Appendix D

Quality Control Summary

D Quality Control Results

This section provides an evaluation of the quality and usability of the environmental data based on the results for the field and laboratory QC samples collected and analyzed during this program. Tables D-2 through D-3 summarize the organic field and laboratory QC results. Tables D-4 and D-5 summarize the inorganic field and laboratory QC results.

In general, no serious data quality issues were noted that would adversely affect the quality or use of the organic and/or inorganic data.

D.1 Field Quality Control

Field QC samples were collected to assess overall precision and representativeness of the sampling and analytical efforts. The results for the field QC sample analyses are presented in Appendices A and B, along with the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

Replicate field samples were collected to assess sample representativeness and precision relative to sample collection procedures and sample matrix.

D.1.1 Field Replicates

Two sets of field replicate samples were generated during the collection of the sediment samples in the form of triplicate samples collected at sampling stations N06 and L06 during the summer 2004 survey. The field replicate results were evaluated to assess analytical precision relative to sample collection procedures and sample matrix.

For the triplicate samples collected at sampling station N06, the precision criterion of less than 50 percent RSD for sediments was met for all PAH, SHC, S/T, and metal results detected at concentrations greater than 5 times the reporting limit with two exceptions. The precision criterion was exceeded for n-C9 (79%) and n-C10 (64%). Overall, the field replicate precision at sampling station N06 was considered to be acceptable.

For the triplicate samples collected at sampling station L06, the precision criterion of less than 50 percent RSD for sediments was met for all PAH, SHC, S/T, and metal results detected at concentrations greater than 5 times the reporting limit with two exceptions. The precision criterion was exceeded for n-C32 (51%) and n-C34 (55%). Overall, the field replicate precision at sampling station L08 was considered to be acceptable.

D.2 Organics Quality Control

Laboratory QC samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. The number and type of laboratory QC samples was based on the total number of field samples and as specified in Battelle SOPs and the Field Sampling and Logistics Plan (Battelle 2004a). For this program, the following laboratory QC

samples and measures were used to evaluate accuracy and precision of the analytical data: surrogate recoveries, procedural blanks, blank spike samples, laboratory duplicates, standard reference materials, and oil reference standards. The results for the organic QC samples and measures are presented in Appendix B, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

In addition to the program-specific QC, Battelle participated in the National Oceanic & Atmospheric Administration/National Institute of Standards & Technology (NOAA/NIST) intercalibration exercises for organics in 2003 and 2005. Triplicate analyses of marine sediment and mussel tissue were analyzed for organics, including PAHs, as part of these exercises. The results of the Battelle analyses were within acceptable criteria for participating laboratories.

D.2.1 Surrogate Results

Surrogate compounds were added to all environmental and QC samples prior to sample preparation. These compounds were added to determine the efficiency of the sample extraction and analysis procedures. Surrogate recoveries were evaluated to assess analytical method accuracy relative to sample matrix and laboratory performance.

For the PAH analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits, with a couple of exceptions. Two laboratory blanks, one blank spike, and five sediment samples had slightly low recoveries for one or two of the four surrogates. The low surrogate recoveries in these samples do not appear to adversely affect the quality or usability of the data. Sample 04-N08-01-PHC-S had very low recoveries (<10%) for all four surrogates. The PAH results for this sample are outliers when assessed against the complete dataset, thus, this sample was considered an outlier and not used for statistical evaluation of the data or presented in graphics. Sample 05-4A-01-PHC-S had very low recoveries for two of the four surrogates; the sample results do not appear to be outliers, thus, the results for this sample were used.

For the SHC analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits, with one exception. Both SHC surrogates in sample 04-N02-01-PHC-S had low recoveries. The low surrogate recoveries in this sample do not adversely affect the quality or usability of the associated data.

For the S/T analyses, all of the environmental and QC sample surrogate recoveries were within the recovery acceptance limits without exception.

D.2.2 Procedural Blanks

A laboratory procedural blank (PB) was prepared with each sample preparation batch by extracting a blank sample matrix (sodium sulfate) as if it were one of the environmental samples. Procedural blanks are used to assess the potential of contamination introduced during sample preparation and analysis. PAH, S/T, and SHC analyses were performed on each PB.

Between 9 and 11 PAH target compounds were detected at trace concentrations (less than the minimum reporting limit [MRL]) in all of the sediment PBs, with the exception of the naphthalenes, alkylated naphthalenes, biphenyl, phenanthrene, and C1-fluorene which were

detected at concentrations greater than the MRL in one or more of the PBs. Naphthalene and C1-naphthalene were identified in all the blanks and are common contaminants associated with the solvents used during sample preparation. Individual SHC target compounds ranging from n-C9 to n-C30 and Total SHC were detected at trace concentrations less than the MRL in the sediment PBs. No S/T target compounds were detected in the PBs. One of the procedural blanks associated with a batch of 2006 samples was lost during preparation and could not be recovered.

Environmental sample results that were within 5 times the associated PB concentration were qualified with a "B" to indicate that the compound was also present in the blank. Overall, the PB results met the DQOs specified in the laboratory QA plan for the program, and do not indicate concentrations of laboratory contamination that would adversely affect the quality or usability of the associated sample data. Results that were qualified with a "B" may be biased high or may be false positives.

D.2.3 Blank Spike Sample Recoveries

A blank spike sample (BS) was prepared with each sample preparation batch by spiking a blank sample matrix with known concentrations of a subset of the target compounds. BSs are used to assess the accuracy of the sample preparation and analysis procedures independent of sample matrix effects. PAH and SHC analyses were performed on each BS; S/T analyses were not performed. The BS results are adjusted based on the response of the associated surrogate recoveries.

For the PAHs analyses, the recovery of naphthalene in one 2004 sediment BS exceeded the acceptance criteria. This high recovery is likely the result of low d8-naphthalene surrogate recovery in the BS. The recovery of several heavy PAHs in one 2005 sediment BS exceeded the acceptance criteria (160 – 300%). The recovery of the surrogate associated with these compounds (d12-benzo[a]pyrene) was 34%, thus, these high recoveries are likely the result of the low surrogate response. These BS recovery exceedances do not adversely affect the quality or usability of the associated sample data.

For the SHC analyses, the recoveries for one or more low molecular weight alkanes (n-C9, n-C10, n-C12, n-C14, and pristine) were recovered below acceptance limits in most of the blank spike samples. Overall, this data quality issue does not adversely affect the quality or usability of the associated sample data since these individual alkanes are only minor components of the SHC distribution and TPHC concentration.

D.2.4 Laboratory Duplicates

Laboratory duplicates were prepared with several sample preparation batches by extracting a second separate aliquot of an environmental sample. Laboratory duplicates were evaluated to assess analytical precision related to laboratory performance and sample matrix. For this project, one laboratory duplicate was prepared and analyzed with each sediment sample batch. PAH, S/T and SHC analyses were performed on each laboratory duplicate.

For the sediment PAH, SHC, and S/T analyses, good laboratory duplicate precision was noted, with relative percent differences (RPDs) less than 30 percent for all of the compounds detected

at concentrations above the MRL and for the majority of the compounds detected at concentrations below the MRL with the exception of the SHC and S/T laboratory duplicate analyses for 04-N16-01-PHC-S. The PAH analyses for sample 04-N16-01-PHC-S showed good duplicate precision thus, the high variability noted for the SHC and S/T laboratory duplicate analyses may be related to laboratory error. The SHC and S/T data for the original and duplicate analyses were compared against the PAH data; the SHC and S/T results from the duplicate analysis were more consistent with the PAH. Battelle reanalyzed this sample with the 2006 sediments and the reanalyzed results were used for statistical analyses. The mean RPDs for the other laboratory duplicate pairs were less than 30 percent with the exception of Total SHC and C2- and C3-fluoranthene/pyrene in sample 06-L08-01-PHC-S. These laboratory duplicate precision exceedances do not adversely affect the quality or usability of the associated sample data.

The laboratory duplicate precision criterion does not apply to compounds detected below the MRL and/or less than 10 times the MDL due to increased variability at low concentrations. RPD was calculated as the absolute difference between the two measurements divided by the mean of the two measurements.

D.2.5 Standard Reference Materials

Instrument SRMs were analyzed with each instrumental analytical sequence to assess accuracy of the instrument calibration (PAH only). A matrix-specific SRM was prepared and analyzed with each sample preparation batch to assess accuracy of the analytical method relative to sample preparation and analysis procedures. PAH analyses were performed on each SRM. SHC and S/T analyses were not performed on the SRMs since there are no certified values for these compounds.

Sediment SRM. SRM 1944 (a freeze-dried marine sediment with certified concentrations for PAHs) was prepared and analyzed for PAHs along with each of the sediment sample batches. The %Ds of the measured values versus the certified values for the PAH compounds were within the acceptance criteria of 30 percent on average per SRM and 35 percent for the individual compounds for the 2004 and 2006 analyses. Three of the four 2005 sediment SRM analyses exhibited low recoveries for many or all of the certified target analytes. The SRM material analyzed in 2005 appears to be from a different NIST preparation batch based on the accompanying documentation. The preparation laboratory noted unusual difficulties preparing this standard in 2005 and low SRM recoveries were also noted for other projects performed at the laboratory during 2005. This quality control issue appears to be limited to the SRMs as the surrogate recoveries of the associated samples and the recoveries for the blank spikes and control oils prepared and analyzed along with the 2005 SRMs were acceptable.

D.2.6 Control Oil Analyses

A North Slope Crude oil sample was analyzed prior to each analytical sequence for PAH, SHC, and S/T analysis. The results of the North Slope Crude oil analyses were used to evaluate the accuracy of the analytical methods, provide a chromatographic pattern for comparisons with samples, and provide an independent check of the quantitation for alkyl PAHs, S/Ts, and SHCs. Results of the control oil analyses were compared to laboratory mean values generated from

multiple analyses of the oil. For the PAH, SHC, and S/T analyses, all of the results were within the acceptance limits with the exception of high recoveries of alkylated naphthalenes, alkylated chrysenes, alkylated fluorene, and/or fluoranthene in several of the analyses. Overall, this data quality issue does not adversely affect the quality or usability of the associated sample data.

D.3 Metals Laboratory Quality Control

Laboratory QC samples were analyzed to assess precision and accuracy of the sample preparation and analytical procedures. For this program, the following laboratory QC samples and measures were used to evaluate accuracy and precision of the analytical data: procedural blanks, matrix spike samples, laboratory duplicates, and standard reference materials. The results for the inorganic QC samples and measures are presented in Tables D-4 and D-5 and Appendix A, along with the results for the associated environmental samples. Discussion and interpretation of the results are provided in the following sections.

In addition to the program-specific QC, the Marine & Environmental Chemistry Laboratories at FIT participated in the most recent NOAA/NIST Intercomparison for Trace Metals that was organized by the National Research Council of Canada. FIT ranked at the top of the laboratories in the exercise. Each laboratory was given two sediment samples and two fish tissue samples to analyze for 15 trace metals including mercury, lead, copper, cadmium, tin, thallium, beryllium and others. Concentrations of some elements were required to be within 5% of established concentrations, while others were to be determined within 10-20%. FIT was one of several laboratories given a Superior rating for the analysis of both sediment and tissue samples.

D.3.1 Procedural Blanks

Two method blanks were processed and analyzed with each batch of samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. No contamination from any of these sources was noted and concentrations of analytes in the blanks do not exceed 5 times the MDL.

D.3.2 Matrix Spike Sample

Matrix spike samples were analyzed with each batch of sediment samples using the method of standard additions. Results from these analyses provide information on the extent of any signal suppression or enhancement due to the matrix. Spike results for the sediment samples are shown in Table D-5, and are within the 70 to 130 percent range specified in the DQOs (Table D-4)

D.3.3 Laboratory Duplicates

Duplicate subsamples taken from individual sediment and water samples in the laboratory were analyzed to estimate analytical precision. Analytical precision for sediment metal analyses ranged from 0.5 percent RSD for Al to ~10 percent RSD for low levels of Ag.

D.3.4 Standard Reference Materials

SRMs were processed and analyzed for trace metals along with the experimental samples as described in the Methods section (Appendix C and Section 2). The results of these analyses are shown in Table D-5. The metal and TOC concentrations determined for each SRM, were all within the range of certified values or within the DQO limits of the reference values provided by the certifying agencies.

Table D-1. Organic Quality Control Result Summary – Polynuclear Aromatic Hydrocarbon Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met	None
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met	None
Surrogate Recoveries	45 to 125% recovery (35 – 125% for d8-naphthalene)	All criteria were met with a few exceptions. Two laboratory blanks, one blank spike, and four sediment samples had slightly low recoveries for one or two of the four surrogates. Sample 04-N08-01-PHC-S had very low recoveries (<10%) for all surrogates and sample 05-4A-01-PHC-S had very low recoveries to two surrogates.	Minor for all affected samples except N08. The results for sample N08 were considered to be unusable based on the very low surrogate recoveries.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	Naphthalene, alkylated naphthalenes, biphenyl, acenaphthylene, phenanthrene, fluorene, C1-fluorene, fluoranthene, and pyrene were detected at concentrations greater than the MRL in one or more blanks.	Minor. Results within 5 times the blank result were qualified “B” and may be biased high or false positives.
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	All criteria were met with the two exceptions: 1) a high naphthalene recovery in one BS from 2004, 2) high recoveries for heavy PAHs in one BS from 2005.	Minor. Results for affected compounds in associated samples may be biased high.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	All criteria were met with the exception of the Total SHC and C2- and C3-fluorene in sample 06-L08-01-PHC-S.	Minor. The positive results for these compounds are considered estimated values in sample 06-L08-01-PHC-S.
Sediment SRM (1944)	Measured values must be within 30% of the true value on average for all compounds, not to exceed 35% of true value for more than 30% of the compounds	All criteria were met in 2004. Three of four SRMs did not meet criteria in 2005 due to low recoveries of 5, 9, and 14 of the 14 certified compounds.	Minor. Results for associated samples may be biased low.
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met with the exception of high C2- and C3- chrysene in two 2004 analyses; three of four NSCs did not meet criteria in 2005 due to high recoveries of 3 or 4 of the reference compounds; and one 2006 analysis had high C1 to C3 fluoranthene/pyrene recoveries.	Minor. The affected results in the associated samples may be biased high.

Table D-2. Organic Quality Control Result Summary – Saturated Hydrocarbon Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met with four exceptions. The results for n-C9 and n-C10 in one field replicate set and n-C32 and n-C34 in one field replicate set exceeded the precision criterion.	Minor. The positive results for these compounds are considered estimated values in the affected samples.
Initial Calibration	%RSD <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds (up to 10% of compounds can be >25%, but <35%)	All criteria were met.	None
Surrogate Recoveries	45 to 125% recovery	All criteria were met, with the exception of low surrogate recoveries in sample 04-N02-01-PHC-S.	Minor. The results in this sample are considered estimated values.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All criteria were met. Several SHCs were detected at trace concentrations less than the MRL in all 2004 procedural blanks.	Minor. Results within 5 times the associated blank result were qualified with a “B” and may be biased high or may be false positives.
Blank Spike Sample Recoveries	35 to 125% recovery for spiked compounds	All criteria were met with the exception of low recoveries for one or more low molecular weight alkanes (n-C9, n-C10, and n-C12, n-C14, and pristine) in many of the sediment blank spikes.	Minor. The low molecular weight alkane results in the associated samples may be biased low.
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	All criteria were met with the exception of sample 04-N16-01-PHC-S, which showed high variability possibly related to sample heterogeneity.	Minor. The analysis with the higher results was used for data analysis and reporting to be most conservative.
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None

Table D-3. Organic Quality Control Result Summary – Sterane and Triterpane Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Field Replicate	RSD < 50% for all compounds >5 times the RL	All criteria were met.	None
Initial Calibration	%RSD <25% for all compounds	All criteria were met.	None
Continuing Calibration	%D <25% for all compounds	All criteria were met.	None
Surrogate Standards	45 to 125% recovery	All criteria were met.	None
Laboratory Duplicate	RPD <30% for all compounds >10 times the MDL; mean RPD <30%	All criteria were met with the exception of sample 04-N16-01-PHC-S, which showed high variability possibly related to sample heterogeneity.	Minor. The analysis with the higher results was used for data analysis and reporting to be most conservative.
Procedural Blank	No compound to exceed 5 times the MDL unless sample amount is >10 times blank amount	All criteria were met.	None
Oil Reference Standard (North Slope Crude)	%D <35% for compounds above the RL	All criteria were met.	None

Table D-4. Inorganic Quality Control Result Summary – Trace-Metal Analyses

QC Sample or Measurement Type	Acceptance Criteria	Quality Control Result Summary	Impact to Data Quality and Usability
Field Replicates	RSD <50% for all trace metal concentrations >5 times the MDL	All criteria were met.	None
Initial Calibration	Standard Curve correlation coefficient $r \geq$ 0.999 for a 3 to 5 point curve for all trace metals	All criteria were met.	None
Continuing Calibration	%D <15% for all trace metals or repeat Initial Calibration and sample analyses	All criteria were met.	None
Matrix Spike Recoveries	70 to 130% recovery for all trace metals	All criteria were met.	None
Procedural Blanks	No trace metal concentration to exceed 5 times the MDL unless the sample amount is >10 times the blank concentration	All criteria were met.	None
Laboratory Duplicates	RSD <25% for all trace metal concentrations >10 times the MDL; mean RSD <25%	All criteria were met.	None
Sediment SRMs (MESS-3, 1643d)	Measured values must be within 20% of the certified or reference values for >85% of the SRM analyses.	All criteria were met.	None

Table D-5. SRM Results for Sediment Metal Analyses: CRM MESS-3 and SRM 1643d

Standard Reference Material	Ag (µg/g)	Al (%)	As (µg/g)	Ba (µg/g)	Be (µg/g)	Cd (µg/g)	Co (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)
CRM MESS-3 This Study (n = 16)	0.18 ±0.01	8.63 ±0.21	20.8 ±0.8	(1025) ±27	2.28 ±0.06	0.24 ±0.01	13.3 ±0.8	107 ±1	34.0 ±0.8	4.27 ±0.11
CRM MESS-3 NRC Certified	0.18 ±0.02	8.59 ±0.23	21.2 ±1.1	--	2.30 ±0.12	0.24 ±0.01	14.4 ±2.0	105 ±4	33.9 ±1.6	4.34 ±0.11
SRM 1643d This Study (n = 4)	--	--	--	501 µg/L ±8	--	--	--	--	--	--
SRM 1643d NIST Certified	--	--	--	506.5 µg/L ±8.9	--	--	--	--	--	--
Spike Recovery (%) (Sediment) (n = 16)	95.3 ±3.3	99.2 ±0.5	100.0 ±0.9	116.5* ±17	98.5 ±2.8	97.4 ±3.2	95.1 ±4.1	99.5 ±.0.6	99.2 ±0.9	98.3 ±0.4

Standard Reference Material	Hg (µg/g)	Mn (µg/g)	Ni (µg/g)	Pb (µg/g)	Sb (µg/g)	Tl (µg/g)	V (µg/g)	Zn (µg/g)	TOC (%)
CRM MESS-3 This Study (n = 16)	0.094 ±0.004	323 ±4	46.1 ±1.0	21.4 ±0.4	1.04 ±0.05	0.89 ±0.04	241 ±4	155 ±3	2.1 ±0
CRM MESS-3 NRC Certified	0.091 ±0.009	324 ±12	46.9 ±2.2	21.1 ±0.7	1.02 ±0.09	0.90 ±0.06	243 ±10	159 ±8	2
Spike Recovery (%) (Sediment) (n = 16)	87.1* ±2.6	96.8 ±2.2	97.1 ±3.2	97.0 ±4.6	108.6 ±13.7	70.1* ±28	115.0* ±1.8	96.4 ±1.1	NA

Notes: CRM MESS-3 - Marine sediment issued by NRC; SRM 1643d – Trace Elements in Water issued by NIST.
Values in parenthesis are for reference only; SRM not certified by the NRC.
Mean results ± standard deviation are presented.
*Final concentrations are corrected for percent spike recovery