0.01%. Reporting limit for grain size will be 0.1% or lower. The reporting limit will be demonstrated by the laboratory to be greater than 5X the detection limit.

Target detection limits, as shown at the bottom of **Tables 1.1a through 1.1e** and in **Table 1.1h**, 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. During validation, these results will be qualified as "F" (found) to indicate that the value is less than the MDL (see Table 7.2).

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 – 6.1h**. 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.

At this time, no criteria for evaluating the target analyte concentrations in the MC252 Reference Oil have been established. Chromatographic resolution criteria for specific compound (peaks) are specified in **Tables 6.1a through 6.1e** and **Table 6.1g** below. When additional criteria are developed they will be added to this Analytical QAP.

TABLE 6.1a
Method Performance Criteria for Extended PAH (Parent and Alkyl Homologs) 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	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.
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%[14]	Resolve before proceeding.
Oil SRM 1582 (Oil and Water only)	One per batch of oil/every 20 field samples	Within ±20% of NIST 95% uncertainty range for analytes within the quantitation range. 2 analytes may be greater than 20% outside, however average %D must be <35%	Resolve before proceeding.
MC 252 Reference Oil	One per batch/every 20 field samples	Peak resolution >80% of 9-methylphenanthrene from 1-methylphenanthrene (m/z 192). Plus additional criteria to be developed.	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, and determine if corrective action is needed.
Blank Spike/Blank Spike Duplicate (Aqueous Samples)	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 >10x 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	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% except d12-perylene which is 10-120%	Re-extract affected samples. Evaluate impact to data, discuss with manager, if corrective action is needed.

[14] 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	Resolve before proceeding.
Continuing Calibration (CCAL)	Every 12 hours or every 12 field samples	%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			
MC 252 Reference Oil	One per batch/every 20 field samples	Peak resolution >80% of n-C17 from pristane; Additional criteria to be developed.	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%.	Evaluate impact to data, discuss with manager, and determine if corrective action is needed.
Blank Spike/Blank Spike Duplicate (Aqueous Samples)	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 >10x 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, and determine if corrective action is needed.

TABLE 6.1c
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 12 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			
MC 252 Reference Oil (optional)	One per batch/every 20 field samples	To Be Determined	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, and determine if corrective action is needed.
Blank Spike/Blank Spike Duplicate (Aqueous Samples)	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, 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.
Surrogates	Every sample	%R 70-130%	Re-extract or re-analyze affected samples. Evaluate impact to data, discuss with manager, and determine if corrective action is needed.

TABLE 6.1d
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.
MC 252 Reference Oil	One per batch/every 20 field samples	Peak resolution (*m/z* 191): 30-Norhopane (T15) from 30-Norneohopane (T16) from Diahopane (X). Add'l. criteria To Be Determined.	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 >10x 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 6.1e
Method Performance Criteria for Qualitative Biomarkers

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Oil SRM 1582 (Oil and Water only)	One per batch of oil/every 20 field samples	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.
MC 252 Reference Oil	One per batch/every 20 field samples	Peak resolution (*m/z* 191): 30-Norhopane (T15) from 30-Norneohopane (T16) from Diahopane (X). Add'l. criteria To Be Determined.	Resolve before proceeding.
Method Blank	One per batch/every 20 field samples	No interference with biomarker patterns	Resolve before proceeding. QA coordinator may be contacted to resolve issues surrounding 'minor exceedance'.
Sample Duplicate	One per batch/every 20 field samples	Qualitative comparison meets laboratory SOP	Evaluate impact to data, discuss with manager, and 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, Total Solids
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
Blank Spike 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[15]	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[16]	One per batch/every 20 field samples	RPD ≤ 25% for analyte concentrations greater than QL	TOC, Grain Size, TS, 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 or SW 846 Method 9060A or Standard Methods 5310C or ASTM D4129-82M, or equivalent
Grain Size	ASTM D422 or PSEP 1986 Particle Size. If using sieve analysis only, report as percent gravel, coarse sand, medium sand, fine sand, very fine sand, and silt/clay. If using sieve with hydrometer or sieve with pipette, report as percent gravel, coarse sand, medium sand, fine sand, very fine sand, silt, and clay. Additionally, grain size must be reported as "True" for sediment treated with hydrogen peroxide prior to analysis or "Apparent" for sediment not treated with hydrogen peroxide.
TS (percent)	EPA 160.3

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 (1981) - U.S. EPA/U.S. Army Corps of Engineers Technical Report EPA/CE-81-1:
http://yosemite.epa.gov/r10/CLEANUP.NSF/ph/T4%20Technical%20Documents/$FILE/Plumb.pdf
PSEP. 1986. "Recommended Protocols for Measuring Conventional Sediment Variables in Puget Sound." Prepared for the Puget Sound Estuary Program.

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[15] Method SW9060 requires quadruplicate analyses, however duplicate or triplicate analyses are acceptable. Standard Method 5310C requires that injections be repeated until consecutive measurements within 10% are obtained for a water matrix, however, duplicate analyses < 20% RPD are acceptable based on a sediment matrix.

[16] 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%.

TABLE 6.1g
Method Performance Criteria for Analysis of Dioctylsulfosuccinate sodium salt (DOSS)

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
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	%D ≤ 30	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 70-130%	Resolve before proceeding.
MC 252 Reference Oil (optional)	One per batch/every 20 field samples	Criteria to be developed	Resolve before proceeding.
Matrix Spike/Matrix Spike Duplicate (Sediments, Soils, Tissues only)	One per batch/every 20 field samples	%R 50% - 125% if sample concentration detected at >5X the spiked amount; RPD ≤30%	Evaluate impact to data, discuss with manager, and determine if corrective action is needed.
Blank Spike/Blank Spike Duplicate (Aqueous Samples)	One per batch/every 20 field samples	%R 50% - 125; RPD ≤30%	Resolve before proceeding.
Method Blank	One per batch/every 20 field samples	Not to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration >10x blank value	Resolve before proceeding.
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.
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.

TABLE 6.1h
Measurement Quality Objectives for Metals by ICP-AES & ICP-MS and Mercury by CVAA/CVAFS

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
ICP-MS Tune	Daily at the beginning of each 24 hour shift. Must start each analytical sequence.	Tuning solution must contain elements spanning all the mass regions of interest (see EPA methods 200.8 & 6020). Analyze 5 times with RSD ≤ 5% Resolution <0.9amu at 10% peak height Mass calibration < 0.1 amu difference from target mass	Resolve before proceeding
Initial Calibration	Daily prior to sample analysis.	Minimum of a 2 point curve for ICP-AES/ICP-MS (1 blank + 1 standard containing all target analytes) Min 5 point curve for CVAA/CVAFS r>0.995 for multi-point curves	Resolve before proceeding
Independent (Initial) Calibration Verification (ICV)	Analyzed immediately after calibration and prior to samples	Different source than calibration standards Concentration near mid-point of calibration curve Must contain all target analytes to be reported %R[1] = 90% - 110%	Resolve before proceeding
Initial Calibration Blank (ICB)	Must be analyzed after each ICV	ICB < RL for all target analytes	Resolve before proceeding
Reporting Limit Standard (CRI)	Daily prior to sample analysis if initial calibration did not contain a low-level standard at the RL for each target analyte. If initial calibration includes the RL as the low-level standard in the initial calibration curve, then RL Std is not required.	Prepare using same source as calibration standards all target analytes at a concentration = RL %R[1] = 70% - 130%	Resolve before proceeding unless all target analytes in associated samples are > 10x RL
Interelement Interference Check Standards (ICSA & ICSAB)	Daily prior to sample analysis	See EPA methods for ICSA & ICSAB concentrations of interferents and other analytes; for ICP-AES checks on background points and instrument interelement interference corrections; for ICP-MS checks on isobaric interference corrections. ICSA & ICSAB: %R[1] = 80% - 120%	Resolve before proceeding
Continuing Calibration Verification (CCV)	Must be analyzed before samples, after every 10 samples, and at end of each analytical sequence	CCV concentration should be near mid-point of calibration curve and contain all target analytes %R = 90% - 110%	Perform instrument maintenance. Re-analyze affected samples.
Continuing Calibration Blank (CCB)	Must be analyzed after each continuing calibration verification (CCV)	CCB < RL for all target analytes Unless: analyte not detected in associated sample(s) or sample analyte concentrations are >10x the blank value	Resolve before proceeding

TABLE 6.1h
Measurement Quality Objectives for Metals by ICP-AES & ICP-MS and Mercury by CVAA/CVAFS

Element or Sample Type	Minimum Frequency	Measurement Quality Objective/ Acceptance Criteria	Corrective Action
Method Blank	Every batch (max. 20 field samples).	No analytes to exceed the reporting limit unless analyte not detected in associated sample(s) or detected in samples at >10x the blank value	Resolve before proceeding
Laboratory Control Sample or Reference Material Possible sediment RMs: NRCC MESS-3 or PACS-2 NIST 1646A*, 1944*, 2702 ERA 540 Possible tissue RMs: NRCC DOLT-4, DORM-3, or TORT-2; NIST 2976 or 1947	Every batch (max. 20 field samples).	Reference Material or laboratory control sample must be matrix-matched to the field samples and prepared/analyzed with the sample batch. Aqueous: %R = 80% - 120% Sediment & Tissue: Values must be within ±30% of the vendor 95% confidence limits for true values >RL	Resolve before proceeding
Matrix Spike (MS)	Every batch (max. 20 field samples).	Must be performed on a NOAA sample from same preparation/analysis batch. Must contain all target analytes to be reported. Sediment/Tissue: %R[2] = 70% - 130% (For native conc. < 4X spike added)	If a MS %R is <30%, a post digestion spike should be analyzed and fall within 75%-125%. See EPA Method 6010C and 6020A for details on spike levels and evaluation. Report QC exceedance in data package narrative.
Sample Duplicate (or matrix spike duplicate) [3]	Every batch (max. 20 field samples).	Sediment/Tissue: RPD[3] ≤ 30% if value > RL	Report this QC exceedance in data package narrative.
Internal Standards (ICP-MS only)	Every sample (QC & field samples)	See EPA methods 200.8 and 6020 for recommended IS elements.Relative intensity of IS %R = 70% - 130% compared to IS of standard in calibration curve (or mid-point standard of calibration for multi-level curve).	Check for instrument drift. If IS in assoc. CCB is acceptable, then dilute sample 5X and re-analyze until IS in control for affected analyte(s). If instrument drift is indicated, recalibrate and re-analyze.
General Reporting	Every sample	* Non-detected values should be reported to the sample-specific MDL or RL to achieve the target sensitivity levels listed in Table 1.1h for each target analyte (using all preparation/dilution factors). * Reporting of detected results less than the RL must be qualified "J" as estimated values. * Results > the linear range must be diluted to within the LR; the diluted result will be reported for the affected analyte.	Include explanation of all non-compliances observed in sample receipt, holding times, preparation, or analysis in the laboratory narrative of the data report.

* These SRMs do not have a certified value for Mercury

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 – 6.1d and 6.1f - 6.1h**. 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 – 6.1d and 6.1f - 6.1h**. 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, SRM1582 is not extracted, but only diluted and analyzed on the instrument, thus the laboratory's value must be within 20% of the NIST uncertainty range. The MC252 Reference Oil will be run with each batch of samples (e.g., GU2988-A0521-O9805 or equivalent as approved by the QA Coordinator). Chromatographic resolution criteria of selected peak pairs in the Reference Oil are indicated in **Tables 6.1a-6.1e, and 6.1g**. After initial data sets are acquired, additional criteria for the Reference Oil will be determined.

6.3.4 Method Blanks

Method (procedural) blanks are laboratory derived samples which have been subjected to the same preparation or extraction procedures and analytical protocols as project samples. A method blank will be analyzed with every 20 field samples analyzed. Acceptance criteria are provided in **Tables 6.1a – 6.1g**. 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 subsampling representative aliquots. If duplicate VOA vials are collected, then volatile organic analyses may be performed in duplicate. Acceptance criteria are provided in **Tables 6.1a – 6.1h**.

6.3.6 Matrix Spike/Matrix Spike Duplicates or Blank Spike/Blank Spike 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 subsampling representative aliquots from a sample container. Instead, blank spike/blank spike duplicates (BS/BSDs) 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. Acceptance criteria are provided in **Tables 6.a – 6.1c, 6.1g, and 6.1h.** Acceptance criteria for conventionals matrix spike and blank spike samples are provided in **Table 6.1f**.

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, 6.1c, 6.1d, and 6.1g**.

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 – 6.1d, and 6.1g**. For the PAH and saturated hydrocarbon analyses, the target analyte concentrations will be corrected for surrogate recovery as specified in the laboratory SOPs.

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 Contractor 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/ Sample Receipt Checklist	
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
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:	As specified in laboratory contract.

Three levels of data validation will be performed (see USEPA, *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use.* EPA-540-R-08-005. January 2009 for definitions): full (stage 4), summary (stage 2B), or cursory (stage 2A) validation. 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. Summary validation will consist of a review of all the following items, but without recalculations. Cursory validation will consist of a review of only the starred (*) items:

- 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)*

As the project proceeds and the quality of the data is verified and documented, the level of validation will decrease at the discretion of the QA Coordinator. At a minimum, cursory validation will be performed on all data packages, i.e., only the starred items will be reviewed.

Qualifiers (**Table 7.2**) may be assigned to individual data points by the QA Contractor. These validation qualifiers will not replace qualifiers or footnotes provided by the laboratory, but will be added to the data summary tables to inform the data user whether or not the data met all project quality objectives. Both sets of qualifiers will be maintained in the database.

TABLE 7.2 Data Validation Qualifier Codes

U	Analyte concentration is not significantly greater than the associated blank result. The result is judged to be the detection limit.
R	Unreliable result. Data should not be used.
N	The analysis indicates the present of an analyte for which there is presumptive evidence to make a "tentative identification".
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
J	Reported concentration is an estimate with potentially more bias or less precision than an unqualified result, as determined by the associated quality control results.
UJ	Not detected. Detection limit is an estimate with potentially more bias or less precision than an unqualified detection limit as judged by the associated quality control results
DNR	Do not report; A more appropriate result is reported from another analysis or dilution.
F	Found. Analyte detected at less than the MDL, however, peak height is greater than 3 times the noise level and ID criteria are met.

All discrepancies and requests for additional corrected data will be discussed with the laboratory prior to issuing the formal data validation report. Review procedures and findings during data validation will be documented on worksheets. A validation report will be prepared for each data group/data package summarizing QC results, qualifiers, and possible data limitations. Only validated data with appropriate qualifiers will be released for general use. Data are not considered final until QA Coordinator has performed assessment and accepted the data.

In addition, the validated data will be reviewed by the QA Reviewer on behalf of BP America. The following process shall be used should the independent validation of the laboratory data results in a material difference in how qualifiers have been assigned or in the actual value itself:

- The QA Coordinator and QA Reviewer will meet to determine the source of the difference, and resolve. No changes to validated results will be made if the differences are considered immaterial to both the QA Coordinator and QA Reviewer.

- If the validated data have already been released by the QA Coordinator, then the data will be updated in accordance with the resolution and reposted.

- Should there be no agreement on how to resolve the difference, the QA Coordinator and QA Reviewer shall request further assistance from the Assessment Managers and BP America, respectively.

- The basis for all material changes to validated results will be documented along with the resubmitted validated data.

8.0 CORRECTIVE ACTION AND PROCEDURE ALTERATION

The analytical laboratories are required to adhere to the SOPs submitted by them to the QA Coordinator for this project. 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 accepted SOP is warranted, the laboratory will revise the SOP and resubmit the SOP to the QA Coordinator 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.

9.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Quality Assurance/Quality Control (QA/QC) reports will be submitted periodically to the Assessment Manager(s) by the QA Coordinator. These reports may be either formal or informal in response to the Assessment Manager's request. Upon termination of the analytical work for this damage assessment, a formal QA report will be submitted. This report will include:

- General compliance with QA objectives
- Summary of technical and performance evaluation audits
- Summary of data validation reports
- Summary of laboratory control charts

10.0 REFERENCES

Bence, A.E., K.A. Kvenvolden, and M.C. Kennicutt, II. 2006. Organic geochemistry applied to environmental assessments of Prince William Sound, Alaska, after the Exxon Valdez oil spill--a review. *Org. Geochem.* 24(1):7-42.

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USEPA, 2002. *Guidance for Quality Assurance Project Plans*, (EPA QA/G-5) EPA/240/R-02/009, December 2002. http://www.epa.gov/quality/qs-docs/r5-final.pdf

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