

**APPENDIX H-5A**

**Finfish—Fillet, Liver and Bone Analytical Results:  
Final Report**

**Prepared for**

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**August, 2002**



US ARMY CORPS  
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New England District

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\_\_\_\_\_ August 2002

## *Final Report*

# **Finfish – Fillet, Liver and Bone Analytical Results**

## **Long Island Sound Disposal Site Study**

**Final Report**  
**for**  
**Finfish Fillet, Liver and Bone Analytical Results**  
**Long Island Sound Disposal Site Study**

**Submitted to**  
**Department of the Army**  
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## 1.0 INTRODUCTION

The following validated data report is for Delivery Order 13, *Long Island Sound Disposal Site Study*. This report includes pesticide/PCB, PAH and Bis(2-ethylhexyl)phthalate, butyltins, metals, dioxin/furan, dioxin-like PCB congeners, radionuclide, percent dry weight and lipid content results for the finfish samples (fillet, liver and bone) analyzed in support of the Finfish Chemistry Testing (Task 3).

### 1.1 Background

To support the production of the Long Island Sound Environmental Impact Statement (LIS EIS), finfish were collected to assess the bioaccumulation of sediment contaminants in organisms that are exposed to the sediments of the disposal sites versus non-disposal areas. Finfish were collected from trawls grouped around seven sites in LIS (see Figure 1) in June and September of 2000. Collections were performed by ENSR of Acton, MA; details of the fish collection are provided in the "Finfish survey, June and September 2000" (ENSR 2000).

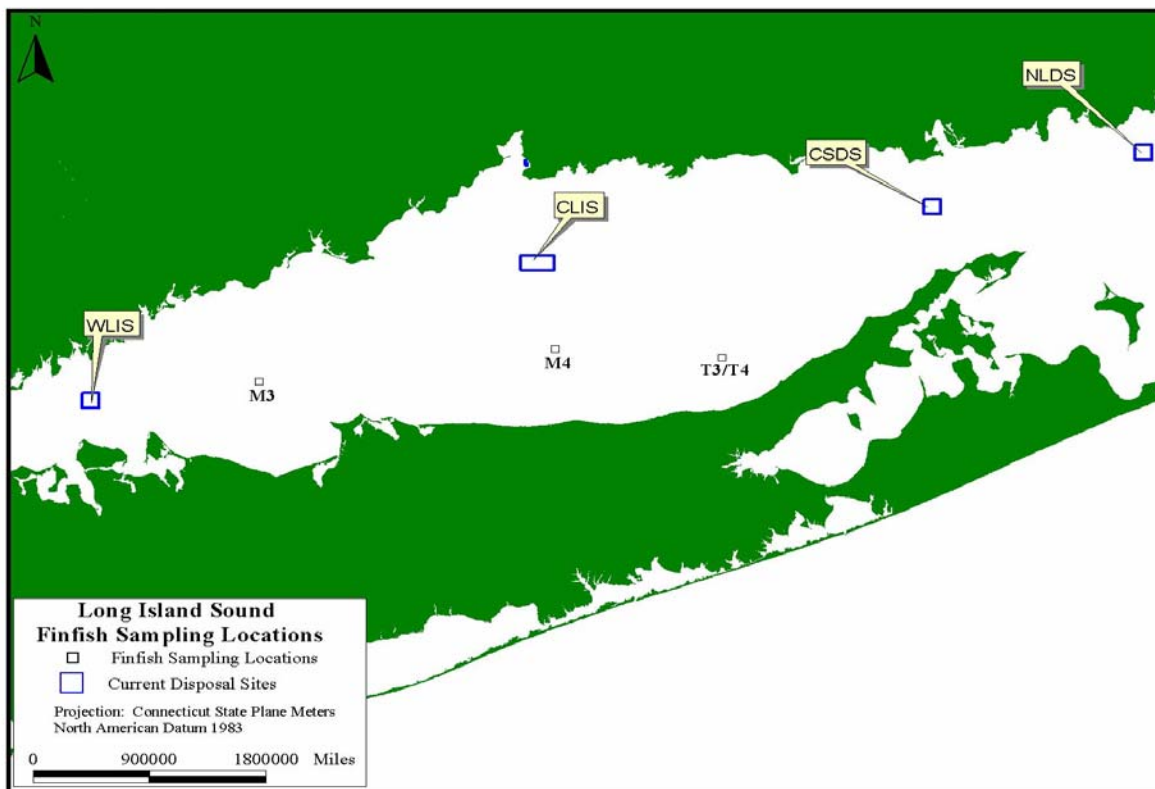
The objective of the sampling was to collect a representative sample of finfish tissue sufficient to conduct chemical analyses on tissue from the most common large demersal species available in June and September. In addition, four sites were sampled for a migratory top predator (striped bass and bluefish) to evaluate bioaccumulation within LIS as a whole. The rationale was to collect finfish that are at least temporarily resident or migrating past the general area of the site. Finfish target species were selected in accordance with project goals as detailed in a technical memorandum by Dr. Drew Cary, dated May 16, 2000. The species collected were: winter flounder (*Pseudopleuronectes americanus*), scup (*Stenotomus chrysops*), bluefish (*Pomatomus saltatrix*), striped bass (*Morone saxatilis*), windowpane flounder (*Scophthalmus aquosus*) and striped searobin (*Prionotus evolans*).

At least three individuals per species and up to 10 were collected to reach a target tissue weight of 1500 g. Samples were shipped daily to Aquatech Biological Sciences, Inc. in Burlington, VT. for processing. At the lab, winter flounder samples were filleted and livers removed. Bone and spleen samples were also removed and stored separately. Striped bass and bluefish were also filleted. Scup, windowpane flounder and striped searobin were frozen for potential future analyses. From fish that were filleted, a composite was formed with one fillet from each individual and the remaining fillet was frozen and archived.

All samples, fillet, liver, bone and whole fish, remained frozen at Aquatech until January 2002, when custody was transferred to Battelle. At that time the original compositing and analysis scheme was reviewed with EPA, Region I. Battelle was instructed to modify the original compositing scheme to include a number of additional composites and some composites previously made were precluded from analysis. The final compositing plans for both June and September fish are included in Attachment 10 to this report.

### 1.2 Summary of Sample Processing and Analyses

All finfish samples were received at Battelle in good condition. Samples were stored frozen (at, or below -20°C) until processing. Finfish samples originally targeted for chemical analyses were already composited and stored in separate glass jars with the exception of scup, which were received whole (though fish targeted to be composited were placed in the same ziplock bag). Winter flounder carcasses (minus fillets) were received bagged by composite. Some additional winter flounder samples received as whole archived samples, subsequently were filleted at Battelle upon instruction from EPA to create additional composites. Scup were also filleted and composited based initially on the original ENSR compositing plan and subsequently, additional composites were made based on instructions from EPA. Fillet and liver composites selected for chemical analyses were homogenized at Battelle (Duxbury) using titanium



**Figure 1. Finfish Sampling Locations.**

instrumentation to allow for splits for metals analyses. Aliquots for the various analyses were removed, placed in appropriate jars, and forwarded to the specified laboratories for analyses.

Table 1 lists the laboratories that performed sample analyses. Tables 2, 3 and 4 summarize the analytical tasks performed on each sample of fillet, liver and bone, respectively. All samples were not tested for all analytical parameters.

**Table 1. Summary of Analytical Labs.**

Analysis Parameters	Laboratory	Third Party Validator
Pesticides/PCB	Battelle, Duxbury, MA	NA
PAH & Bis(2-ethylhexyl)phthalate	Battelle, Duxbury, MA	NA
Butyltins	Battelle, Duxbury, MA	NA
Metals	Battelle, Sequim, WA	NA
Dioxin/Furan, Dioxin-like PCB congeners	PSC Analytical Services, Ontario, Canada	Ecochem, Inc., Seattle WA. (1)
Radionuclide	STL St. Louis, Earth City, MO	NA
Percent Dry Weight & Lipids	Battelle, Duxbury, MA	NA

NA indicates Not Applicable

(1) Only one batch per matrix was sent to Ecochem for Tier III level validation.


Table 2. Finfish Fillet Summary Of Analyses.

Sample ID	Study Area	Station	Species	PCB Aroclor, Pest, PAH, % Dry Weight	Butyltins	Metal	Dioxin/furan and Dioxin like PCBs	Radionuclide	Lipid
LIS02WL000F3C1	WLIS	59-07	Striped Bass	X		X	X		X
LIS02WL808F2C1		58-08	Scup	X		X	X		X
LIS02WL805F1C1		58-05	Winter Flounder	X	X	X	X	X	X
LIS02CL722F1C1	CLIS	07-22	Winter Flounder	X	X	X	X	X	X
LIS02CL722F2C1			Scup	X		X	X		X
LIS02CL024F3C1		10-24	Striped Bass	X		X	X		X
LIS02CS831F1C1	CSDS	8-31	Winter Flounder	X	X	X	X	X	X
LIS02CS831F2C1			Scup	X		X	X		X
LIS02NL740F1C1	NLDS	17-40	Winter Flounder	X	X	X	X	X	X
LIS02NLTD2F3C1		TD2	Striped Bass	X		X	X		X
LIS02M4220F1C1	Strata M4	02-20	Winter Flounder	X	X	X	X	X	X
LIS02M4322F1C1		03-22	Winter Flounder	X		X	X		X
LIS020M4223F2C1 + LIS02M4322F2C1		02-23 + 03-22	Scup	X		X	X		X
LIS02M3212F1C1	Strata M3	02-12	Winter Flounder	X	X	X	X	X	X
LIS02M3212F2C1			Scup	X		X	X		X
LIS02T4125F1C1	Strata T4/T3	1-25	Winter Flounder	X	X	X	X	X	X
LIS02T4125F2C1			Scup	X		X	X		X
LIS07WL907F2C1	WLIS	59-07	Scup	X		X	X		X
LIS07WL0505F1C1 + LIS07WL008F1C1		55-05 + 00-08	Winter Flounder	X	X	X	X	X	X
LIS07CL920F1C1		CLIS	9-20	Winter Flounder	X	X	X	X	X
LIS07CL920F2C1	Scup			X		X	X		X
LIS07CL124F6C1	11-24		Bluefish	X		X	X		X
LIS07CS730F2C1	CSDS	7-30	Scup	X		X	X		X
LIS07NL740F1C1 + LIS07NL740F1C2	NLDS	17-40	Winter Flounder	X	X	X	X	X	X
LIS07NL740F2C1			Scup	X		X	X		X
LIS07M4522F1C1	Strata M4	5-22	Winter Flounder	X	X	X	X	X	X
LIS07M4522F2C1			Scup	X		X	X		X

**Table 2. Finfish Fillet Summary Of Analyses (continued).**

Sample ID	Study Area	Station	Species	PCB Aroclor, Pest, PAH, % Dry Weight	Butyltins	Metal	Dioxin/furan and Dioxin like PCBs	Radionuclide	Lipid
LIS07M3212F1C1	Strata M3	2-12	Winter Flounder	X	X	X	X	X	X
LIS07M3212F6C1	Strata M3	2-12	Bluefish	X		X	X		X
LIS07M3212F2C1	Scup		X		X	X		X	
LIS07T4724F1C1	Strata T4/T3	7-24	Winter Flounder	X	X	X	X	X	X
LIS07T4724F2C1			Scup	X		X	X		X
LIS07T4725F1C1	Strata T4/T3	7-25	Winter Flounder	X	X	X	X	X	X
LIS07T4725F2C1			Scup	X		X	X		X


X Indicates analysis performed

 Indicates analysis not performed

**Table 3. Winter Flounder Liver Summary Of Analyses.**

Sample ID	Study Area	Station	PCB Aroclor, Pest, PAH, % Dry Weight	Butyltins	Metal	Dioxin/furan and Dioxin like PCBs	Radionuclide	Lipids
LIS02CL722F1C1	CLIS	07-22	X		X	X		
LIS07CL920F1C1		9-20	X		X			X
LIS02CS831F1C1	CSDS	8-31	X		X	X		X
LIS02NL740F1C1	NLDS	17-40	X		X	X		X
LIS07NL740F1C1 + LIS07NL740F1C2			X		X	X		X
LIS02M3212F1C1			Strata M3	02-12	X		X	X
LIS07M3212F1C1	Strata M3	02-12	X		X			X
LIS02M4220F1C1	Strata M4	02-20	X		X	X		X
LIS02M4322F1C1		03-22	X		X	X		X
LIS07M4522F1C1		5-22	X		X			X
LIS02T4125F1C1	Strata T4/T3	1-25	X		X	X		X
LIS07T4724F1C1		7-24	X		X			
LIS07T4725F1C1		7-25	X		X			
LIS02WL805F1C1	WLIS	58-05	X		X			
LIS07WL505F1C1 + LIS07WL008F1C1		55-05 + 00-08	X		X			

X Indicates analysis performed

 Indicates analysis not performed

**Table 4. Winter Flounder Summary Of Bone Analyses.**

Sample ID	Study Area	Station	Radionuclide Sr-90
LI02WL0805F1C1	WLIS	58-05	X
LIS02CL722F1C1	CLIS	07-22	X
LIS03CS831F1C1	CSDS	8-31	X
LIS02NL740F1C1	NLDS	17-40	X
LIS02M4220F1C1	Strata M4	02-20	X
LIS02M3212F1C1	Strata M3	02-12	X
LIS02T4125F1C1	Strata T4/T3	1-25	X

X Indicates analysis performed

### 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 2002). The dioxin/furan and dioxin-like PCB congener fillet and liver data were submitted to Ecochem Inc, of Seattle, WA for third party validation (Tier III). The validation report is included as Attachment 8 of this report.

## 2.0 METHODS

Chemical analysis of finfish samples for pesticide/PCB, PAH, Bis(2-ethylhexyl)phthalate, butyltin, metal, dioxin/furan and dioxin-like PCB congener, radionuclide, percent dry weight and lipid were conducted following methods and SOPs as described in *Quality Assurance Project Plan : Long Island Sound Study* (January, 2002). Due to limited liver tissue mass not all liver samples were analyzed for all parameters (see Table 3). Detection limits for some parameters in liver samples were elevated, also due to limited tissue mass. Exceptions and unusual circumstances have been documented and are noted.

### 2.1 Pesticide/PCB

Tissue samples were extracted for Pesticide/PCB analysis following general NS&T methodologies. Briefly, tissue samples were homogenized and approximately 30 g of fillet, or 5 g of liver tissue was extracted three times with dichloromethane using maceration techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and quantitatively split for further cleanup by GPC HPLC. The post-HPLC extract was concentrated, fortified with recovery internal standards (RIS) and split qualitatively for Pesticide/PCB and PAH 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 on a wet-weight concentration basis.

### 2.2 PAH and Bis(2-ethylhexyl)phthalate

Tissue samples were extracted for PAHs and Bis(2-ethylhexyl)phthalate following general NS&T methodologies, as described in Section 2.1. 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 on a wet-weight concentration basis.

Note that the pre-HPLC extracts were analyzed separately for Bis(2-ethylhexyl)phthalate due to potential loss of this compound to the HPLC column, and data were incorporated into the final reports.

### 2.3 Butyltins

Approximately 20 to 25 g of fish fillet tissue was spiked with a Surrogate Internal Standard (SIS: triphenyltin (TPET)) to monitor laboratory efficiency and extracted with hexane and the chelating agent tropolone. Following extraction, the cationic butyltin compounds were converted to nonpolar *n*-hexyl derivatives with commercially available *n*-hexylmagnesium bromide via a Grignard reaction. The extract was cleaned up through a Silica/Florisil gel liquid chromatography column. The butyltins were collected in a conventional hexane eluate from the Silica/Florisil column. The extracts were analyzed by gas chromatography with flame photometric detection (GC/FPD) using a tin-specific photometric filter.

Sample data were quantified by the method of internal standards, using the SIS compounds thereby correcting for sample loss during extraction and cleanup. All peaks were manually integrated due to the extreme fluctuations in baseline noise associated with this analysis. Sample data were reported on a wet-weight concentration basis.

### 2.4 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). To prepare the tissues for analysis, they were freeze-dried then blended in a Spex mixer-mill. Sample percent moisture/dry weight was determined according to Battelle SOP MSL-C-003. Tissue samples were digested using aqua regia according to Battelle SOP MSL-I-024, *Mixed Acid Tissue 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 tissue 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, Se 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*. This procedure is based on two methods modified and adapted for analysis of solid sample digestates: EPA Method 1693, *Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry* and EPA Method 1640, *Determination of Trace Elements in Water by Preconcentration and Inductively Coupled Plasma-Mass Spectrometry*. Cr was analyzed separately by ICP-MS using the method of standard additions (MSA), which is used in samples when interference is suspected. Carbon typically causes interference in Cr analysis of tissue samples. The procedure involves taking two aliquots of each sample, adding a known, low concentration of standard to one, and a volume of acid blank equal to the standard addition to the second. The sample concentration is calculated using the differences in intensities between the fortified and unfortified samples.

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*.

Sample results were reported on a dry-weight basis and converted to a wet-weight basis using the percent dry weight of each sample. QC results were evaluated on a dry-weight basis. The results were not blank corrected for any of the metals.

## 2.5 Dioxin/Furan and Dioxin-like PCB Congeners

Fish fillet and liver extracts were cleaned, and analyzed for the seventeen 2,3,7,8 – substituted PCDD/PCDF following the general procedures in EPA Method 1613, Revision B, as described in PSC Analytical Services SOP ORG-310. Fish fillet and liver 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 2mL for analysis. Final volume for injection was 20uL. 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 on a wet-weight concentration basis.

## 2.6 Radionuclides

### 2.6.1 $^{60}\text{Co}$ and $^{137}\text{Cs}$

Severn Trent Laboratory analyzed a subset of fish fillet samples for radiochemical parameters following STL SOP's STL-RC-0025, STL-RC-5016, and STL-RD-0101. Finfish fillet samples were placed in either a 25 mL or 100 mL counting geometry.

### 2.6.2 Isotopic U

A subset of fish fillet samples was analyzed for isotopic uranium following, SOPs STL-RC-5016, STL-RC-0238, and STL-RC-0100 for sample preparation and SOP STL-RD-0201 for the analysis. The appropriate aliquot of fish tissue was placed in a quartz crucible and U-232 tracer, used as a yield monitor, was added to the sample. The crucible was placed on a hotplate at low heat to dry. The crucible containing the dry sample was placed in a muffle furnace and burned in a controlled fashion. The temperature was increased to 150°C and held at this temperature for 1 hour. The temperature was then ramped at the rate of 1°C/minute to 575°C. The sample was kept at this temperature for 7.5 hours. After cooling, 3M nitric acid + 1M Al(NO<sub>3</sub>)<sub>3</sub> was added to the crucible and refluxed on a hotplate at low temperatures. This solution was taken through the separation procedure.

### 2.6.3 <sup>90</sup>Sr

Bone samples were analyzed for <sup>90</sup>Sr following SOPs STL-RC-00050, STL-RC-5016, and SL 13021.

## 2.7 Lipids

Percent total lipids found in fish fillet and liver samples were determined using a procedure based on the original Bligh and Dyer method for extracting lipids, Battelle Duxbury SOP 5-299. Modifications included using a much smaller sample aliquot (<10 grams wet) and using centrifugation rather than filtering to separate and isolate the appropriate solvent layers. Lipids are extracted using specific ratios of sample moisture: chloroform: methanol. The method is described in Battelle SOP 5-299 *Determination of Tissue Lipid Concentration Using the Modified Bligh and Dyer Method*. Sample results were reported on a percent wet-weight basis.

## 2.8 Percent Dry Weight

Percent dry weight was determined in conjunction with the Pest/PCB and PAH/Bis(2-ethylhexyl)phthalate sample extraction procedure (SOP 5-190). Briefly, 1 to 5-g of well-mixed tissue homogenate 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 percent dry weight determined as defined in Section 4.0 of the SOP.

## 3.0 RESULTS

This data report is organized in 11 sections as follows:

- Attachment 1—Pesticide/PCB Congener Results**
- Attachment 2—PAH and Bis(2-ethylhexyl)phthalate Results**
- Attachment 3—Butyltin Results**
- Attachment 4—Metal Results**
- Attachment 5—Dioxin/Furan and Dioxin-like PCB Congener Results**
- Attachment 6—Radionuclide Results**
- Attachment 7—Lipid and Percent Dry Weight Results**
- Attachment 8—Third Party Validation Report**
- Attachment 9—Chain of Custody**
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Attachments 1 through 7 of this document 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 wet weight, concentration basis.

## 4.0 QC SUMMARY

All results were reviewed following an EPA Tier II-like validation. The results of all Quality Control (QC) samples and procedures were evaluated against established project specific MPCs (Battelle 2002) and used to assess and qualify sample results. Detailed QA/QC narratives are included with the analytical data in Attachments 1 through 7, as described above. However, because of the intended use and interpretation of the data, some qualifiers were changed from what was originally stated in the QAPP. Specifically, a "B" qualifier now only pertains to blank concentrations that are greater than the reporting limit and a "U" qualifier is for data detected at or below the sample specific MDL or sample concentrations that are within five times detected blank concentrations. The results from the analysis of QC samples, with few exceptions, met MPCs specified in the QAPP. Exceedences are flagged appropriately on the data tables. Of particular note:

### 4.1 Pesticide/PCB

Matrix spike/matrix spike duplicate recoveries exceeded the MPC in some cases due to high native concentrations, however, in fillet batch 02-142 and liver batch 02-145, the original MS/MSD recoveries were very high. It appeared that the native sample recorded as the sample used to prepare the MS/MSD (e.g., background sample spiked with target compounds) might have been incorrect. The native sample and associated MS/MSD for fillet batch 02-142 was re-extracted in batch 02-203 and MS/MSD recoveries in this batch were acceptable. No liver sample from batch 02-145 was available for re-extraction; however, all other QC associated with this batch was acceptable.

The relative standard deviation (RSD) between pesticide/PCB concentrations in the liver triplicate samples exceeded the MPC for many compounds. Pesticide/PCB concentrations for replicates #2 and #3 agreed well, but were very different from replicate #1 values, suggesting that either the sample was not homogenous or, more likely, replicate #1 was mislabeled in the laboratory. No liver tissue material was available for re-extraction and as a result no further corrective action could be taken.

Surrogate PCB 112 recoveries were compromised in fillet batch 02-142 due to matrix interference; therefore alternate surrogate PCB 34 was reported with this batch with acceptable recovery for all but one sample.

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

Fillet samples, prepared in batch 02-142, were re-extracted and re-analyzed (in batch 02-203) due to high concentrations of a number of PAH compounds in the procedural blank (especially the naphthalenes). With three exceptions, results for all fillet samples were reported from the re-extract analysis (batch 02-203). Exceptions included:

- Initial extraction results were reported for fillet samples LIS02M3212F1C1 (Battelle ID V0767) and LIS02WL805F1C1 (Battelle ID V0776), as insufficient tissue material was available for re-extraction;
- Initial extraction results for Benzo(g,h,i)perylene were reported for all samples (batch 02-142) due to a loss of this compound on the HPLC clean-up column used for the re-extracts.
- Initial extraction results for Bis(2-ethylhexyl)phthalate were reported for all samples (batch 02-142). QA/QC results are reported from both the original and the re-extract batches.

Concentrations of PAHs and phthalate in the re-extracted blanks were low.

Note that two laboratory blanks were reported with batch 02-203. One sample extract from this batch was lost during preparation and the sample was re-extracted along with a second laboratory blank.

### 4.3 Butyltins

TBT was detected in the method blank at 2.81 : g/kg-wet weight. While this value is below the method reporting limit (RL), all sample results, except for LIS02M3212F1C1 (V0767TBT) were  $\leq 5$  times this value and may be biased due to background contamination. All sample results were flagged with a "U" to indicate this potential bias. Low levels of TBT are often found in the method blank due to contamination both from ambient sources of TBT and from small quantities present in one of the reagents used in the derivitization step of the method.

### 4.4 Metals

Cu, Ni, Se, and Zn were detected in at least one of the method blanks associated with the fish fillet samples, however; only Cu, Se and Zn were detected at levels near or above the RL. All data were flagged "U" that were  $\leq 5$  times the blank concentrations. Zn, As and Cd were detected above the RL in the method blank associated with the liver samples. Ag, Pb, Hg and Cu were also detected in the blank associated with the liver samples; however, blank concentrations were below the RL. Most sample concentrations were well above 5 times the blank concentration, with the exception of Cu, Ni and Se for the fillet samples and Cd and Pb for the livers. Remaining QA/QC results for both fillet and liver samples were acceptable.

### 4.5 Dioxin/Furan and Dioxin-like PCB Congener

A number of dioxin-like PCB congeners and dioxin/furans were detected in the procedural blanks, however in most cases concentrations were below the RL. This blank contamination was a result of running the procedural blanks immediately after the ongoing precision and recovery (OPR) standard. All blanks (for both dioxin/furan and dioxin-like PCB congeners) were re-analyzed with a solvent blank run prior to the procedural blanks along with two representative samples from each batch, to ensure carryover was only an issue associated with the blanks. The result for field samples remained essentially the same while blank results were much improved. Target analyte concentrations for all PCB blank re-runs were lower, in some cases by an order of magnitude. As a result of the re-analysis, the original data reported for the procedural blanks was qualified with an "R" to indicate the data has been rejected and the new blank data has been reported. Sample data was re-evaluated against the new procedural blank data and reported in the data tables. All sample concentrations of both dioxin/furans and dioxin-like PCB congeners that were within five times the blank concentration (using the EPA Region II Tier III validation action levels) were flagged with a "U" to indicate possible bias due to the blank.

The SRM (EDF 2525) analyzed with these samples is a highly contaminated natural fish matrix with relatively low levels of dioxin/furans and dioxin-like PCBs. Because of the nature of the material (high background contamination) SRM recoveries were variable for both dioxin/furans and one dioxin-like PCB congener. All dioxin/furan target analytes are certified in SRM 2525; however, they are certified at relatively low levels, many below the RL, resulting in percent differences (PDs) greater than 30% from the certified value. Only five of the dioxin-like PCBs are certified, one of which (PCB 169) is just above the RL. The SRM MDL for 1,2,3,4,7,8-HxDF was elevated due to interference caused by coelution with diphenyl ether. PCB 169 and 1,2,3,4,7,8,9-heptafuran in the SRM are routinely recovered above certified values. The lab had made effort to remove the matrix interference, without success. Another SRM, EDF 2526, a fortified clean natural fish matrix, with more attainable target levels, has been analyzed with much better results.

#### 4.6 Radionuclides

All QA/QC results for radionuclide analyses were within control limits.

#### 4.7 Lipids

For fish fillets, two pairs of duplicates (rather than triplicates) were prepared with batch 02-181. The relative percent difference (RPD) between lipid concentrations in the two laboratory duplicates was 33% and 21%. A third batch of fillet samples was prepared in the laboratory that consisted of two fillet samples each extracted in triplicate. The RSD between lipid concentrations in the two sample triplicates was 6.5% and 1.4%.

For fish livers, one sample triplicate was prepared with the samples and the RSD between lipid concentrations (5.1%) of was well within the precision MPC.

No SRM is available for lipids and no certified spike standard is available for measurement of accuracy.

### 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 one batch of fish fillet and the single batch of liver samples is provided in Attachment 8 of this report. The data validation is based on QC criteria documented in the above listed methods; the *Quality Assurance Project Plan: Long Island Sound Study, Task I QAPP (Final)*, Battelle, January 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

**Fillet** - Minor calculation errors were noted for the PCB MS/MSD RPD values (results were calculated using the recovery values rather than the actual concentrations). Since the errors did not significantly impact the reported results, no further action was taken.

**Livers** - Minor calculation errors were noted for the PCB MS/MSD RPD values (results were calculated using the recovery values rather than the actual concentrations). Since the errors did not significantly impact the reported results, no further action was taken.

No other correctable deficiencies were noted.

#### 5.2 Non-Correctable Deficiencies

**Fillet** - Low levels of target compounds were present in all method blanks, for both the dioxin-like PCB congener and dioxin/furan analyses. All concentrations were also less than the PQL, so no additional corrective action was required. For both the dioxin and dioxin-like PCB analyses, several of the recovery values for the labeled compounds were outside the control limits specified in the QAPP. For the dioxin-like PCB congener analysis, several recovery and RPD values were outside the control limits for the MS/MSD analysis. For the SRM prepared with the dioxin/furan analysis, one concentration was outside than the  $\pm 35\%$  (of the true value) control limit. The outliers described were correctly flagged by the laboratory as required in the QAPP. No data were qualified as the MS/MSD and LCS recoveries were acceptable. During validation, the data were qualified as detailed in the data validation reports.

**Liver** - Low levels of target compounds were present in all method blanks, for both the dioxin-like PCB congener and dioxin/furan analyses. Two dioxin-like PCB congener concentrations were also greater than the PQL. The laboratory did not perform any additional corrective action. For both the dioxin and dioxin-like PCB analyses, several of the recovery values for the labeled compounds were outside the control limits specified in the QAPP. For the dioxin-like PCB congener analysis, two recovery values were less than the lower control limits for the MS/MSD analysis. For the triplicate analyses performed with the dioxin/furan analyses, one %RSD value was greater than the 25% upper control limit (at 27%). All outliers described here were correctly flagged by the laboratory. During validation, the data were qualified as detailed in the data validation reports.

### **5.3 Comments**

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

## **6.0 REFERENCES**

Battelle, 2002. Tasks 1 Quality Assurance Project Plan for Long Island Sound Disposal Site Study. 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. January 11, 2002.

ENSR, 2000. "Finfish Survey, June and September 2000, Summary Report". Prepared for the USACE NAE under contract DACW33-96-D-004. ENSR Document No. LIS-2000-F06-F, TC. December 2000.