Appendix C

Sample Preparation and Analytical Methods

C Analytical Methods

C.1 Ancillary Parameters

C.1.1 Grain Size

Grain size analyses were carried out using the classic method of Folk (1974) that includes a combination of wet sieving and pipette techniques. Initially, 10 to 30 grams of wet sediment were placed in a wide-mouth dish using a larger mass for sandy samples and a smaller mass for muddy samples. A small amount of distilled-deionized water (DDW) was added to the dish, clay lumps were broken up with a gloved finger, and the wetted sample was poured into a 200-milliliter (mL) glass bottle and shaken vigorously for a few minutes. Then the sample was poured through 2 millimeter (mm; gravel) and 63 micrometer (μm; sand) sieves and rinsed until the water was clear. The sediment on each sieve was washed into beakers #1 and #2, respectively, allowed to settle and the overlying, clear water was decanted. The weighed beakers were dried at ~105°C and re-weighed.

The glass bottle containing the muddy water (<63 μm) was shaken for about 15 minutes and gently poured into a 1-L cylinder. The cylinder was stirred vigorously with a stirring rod and a timer was started as soon as the rod was removed. Dispersant was not needed to these samples of marine sediment because the mud fraction dispersed extremely well. After 20 seconds, 20 mL of sample were withdrawn from a depth of 20 cm using a Class A pipette. The pipette sample was drained into weighed beaker #3, dried at ~105°C for 24 hours, and weighed for total silt + clay. After 2 hours and 3 minutes, 20 mL of sample was withdrawn from a depth of 10 cm using a Class A pipette. This pipette sample was drained into weighed beaker #4, dried at 105°C for 24 hours, and weighed for total clay. All masses were determined to the nearest 0.0001 g. The total mass of sample was equal to the sum of masses in beakers 1 + 2 + 3(x 50). The individual percentages were calculated as follows:

- % gravel = (beaker #1 sediment/sum) x 100%
- % sand = (beaker #2 sediment/sum) x 100%
- % silt = {[(50 x beaker #3) – (50 x beaker #4)]/sum} x 100%
- % clay = [(50 x beaker #4)/sum] x 100%

C.1.2 Total Organic Carbon

A 0.5 to 1 gram portion of the freeze-dried sediment was placed in a 30-mL Pyrex® beaker. Then, 2-5 mL of 10% (v/v) phosphoric acid (H_3PO_4) was added to remove any inorganic carbon present. The sediment was dried at 105°C and re-weighed to determine the increase in weight due to the formation of hydrated calcium phosphate ($CaHPO_4X2H_2O$) from the addition of H_3PO_4. Then, approximately 200 to 800 mg of pre-treated sediment were weighed into ceramic boats and combusted at 900°C in a Shimadzu® TOC-5050A carbon system with SSM-5000A solid sampling module following the manufacturer's instructions. The total organic carbon (TOC) content of the sediment samples was determined using a four-point calibration curve with pure sucrose as the standard. The TOC concentrations were corrected to account for the

increase in sediment mass following the addition of H_3PO_4. The calibration curve was checked every 10 samples by analyzing certified reference material (CRM) MESS-3, a marine sediment issued by the National Research Council of Canada (NRC).

C.2 Organic Chemical Parameters

Analysis for organic contaminants was conducted by Battelle's environmental chemistry laboratory. The analyses were conducted in accordance with the laboratory's standard operating procedures (SOPs) and generally followed the same procedures used in previous ANIMIDA studies (Brown et al., 2004). The organic analyses for the surficial sediment samples were:

- Saturated hydrocarbons (SHC) by gas chromatography/flame ionization detection (GC/FID)
- Polycyclic aromatic hydrocarbons (PAH) by gas chromatography/mass spectrometry detection (GC/MS)
- Geochemical biomarkers (steranes/triterpanes [S/T]) by GC/MS.

Targeted compounds are listed in Tables 2-5, 2-6, and 2-7. This section describes the analytical methods that were used in performing the organic chemical analyses.

C.2.1 Sediment Sample Preparation

The sediment samples were prepared according to Battelle SOP: 5-203-04 Extraction of Soil/Sediment Samples for Petroleum Analysis. The following is a summary of the method.

Approximately 30 grams (wet weight) of the homogenized sediment were weighed into pre-cleaned glass jars with Teflon®-lined caps, dried with sodium sulfate, and spiked with the appropriate surrogate standards. Another 10-gram subsample was placed into a pre-weighed aluminum-weighing pan and baked overnight at 105°C to determine percent moisture. Extraction solvent (100 mL) was added and samples were shaken on an orbital shaker table for ~12 hours. The extracts were then collected into Erlenmeyer flasks and the samples were serially extracted two more times with 100 mL solvent, for at least 4 hours and at least 30 minutes, respectively. Between extractions the samples were broken up to ensure sediment and sodium sulfate were freely flowing.

The surrogates used were: naphthalene-d8, acenaphthene-d10, phenanthrene-d10, and benzo[a]pyrene-d12 for PAH analysis; 5a-androstane, d50-tetracosane, and o-terphenyl for SHC analysis, and 5β(H)-cholane for S/T analysis.

After extraction, samples were concentrated using a Kuderna-Danish (K-D) concentrator on a hot water bath. An extract weight was taken if necessary to determine general organic content levels prior to column cleanup. Extracts were then treated with copper to remove sulfur processed through a silica gel column as described in the Extract Fractionation subsection.

C.2.2 Extract Fractionation

The sediment extracts were fractionated in order to remove potential interferences and to improve the quality of the analysis at trace levels. The procedure used for fractionation was similar to that used for previous ANIMIDA investigations (Brown, et.al, 2004). Prior to fractionation, the sample extracts were exchanged from methylene chloride to hexane under nitrogen.

The fractionation was performed using a 30-cm by 1-cm column that was wet-packed in methylene chloride with 100 percent activated silica gel/5 percent deactivated alumina/activated copper (approximately 11:1:2) and preconditioned with 30 mL methylene chloride followed by 30 mL of hexane. The sample extract (which had been verified to be less than 50 mg extractable material per 1 mL) was loaded onto the column. The sample was eluted with 18 mL of hexane and the isolated saturate (f1) fraction was collected. This was followed by 21 mL of hexane:methylene chloride (1:1) to isolate the aromatic fraction.

C.2.3 Internal Standard Addition

The extracts (or extract fractions) were reduced to a measured final volume under a stream of nitrogen. The final sample extracts were spiked with SHC, PAH, and S/T internal standards, as appropriate for each extract or fraction. In general, the extracts were concentrated to approximately 500 microliter (µL) before adding the internal standards in order to lower detection limits. The internal standard compounds used were: chrysene-d12 and fluorene-d10 for PAH; chrysene-d12 for S/T; and d62-triacontane for SHC. The amount of SHC internal standard added to the extracts was adjusted to obtain a target concentration of 50 microgram (µg) per mL. The amount of PAH and S/T internal standard added to the extract was adjusted to obtain a target concentration of 1 µg/mL.

C.2.4 Organic Instrumental Analysis

Instrumental analysis of the sediment samples included SHC by GC/FID, PAH by GC/MS, and S/T by GC/MS. The laboratory SOPs include the acceptability criteria for the calibration, procedural blank, surrogate compound recoveries, and spike recoveries, as well as the corrective action if the criteria are not met, reporting requirements, and method detection limit (MDL) protocols. The data quality objectives (DQO) for these analyses are summarized in Section 2.3.

C.2.5 Saturated Hydrocarbons by Gas Chromatography/Flame Ionization Detection

Analysis for SHCs was performed using a GC/FID method based on United States Environmental Protection Agency Method 8015 (USEPA 1993) and according to Battelle SOP No. 5-202-06, *Determination of Low Level Total Petroleum Hydrocarbon (Diesel Range Organics – DRO) and Individual Hydrocarbon Concentration in Environmental Samples*. Target compounds for the method are SHCs, including normal alkanes from n-C8 through n-C40, pristane, phytane, and selected isoprenoids (Table 2-5). Instrument analysis was performed by injection of a portion of the prepared sample extract onto a 30-m long by 0.25-mm inner-diameter (ID) fused-silica capillary column with DB-5 bonded phase, or equivalent. This column provides baseline resolution of n-alkanes from n-C8 to n-C40 and n-C17/pristane and n-C18/phytane pairs (in the n-alkane nomenclature n-C8 refers to a straight chained hydrocarbon, eight carbons in length). The injection port is designed for splitless injection and includes a

silanized wide-bore glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination.

Qualitative identification of target compounds was made by comparison to a standard mixture of calibration standards. Quantitation of the analytes was based on the internal standard compound (d62-triacontane), which was spiked into the sample just prior to analysis. The target compound concentrations were corrected based on surrogate recovery.

C.2.6 Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry

Analysis for PAHs was performed according to Battelle SOP 5-157-08 *Identification and Quantification of Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry*, which is based on USEPA Method 8270 (USEPA 1993) with modifications to expand the list of PAH (Table 2-6) and to lower detection limits using selected ion monitoring (SIM).

The sample extract was injected onto a 30-m long by 0.25-mm ID fused-silica capillary column with DB-5 bonded phase, or equivalent. This column provides baseline resolution of target parent PAHs. The injection port is designed for splitless injection and includes a silanized wide-bore glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination.

Qualitative identification of target compounds was made by comparison to a standard mixture of target PAHs. Identification of alkyl PAHs was made by comparison to reference oil samples analyzed with each batch of samples. The concentrations of the individual PAHs were calculated relative to one of the two internal standards that were spiked into the sample just prior to instrumental analysis. The target PAH concentrations were quantified using average response factors (RFs) generated from the five-point calibration curve. To quantify the alkyl PAH, homologue groups were assigned the RF of their respective parent PAH compound. Compound concentrations were corrected based on surrogate recoveries. Total PAH concentration was calculated as the sum of all target and alkyl PAH concentrations (Table 3-7). For some data analyses, the Total PAH concentration was modified to exclude perylene (a biogenic PAH) – in such a case the parameter is identified as Total PAH less perylene.

C.2.7 Steranes and Triterpanes

Analysis for S/Ts was performed by GC/MS in the SIM mode using a method similar to that used for PAH analysis. Qualitative identification of the target S/Ts (Table 2-7) was made by comparison to a reference oil analyzed with each batch.

The concentrations of the identified S/Ts were calculated versus the internal standard chrysene-d12. All target triterpane concentrations were quantified using the average RF of 17b(H), 21b(H)-hopane (T23) generated from the initial calibration. All target sterane concentrations were quantified using the average RF of cholestane (S17) in the initial calibration. Surrogate recovery of 5β(H)-cholane was calculated relative to the internal standard. Compound concentrations were corrected based on surrogate recovery.

C.3 Inorganic Parameters

Analysis for inorganic parameters was conducted by FIT. The analyses were conducted in accordance with FIT's SOPs. The inorganic analytes for the sediment and source samples were trace and major metals. Target analytes and associated MDLs are listed in Tables 2-8a through 2-8c. This section describes the analytical methods that were used in performing the chemical analyses.

C.3.1 Trace and Major Metals Analysis in Sediment

Sediment samples were initially brought to room temperature; then, each wet sediment sample was homogenized in the original 75-mL plastic vial using a Teflon® mixing rod. Approximately 20 grams of sediment were transferred into pre-weighed plastic vials to determine water content. Once transferred, the wet sediment and the vial were re-weighed. In addition, about 2 to 4 grams of sample were transferred into glass centrifuge tubes to determine the Hg content of the sediments. The portion used for determining water content was frozen, freeze-dried, and re-weighed. The dried sediment samples were again homogenized using a Teflon® mixing rod.

About 0.45 gram of freeze-dried, homogenized sediment and CRM sediment (MESS-3) were totally digested in Teflon® beakers using concentrated, high-purity hydrofluoric acid (HF), nitric acid (HNO_3) and perchloric acid ($HClO_4$). Complete digestion of the sediment was chosen because it accounts for the entire amount of metal in the sample. In the digestion process, 1 mL $HClO_4$, 2 mL HNO_3, and 3 mL HF were added to the sediment in the Teflon® beaker, covered with a Teflon® watch cover, and heated at 50°C until a moist paste formed. The mixture was heated for another 3 hours at 80°C with an additional 2 mL HNO_3 and 3 mL HF before bringing the sample to dryness. Finally, 1 mL HNO_3 and ~30 mL DDW were added to the sample and heated strongly to dissolve perchlorate salts and reduce the volume. The completely dissolved and clear samples were diluted to 20 mL with DDW.

Sediment samples to be analyzed for Hg (element symbols are defined in Table 2-8) were digested by heating 2 to 4 grams of wet sediment in acid-washed, glass centrifuge tubes with 4 mL HNO_3 and 2 mL sulfuric acid (H_2SO_4). Sample tubes were heated for 1 hour in a 90°C water bath and allowed to cool. Each tube was centrifuged at 2,000 revolutions per minute (rpm) and the supernatant decanted into a 25-mL graduated cylinder. The sediment pellet was rinsed twice with 5 mL DDW, centrifuged, and decanted into the graduated cylinder before diluting to a final volume of 20 mL with DDW.

Labware used in the digestion process was acid-washed with hot 8 Normal (N) HNO_3 and rinsed three times with DDW. Two procedural blanks, two duplicate samples, and two portions of the CRM MESS-3 were prepared with each set of 40 samples.

Sediment samples, CRMs, and procedural and reagent blanks were analyzed by flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS; Zeeman or Continuum background correction), cold vapor atomic absorption spectrometry (CVAAS), or inductively coupled plasma/mass spectrometry (ICP/MS). Mercury concentrations were measured by CVAAS. The method used for each element and the corresponding MDLs are presented in Tables 2-8a to 2-8c. During 2004-2006, GFAAS and

ICP-MS were used interchangeably for analysis of selected metals (Tables 2-8a to 2-8c) because an older ICP-MS unit was being replaced with a newer instrument and no ICP-MS was available during a portion of the project. Uniform results for CRMs (Table 3-16 and Appendix A) and for metal versus Al plots (Sections 3 and 4) with the two different instruments provide a great test of the concept that as long as proper QA/QC and data interpretation techniques are followed, the metal data will be able to stand the test of time well into the future when different, more advanced instrumentation may be used for metal analysis. All analytical techniques followed manufacturers' specifications, laboratory SOPs, and the details provided in Section 2.3 below. These methods are based on USEPA methods described for Series 7000 (FAAS and GFAAS), Series 7470 (CVAAS), and Series 6010A (ICP/MS) (USEPA 1991).

C.3.2 Radionuclides in Surface Sediment and Geochronology of Sediment Core

Surface sediment samples also were analyzed for excess ^{210}Pb and total ^{137}Cs in an effort to determine whether sediment at a particular location was recently deposited. Sediment core samples were sub-sectioned in 0.5-cm intervals in an effort to age-date the cores. Approximately 8-10 grams of freeze dried sediment were ground to a fine powder using a SPEX 8000 mixer mill. The samples were then tightly packed into a 2 cm diameter, 5 cm long polycarbonate vial to a depth of 3 cm. A rubber stopper was used to seal the vial and was cemented into place with two-part epoxy to prevent leakage of ^{222}Rn and disruption of secular equilibrium between ^{226}Ra and ^{210}Pb. The samples were then set aside for at least 20 days to establish secular equilibrium and the activities of the various radionuclides were then determined by counting.

For counting, the sealed vial was placed in a well-type intrinsic germanium detector (WiGe, (Princeton Gamma Tech Model IGW11023). Each sample was counted for 2-3 days or until sufficient counts of the pertinent radionuclides were obtained (>1000 net counts for ^{210}Pb). The peaks monitored for the purposes of this study were: ^{210}Pb at 46.5 KeV, ^{214}Pb at 295.2 KeV and 351.9 KeV, ^{214}Bi at 609.3 KeV, and ^{137}Cs at 661.6 KeV. The ^{226}Ra daughter isotopes ^{214}Pb (2 peaks) and ^{214}Bi are used to determine the activity of ^{226}Ra. The activity of excess ^{210}Pb was calculated by subtracting the $A_{(214Pb,214Bi)}$ from the A_{210Pb}. Detector efficiency and counting accuracy were standardized using standard reference river sediment 4350B (^{137}Cs) from the U.S. National Institute of Technology and Standards (NIST) and RGU-1 (^{210}Pb) from the International Atomic Energy Agency. The specific activity [disintegrations per minute per gram (dpm/g)] of each sediment sample was calculated from the detector efficiency, gamma intensity, geometry factor and sample weight (Kang et al., 2000). All values are reported as the activity on the date of sampling. Errors shown are based on 1-sigma counting statistics.

Sediment core sedimentation rates (S) in cm/year were calculated using the following equations with the assumptions being made that there is no sediment mixing:

Cs-137:

$$S = \frac{\text{Depth in cm at which Activity}_{Cs\text{-}137} = \text{maximum}}{\text{[Year – (1963 and/or 1950)] in years}}$$

Pb-210:

$$S = \frac{\text{(-) decay constant for Pb-210 (0.0311 year}^{-1}\text{)}}{\text{Slope for plot of natural logarithm (ln) excess Pb-210 vs. sediment depth}}$$

The excess Pb-210 is calculated by subtracting the mean of $A_{(Pb\text{-}214,\ Bi\text{-}214)}$ from $A_{Pb\text{-}210.}$

C.4 Quality Assurance/Quality Control

A quality assurance (QA) plan, which included quality control (QC) measures, was employed for the program. This section presents the key elements of the plan.

C.4.1 Quality Assurance

The procedures for monitoring the activities of key staff, meeting contract requirements, submission of all deliverables, budget control, and communications are detailed in the various documents that together compose the project management plan:

- A detailed work breakdown structure (WBS) for all tasks, designating primary task leader and responsibilities for key personnel and staff;
- A field sampling and logistics plan for field operations, including scheduling, staffing, training, QC sample collection and analysis procedures, sample chain-of-custody (COC) specifications, and sample shipping; and
- A laboratory work plan for laboratory analysis, including laboratory procedures, analytical DQOs, QC procedures, corrective action criteria, and data entry/data management.

The supporting quality assurance documentation includes the general company policies and procedures (hiring practices, performance evaluations, program management and control tools, and technical review procedures), the Quality Assurance Manual (QAM) for the respective laboratories, and SOPs for field and laboratory operations.

C.4.2 Field Quality Control

C.4.2.1 Sample Handling

Equipment decontamination procedures were strictly followed during the sampling. The decontamination included a physical scrub with soap and water, rinses with seawater and distilled water, and a rinse with isopropanol.

C.4.2.2 Quality Control Samples

As part of the QA program, several types of field QC samples were collected during the survey.

Blanks

No field or equipment blank samples were collected along with the sediment samples to characterize potential influences from equipment and the sampling activities.

Field Replicates

As a QC measure, replicate samples were collected as part of the field sampling design at sample stations L06 and N06 in 2004 and station N11 in 2005. At these locations, sediment samples were collected in triplicate (N11 collected in duplicate) so that the reproducibility and range of results could be evaluated.

C.4.2.3 Documentation

Throughout the field surveys, field notes were maintained by the scientists in log books and on station logs. Exceptions to procedures specified in the sampling and analysis plans, if any, were recorded on the forms.

Film and digital media were used to photo-document the surveys. This documentation recorded specific samples, sampling procedures, and unusual sediment types.

C.4.3 Organic Chemistry Laboratory Quality Control

C.4.3.1 Data Quality Objectives and Quality Control Samples

A set of DQOs was established for the program to ensure that the analytical data would be of the quality necessary to achieve the project objectives. The DQOs were also designed to enhance the ability of the methods to identify and accurately quantify source-specific oils. The DQOs were adapted from the specific laboratory analytical SOPs and were included in the laboratory workplan specific for the program. They are included here as Tables C-1 and C-2.

For processing, samples were grouped together in batches of approximately 20 field samples, plus associated QC samples. In general, the QC samples processed along with the sediment samples included one procedural blank, one blank spike (BS), and one SRM (Sediment SRM 1941a) per batch. The BS sample was fortified with PAH matrix spike solution and SHC matrix spike solution.

There were a number of additional measures added to the processing of the samples to monitor QC and to aid in the assessment of the data's usability. An important part of this is the evaluation of specific QC samples for accuracy, precision, and potential contamination. The following is a general description of some elements.

Solvent and Standard Checks

Prior to sample analysis, every lot of solvent used in the analytical process was analyzed to verify that it was free of contamination and acceptable for use. Likewise, prior to spiking the samples with surrogates and internal standards, all standard preparation records were checked. No standards were used for an analysis unless they had been approved for use.

Instrument Calibration

Before instrumental analysis of sample extracts, a multi-level calibration was analyzed and the linearity of the analyte response factors was evaluated. A continuing calibration standard was

analyzed regularly to check the stability of the instrument response. If the relative standard deviations (RSDs) for the initial calibration or the percent difference (%D) of the daily calibration did not meet the criteria set in the SOP, a new calibration was run and the affected samples re-analyzed.

Reference Samples

To assess the accuracy of the mixture used to calibrate the method, an independently verified instrument reference material (IRM) was analyzed against the calibration standard for PAH samples. The values of the analytes had to be within 15 percent of the target value for the calibration solution to be valid.

In addition, a solution of an assayed crude oil was analyzed with each initial calibration sequence and the results were compared to a laboratory-established mean to assess method accuracy. The solution was also used to provide petroleum pattern information and to aid in qualitative identification of target compounds.

Procedural Blank

A procedural blank was processed and analyzed with each analytical batch in order to monitor potential contamination resulting from laboratory solvents, reagents, glassware, and processing procedures.

Blank Spike Samples

A blank matrix was spiked with representative target compounds prior to extraction of each sample batch to assess the effect of the sample processing procedure independent of sample matrix effects.

Duplicate Samples

A field sample in each sample batch was analyzed in duplicate to assess the precision of the method in the target matrix.

Standard Reference Materials

A Standard Reference Material of a well-characterized sample of known concentration was processed through sample preparation and instrumental analysis with each batch of samples. The results were compared to externally certified values to assess method accuracy. This program used SRM 1944 for sediment samples provided by National Institute of Standards and Technology (NIST).

C.4.3.2 Laboratory Records

The laboratory maintained detailed records throughout the processing of the samples. All raw instrumental data were archived electronically. Completed records or copies of forms were collated into a binder for final archive storage. The final laboratory data package contains sufficient detail so that an external audit could be performed. The documentation in the final data package includes:

- Lot numbers, vendor, and preparation records for reagents and standards
- Sample preparation records
- Analytical procedures used that are not documented in laboratory SOPs
- Instrument analysis records
- Instrument raw data hardcopy
- Documentation of observations or deviations encountered

C.4.3.3 Laboratory Data Review

The following describes the process of data reporting and review by the laboratory. The chemistry data for each analysis were reduced and reviewed by the laboratory staff and then assembled into the final data package. The assembled package was peer reviewed and checked to ensure that the DQOs were met, that the analyses met the program objectives, and that the data were traceable and defensible. The data were also reviewed for compliance with the documented procedures and quality objectives in the work plan. Data were also reviewed for internal consistency and against expected or known values.

The final laboratory data packages were subjected to a formal audit. The audit process is coordinated by the QA Manager and follows the procedure outlined in the Battelle Data Review SOP. The formal audit process included a partial review of all hand-calculated and computer-generated results. The process also checked the traceability of a final result through the instrument calibration and to the sample preparation steps. A formal report was issued to the facility supervisors at the completion of the audit for response. Upon completion of the responses, the auditor released the results to the Program Manager for review and reporting. The final laboratory data package and the audit report are maintained in the laboratory files

C.4.4 Metals Chemistry Laboratory Quality Control

C.4.4.1 Quality Control Measurements for Analysis

For this project, QC measures included balance calibration, instrument calibration (FAAS, GFAAS, Zeeman Graphite Furnace Atomic Absorption Spectrometry [ZGFAAS], CVAAS, ICP/MS, TOC analyzer, turbidimeters, and *in-situ* instrument sensors), matrix spike analysis for each metal, duplicate sample analysis, SRM analysis, procedural blank analysis and standard checks. With each batch of up to 40 samples, 2 procedural blanks, 2 SRMs, 2 duplicate samples and 2 matrix-spiked samples were analyzed. Because CRM MESS-3 does not have a certified value for Ba, the NIST SRM #1643d was used as a check on the analyses. DQOs for these QC measurements are provided in Table C-3.

C.4.4.2 Instrument Calibration

Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified (NIST-traceable) standard weights. All pipettes (electronic or manual) were calibrated prior to use. Each of the spectrometers used for metals analysis was initially standardized with a three- to five-point calibration with a linear correlation coefficient of $r \geq 0.999$ required before experimental samples could be analyzed. Analysis of complete three- to five-point calibrations and/or single standard checks alternated every 5 to 10 samples until all of the analyses were complete. The RSD between complete calibration and standard check was

required to be <15 percent or recalibration and reanalysis of the affected samples was performed.

C.4.4.3 Matrix Spike Analysis

Matrix spikes were prepared for a minimum of 5% of the total number of samples analyzed and included each metal to be determined. Results from matrix spike analysis using the method of standard additions provide information on the extent of any signal suppression or enhancement due to the sample matrix. If necessary (i.e., spike results outside 80 to 120% limit), spiking frequency was increased to 20% and a correction applied to the metal concentrations of the experimental samples.

C.4.4.4 Duplicate Sample Analysis

Duplicate samples from homogenized field samples (as distinct from field replicates) were prepared in the laboratory for a minimum of 5% of the total samples. These laboratory duplicates were included as part of each set of sample digestions and analyses and provided a measure of analytical precision.

C.4.4.5 Procedural Blank Analysis

Two procedural blanks were prepared with each set of 40 samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. These blanks were processed using the same analytical scheme, reagents, and handling techniques as used for the experimental samples.

C.4.4.6 CRM and SRM Analysis

A common method used to evaluate the accuracy of environmental data is to analyze CRMs and SRMs, samples for which consensus or "accepted" analyte concentrations exist. The following CRM was used: Marine Sediment MESS-3 (NRC). Metal concentrations obtained for the CRMs were required to be within $\pm$20% of accepted values for >85% of other certified analyses. When no certified values existed for a metal (e.g., Ba), the SRM Trace Elements in Water #1643d and matrix spikes were used to evaluate analytical accuracy.

Table C-1. Data Quality Objectives for Saturated Hydrocarbon and Polynuclear Aromatic Hydrocarbon Analyses

Element or Sample Type	Minimum Frequency	DQO/Acceptance Criteria
Initial Calibration	Prior to every instrument sequence for PAH analysis and as needed for SHC analysis	5-point curve, %RSD < 35% for all target analytes; 90% must be < 25%
Continuing Calibration	After every 10 samples and at end of instrument sequence	%D < 35% for all target analytes; 90% must be < 25%
Oil Reference Standard (North Slope Crude)	One with each instrument sequence (North Slope Crude)	%D < 30% from laboratory mean for target compounds (use surrogate-corrected values) except for compounds below the reporting limit
Procedural Blank	One per batch	No analyte to exceed 5 times the MDL unless sample amount is >5 times blank amount
Laboratory Control Sample (LCS)	One per batch	Recovery between 70 and 130% for PAH and SHC
Instrument SRM (1491)	One per instrument sequence (PAH only)	Values must be <15% difference of true value for all certified analytes
Sediment SRM (1941a)/Tissue SRM (1974a)	One per batch as appropriate (PAH only)	Values must be within 30% of the true value on average for all analytes, not to exceed 35% of true value for more than 30% of the analytes
Duplicate Analysis	One per batch	Relative percent difference (RPD) < 30% for all analytes >5 times the MDL; Mean RPD <30%
Surrogate Recovery	Every sample	Recovery between 40 and 12% (35% for d8-naphthalene)

Table C-2. Data Quality Objectives for Sterane and Triterpane Analyses

Element or Sample Type	Minimum Frequency	DQO/Acceptance Criteria
Initial Calibration	Prior to every instrument sequence	4-point curve, %RSD < 25% for all target analytes
Continuing Calibration	After every 12 samples or 16 hours, whichever is more frequent, and at end of instrument sequence	%D < 25% for all analytes
Oil Reference Standard (North Slope Crude)	One with each instrument sequence (North Slope Crude)	%D < 30% from laboratory mean for target compounds (use surrogate-corrected values) except for compounds below the reporting limit
Procedural Blank	One per batch	No analyte to exceed 5 times the MDL unless sample amount is > 5 times blank amount
Duplicate Analysis	One per batch	RPD < 30% for all compounds >5 times the MDL; mean RPD <30%
Surrogate Recovery	Every sample	Recovery between 40 and 120%

Table C-3. Data Quality Objectives and Criteria for Metals Analyses

Element or Sample Type	Minimum Frequency	DQO/Acceptance Criteria
Initial Calibration	Prior to every batch of samples	3- to 5-point curve depending on the element and a blank. Standard Curve correlation coefficient r $\geq$0.999 for all analytes
Continuing Calibration	Must end every analytical sequence; for flame, repeat all standards every 5 samples; for graphite furnace and ICP/MS recheck standard after every 8 to 10 samples	%RSD <15% for all analytes
Standard Reference Materials	One per batch of 20 samples	Values must be within 20% of accepted values for >85% of the certified analytes and within 25% for Hg.
Method Blank	One per batch of 20 samples	No more than 2 analytes to exceed 5 times MDL unless analyte not detected in associated samples
Matrix Spike and Spike Method	One per batch of 20 samples	%RSD 70 to 130%
Laboratory Duplicate	One per batch of 20 samples	RPD <25% for 65% of the analytes