

**APPENDIX F-2**

**Sediment Chemistry and Physical Measurement Report  
for Bridgeport and Milford**

**Prepared for**

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**November, 2002**



US ARMY CORPS  
OF ENGINEERS  
New England District

Contract No. DACW33-01-D-0004

Delivery Order No. 13

November 2002

## *Final Report*

# **Sediment Chemistry and Physical Measurement Report for Bridgeport and Milford**

**Long Island Sound Dredged Material  
Disposal Site Designation  
Environmental Impact Statement**

**Sediment Chemistry and Physical Measurement  
Data Report for Bridgeport and Milford**

**Long Island Sound Dredged Material Disposal Site Designation  
Environmental Impact Statement**

**Submitted to  
Department of the Army  
U.S. Army Corps of Engineers  
North Atlantic Division  
New England District**

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**November 20, 2002**

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## 1.0 INTRODUCTION

The following validated data report includes the results of data analyzed from sediment and QC water (rinstate blank and ambient blank) samples collected in support of the *Long Island Sound Dredged Material Disposal Site Designation Environmental Impact Statement (LIS EIS)*. Data have been reported for the following analyses: pesticides/ polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) and bis(2-ethylhexyl)phthalate, metals, AVS/SEM, dioxins/furans, dioxin-like PCB congeners, grain size, specific gravity, total organic carbon (TOC), and moisture content.

### 1.1 Background

To support the production of the LIS EIS, sediment and QC water samples were collected to assess the chemical, physical, and biological conditions at two alternative dredge material disposal sites known as Bridgeport and Milford (Figure 1). Sediment was collected from within the boundary of the two sites and at two reference locations located outside of each site boundary (Figures 2 and 3) on July 29, and July 30, 2002. Collections were performed by Battelle Duxbury, MA; details of the sediment collection are provided in the "Final Survey Report, Summer 2002 Sediment Sampling Survey Long Island Sound EIS Alternative Disposal Site Study" (Battelle 2002a).

The objective of the sampling was to characterize chemical, physical, and biological conditions at the two sites and two reference locations. The data will also be used in an Environmental Impact Statement to identify, select, and designate dredged material disposal site(s) in the western and central portions of Long Island Sound. Site characterization efforts at Bridgeport and Milford are designed to fulfill the baseline monitoring requirements defined in 40 CFR, Section 228.13 of the Marine Protection Research and Sanctuaries Act (MPRSA). Samples were collected for benthic infauna, toxicity, chlorinated pesticides, PCBs, PAHs, bis(2-ethylhexyl)phthalate, trace metals, acid volatile sulfide/simultaneously extracted metals (AVS/SEM), dioxins/furans, dioxin-like PCB congeners, grain size, specific gravity, and total organic carbon (TOC) testing and analysis. This report only includes the chemical and physical measurement data results. The benthic infauna results and toxicity testing and evaluation results will be presented in separate reports.



**Figure 1. Location of Existing and Alternative Dredged Material Disposal Sites under Consideration in Western and Central Long Island Sound.**

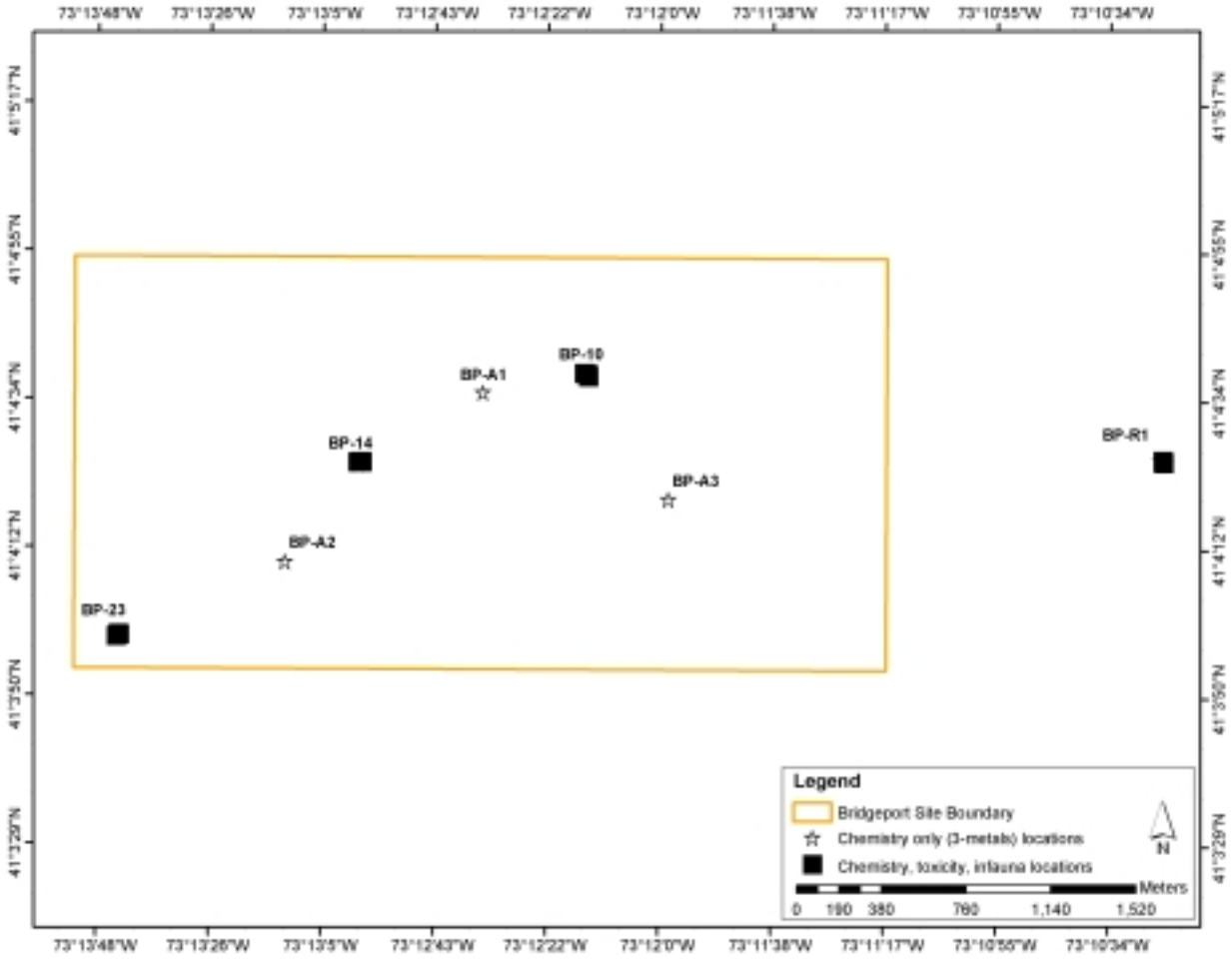
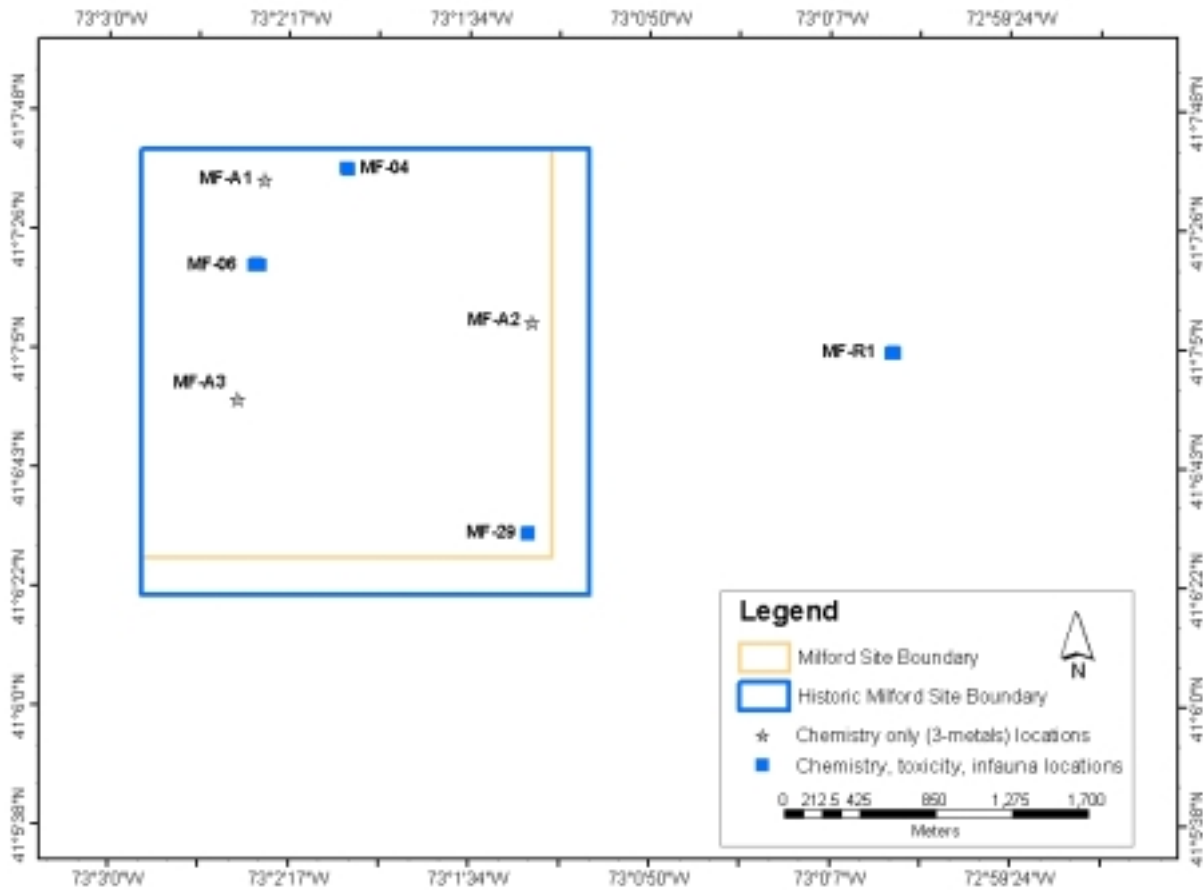


Figure 2. Actual Sediment Sampling Locations of Bridgeport Site – July 2002.



**Figure 3. Actual Sediment Sampling Locations of Milford Site – July 2002.**

For the purpose of this LIS study, the Milford Site is defined as 7500 ft × 7500 ft anchored on the northwest corner of the historic Milford Site as defined in GIS record (41°7.68155'N, 73°2.87043'W). The historic Milford Site is presented for reference.

## 1.2 Summary of Sample Processing and Analyses

All sediment and QC water samples were received at Battelle in good condition and processed per the project Quality Assurance Project Plan (Battelle 2002b). Sediment samples were stored frozen (at, or below  $-20^{\circ}\text{C}$ ), and water samples were stored refrigerated (at approximately  $4^{\circ}\text{C}$ ) until processing. Equipment rinsate blank and ambient blank water samples were collected at each site for pesticides/PCBs, PAHs and bis(2-ethylhexyl)phthalate, metals, dioxins/furans, and dioxin-like PCB congeners. All samples were processed with the exception of one rinsate blank sample collected for dioxins/furans, and dioxin-like PCB congeners at the Milford site which was lost during transportation in the field. Analysis proceeded per communication with EPA and the Corps.

Sediment samples for dioxins/furans and dioxin-like PCBs were received at PSC outside the temperature control limit of  $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$  (coolers were at  $8.9^{\circ}\text{C} - 12.1^{\circ}\text{C}$ ). PCBs and dioxins/furans are extremely stable and since the samples were stored at the correct temperature upon receipt at the laboratory, this outlier should have no significant impact on data quality.

Sediment samples for the various analyses were homogenized, split into appropriate containers, and forwarded to the specified laboratories for analyses.

Table 1 lists the laboratories that performed sample analyses. Tables 2 and 3 summarize the analytical tasks performed on each sample of sediment and QC water, respectively.

**Table 1. Summary of Analytical Laboratories.**

Analysis Parameters	Laboratory	Third Party Validator
Pesticides/PCBs	Battelle, Duxbury, MA	NA
PAHs & Bis(2-ethylhexyl)phthalate	Battelle, Duxbury, MA	NA
Metals and AVS/SEM	Battelle, Sequim, WA	NA
Dioxins/Furans, Dioxin-like PCB congeners	PSC Analytical Services, Ontario, Canada	Ecochem, Inc., Seattle WA. (1)
Grain Size, Specific Gravity and TOC	Applied Marine Sciences, Inc. League City, TX	NA
Moisture Content	Battelle, Duxbury, MA	NA

NA indicates Not Applicable

(1) Only sediment data were sent to Ecochem for Tier III level validation.

## 1.3 Data Verification/Validation

Laboratory data generated for this study received internal verification and validation by the Quality Assurance (QA) officers from each participating laboratory. Second-level verification of all data was performed at Battelle, Duxbury by comparing results with specific measurement performance criteria (MPCs) defined in the Quality Assurance Project Plan prepared for this study (Battelle 2002b). The dioxin/furan and dioxin-like PCB congener sediment data were submitted to EcoChem Inc, of Seattle, WA for third party validation (Tier III). The validation reports are included as Attachment 8 of this report.

**Table 2. Sediment Samples Summary of Analyses.**

Sample ID	Site	Station	Battelle ID	PCBs/Pest, PAHs and phthalate	Metal	AVS/SEM	Dioxins/ furans and Dioxin like PCBs	Grain Size and TOC	Moisture
LIS1S010	Bridgeport	BP-14	V7190	X	X	X	X	X	X
LIS1S011			V7191	X	X	X	X	X	X
LIS1S012			V7192	X	X	X	X	X	X
LIS1S01C		BP-10	V7193	X	X	X	X	X	X
LIS1S01F			V7194	X	X	X	X	X	X
LIS1S020			V7195	X	X	X	X	X	X
LIS1S029		BP-R1 <sup>a</sup>	V7196	X	X	X	X	X	X
LIS1S02A			V7197	X	X	X	X	X	X
LIS1S02B			V7198	X	X	X	X	X	X
LIS1S018		BP-A1	NA		X			X	X
LIS1S015		BP-A2	NA		X			X	X
LIS1S026		BP-A3	NA		X			X	X
LIS1S034		Milford	MF-06	V7199	X	X	X	X	X
LIS1S035	V7200			X	X	X	X	X	X
LIS1S036	V7201			X	X	X	X	X	X
LIS1S048	Bridgeport	BP-23	V7202	X	X	X	X	X	X
LIS1S049			V7203	X	X	X	X	X	X
LIS1S04A			V7204	X	X	X	X	X	X
LIS1S050	Milford	MF-29	V7205	X	X	X	X	X	X
LIS1S052			V7206	X	X	X	X	X	X
LIS1S053			V7207	X	X	X	X	X	X
LIS1S03D		MF-A1	NA		X			X	X
LIS1S040		MF-A2	NA		X			X	X
LIS1S039		MF-A3	NA		X			X	X
LIS1S060		MF-R1	V7208	X	X	X	X	X	X
LIS1S061			V7209	X	X	X	X	X	X
LIS1S062			V7210	X	X	X	X	X	X
LIS1S066		MF-04	V7211	X	X	X	X	X	X
LIS1S067			V7212	X	X	X	X	X	X
LIS1S068			V7213	X	X	X	X	X	X

Indicates analysis not required.

<sup>a</sup> Station ID was originally labeled as BP-RF, and corrected to BP-R1 per communication with the Field Task Leader.

**Table 3. Water Samples Summary of Analyses.**

Sample ID	Sample Description	Site	Station	Battelle ID	PCBs/Pest, PAHs, phthalate	Metals	Dioxins/furans and Dioxin like PCBs
LIS1S065BO1	Rinsate Blank	Milford	MF-04	V7214	X	X	No analysis done <sup>a</sup>
LIS1S01BBO1	Rinsate Blank	Bridgeport	BP-10	V7215	X	X	X
LIS1S065OA1	Ambient Blank	Milford	MF-04	V7216	X	X	X
LIS1A01BOA1	Ambient Blank	Bridgeport	BP-10	V7217	X	X	X

<sup>a</sup>Sample broke during transit. No analysis was possible.

## 2.0 METHODS

Analysis of sediment samples for pesticides/PCBs, PAHs and bis(2-ethylhexyl)phthalate, metals, AVS/SEM, dioxins/furans, dioxin-like PCB congeners, grain size, specific gravity, total organic carbon (TOC), and moisture content, and QC water samples for pesticides/PCBs, PAHs and bis(2-ethylhexyl)phthalate, metals, dioxins/furans and dioxin-like PCB congeners were conducted following methods and SOPs as described in the project Quality Assurance Project Plan (Battelle 2002b).

The following definitions regarding the electronic data deliverable (EDD) specification were added:

- Qualifier “G” is used for “Co-eluting compound interferes with peak of interest”
- Qualifier “R” is used for “Data rejected, due to QC exceedance”
- The PARAM\_CODE for AVS (Acid Volatile Sulfide) is "NED414".
- Prep Code "SOP MSL-C-001" in the SAMP\_PREP\_METH field is used to distinguish the AVS/SEM metals preparation method.

### 2.1 Sediment Sample Analysis

#### 2.1.1 Pesticides/PCBs

Sediment samples were extracted for Pesticide/PCB analysis following general NS&T methodologies. Briefly, sediment samples were homogenized and approximately 30 g of sediment was fortified with surrogate internal standard (SIS) compounds. The sample was extracted three times with dichloromethane using shaker table techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further cleaned up by GPC HPLC. The post-HPLC extract was concentrated, fortified with recovery internal standards (RIS) and split qualitatively for Pesticide/PCB and PAH/phthalate analyses. Pesticide/PCB extracts were solvent exchanged into hexane prior to analysis. Extracts were analyzed using gas chromatography/electron capture detection (GC/ECD), following general NS&T methods. Sample data were quantified by the method of internal standards, using the RIS compounds. Sample data were reported in units of  $\mu\text{g}/\text{kg}$  on a dry-weight concentration basis.

#### 2.1.2 PAHs and Bis(2-ethylhexyl)phthalate

Sediment samples were extracted for PAHs and Bis(2-ethylhexyl)phthalate following general NS&T methodologies, as described in Section 2.1.1. Extracts were analyzed for PAHs and Bis(2-ethylhexyl)phthalate following general NS&T methods. Briefly, extracts were analyzed by gas chromatography/mass spectrometry detection (GC/MS) in the selected ion monitoring (SIM) mode. Sample data were quantified by the method of internal standards, using the RIS compound Acenaphthene d-10. Sample data were reported in units of  $\mu\text{g}/\text{kg}$  on a dry-weight concentration basis.

#### 2.1.3 Metals

Eleven metals were analyzed: silver (Ag), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn). Samples were freeze dried and homogenized using a ball-mill prior to digestion. Sediment samples were digested using aqua regia according to Battelle SOP MSL-I-006, *Mixed Acid Sediment Digestion*. An approximately 500-mg (dry weight) aliquot of each sample was combined with nitric and hydrochloric acids (aqua regia) in a Teflon bomb and heated in an oven at 130°C ( $\pm 10^\circ\text{C}$ ) overnight. After heating and cooling, deionized water was added to the sediment digestate to achieve analysis volume, and the digestates were submitted for analysis.

Sample digestates were analyzed for Ag, As, Be, Cd, Cr, Cu, Ni, Pb, and Zn using inductively coupled plasma-mass spectrometry (ICP-MS) according to Battelle SOP MSL-I-022, *Determination of Elements in Aqueous and Digestate Samples by ICP/MS*.

Sample digestates were analyzed for Se using hydride generation atomic absorption (HGAA) spectroscopy with flow injection analysis system (FIAS) according to Battelle SOP MSL-I-030, *Determination of Metals in Aqueous and Digestate Samples by HGAA*.

Sample digestates were analyzed for Hg using cold-vapor atomic absorption spectroscopy (CVAA) according to Battelle SOP MSL-I-016, *Total Mercury in Tissues and Sediments by Cold Vapor Atomic Absorption*.

All results were reported in units of  $\mu\text{g/g}$  on a dry-weight basis. The results were not blank corrected for any of the metals.

#### **2.1.4 AVS/SEM**

**AVS:** Samples were processed and analyzed for AVS and prepared for SEM analysis following Battelle SOP MSL-C-001, *Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM) in Sediments and Dissolved Sulfide in Aqueous Samples by a Colorimetric Method*. AVS is converted to hydrogen sulfide by the addition of hydrochloric acid. A portion of the acid solution produced is then analyzed for the soluble metals, or the SEM. The hydrogen sulfide is purged from the sample by an inert gas and trapped in a sodium hydroxide solution. With the addition of a mixed-diamine reagent, the sulfide is converted to methylene blue and measured on a spectrometer.

**SEM:** Six metals were analyzed: Ag, Cd, Cu, Ni, Pb, and Zn. SEM extracts were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) according to Battelle SOP MSL-I-022 *Determination of Elements in Aqueous and Digestate Samples by ICP/MS*. This procedure is based on two methods modified and adapted for analysis of solid sample digestates, EPA Method 1638 *Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry* (EPA 1996) and EPA Method 1640 *Determination of Trace Elements in Water by Preconcentration and Inductively Coupled Plasma-Mass Spectrometry* (EPA 1997).

The data generated are used to calculate the molar ratio of SEM to AVS. All results were reported as blank corrected in units of  $\mu\text{g/g}$  on a dry-weight basis.

#### **2.1.5 Dioxins/Furans and Dioxin-like PCB Congeners**

Sediment extracts were cleaned, and analyzed for the seventeen 2,3,7,8 – substituted PCDDs/PCDFs following the general procedures in EPA Method 1613, Revision B, as described in PSC Analytical Services SOP ORG-310. Sediment samples were also extracted and analyzed for dioxin-like PCBs (also referred to as 12 WHO congeners) following the general procedures in EPA Method 1668, Revision A, as described in PSC Analytical Services SOP ORG-307. The extraction allows for both dioxins/furans and the dioxin-like PCB congeners, with subsequent splitting of the extract into thirds for separate clean-up and analysis of the dioxins/furans from the dioxin-like PCB congeners and archive.

The PCDDs and PCDFs were extracted from solid samples with a solvent mixture of 50:50 hexane/dichloromethane. Following extraction, the samples were cleaned up via GPC and/or carbon (if sample necessitated) and passed through a series of columns, which removed the bulk of the organic matrix, which co-extracted with the PCDD/Fs. The resulting fraction was concentrated to 2 mL for

analysis. Final volume for injection was 20  $\mu\text{L}$ . Qualitative/quantitative analysis for PCDD/Fs was performed using separation by high-resolution capillary gas chromatography, and measured by high-resolution mass spectrometry (HRMS). PCDD/Fs were identified by comparing gas chromatograph retention times and the ion abundance ratios of the  $m/z$ 's with the corresponding values obtained for standards.

The GCMS system was calibrated and the analyte concentrations were determined using an isotope dilution technique. Quantitation was based on the use of internal standards and relative response factors (RRFs). Sample data were reported in units of  $\text{pg/g}$  for dioxins/furans and  $\text{ng/g}$  for dioxin-like PCBs on a dry-weight concentration basis.

### **2.1.6 Grain Size**

Grain size aliquots were analyzed following AMS SOP 2103, *Wet Preparation of Soil Samples for the Quantitative Determination of Particle Size Analysis (Sieve and Hydrometer Method)*. Each sediment sample was homogenized using a stainless steel spatula. Separate grain size and water content aliquots were secured. The grain size aliquots were treated with 30% hydrogen peroxide to remove organic matter and dispersed in a solution of sodium hexametaphosphate. The coarse-grained fraction ( $>74 \mu\text{m}$ ) was separated from the fine-grained fraction ( $<74 \mu\text{m}$ ) by sieving through a No. 200 sieve. The portion remaining on the No. 200 sieve was then washed into a beaker and dried. This dried fraction was sorted through a series of nested sieves to provide the distribution of coarse-grained particles.

The fraction passing the No. 200 sieve was washed directly into a hydrometer cylinder, stirred, and then brought to volume. The sample was stirred again and hydrometer readings were taken at 2, 5, 15, 60, 250, and 1440 minute intervals. The resulting data were combined with the sieve data to generate a grain size distribution curve. Percent gravel and sand values were calculated directly from the sieve data, while silt and clay values were read from the graph. Sample data were reported in units of percentage on a dry-weight concentration basis.

### **2.1.7 Specific Gravity**

Sediment samples were analyzed for specific gravity following the general procedure in ASTM D854, as described in AMS SOP 2302. Briefly, a known mass of dry sediment was placed in a beaker and soaked with RO/DI water for no less than 12 hours. The sediment slurry was then transferred to a pycnometer flask. After air bubbles were removed, the weight of the pycnometer flask plus sediment was recorded. Specific gravity is defined as the ratio of the mass of a unit volume of a material at a specific temperature to the mass in air of an equivalent volume of pure water at the same temperature. Specific gravity measurements were reported as a ratio, and thus have no reporting units.

### **2.1.8 TOC**

Sediments requiring Total Organic Carbon (TOC) analysis were processed according to AMS SOP 2201, *Total Organic Carbon Content of Sediments by Coulometric Detection*. Aliquots of sediment were secured and dried at a low temperature, approximately  $70^\circ\text{C}$ . The samples were then ground and acidified ( $\text{pH}<2$ ) with a dilute solution of HCl to remove inorganic carbon. Next, the samples were rinsed with distilled water until the pH was found to be 7. After samples were dried to remove water, a small aliquot was weighed into a pre-combusted sample boat and combusted at  $900^\circ\text{C}$  in a stream of oxygen to convert organic substances to  $\text{CO}_2$ . The  $\text{CO}_2$  stream was scrubbed to remove interferants such as water vapor,  $\text{NO}_x$ , and  $\text{SO}_x$ , and swept into the coulometer cell. The amount of  $\text{CO}_2$  produced was measured, recorded digitally, and printed as a hard copy report. Sample data were reported in units of percentage on a dry-weight concentration basis.

### **2.1.9 Moisture Content**

Moisture content was determined in conjunction with the Pesticides/PCBs and PAHs/Bis(2-ethylhexyl)phthalate sample extraction procedure (SOP 5-192). Briefly, 5 to 10-g of well-mixed sediment was weighed into a pre-weighed, pre-baked, aluminum weighing pan. The pan was placed in a drying oven and dried overnight at approximately 105 °C. After approximately 24 h, the pan was removed from the drying oven and allowed to cool at room temperature for at least 30 min. The pan was reweighed and moisture content determined as defined in Section 4.0 of the SOP.

## **2.2 Rinsate Blank and Ambient Blank Water Sample Analysis**

### **2.2.1 Pesticides/PCBs**

Water samples were extracted for Pesticide/PCB analysis following general NS&T methodologies. Briefly, 1-L of water (measured using a graduated cylinder) was transferred to a separatory funnel, extraction solvent was added (60 mL methylene chloride), and the sample was fortified with surrogate internal standard (SIS) compounds. Each sample was serially extracted three times using separatory-funnel techniques. The combined extract of each sample was dried over sodium sulfate and concentrated to 900 µL using Kuderna-Danish and nitrogen evaporation techniques. The extract was then fortified with RIS and split qualitatively for Pesticide/PCB and PAH/phthalate analyses. Pesticide/PCB extracts were solvent exchanged into hexane prior to analysis. Extracts were analyzed using GC/ECD, following general NS&T methods. Sample data were quantified by the method of internal standards, using the RIS compounds. Sample data were reported in units of ng/L on a volume basis.

### **2.2.2 PAHs and Bis(2-ethylhexyl)phthalate**

Sediment samples were extracted for PAHs and Bis(2-ethylhexyl)phthalate following general NS&T methodologies, as described in Section 2.2.1. Extracts were analyzed for PAHs and Bis(2-ethylhexyl)phthalate following general NS&T methods. Briefly, extracts were analyzed by GC/MS in the selected ion monitoring (SIM) mode. Sample data were quantified by the method of internal standards, using the RIS compound Acenaphthene d-10. Sample data were reported in units of ng/L on a volume basis.

### **2.2.3 Metals**

Eleven metals were analyzed: Ag), As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn. For analysis of total recoverable metals (TRM) by ICP-MS, a 9.6-mL aliquot of each water sample was combined with 0.2 mL concentrated nitric acid and internal standards, then heated for 2.5 h in a sealed tube. The sample was then analyzed directly by inductively coupled plasma-mass spectrometry (ICP-MS) following Battelle SOP MSL-I-022, *Determination of Elements in Aqueous and Digestate Samples by ICP-MS*, which is based on EPA Method 200.8

Hg was analyzed directly (with no preconcentration step) using cold-vapor atomic fluorescence (CVAF) spectroscopy according to Battelle SOP MSL-I-013, *Total Mercury in Aqueous Samples by CVAF*, which is derived from EPA Method 1631.

All results were reported in units of µg/L. None of the results were blank corrected. Note that the only QC samples requested for analysis with equipment blanks are method blanks and blank spike samples, however, results of SRMs analyzed with the sample batch were also provided.

#### **2.2.4 Dioxins/Furans and Dioxin-like PCB Congeners**

Water samples were extracted and analyzed for the seventeen 2,3,7,8-substituted PCDDs/PCDFs following the general procedures in EPA Method 1613, Revision B, as described in PSC Analytical Services SOPs ORG-310. Water samples were also extracted and analyzed for dioxin-like PCBs (also referred to as the 12 WHO congeners) following the general procedures in EPA Method 1668, Revision A, as described in PSC Analytical Services SOPs ORG-307.

The extraction method allows for one extraction for both dioxins/furans and the dioxin-like PCB congeners, with subsequent 50:50 splitting of the extract for archival and separate cleanup and analysis of the dioxins/furans from the dioxin-like PCB congeners.

Following extraction, the samples were cleaned up via GPC and/or carbon (if sample necessitated) and passed through a series of columns, which removed the bulk of the organic matrix, which co-extracted with the PCDD/Fs. The resulting fraction was concentrated to 2 mL for analysis. Final volume for injection was 20  $\mu$ L. Qualitative/quantitative analysis for PCDD/Fs was performed using separation by high-resolution capillary gas chromatography, and measured by high-resolution mass spectrometry (HRMS). PCDD/Fs were identified by comparing gas chromatograph retention times and the ion abundance ratios of the m/z's with the corresponding values obtained for standards.

The GCMS system was calibrated and the analyte concentrations were determined using an isotope dilution technique. Quantitation was based on the use of internal standards and relative response factors (RRFs). Sample data were reported in units of pg/L for dioxins/furans and ng/L for dioxin-like PCBs on a volume basis.

### **3.0 RESULTS**

The study data are presented in eight sections as follows:

- Attachment 1 — Pesticide/PCB Congener Results**
- Attachment 2 — PAH and Bis(2-ethylhexyl)phthalate Results**
- Attachment 3 — Metal and AVS/SEM Results**
- Attachment 4 — Post-third Party Validated Dioxin/Furan and Dioxin-like PCB Congener Results**
- Attachment 5 — Grain Size, Specific Gravity and TOC Results**
- Attachment 6 — Moisture Content Results**
- Attachment 7 — Chain of Custody Forms**
- Attachment 8 — Third Party Validation Reports**

Attachments 1 through 5 are organized as follows:

1. A QA/QC narrative, which includes a discussion of the QC results and a description of any MPC exceedances, including the impact, if any, they may have on the overall field sample data.
2. Summary report tables for all QC samples, presented on a concentration (blanks and laboratory triplicates), recovery (LCS, MS, MSD) and/or percent difference (SRM) basis.
3. Summary report tables for all authentic samples, presented on a dry weight or volume, concentration basis.

## 4.0 QC SUMMARY

Pesticide/PCB, PAH/phthalate, metals, AVS/SEM and TOC results were reviewed following an EPA Tier II-like validation. Grain size and specific gravity results were reviewed following an EPA Tier I-like validation. The results of all Quality Control (QC) samples and procedures were evaluated against established project specific MPCs (Battelle 2002b) and used to assess and qualify sample results. Detailed QA/QC narratives are included with the analytical data in Attachments 1 through 5, as described in Section 3.0. The results from the analysis of QC samples, with a few exceptions, met MPCs specified in the QAPP. Exceedences are flagged appropriately on the data tables.

### 4.1 Pesticides/PCBs

Laboratory control sample (LCS) and matrix spike/matrix spike duplicate (MS/MSD) recoveries in the sediment samples (Batch 02-463 and 02-464) exceeded the MPC for endosulfan II due to the target retaining (or breaking down) on the alumina cleanup column, however, endosulfan II has been historically undetected in LIS samples. Coincidentally, surrogate PCB 34 failed in the LCS/MS/MSD samples. It appeared that an interference peak, probably a result of breakdown of the endosulfan II, is eluting at the same time as PCB 34 on the GC column, causing the high recoveries of PCB 34. Recoveries of PCB112, as well as the alternate surrogate PCB104 met MPC in the LCS/MS/MSD samples.

The percent difference (PD) for selected compounds in the standard reference materials (SRM) prepared with both sediment batches exceeded the MPC. There have been repeated historical occurrences of these analytes failing criteria in this particular SRM, NIST1944. Coincidentally, surrogate PCB 104 failed in the SRM samples. The high recoveries of PCB 104 in both sediment batches have been attributed to matrix interference and were exclusive to the SRM sample. The other two surrogate recoveries in the SRM sample met MPC.

All other QCs associated with these two batches of sediment samples, and all QCs associated with the water samples were acceptable.

### 4.2 PAHs and Bis(2-ethylhexyl)phthalate

Bis(2-ethylhexyl)phthalate was detected at a low level (<RL) in the procedural blank (PB) samples of all three batches (two sediment batches and one water batch). Sample data have been "B" flagged in these cases where the sample concentration of bis(2-ethylhexyl)phthalate was less than five times the blank value.

The relative standard deviation (RSD) between PAHs/phthalate concentrations in the sediment triplicate samples exceeded the MPC for bis(2-ethylhexyl)phthalate for one of the two sediment batches prepared in the laboratory.

Surrogate recovery of naphthalene-d8 in sample V7205 and V7208 were just slightly under the PMC (36% and 39%, respectively). The exceedences may be related to the complexity of the sediment matrix as noted in the sample preparation record. The recovery was flagged with a "N" for naphthalene-d8, and recoveries of the other two PAH surrogates and all three PCB surrogates in these two samples met MPC.

All other QCs associated with the sediment and water samples were acceptable.

### **4.3 Metals**

The laboratory blanks exhibited low level contamination for Cr (sediment only), Ag and As (water only). Sample data (sediment and water) were evaluated against the blank action limits, and sample data were “B” flagged in those cases where the sample values were less than five times the blank values.

### **4.4 AVS/SEM**

The AVS sample analysis holding time was exceeded by one day for 10 of the sediment samples. It is unlikely that this exceedance (one-day beyond holding time) had any effect on the sample results, as the samples were extracted within the required holding time. Samples exceeding the analysis holding time were flagged with a “T.”

The precision between AVS triplicates slightly exceeded the MPC for one of the two AVS sample analyses in triplicate (31% and 25%). Note that achieving acceptable precision in lab replicates is difficult in AVS analysis because each time the sample container is opened to remove an aliquot of sediment for analysis, the sediment is exposed to air, which can potentially alter the sample.

### **4.5 Dioxins/Furans and Dioxin-like PCB Congeners**

A number of dioxins/furans and one to two of dioxin-like PCB congeners were detected in the procedural blanks at the levels below the RL. However, concentrations of sediment field samples were greater than five times the concentrations detected in the associated PB, suggesting that the impact on the data quality is minimum. All water sample concentrations of both dioxins/furans and dioxin-like PCB congeners that were within five times the blank concentration were flagged with a “B” to indicate possible bias due to the blank.

Matrix spike/matrix spike duplicate recoveries were low in both sediment batches for 1,2,3,4,6,7,8,9-Cl<sub>8</sub>-Dibenzo-p-dioxin (OCDD) and 1,2,3,4,6,7,8,9-Cl<sub>8</sub>-Dibenzofuran (OCDF). However, this effect was not seen in the blank spike sample in the same extraction batch, suggesting that the exceedances may be matrix related.

Because of the nature of the material (high background interference) SRM NIST 1944 recoveries were variable for dioxins/furans. SRM was re-extracted and re-analyzed, without improved results. In addition, these values are listed as reference values only, which may indicate that there is more variability associated with the values.

### **4.6 Grain Size, Specific Gravity and TOC**

All QA/QC results for grain size, specific gravity and TOC analyses were within control limits.

### **4.7 Moisture Content**

All QA/QC results (duplicate and triplicate samples) for percentage dry weight analyses were within control limits.

## **5.0 TIER III VALIDATION SUMMARY**

The report summarizing the results of full Tier III data validation performed on the dioxin/furan and dioxin-like PCB results for the two batches of sediment samples is provided in Attachment 7 of this report.

The data validation is based on QC criteria documented in the above listed methods; the *Quality Assurance Project Plan for Long Island Sound Dredged Material Disposal Site Evaluation Project, Tasks*

8 QAPP, Field Sampling, Chemical, Benthic, and Toxicity Testing, Battelle, August 2002; the U.S. EPA Region II Data Validation SOP for EPA Method 1613, Revision A, U.S. EPA, September 1999; and the U.S. EPA Region 10 SOP for the Validation of Method 1668, Toxic, Dioxin-like, PCB Data, U.S. EPA, December 1995.

### **5.1 Correctable Deficiencies**

For the PCB congener analysis, the results for the method blanks analyzed on August 20, 2002 and August 26, 2002 were switched. The laboratory resubmitted the forms and EDDs with the correct results reported for each blank. The laboratory qualifier flags were corrected by the reviewer.

Calculation errors were noted for several dioxin/furan compounds in both SDGs. The laboratory resubmitted the summary forms and EDDs with the corrected values.

No other correctable deficiencies were noted.

### **5.2 Non-Correctable Deficiencies**

Low levels of target compounds were present in all method blanks, for both the PCB congener and dioxin/furan analyses. The laboratory did not perform any additional corrective action. During validation, the data were evaluated as detailed in the data validation reports.

For the dioxin/furan analyses, several of the recovery values for the matrix spike/matrix spike duplicate (MS/MSD) compounds were outside the control limits specified in the QAPP. The outliers were flagged by the laboratory as required in the QAPP. During validation, the data were qualified as detailed in the data validation reports.

The dioxin laboratory control sample (LCS) recovery for 1,2,3,7,8,9-HxCDD in SDG 2H0070 was greater than the QAPP specified upper control limit. The outlier was flagged by the laboratory as required in the QAPP. During validation, the data were qualified as detailed in the data validation reports.

For the standard reference material (SRM) analysis performed with the PCB and dioxin/furan analyses, some concentrations were outside of the  $\pm 35\%$  (of the true value) control limit. The outliers were correctly flagged by the laboratory. No data were qualified as the MS/MSD and LCS recoveries were acceptable.

### **5.3 Comments**

No data were rejected. Overall, the data are useable for the intended purposes.

## **6.0 REFERENCES**

Battelle, 2002a. "Final Survey Report, Summer 2002 Sediment Sampling Survey Long Island Sound EIS Alternative Disposal Site Study". Prepared for the USACE NAE under contract DACW33-01-D-0004, Delivery Order No. 13. September 2002.

Battelle, 2002b. Quality Assurance Project Plan for Long Island Sound Dredged Material Disposal Site Evaluation Project, Tasks 8 QAPP, Field Sampling, Chemical, Benthic, and Toxicity Testing. Prepared under contract for U.S. Army Corps of Engineers North Atlantic Division, New England. Contract No. DACW33-01-D-0004, Delivery Order No. 13. August 5, 2002.