Combined Work/Quality Assurance Project Plan (CWQAPP)

for

Sediment Chemistry Analyses for Harbor and Outfall Monitoring

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for
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1.0 PROJECT MANAGEMENT

1.1 Project Organization

Figure 1 presents the project management structure for sediment chemistry analyses by the MWRA Department of Laboratory Services (DLS) for outfall monitoring. This project is part of the Harbor and Outfall Monitoring (HOM) project of the MWRA Environmental Quality Department (ENQUAD). It includes onshore sample handling, sample analysis, and data loading for the sediment chemistry analyses that are part of the benthic study in the MWRA's outfall ambient monitoring program (bay soft-bottom monitoring study, or BMBSOFT) and harbor monitoring program (harbor soft-bottom monitoring program, or BHSOFT.)

ENQUAD Mr. Kenneth Keay is the Deputy Outfall Monitoring Program Manager for ENQUAD and is also primarily responsible for benthic/sediment studies within that program. He is responsible for general coordination of monitoring activities and for reviewing monitoring data before it is loaded into the EM & MS database. His responsibility is also to ensure that the data collected as part of the monitoring project satisfies the quality objectives set forth in this CWQAPP. Ms. Wendy Leo leads the data management group and serves as ENQUAD's Quality Assurance Manager. She is responsible for assigning staff to transfer data from the DLS Laboratory Information Management System (LIMS) into the ENQUAD environmental monitoring and management database (EM&MS) and transmitting them to Battelle. Dr. Douglas Hersh is ENQUAD's Database Administrator for the EM&MS database. Dr. Andrea Rex is the Director of the Environmental Quality Department.

DLS Mr. Yong Lao is the Laboratory's Project Manager and is DLS' primary point of contact for this project. Mr. Steve Rhode is the Section Manager responsible for client services and the Violet Team. Ms. Polina Epelman is the Section Manager responsible for the Red, Orange, and Green Teams. Mr. Edward Caruso is Acting Supervisor of the Violet team, responsible for sample management. Ms. Nancy McSweeney is the Supervisor of the Red Team, responsible for solids analyses. Ms. Patricia Sullivan is the Supervisor of the Orange Team, responsible for metals and Total Organic Carbon (TOC) analyses. Mr. Mark Lambert is the Supervisor of the Green Team, responsible for organics analyses. Dr. William Andruchow is the Quality Assurance Manager for Laboratory Services and is responsible for overseeing the QA/QC and Supervising the Yellow Team. Ms. Jennifer Prasse is the QA Coordinator and is responsible for the laboratory's Proficiency Testing programs and laboratory oversight/audit programs. Dr. Michael Delaney is the Director of Laboratory Services. The DLS reporting relationships and functional responsibilities are shown in Table 1.

Table 1. DLS Reporting Relationships

<table>
<tr><td colspan="5">Michael Delaney, Director of Laboratory Services</td></tr>
<tr><td colspan="3">Polina Epelman, Lab Manager
(Operations)</td><td>Steve Rhode, Lab Manager
(Client Services)</td><td>William Andruchow, Lab Manager
(Quality Assurance)</td></tr>
<tr><td rowspan="2">Nancy McSweeney, Supervisor, Red Team</td><td rowspan="2">Patricia Sullivan, Supervisor, Orange Team</td><td rowspan="2">Mark Lambert, Supervisor, Green Team</td><td>Yong Lao, Project Manager (Client Services)</td><td rowspan="2">Jennifer Prasse QA Coordinator</td></tr>
<tr><td>Edward Caruso Acting Supervisor, Violet Team</td></tr>
<tr><td>Total Solids</td><td>Metals, TOC</td><td>Organic Contaminants</td><td>Sample Management</td><td>Performance Testing, Oversight and Document Control</td></tr>
</table>

Battelle Ocean Sciences (BOS) Ms. Ellen Baptiste-Carpenter is the HOM project manager for BOS, and also leads the BOS data management group. She is responsible for the overall performance of the HOM project. Dr. Carlton Hunt is the Battelle Technical Director and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise. The Battelle Quality Assurance Officer for the project is Ms. Rosanna Buhl. For this task, Ms. Buhl is responsible for reviewing data submitted by ENQUAD and QA Statements submitted by DLS for completeness and adherence to the Benthic CWQAPP (Williams *et al.* 2002, 2004 in prep.) Ms. Deirdre Dahlen is the consultant team's Laboratory Manager for the HOM program, responsible for overseeing all HOM laboratory activities.

The key contacts at each of the organizations are shown in Figure 1. Addresses, telephone (and fax) numbers, and Internet addresses are given in Table 2.

Figure 1 Organizational Chart for Metals, Organic, TOC, and Solids for the Outfall Monitoring Program

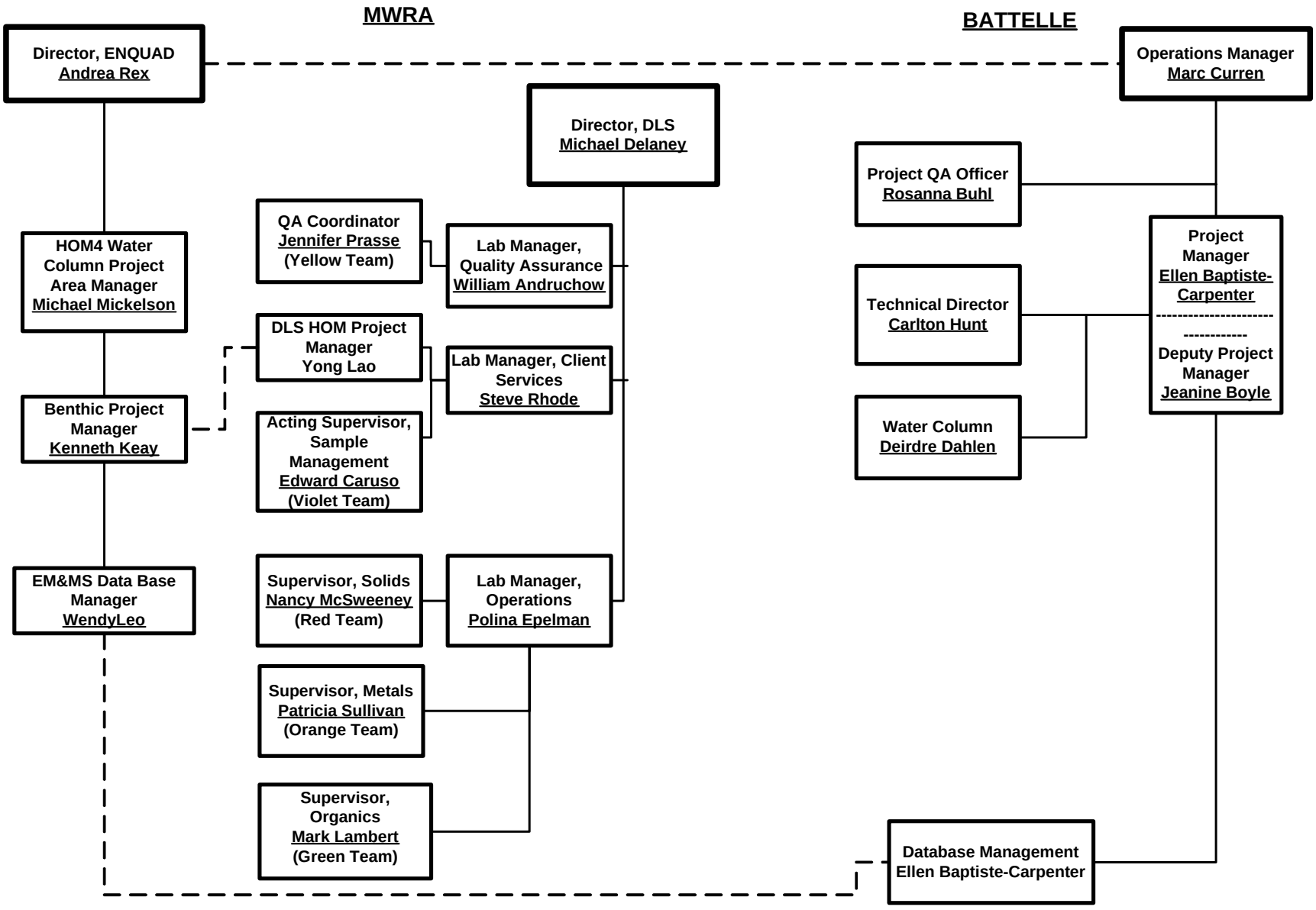

Table 2.		**Contact Information**		
Name	Title/Role	Location	email	Phone
William Andruchow	Laboratory QA Manager (Yellow)	DLS[1]	william.andruchow[at]mwra.state.ma.us	617-660-7804
Edward Caruso	Acting Supervisor (Violet)	DLS	edward.caruso[at]mwra.state.ma.us	617-660-7807
Ellen Baptiste-Carpenter	HOM4 Project Manager	BOS[2]	baptiste[at]battelle.org	781-952-5361
Deirdre Dahlen	HOM Laboratory Manager	BOS	dahlend[at]battelle.org	781-952-5253
Mike Delaney	Laboratory Director	DLS	mike.delaney[at]mwra.state.ma.us	617-660-7801
Matt Fitzpatrick	Field Sample Custodian	BOS	fitzpatrickm[at]battelle.org	781-952-5351
Polina Epelman	Laboratory Manager (Red, Orange, Green)	DLS	polina.epelman[at]mwra.state.ma.us	617-660-7802
Chris Gagnon	Field Manager	BOS	gagnonc[at]battelle.org	781-934-0571
Doug Hersh	EM&MS Database Administrator	ENQUAD[3]	douglas.hersh[at]mwra.state.ma.us	617-788-4738
Kenneth Keay	Program Manager ENQUAD/Operations	ENQUAD	kenneth.keay[at]mwra.state.ma.us	617-788-4742
Mark Lambert	Team Supervisor (Green)	DLS	mark.lambert[at]mwra.state.ma.us	617-660-7817
Yong Lao	Project Manager	DLS	yong.lao[at]mwra.state.ma.us	617-660-7841
Wendy Leo	EM&MS Manager	ENQUAD	wendy.leo[at]mwra.state.ma.us	617-788-4743
Nancy McSweeney	Team Supervisor (Red)	DLS	nancy.mcsweeney[at]mwra.state.ma.us	617-660-7846
Jennifer Prasse	QA Coordinator (Yellow)	DLS	jprasse[at]mwra.state.ma.us	617-660-7808
Steve Rhode	Laboratory Manager (Violet)	DLS	steve.rhode[at]mwra.state.ma.us	617-660-7803
Pat Sullivan	Team Supervisor (Orange)	DLS	patricia.sullivan[at]mwra.state.ma.us	617-660-7838

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1.2 Communication Plan

Mr. Kenneth Keay is the primary contact with the monitoring prime consultant Battelle and benthic studies sub-consultant ENSR Consulting and Engineering (ENSR) on technical issues. Mr. Steve Rhode is DLS' primary contact with ENQUAD. Communication between DLS and Battelle/ENSR staff at all levels of the team is encouraged and it is important to keep ENQUAD informed (Table 3).

Mr. Steve Rhode attends HOM project meetings, held quarterly at Battelle in Duxbury (March, June, September, and December) and in other months at MWRA in the Charlestown Navy Yard. Generally these meetings are held on the last Wednesday morning of the month. DLS holds an

Table 3.	**Email cc: List**
If the subject is...	*Copy the email to...*
Any	**Kenneth Keay, Steve Rhode, Yong Lao**
transfer of samples	Matt Fitzpatrick, Edward Caruso (Violet)
data interpretation	Kenneth Keay, Deirdre Dahlen
laboratory technical issues	Relevant DLS Team Manager(s): ▪ M. Lambert (Green-organics) ▪ P. Sullivan (Orange-metals, TOC) ▪ N. McSweeney (Red- solids) Polina Epelman, Steve Rhode Deirdre Dahlen (issues affecting data interpretation or data quality)
data management/database	Wendy Leo
cost/schedule	Kenneth Keay, Mike Delaney Ellen Baptiste-Carpenter (issues affecting cost/schedule of Battelle contract)
quality assurance	Bill Andruchow, Wendy Leo Rosanna Buhl (issues affecting data quality not resolved internal to DLS)

internal weekly scheduling and coordination meeting on Tuesdays, which are attended by the DLS Lab Managers and Supervisors.

Email is the primary day-to-day communication method.

The individuals listed in Table 3 take responsibility for forwarding the email to any other relevant staff not on the cc: list. Emails between MWRA and Battelle should also be copied to the HOM4 archive HOM4@battelle.org.

If time is of the essence or if emails fail to produce a response, a telephone call is appropriate. Conversations/contacts affecting scope, schedule, or significant technical issues should be documented in email or memoranda summarizing key items discussed, decisions made, and any actions to be taken.

If expected samples are missing, Mr. Edward Caruso immediately notifies the Battelle Field Manager, Mr. Chris Gagnon and the Battelle Field Sample Custodian, Mr. Matt Fitzpatrick as well as Mr. Steve Rhode, and Mr. Kenneth Keay.

Changes to the number of planned samples should be communicated to the Violet Team, Mr. Steve Rhode, and Mr. Kenneth Keay in advance. It may occur that unusual environmental conditions lead to a decision during field sampling to collect extra samples. In this case, the field team should notify the Violet Team before delivering the samples if possible. If this is not

possible, the fact that there are extra samples should be clearly indicated on the chain-of-custody forms to avoid sample mix-ups.

DLS staff usual work hours are 7 am – 3 pm.

Plans for sample custody and transfer are described in Section 2.3.

1.3 Project Background

The background of the HOM project can be found in the HOM Project Management Plan (Battelle, 2002), and more comprehensive background for the benthic monitoring in the CWQAPP for Benthic Monitoring (Williams *et al.* 2002, Williams *et al.* 2004 in prep.)

From 1992-2003 the sediment chemistry analyses were conducted by subcontractor laboratories to the HOM consultant (currently, Battelle Ocean Sciences and ENSR). This CWQAPP reflects a change in analytical laboratories and describes the quality system implemented for analytical procedures that are performed for the HOM project by the MWRA DLS.

1.4 Project Description and Schedule

Harbor and Outfall Monitoring (HOM) Project benthic surveys have been conducted since 1991 and are scheduled to continue through 2005. The benthic CWQAPP (Williams *et al.*, 2002) describes activities specific to the benthic surveys of Massachusetts Bay and Cape Cod Bay, and of Boston Harbor, conducted annually.

MWRA's benthic studies include: (1) monitoring the recovery of the benthic communities in Boston Harbor and (2) obtaining data on the communities and sediment quality at sites in Massachusetts Bay and Cape Cod Bay between 2000 and 2005.

The principal aim of the Harbor studies is documentation of continuing recovery of benthic communities in areas of Boston Harbor in response to decreases in wastewater discharges, for example, reductions in combined sewer overflow (CSO) releases. The Harbor recovery monitoring includes evaluation of local and area-wide changes in the Boston Harbor system that have resulted from (1) improvements in wastewater treatment practices (*e.g.,* cessation of sludge discharge and conversion from primary to full secondary treatment), (2) diversion of effluent to the new ocean outfall, and (3) improvements to (CSO) control systems.

Outfall studies include monitoring the response of benthic communities in Massachusetts and Cape Cod Bays to effluent discharge that began in September 2000. This monitoring program focuses most intensely on nearfield sites in western Massachusetts Bay (0˜8 km from the outfall), where changes in water and sediment quality were predicted to occur following initiation of the discharge. Farfield areas (typically >8 km from the outfall), which serve primarily as reference areas for the nearfield, are also examined as part of the monitoring studies.

Such sites can become monitoring stations if the discharge is shown to affect sites a distance from the diffuser.

Relevant to this CWQAPP, the benthic studies include sediment sampling in the Harbor and Bays for analysis of sedimentary organic matter content and chemical contaminant concentrations. Sedimentary physical characteristics and sewage tracer levels are also measured by other parts of the Harbor and Outfall Monitoring Program. The present status and variability of the benthic environmental quality within the Harbor and Massachusetts Bays system is evaluated by examination of the interrelationships among these parameters. Particular importance is placed on the rapid evaluation of benthic data with respect to monitoring thresholds described in the Contingency and Outfall Monitoring Plans (MWRA 2001a, 2004a).

Twelve or thirteen stations in the nearfield and four stations in the farfield (depending on year, see Table 4) are sampled in August. Samples from stations NF12, NF17, and C019 are analyzed for chemical constituents including polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, metals, and total organic carbon (TOC). Harbor samples are collected in August and analyzed for total organic carbon only. Samples collected at each location (relevant to this CWQAPP) are listed in Table 4 and total number of samples for even years and odd years are listed in Table 5.

Table 4. Benthic Station Sampling and Replication

Station group name	Stations	Year sampled	Replication: chemistry	Replication: TOC
Harbor traditional (8 stations)	T01, T02, T03, T04, T05A, T06, T07, T08	all	0	1
Harbor chemistry (1 station)	C019	all	3	3
Bay Core (2 stations)	NF12, NF17	all	2	2
2004 replicated nearfield (2 stations)	FF10, FF13	even	0	2
2004 unreplicated nearfield (9 stations)	NF05, NF07, NF08, NF09, NF16, NF18, NF19, NF22, NF23	even	0	1
2004 farfield (4 stations)	FF04, FF05, FF07, FF09	even	0	2
2005 replicated nearfield (2 stations)	FF12, NF24	odd	2	2
2005 unreplicated nearfield (8 stations)	NF02, NF04, NF10, NF13, NF14, NF15, NF20, NF21	odd	1	1
2005 farfield (4 stations)	FF01A, FF06, FF11, FF14	odd	2	2

Table 5. Parameters Measured, Units, and Number of Samples per Survey

Parameter	Reporting Units	# Samples (Even Year)	# Samples (Odd Year)
Percent dry weight	%	8x1 +1x3 + 2x2 + 2x2 + 9x1 + 4x2 = 36	8x1 +1x3 + 2x2 + 2x2 + 8x1 + 4x2 = 35
TOC	% dry wt.	36	35
Metals	µg/g	1x3 + 2x2 = 7	1x3 + 2x2 + 2x2 + 9x1 + 4x2 = 27
PCBs	µg /kg	7	27
PAHs	µg /kg	7	27
Pesticides	µg /kg	7	27

1.5 Quality Objectives and Criteria for Measurement Data

The parameters measured, the concentration reporting units, and the number of samples taken per survey are listed in Table 5, above.

1.5.1 Quality Objectives

Data quality objectives are as follows:

- To ensure that parameters measured adequately describe the effects of effluent and CSO discharge on contamination of Boston Harbor and Massachusetts Bay sediments, and the quality of these sediments as habitat, and

- To ensure that sample results are representative of the location sampled and are accurate.

1.5.2 Measurement Performance Criteria

The objectives are met by examining data collected on BMBSOFT and BHSOFT surveys to quantify chemical concentrations in the sediments of the receiving waters of interest; by analyzing laboratory QC sample to determine precision and accuracy, comparability, representativeness, sensitivity, and completeness; by analyzing laboratory replicates to ensure reproducibility of results; and by repeated measurements collected at the same locations over time to quantify the variability of results at each station. Definitions of quality control samples are provided in Section 2.4.2.

1.5.2.1 Precision and Accuracy

Precision and accuracy of laboratory procedures are ensured by the analysis of quality control (QC) samples including procedural blanks, prepared standards, standard reference materials (SRMs), where available, Laboratory Control Samples (LCS), and laboratory spikes and

duplicates, as applicable. Table 6 lists the desired precision, accuracy, and detection limit goals for each parameter being measured. QC samples to be analyzed in the laboratory to assess precision and accuracy are listed in Table 9.

1.5.2.2 Comparability

Data is directly comparable to results obtained previously at the same or similar sites in Massachusetts Bay, Cape Cod Bay, and Boston Harbor (see Williams *et al.* 2002) because field program design and analytical procedures are similar or identical. In addition, the use of written standardized procedures ensures that sample preparation and analyses are comparable throughout the project and with other projects.

To verify that data generated by DLS are comparable to those generated by BOS and its subcontractors during the HOM contract, an inter-comparison study was performed in 2003. The results of the study showed that the data were comparable.

Reporting units for concentrations follow standard convention for most oceanographic studies. (See Table 5).

1.5.2.3 Representativeness

Representativeness is addressed primarily in sampling design. The sampling practices and laboratory measurements that are performed during the benthic monitoring have already been used in many systems to characterize marine sediment quality and are, therefore, considered to yield data representative of the study area. Representativeness is also ensured by proper handling, storage (including appropriate preservation and holding times), and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

Deviations from the analytical scheme described in this CWQAPP are noted in the laboratory records associated with analytical batches and in the QA statements.

1.5.2.4 Sensitivity

Sensitivity is the capability of methodology or instrumentation to discriminate among measurement responses for quantitative differences of a parameter of interest. The method detection limits (MDLs) (Table 6) provide the sensitivity goals for the procedures. With the exception of PAHs, the MDLs listed in Table 6 are comparable to those listed in Williams, et al. (2002). The DLS will rerun PAH MDLs to try to achieve lower results.

Table 6. Desired Precision, Accuracy, and MDL for each Parameter based on Quality Objectives

Parameter	Lab Precision	Accuracy	Blank Cleanliness	MDL[1,6,5] (Current)	
TOC	≤ 25% RPD	±5% PD	≤ 10% of lowest sample concentration	0.00648%	
% dry weight	≤ 10% RPD	89%-115%	< 0.0125%	NA	
Metals (MDL/RL source)	≤ 25% RPD if value > 5*MDL	≤ 20% PD vs. SRM certified values	≤ 10% of the lowest sample concentration	MDL	RL[4]
Aluminum (ICP)				4.5 µg/g	4.5 µg/g
Iron (ICP)				0.04 µg/g	1.5 µg/g
Silver (GFA)				0.0045 µg/g	0.045 µg/g
Cadmium (GFA)				0.005 µg /g	0.005 µg/g
Chromium (ICP)				0.20 µg /g	0.20 µg/g
Copper (ICP)				0.525 µg/g	1.5 µg/g
Mercury (CVA)				0.001 µg /g	0.001µg/g
Nickel (ICP)				0.15 µg /g	0.15 µg/g
Lead (ICP)				0.60 µg /g	0.75 µg/g
Zinc (ICP)				0.285 µg /g	0.30 µg/g
PCBs					
2,4-Cl_2(8)	≤ 30% RPD	≤ 35% vs. SRM range	≤ RL[4] (0.100 ng/g)	0.0549 ng/g	
2,2',5-Cl_3(18)				0.0564 ng/g	
2,4,4'-Cl_3(28)				0.0688 ng/g	
2,2',3,5'-Cl_4(44)				0.0795 ng/g	
2,2',5,5'-Cl_4(52)				0.0682 ng/g	
2,3',4,4'-Cl_4(66)				0.0760 ng/g	
3,3',4,4'-Cl_4(77)				0.0814 ng/g	
2,2'4,5,5'-Cl_5(101)				0.0840 ng/g	
2,3,3',4,4'-Cl_5(105)				0.0696 ng/g	
2,3',4,4'5-Cl_5(118)				0.0692 ng/g	
3,3',4,4',5-Cl_5(126)				0.0637 ng/g	
2,2',3,3,4,4'-Cl_6(128)				0.0535 ng/g	
2,2',3,4,4',5-Cl_6(138)				0.0556 ng/g	
2,2'4,4',5,5'-Cl_6(153)				0.0598 ng/g	
2,2'3,3,4,4',5-Cl_7(170)				0.0929 ng/g	
2,2',3,4,4',5,5'-Cl_7(180)				0.0524 ng/g	
2,2',3,4,5,5',6-Cl_7(187)				0.0554 ng/g	
2,2',3,3',4,4',5,6-Cl_8(195)				0.0865 ng/g	
2,2',3,3'4,4',5,5',6-Cl_9(206)				0.0626 ng/g	
Decachlorobiphenyl-Cl_{10}(209)				0.0556 ng/g	
PAH					
Naphthalene	≤ 30% RPD	≤ 35% vs. SRM range	≤ RL[4] (0.500 ng/g)	0.242 ng/g	
C_1-naphthalenes				0.242 ng/g	
C_2-naphthalenes				0.242 ng/g	
C_3-naphthalenes				0.242 ng/g	
Acenaphthylene				0.428 ng/g	
Acenaphthene				0.468 ng/g	
Fluorene				0.432 ng/g	
C_1-fluorenes				0.432 ng/g	
C_2-fluorenes				0.432 ng/g	
C_3-fluorenes				0.432 ng/g	
Anthracene				0.317 ng/g	
Phenanthrene				0.430 ng/g	
C_1-phenanthrenes/anthracene				0.430 ng/g	
C_2-phenanthrenes/anthracene				0.430 ng/g	
C_3-phenanthrenes/anthracene				0.430 ng/g	
C_4-phenanthrenes/anthracene				0.430 ng/g	
Dibenzothiophene				0.148 ng/g	
C_1-dibenzothiophenes				0.148 ng/g	
C_2-dibenzothiophenes				0.148 ng/g	
C_3-dibenzothiophenes				0.148 ng/g	

Table 6. Desired Precision, Accuracy, and MDL for each Parameter based on Quality Objectives

Parameter	Lab Precision	Accuracy	Blank Cleanliness	MDL[1,6,5] (Current)
Fluoranthene	≤ 30% RPD	≤ 35% vs. SRM range	≤ RL[4] (0.500 ng/g)	0.400 ng/g
Pyrene				0.361 ng/g
C_1-fluoranthenes/pyrenes				0.361 ng/g
benzo(a)anthracene				0.420 ng/g
Chrysene				0.495 ng/g
C_1-chrysene				0.495 ng/g
C_2-chrysene				0.495 ng/g
C_3-chrysene				0.495 ng/g
C_4-chrysene				0.495 ng/g
benzo(b)fluoranthene				0.477 ng/g
benzo(k)fluoranthene				0.281 ng/g
benzo(a)pyrene				0.469 ng/g
dibenzo(a,h)anthracene				0.293 ng/g
benzo(g,h,i)perylene				0.380 ng/g
Indeno(1,2,3-c,d)pyrene				0.468 ng/g
Perylene				0.167 ng/g
Biphenyl				0.186 ng/g
benzo(e)pyrene				0.588 ng/g
Dibenzofuran				0.451 ng/g
Benzothiazole				0.581 ng/g
Pesticides				
Hexachlorobenzene	≤ 30% RPD	≤ 35% vs. SRM range	≤ RL[4] (0.100 ng/g)	0.0475 ng/g
Lindane (gamma- BHC)				0.0474 ng/g
Heptachlor				0.0416 ng/g
Aldrin				0.0503 ng/g
Heptachlorepoxide				0.0391 ng/g
Alpha-chlordane				0.0407 ng/g
Trans-Nonachlor				0.0787 ng/g
Dieldrin				0.0392 ng/g
Endrin				0.0624 ng/g
Mirex				0.1043 ng/g
2,4'-DDD				0.0764 ng/g
4,4'-DDD				0.0566 ng/g
2,4'-DDE				0.0707 ng/g
4,4'-DDE				0.0612 ng/g
2,4'-DDT				0.0570 ng/g
4,4'-DDT				0.0673 ng/g
DDMU				0.0693 ng/g
Gamma-Chlordane				0.0521 ng/g
Cis-Nonachlor				0.0561 ng/g
Oxychlordane				0.0583 ng/g

[1] MDL = method detection limit. The actual MDL may be updated periodically. Contact the MWRA Central Laboratory for the most current MDL information.

[2] Relative Percent Difference (RPD)% = $\left|$ (replicate 1 - replicate 2)/(replicate 1 + replicate 2)/2 $\right|$ x 100.

[3] Percent Difference (PD)% = [(true concentration – measured concentration)/true concentration] x 100.

[4] Reporting Limit (RL): The RL is the typical reporting limit, which is based on the low point of the calibration curve. Concentrations below the RL are reported, so long as all identification criteria are met.

[5] For organics SRM: If the detected value falls within the SRM certified range, then PD=0. If the detected value falls outside the SRM certified range, then the PD is determined against either the upper or lower limit of the range.

[6] Metals MDLs are based on 1 g initial weight, 100% solids, and 50 mL final volume (except mercury, which has a final volume of 100 mL). Organics MDLs are based on a 20 g initial weight, 100% solids. TOC MDLs are based on 0.25 g initial weight, 100% solids, and 5 mL final volume.

[7] MDL concentrations for alkyl homologues are based on the MDL of the unsubstituted, parent compound.

1.5.2.5 Completeness

It is expected that 100% of the samples collected and intended for analysis be analyzed. However, a sample loss of <5% for the entire project does not compromise the objectives of the project.

1.6 Special Training Requirements and Certification

Organic contaminant measurements, metals analysis, and total solids analysis for the HOM Benthic study use routine laboratory analyses (for sediment samples) and data validation. Therefore, specialized training is not required. Metals (except mercury) preparation of sediment samples for the HOM project however, involves a digestion with hydrofluoric acid, which requires specialized training. Once analysts have undergone the proper training in handling, storing, preparing, and analyzing sediment samples as specified in MWRA's Department of Laboratory Services Quality Assurance Management Plan (QAMP, DCN #5000, Section 3.0), they can be certified to perform the analysis.

1.7 Documentation and Records

Documents and records are created and maintained according to the guidance and requirements found in the following DLS documents: QAMP, Section 12.0 (DCN #5000), SOP (DCN #5006), "Guidance for Writing, Revising and Approving Standard Operating Procedures", and SOP (DCN #5007), "Procedures and Guidelines for the Handling, Storage and Archiving of Hardcopy and Electronic Records."

1.7.1 Document Control

MWRA DLS maintains documents relevant to laboratory analysis activities and entry of data into LIMS. The DLS document retention system includes all logbooks, raw data, instrument reports, calculated data, and COC forms.

The pertinent documents applicable to the HOM analyses are this CWQAPP, the DLS QAMP (DCN #5000) and the analysis SOPs (See Table 8). The guidance for the control of DLS' SOPs is set forth in the DLS SOP DCN: 5006. "Guidance for Writing, Revising, and Approving Standard Operating Procedures". After revision and approval, all SOPs are immediately distributed to the respective Team/Supervisor/analyst. A copy of the most current analysis SOP is kept in the lab area where the analysis is being performed.

Document Control is the responsibility of DLS' Quality Assurance Manager.

1.7.2 Analysis Records

All data are recorded initially into bound laboratory logbooks, onto established data forms or onto electronic file, where applicable. Sampling logs associated with custody and tracking are held in the custody of the Violet Team Supervisor responsible for sample management. Field measurements and laboratory analytical results are subsequently entered into LIMS.

1.7.3 Records Retention and Storage

All hardcopy records are stored, secured, and protected in appropriate locations either in the Team areas, the QA File area, or in the DLS Record Retention Room. Subsequently, hard copy records are sent and archived at MWRA's Central Record Storage location in Fore River in Quincy, MA. All records are kept for a period of ten years. The guidance for record handling is set forth in the DLS SOP DCN: 5007, "Procedures and Guidance for the Handling, Storage, and Archiving of Hardcopy and Electronic Records".

1.7.4 LIMS Electronic Records

All records and data stored in LIMS are backed up daily, weekly, and monthly by MWRA's MIS department. Once a month, the records are backed up onto tape and sent to an off-site location where they are kept for a period of ten years.

1.7.5 Records Managed by ENQUAD

ENQUAD maintains all documents relevant to data loading into EM&MS, and to data reviews.

2.0 MEASUREMENT/DATA ACQUISITION

2.1 Sampling Process Design (Experimental Design)

2.1.1 Scheduled Project Activities, Including Measurement Activities

The BMBSOFT and BHSOFT studies are performed on an ongoing basis as specified in Williams *et al.* 2002. They have been ongoing, with slight changes in sampling frequency and sampling locations, since 1991 or 1992, thus including twelve or thirteen years of monitoring. Each currently includes one sampling event per year.

2.1.2 Design Rationale

The objective of the BMBSOFT and BHSOFT studies is to measure sediment quality changes after wastewater discharges were transferred offshore to Massachusetts Bay. The evaluation of sediment quality changes due to the transfer of discharges offshore is assessed through measurement of organic carbon content and of chemical contaminant concentrations, among others. Outfall effects are most likely at the nearfield stations. Farfield stations serve as reference stations as well as documenting the spatial extent of any change due to the outfall. Harbor stations show recovery from past effluent and sludge discharges to the harbor, and changes due to changes in other sources (e.g. CSOs.)

2.1.3 Design Assumptions

Because sediment properties in the nearfield are known to be spatially heterogeneous, stations close to one another are assumed to be replicates of one another. Conversely, Boston Harbor stations are located in distinct areas of the harbor and were selected to be representative of sediment quality for each of these areas. It is assumed that the sediment properties change only gradually over time, except in response to large storms, so annual or biennial sampling is sufficient to characterize the distribution of contaminants and the quality of the sediment as benthic habitat (a complementary study by USGS examines temporal variations in much greater detail.)

2.1.4 Procedures for Locating and Selecting Environmental Samples

The choice of sampling locations is discussed in the Ambient Monitoring Plan (MWRA 2004a) and in the CWQAPP for Benthic Monitoring (Williams *et al.* 2002.) This CWQAPP deals only with laboratory analyses.

2.1.5 Classification of Measurements as Critical or Non-critical

All measurements collected as part of the BWQM surveys are considered critical due to the requirement in MWRA's discharge permit to conduct the measurements described in the Ambient Monitoring Plan (MWRA 2004a).

2.2 Sampling Methods Requirements

2.2.1 Sample Collection, Preparation, Decontamination Procedures

Samples for each suite of analytes are collected in Kynar coated Ted Young-modified Van Veen grab samplers as described in Williams *et al.* 2002. The upper 0-2 cm is subsampled with a Kynar-coated scoop. The sample bottles and the associated analytes are shown in Table 7, along with field preservation method and holding time. DLS provides all sample containers. All other field supplies are provided by BOS.

Table 7. Sample Collection and Storage

Parameter	Sample Volume (Target) (g)[a]	Sample Containers[b]	Shipboard Processing/ Preservation	Maximum Holding Time to Analysis
TOC, % dry weight	50	Clean, labeled glass jar	freeze (-20° C)	28 days
Metals	100	Clean, tared and labeled I-CHEM container	freeze (-20° C)	6 months to preparation and analysis; Hg holding time is 28 days to preparation and analysis
Organic contaminants	125	Clean, labeled glass jar with Teflon-lined cap	freeze (-20° C)	1 year to extract (if samples frozen); 40 days from extraction to analysis

[a] Volume processed for analysis.
[b] Name brand items (*e.g*., I-CHEM) may be substituted with comparable items from a different manufacturer.

2.2.2 Sampling/Measurement System Failure Response and Corrective Action Process

Corrective action in the field is covered in Williams *et al.* 2002.

From time to time, circumstances/conditions (e.g., broken or contaminated sample containers) may be identified prior to check-in or prior to analysis, which, in turn, may dictate that a corrective action be initiated. The corrective action process/procedures are summarized in Section 3.0.

2.3 Sample Handling and Custody Requirements

2.3.1 Sampling Equipment, Preservation, and Holding Times Requirements

Samples collected for laboratory analysis are stored on ice in coolers or frozen and holding times (Table 7) are met to ensure the accuracy of results. The temperatures of sample storage units are monitored to verify that holding temperatures are met.

2.3.2 Sample Custody Procedure

The CWQAPP for benthic studies (Williams *et al.*, 2002) describes sample tracking in the field. The BOS NavSam© system creates the chain of custody (COC) form (Figure 2) from the sample table used to generate sample labels, thereby creating a link between the sample, the data recorded on the chain form, and the sample collection information stored within NavSam© (*i.e.* location, depth, and time.) The COC forms have the same alphanumeric code as the corresponding label on the sample container, ensuring the tracking of sample location and the status.

The Chief Scientist is responsible for verifying each sample ID vs. the COC forms generated by NavSam© prior to delivering the samples to the laboratory. All samples are delivered to the Battelle Field Sample Custodian, who distributes them to the appropriate laboratory personnel by hand or by Federal Express. Hand-delivery may include direct transfer of samples to DLS personnel at the boat, dock, or lab. All frozen samples that must be shipped are placed on dry ice with protective layers of foam or bubble wrap to ensure samples remain intact and frozen during shipment.

Battelle field staff generally drive the samples up to Deer Island a day or two after the survey. On rare occasions they ship via FedEx. Coordinating with the DLS HOM Project Manager, the samples can be dropped off or picked up first thing in the morning (0700) during a multi-day survey.

2.3.3 Sample Receipt and Check-in

Upon receipt of the samples, the MWRA DLS Laboratory Sample Management Team (Violet):

- Inspects the samples to verify that:
  (1) integrity is intact (containers are sealed and intact),
  (2) the sample label and custody forms agree,
  (3) all shipped samples have been received, and
  (4) holding temperatures were maintained.

- Completes the Battelle COC forms, and signs the COC form so that transfer of custody of the samples is complete. Any discrepancies between sample labels and the custody forms, and unusual events or deviations from the project CWQAPP are documented in detail on the COC, and are communicated to the DLS Project Manager who notifies the Battelle Field Manager within 24 hours of receipt. **Note:** The original COC forms are sent to ENQUAD to be forwarded to Battelle along with the data set and other associated documentation; copies are kept at the DLS Laboratory.

- Checks the samples into LIMS to provide a permanent laboratory record. **Note:** This is accomplished by matching up the Battelle ID with the LIMS ID. The Battelle ID is either scanned from the barcoded label or otherwise hand entered into LIMS in the QC lot number field. The LIMS IDs are used throughout the laboratory analysis.

After the samples are received by the DLS laboratory:

- Samples are stored in the secure Sample Bank or a secure freezer at the temperature conditions specified in Table 7. Access to the samples is only allowed to lab analysts, using their electronic pass card, key, or combination lock.

- Samples that are stored in the secure Sample Bank or freezer are in the custody of the Violet Team member who checked-in the samples until they are transferred from the

Sample Bank to a member of laboratory staff for analysis. The receipt of samples by the analyst is documented in LIMS.

MWRA Harbor and Outfall Monitoring Program
Contract No. S366
Sample Custody Form

Today's Date : 2/22/02 9:30:55 AM
Laboratory : Applied Marine Sciences

Chain-of-Custody # : BC021-TC-0006
Survey ID : BC021
Analysis ID : TC
Analysis Description : TOC

502 N. Highway 3, Suite B
League City TX 77573
Mr. Kenneth Davis
281-554-7272 (Phone) 281-554-6356 (Fax)

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Ck 1	Ck 2	Ck 3	Ck 4
[redacted]	BC0210E1TC1	2/20/02 10:06:39 AM	FF10	☐	☐	☐	☐
[redacted]	BC0210ECTC1	2/20/02 10:47:50 AM	FF10	☐	☐	☐	☐
[redacted]	BC0210EETC1	2/20/02 10:59:23 AM	FF10	☐	☐	☐	☐
[redacted]	BC0210F6TC1	2/20/02 11:35:14 AM	NF08	☐	☐	☐	☐
[redacted]	BC0210F8TC1	2/20/02 11:47:34 AM	NF08	☐	☐	☐	☐
[redacted]	BC0210FATC1	2/20/02 12:12:44 PM	NF08	☐	☐	☐	☐
[redacted]	BC021100TC1	2/20/02 12:48:56 PM	NF24	☐	☐	☐	☐
[redacted]	BC021101TC1	2/20/02 12:56:47 PM	NF24	☐	☐	☐	☐
[redacted]	BC021102TC1	2/20/02 1:06:20 PM	NF24	☐	☐	☐	☐
[redacted]	BC021106TC1	2/22/02 1:27:23 PM	NF22	☐	☐	☐	☐
[redacted]	BC021107TC1	2/20/02 1:36:57 PM	NF22	☐	☐	☐	☐
[redacted]	BC021108TC1	2/20/02 1:44:21 PM	NF22	☐	☐	☐	☐

Shipping Condition - Room Temperature: _____ Cold(ice): _____ Frozen(dry ice): _____
Received Condition - Room Temperature: _____ Cold(ice): _____ Frozen(dry ice): _____

Relinquished By / Date / Time / Company / Transport-Airbill #	Received By / Date / Time / Company

Page 1 of 1

Figure 2: Battelle Chain-of-Custody Form

- Internal laboratory documentation in LIMS tracks sample custody and location throughout processing and analysis. Transfer of samples is documented in LIMS, using a password-protected program to document both the person relinquishing the samples as well as the recipient. A copy of the DLS internal LIMS Chain-of-Custody is shown in Figure 3.

- Sample archival and disposal are documented in LIMS.

- All samples covered by this CWQAPP are analyzed by the DLS Central Laboratory following the various DLS SOPs (Table 8).

- When the results are transferred to the EM&MS database (see Section 4.1.2), ENQUAD EM&MS personnel maps the NavSam© Sample ID into the SAMPLE_ID field, and the LIMS Sample_ID into the LAB_SAMPLE_ID field.

Figure 3: DLS LIMS Internal Chain-of-Custody

3/01/2004 MWRA -LIMS 11:03:41
Internal Chain of Custody

ENTRY	Container #	Type	Current Storage Loc.	Responsible Person	Date and Time of Tran
4	04006748-01	FGF-CH	147-SAMPLE BANK	BERGER K	11:00:07 2/23/2004
3	04006748-01	FGF-CH	437-BIOLOGY LAB	BERGER-K	9:20:03 2/17/2004
2	04006748-01	FGF-CH	147-SAMPLE BANK	SEAMAN-C	13:46:2 12/09/2004
1	04006748-01	FGF-CH	141-SAMPLE RECVG	SEAMAN-C	13:44:33 2/09/2004

List of Revisions, Highlighted Fields have Changed

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2.4 Analytical Requirements

2.4.1 Analytical Methods

Table 8 summarizes the methods used for sample analysis. The analyses are conducted as described in the DLS SOPs listed, which are based on literature references or EPA methods as indicated in the SOP.

Table 8. Methods for Sediment Sample Analyses to be Conducted by DLS

Parameter	LIMS test code	Units	Instrument [1]	DLS SOP DCN[2] (Based on Reference)
TOC	TOC-SOCIR	% dry wt.	DC-190	#1168
Dry weight	TS--SOGRV	%	NA	#1094
Metals				
Aluminum	AL--SOFAA	% dry wt.	ICP/FAA	#1193/ #1008/ #1199
Iron	FE—SOICP		ICP/FAA	#1193/ #1008/#1199
Silver	AG--SOGFA	µg/g	ICP/GFA/FAA	#1193/ #1008/ #1150/#1199
Cadmium	CD—SOGFA		ICP/GFA/FAA	#1193/ #1008/ #1150/#1199
Chromium	CR—SOICP		ICP/FAA/GFA	#1193/ #1008/ #1150/ #1199
Copper	CU—SOICP		ICP/FAA/GFA	#1193/ #1008/ #1150/ #1199
Mercury	HG—SOCVA		CVA	#1027/ #1049
Nickel	NI—SOICP		ICP/FAA/GFA	#1193/ #1008/ #1150/ #1199
Lead	PB—SOGFA		ICP/GFA/FAA	#1193/ #1008/ #1150/ #1199
Zinc	ZN—SOICP		ICP/FAA	#1193/ #1008/ #1199
PCBs	PCB-SOSIM	µg/kg	GC/MS	#1188/#1173
Polynuclear Aromatic Hydrocarbons (PAH)	PAHTSOGMS	µg/kg	GC/MS	#1188/ #1030
Pesticides	PES-SOSIM	µg/kg	GC/MS	#1188/#1173

[1] When more than one instrument is listed, this is the order that would be applied. (i.e. First they are run on ICP, then FAA if necessary, then GFA if necessary).

[2] DCN= Document Control Number. The SOP revision number is not included in the DCN. Contact the MWRA Central Laboratory for the most current revision number.

The preparation and analysis of samples are described in detail in the DLS Standard Operating Procedures. The comprehensive QA/QC program is described in the DLS' QAMP (DCN #5000).

Calibration procedures for laboratory instruments are summarized in Table 10. All laboratory calibration records are reviewed by analysts and maintained in the laboratory document retention system.

2.4.1.1 Organic Chemicals Analysis

The MWRA Central Laboratory performs all organic sediment chemistry analyses. Sediment samples are extracted for PAH, chlorinated pesticides, and PCB congeners by following MWRA SOP #1188.0, *Combined Sediment Sample Extraction by Sonication for PAH, Pesticides, and PCB Congener Analyses*. This extraction method utilizes sonication, and is based on EPA Method 3550B. Approximately 20 g of sediment is mixed with sodium sulfate and is serially extracted with methylene chloride (DCM) using sonication techniques. (Approximately 25 g of the original sample is also taken for dry weight determination by the Red Team.) The sample is weighed into an extraction vessel, mixed with the appropriate amount of sodium sulfate to achieve a free-flowing consistency, and spiked with the surrogate compounds. Methylene chloride is added and the sample is sonicated using the ultrasonic disruptor. The extract is decanted into an Erlenmeyer flask through a powder funnel containing glass wool and sodium sulfate to remove any water and sediment particles. After each extraction (total of three solvent additions) the filtered solvent is combined in the flask. The combined extracts are processed through a silica gel cartridge and concentrated to 1 mL using the TurboVap automatic concentrator technique. The extract may then be additionally cleaned using activated copper to remove elemental sulfur, if present. The post-cleanup extracts are concentrated to 2.0 mL and split 50:50 for analysis by the PAH and pesticide/congener methods.

Sample extracts are analyzed for PAH compounds by gas chromatography/mass spectrometry (GC/MS) operating in the selected-ion-monitoring (SIM) mode, using a 30m Rtx-5 column (or equivalent) and an Agilent 5973 detector (or equivalent), according to MWRA SOP #1030, *Trace Level Polynuclear Aromatic Hydrocarbon Analysis by Gas Chromatography/Mass Spectrometry using Selected Ion Monitoring (GC/MS SIM)*. The PAH compounds are quantified using the internal standard method. Sample data are not surrogate corrected prior to entry into the LIMS system, but guidance regarding the surrogate compounds is provided so that the client may later perform surrogate correction if desired. Concentrations of the substituted PAH homologues are determined by summing the total area of each homologue and using the response factor of the parent PAH compound.

Pesticides and PCB congeners are analyzed by gas chromatography/mass spectrometry (GC/MS) operating in the selected-ion-monitoring (SIM) mode, using a 60m Rtx-5 column (or equivalent) and an Agilent 5973 detector (or equivalent), according to MWRA SOP #1173, *Trace Level PCB Congener and Pesticide Analysis by Gas Chromatography/Mass Spectrometry using Selected Ion Monitoring (GC/MS SIM)*. Two separate analyses are performed, one to determine the pesticide compounds and one for the PCB congeners. Concentrations for all target analytes are determined using the internal standard method. Sample data are not surrogate-corrected prior to entry into the LIMS system, but guidance regarding the surrogate compounds is provided so that the client may later perform surrogate correction if desired.

All PAH, PCB congener, and pesticide results are reported in micrograms per kilogram (μg/Kg) on a dry weight basis.

2.4.1.2 Metals Analysis

The MWRA Central Laboratory performs metals digestions and analyses for Ag, Al, Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Sediment samples are digested using a hydrochloric/nitric/hydrofluoric acid digestion according to DLS SOP #1193, *Preparation for Analysis of Total Elements in Sediment Samples by Microwave Digestion*. A 500 to 1000 mg aliquot of each homogeneous wet sample is combined with 5 mL HNO_3, 2.5 mL HCl, and 4 mL HF in a Teflon microwave vessel. Samples are cold-digested in this acid mixture overnight. Samples are microwave digested for approximately 30 minutes. After heating and cooling, samples are filtered through Whatman #541 filters and rinsed with Milli-Q water (final volume is 50 mL). After rinsing, filter paper is transferred back to the digestion vessel and the digestion is repeated (an additional 5 mL HNO_3, 2.5 mL HCl, and 4 mL HF is added and samples are filtered again) to further digest the sample. Both digestates are analyzed by radial ICP according to DLS SOP #1008, *Metals Analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy*. Elements that are undetected by ICP (e.g. Ag, Cd, and Pb) or may be prone to matrix interference are reanalyzed by GFA (DLS SOP #1150, *Graphite Furnace Atomic Absorption Spectroscopy*) for lower reporting limits. Elements with high concentrations (e.g. Al, Fe, Cu) or suspected matrix effects may be analyzed by FAA (DLS SOP 1199, *Analysis of Sediments and Tissues by Flame AA*). Acceptance criteria for the calibration are listed in Table 10. Results are reported as μg/g dry-weight.

CVAA Analysis of Mercury - Samples are digested and analyzed for Hg using cold-vapor atomic absorption spectroscopy (CVAA) according to DLS SOP #1027, *Digestion of Solid Samples for Mercury Analysis* and DLS SOP #1049, *Mercury analysis by Cold Vapor Atomic Absorption Spectroscopy (CETAC M6000A).* A 200 mg aliquot is leached with 15 mL dilute HNO_3 and HCl in a waterbath for 2 minutes. Cooled samples are diluted to 50 mL and oxidized with $KMnO_4$ in a waterbath at 95º C for 30 minutes. Deionized water is added to bring the final sample volume to 100 mL. The digested sample is mixed with a reducing agent in-line to release elemental Hg vapor. Hg is quantified by atomic absorption at 254 nm. Acceptance criteria for the calibration are listed in Table 10. Results are reported as μg/g dry-weight.

2.4.1.3 Total Organic Carbon Analysis

Samples are processed and analyzed by the MWRA Central Laboratory according to DLS SOP #1168, *Total Organic Carbon in Sediment by Combustion with Infrared Detection (Tekmar-Dorhmann DC-190).* Sediment samples for TOC analysis are thawed in the refrigerator. A portion of the wet sample (approximately 250 mg) is transferred to a scintillation vial. The sample is treated with 5 mL of 10% HCl to remove inorganic carbon and the sample is heated in a water bath at 70° C for 10 minutes. The analyzer operates through the high-temperature conversion of all carbon in the treated sample to carbon dioxide in the presence of oxygen. The carbon dioxide is quantified by infrared detection. Acceptance criteria for the calibration are listed in Table 10. Results are reported as %C dry-weight.

2.4.1.4 Total Solids (% Dry Weight)

Percent dry weight is performed by the MWRA Central Laboratory. For this analysis, percent dry weight is determined following SOP #1094, *Percent Total, Volatile, and Fixed Solids in Solid and Semisolid Samples*. A well-mixed representative sample is evaporated to dryness in a pre-weighed dish and dried to constant weight in an oven at 103° to 105° C. The weight of the residue remaining in the dish is the amount of total solids in the sample. Percentages of total solids are calculated according to the formula in SOP #1094. This result is used to determine metals, TOC, and organics results.

2.4.2 Quality Control Requirements

Quality Control (QC) samples are run with every analytical batch of 20 samples or fewer. The suite of QC samples specified for a particular analytical batch depends on the parameters being analyzed. Table 9 lists the quality control samples and data quality acceptance limits for each measurement according to the particular parameter(s) being analyzed. Other QC samples (e.g., instrument QC) may be dictated by the analytical method and are described in Section 8.0 of DLS' QAMP (DCN #5000) and the specific SOP.

The definitions of the QC samples are as follows:

- **Laboratory Control Sample:** A sample of deionized water free from the analytes of interest and interferences, spiked with verified known amounts of analytes. It is processed simultaneously with and under the same conditions as samples through all steps of the preparatory and analytical procedures. The purpose of the LCS is to establish intra-laboratory or analyst specific recovery, precision, and bias and to assess the performance of the entire measurement process. These standards are purchased either from NIST (National Institute of Standards) or from a qualified commercial vendor.

- **Standard Reference Material:** A reference material, which is sufficiently well established for the calibration of procedures and development of methods. Certified values are generally based on the results of determinations by at least two independent methods of analysis. These standards are purchased either from NIST (National Institute of Standards) or NRC (National Research Council Canada).

- **Laboratory Duplicate (Processing):** A second aliquot of a sample taken from the same container as the first aliquot under laboratory conditions and processed and analyzed independently.

- **Method (Procedural) Blanks:** A sample of deionized water that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the preparatory and analytical procedures. The purpose of the Method Blank is to demonstrate that the analytical system is free of target analytes and interferences, or assess any possible contamination.

- **Field Duplicates/Triplicates:** Two/Three subsamples taken from one field sample (grab sample) and processed in the field as two/three separate samples, resulting in two/three sample containers.

- **Matrix Spike:** A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. The purpose of the matrix spike is to determine the effect of the matrix on a method's recovery efficiency.

- **Matrix Spike Duplicate:** A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

2.5 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

All equipment associated with sediment analyses (GC/MS, ICP, GFA, FAA, Cetac, DC-190], analytical balances, thermometers, and incubators) are calibrated and maintained according to manufacturer's specifications. This is done or checked on each day of use as described in Section 10.0 of DLS' QAMP (DCN #5000) or the pertinent SOP. An equipment logbook is maintained to document periodic maintenance of major equipment.

2.6 Instrumentation Calibration and Frequency

Calibration procedures for laboratory instruments are summarized in Table 10. All laboratory calibration records are reviewed by the Team Supervisor as part of the validation process and filed.

DLS policy on calibration standards is described in Section 6.0 of the QAMP (DCN #5000). Specific details are included in the pertinent analytical SOPs.

2.7 Tracking and Quality Verification of Supplies and Consumables

All supplies and consumables are ordered and when received, checked/verified by the analysts according to the requirements of the respective analysis SOP. All reagents and chemicals are Analytical Reagent Grade or higher. Standards are purchased according to the requirements of the respective analysis SOP and all information concerning the standards (purchased or prepared) is kept in the Standards Logbook. Certifications are kept in the team's Standards Certificate File. Expiration dates are assigned by the analyst either according to the manufacturer's specification or according to the requirements given in the respective analysis SOP. Additional information concerning standards and reagents can be found in Section 6.0 of DLS' QAMP (DCN #5000).

Table 9. Quality Control Samples and Data Quality Objectives for Sediment Chemistry			
QC Type	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Procedural Blanks			
Organics	1 per 20 samples	< RL[1]	Results examined by project manager, team supervisor, or lab manager. Corrective action (*e.g.*, re-extraction, reanalysis, data qualifier) is documented in LIMS sample notepad and/or test_comments.
Metals	1 per 20 samples	≤ 10% of the lowest sample concentration	
TOC	1 per day or 1 per 20 samples, whichever comes first	≤ 10% of the lowest sample concentration (total carbon)	
% dry weight	1 per 20 samples	≤ 0.0125%	
Accuracy			
Matrix Spike			
Organics	1 per 20 samples	50-150% recovery[2]	Document, justify deviations. Corrective action (*e.g.*, re-extraction, reanalysis, data qualifier) is documented in LIMS sample notepad and/or test_comments.
Metals	1 per 20 samples	70-130% recovery[2]	
TOC	NA	NA	
% dry weight	NA	NA	
Surrogate standards			
Organics only	Every sample	50-150% recovery[3] (40-150% for Naphthalene-d8)	Document, justify deviations. Corrective action (*e.g.*, re-extraction, reanalysis, data qualifier) is documented in LIMS sample notepad and/or test_comments.
SRMs			
Organics	1 per 20 samples	PD ≤ 35% vs. SRM range[4]	Results examined by project manager, team supervisor, or lab manager. Corrective action (*e.g.*, re-extraction, reanalysis, data qualifier) is documented in LIMS sample notepad and/or test_comments.
Metals	1 per 20 samples	PD ≤ 20% vs. SRM certified values[5]	
TOC	1 per 20 samples (digested); Run once a day with each batch	±5% of certified value	
% dry weight	1 per 20 samples	89%-115% of certified value	
Precision			
Duplicates			
Organics (MS/MSD)	1 per 20 samples	≤ 30% RPD[6]	Document, justify deviations. Corrective action (*e.g.*, re-extraction, reanalysis, data qualifier) is documented in LIMS sample notepad and/or test_comments. Flag with test_comment 'R' (precision does not meet DQO)
Metals	1 per 20 samples	≤ 25% RPD if value is >5 X MDL	
TOC	1 per 20 samples	≤ 25% RPD	
% dry weight	1 per 20 samples	≤ 10%	

[1] Reporting Limit (RL): The RL is the typical reporting limit, which is based on the low point of the calibration curve. (For PCBs and Pesticides this is 0.100 ng/g and for PAHs this is 0.500 ng/g.) Concentrations below the RL are reported only if all identification criteria are met.

[2] For matrix spike and matrix spike duplicates: Percent Recovery =([spiked sample result – unspiked sample result] ÷ spike amount) × 100.

[3] For surrogate standards: Percent Recovery = [(measured concentration)/(true or nominal concentration)] x 100%.

[4]For organics SRM: If the detected value falls within the SRM certified range, then percent difference (PD)=0. If the detected value falls outside the SRM certified range, then the PD is determined against either the upper or lower limit of the range.
[5]Percent Difference = [(SRM Certified value – Laboratory SRM result) ÷ SRM Certified value)]× 100
[6] Relative Percent Difference (RPD) = | (replicate 1 - replicate 2) x 2/(replicate 1 + replicate 2) | x 100%.

Table 10. Calibration Procedures for Laboratory Instruments

Parameter	Instrument Type	Initial Calibration			Continuing Calibration		Corrective Action
		No. Stds.	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	
PCB	GC/MS (SIM)	5	RSD ≤ 20%	Prior to analytical run	PD from initial ≤ 25%	Every 24 hours	Document, justify deviations. Remedial maintenance, new initial calibration, or reanalyze samples as needed.
Pesticides	GC/MS (SIM)	5	RSD ≤ 20%	Prior to analytical run	PD from initial ≤ 25%	Every 24 hours	Document, justify deviations. Remedial maintenance, new initial calibration, or reanalyze samples as needed.
PAH	GC/MS (SIM)	5	RSD ≤ 25%	Prior to analytical run	PD from initial ≤ 25%	Every 24 hours	Document, justify deviations. Remedial maintenance, new initial calibration, or reanalyze samples as needed.
Metals	CVAA (Hg)	3	R ≥ 0.995 [1]	Prior to analytical run	± 15 % Rec.	Every 10 samples	Document, justify deviations. Remedial maintenance, new initial calibration, or reanalyze samples as needed.
	ICP [2]	1	See footnote 1	Prior to analytical run	± 10 % Rec.	Every 10 samples	
	GFAA [2] (as required)	3	R ≥ 0.995 [1]	Prior to analytical run	± 10 % Rec.	Every 10 samples	
	FAA [2] (as required)	3	R ≥ 0.995 [1]	Prior to analytical run	± 10 % Rec.	Every 10 samples	
TOC	Combustion/ Infrared Carbon Analyzer	1 (Check std.)	See footnote 3	Weekly	5 % Rec.	Every 20 samples	Document, justify deviations. Remedial maintenance, new initial calibration, or reanalyze samples as needed.

[1] Instrument Performance Check standard (IPC =±5%), Independent Calibration Verification (ICV = ±10%), and Instrument Calibration Blank (ICB=<MDL) precede each run.
[2] Samples are screened by the ICP but may be analyzed by other methods as required.
[3] Three IPCs are checked after calibration. The mean of the standards must be between 95-105% recovery of the true value.

2.8 Data Management

2.8.1 Acquisition of Non-Direct Measurement Data

Field sample locations are pre-loaded in LIMS as Station IDs. When samples are checked in, the Battelle sample ID is associated with a LIMS sample ID by matching up the Station ID. Except for date and time, no Battelle field measurements are entered in LIMS. Station Ids are given in Table 11. The LIMS location_ID, or an abbreviation of, is equivalent to the station_id (EM&MS STAT_ID).

Table 11. Station Identifiers

FACILITY_ID	LOCATION_ID	EM&MS STAT_ID	Location Description
HARBBNTH	C019	C019	42-21.56, 71-2.72, FORT POINT CHANNEL
HARBBNTH	T01	T01	42-20.95, 70-57.81, OFF DEER ISLAND WEST SIDE
HARBBNTH	T02	T02	42-20.57, 70-60.12, PRESIDENT ROADS
HARBBNTH	T03	T03	42-19.81, 70-57.72, OFF NORTH EAST TIP OF LONG ISLAND
HARBBNTH	T04	T04	42-18.6, 70-62.49, DORCHESTER BAY
HARBBNTH	T05A	T05A	42-20.38, 70-57.64, PRESIDENT ROADS
HARBBNTH	T06	T06	42-17.61, 70-56.66, NANTASKET ROADS
HARBBNTH	T07	T07	42-17.36, 70-58.71, QUINCY BAY
HARBBNTH	T08	T08	42-17.12, 70-54.75, HINGHAM BAY
MASSBNTH	FF1A	FF01A	42-33.84, 70-40.56, SOUTH OF CAPE ANN
MASSBNTH	FF04	FF04	42-17.28, 70-25.50, STELLWAGEN BASIN
MASSBNTH	FF05	FF05	42-07.98, 70-25.38, SOUTHWEST OF STELLWAGEN BANK
MASSBNTH	FF06	FF06	41-53.88, 70-24.18, WESTERN CAPE COD BAY
MASSBNTH	FF07	FF07	41-57.48, 70-16.02, NORTHEASTERN CAPE COD BAY
MASSBNTH	FF09	FF09	42-18.78, 70-39.42, MASS BAY, WEST OF STELLWAGEN BASIN
MASSBNTH	FF10	FF10	42-24.84, 70-52.74, MASSACHUSETTS BAY NEAR NAHANT
MASSBNTH	FF11	FF11	42-39.48, 70-30.00, MASSACHUSETTS BAY EAST OF CAPE ANN
MASSBNTH	FF12	FF12	42-23.40, 70-54.00, MASSACHUSETTS BAY NEAR NAHANT
MASSBNTH	FF13	FF13	42-19.20, 70-49.38, MASSACHUSETTS BAY NEAR THIEVES LEDGE
MASSBNTH	FF14	FF14	42-25.02, 70-39.30, STELLWAGEN BASIN
MASSBNTH	NF02	NF02	42-20.34, 70-49.68, SOUTHWEST OF OUTFALL SITE
MASSBNTH	NF04	NF04	42-24.96, 70-48.42, NORTH OF OUTFALL SITE
MASSBNTH	NF05	NF05	42-25.62, 70-50.04, NORTHWEST OF OUTFALL SITE
MASSBNTH	NF07	NF07	42-24.60, 70-48.90, NORTH OF OUTFALL SITE
MASSBNTH	NF08	NF08	42-24.00, 70-51.84, NORTHWEST OF OUTFALL SITE
MASSBNTH	NF09	NF09	42-24.00, 70-50.70, NORTHWEST OF OUTFALL SITE

Table 11. Station Identifiers			
FACILITY_ID	**LOCATION_ID**	**EM&MS STAT_ID**	**Location Description**
MASSBNTH	NF10	NF10	42-23.58, 70-50.28, WEST OF OUTFALL SITE
MASSBNTH	NF12	NF12	42-23.40, 70-49.86, WEST OF OUTFALL SITE
MASSBNTH	NF13	NF13	42-23.40, 70-49.38, WEST OF OUTFALL SITE
MASSBNTH	NF14	NF14	42-23.22, 70-49.38, WEST OF OUTFALL SITE
MASSBNTH	NF15	NF15	42-22.92, 70-49.68, WEST OF OUTFALL SITE
MASSBNTH	NF16	NF16	42-22.68, 70-50.28, WEST OF OUTFALL SITE
MASSBNTH	NF17	NF17	42-22.86, 70-48.90, WEST OF OUTFALL SITE
MASSBNTH	NF18	NF18	42-23.82, 70-49.32, NORTHWEST OF OUTFALL SITE
MASSBNTH	NF19	NF19	42-22.32, 70-48.30, SOUTH OF OUTFALL SITE
MASSBNTH	NF20	NF20	42-22.68, 70-50.70, WEST OF OUTFALL SITE
MASSBNTH	NF21	NF21	42-24.18, 70-50.22, NORTHWEST OF OUTFALL SITE
MASSBNTH	NF22	NF22	42-20.88, 70-48.90, SOUTH OF OUTFALL SITE
MASSBNTH	NF23	NF23	42-23.88, 70-48.12, NORTH OF OUTFALL SITE
MASSBNTH	NF24	NF24	42-22.86, 70-48.12, SOUTH OF OUTFALL SITE

2.8.2 Data Recording

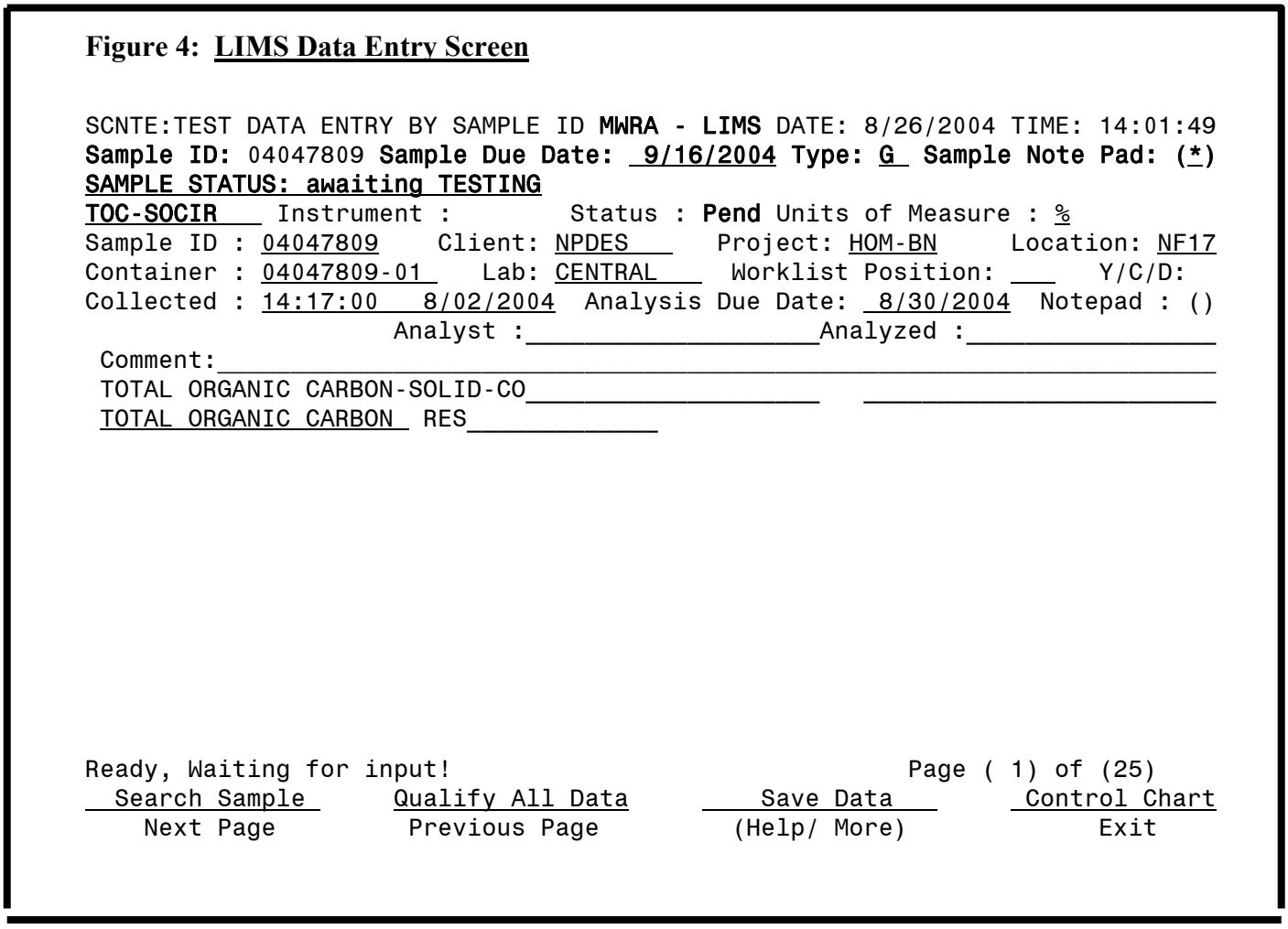
All documentation conforms to the DLS QAMP (DCN #5000), including:

- All original data are recorded in permanent ink in a bound notebook, on standardized forms, or, where applicable, in electronic files.
- Corrections are made by placing a single line through the incorrect entry.
- Corrections are initialed and dated at the time the correction is made.
- All QC data (precision, accuracy) are recorded in laboratory notebooks.

For this project, all test results are manually entered into LIMS from laboratory logbooks, spreadsheets, or instrument data system printouts. The LIMS worklist module (WKLIST) is used to create sample/test fields for routine internal laboratory QC parameters (method blanks, laboratory control samples, and laboratory duplicates). These QC tests are programmed in LIMS with test-specific warning and control limits. As results are entered, the field and QC tests are checked against limits, and the analyst is informed of any parameter that exceeds a warning or control limit. This allows gross typographical errors to be detected and as an early notification of any limit exceedance.

Completed data forms or other types of hand-entered data are signed and dated by the individual entering the data. Direct-entry and electronic data entries identify the person collecting or entering the data. An example LIMS data entry screen for this project is shown in Figure 4. It is the responsibility of the Team Supervisor to ensure that all data entries and hand calculations are verified in accordance with procedures described in Section 2.8.5.

Figure 4: LIMS Data Entry Screen



2.8.3 Analysis Comments

Comments, where necessary and appropriate are made in LIMS for sample measured/non-measured information to provide the data validator/reviewer with an explanation or description of the test results or sample characteristics. All LIMS entered comments associated with a sample/test are part of the LIMS database record for the analysis of the respective sample.

2.8.3.1 Comment Types

Comments are entered as either as free-flowing text (SAMPLE NOTEPAD COMMENTS) or as predefined text (TEST COMMENTS). Further, TEST COMMENTS for HOM analyses are only used to qualify data and are entered either by the analyst or validator.

2.8.3.1.1 Sample Notepad Comments

From time to time, the Analyst, Validator, and/or the Approver need to comment on the analyses. In such circumstances, the Validator/Approver uses the SAMPLE NOTEPAD COMMENT to enter a free-flowing text descriptive.

2.8.3.1.2 Test Comments

From time to time, a test result is reported as invalid or is qualified by the DLS. When such a situation occurs, the analyst/validator/approver annotates the reason for the invalidation or qualification by entering pre-defined text into the appropriate test comment field. The pre-defined qualifiers are listed in Table 12, below. If more than one test comment (qualifier) needs to be annotated, the pre-defined qualifier = X (See Sample Notepad) is used. The entry into the Sample Notepad contains the multiple qualifier codes and any free text deemed necessary. Note: When using the sample notepad in this manner, the comment must be prefaced with the test_code identifier. For example:

TOC-SOCIR: R; Precision does not meet data quality objectives.

Note: The EM&MS qualifiers, which are used for reporting data to Battelle, are not the same as the pre-defined LIMS test comments used to qualify analytical results.

Table 12. Test Comments Qualifiers for Qualifying/Annotating Sample Test Results

LIMS Test Comment	Description
A	Not detected - value reported as negative or missing
B	Not blank corrected, blank ≥5x MDL
E1	Calibration level exceeded
E2	Results not reported, value given is NULL, see comments field
F	Value reported <MDL, See Sample Notepad
G1	Recovery outside data quality objectives
G2	Co-eluting compound interferes with peak of interest
J	Estimated value [1]
K	Matrix interference
L	Analytical concentration reported from dilution
P	Lab sample bottles mislabeled - caution data use
Q	Accuracy does not meet data quality objectives
R	Precision does not meet data quality objectives
S	Suspect/Invalid. Not fit for use
T	Holding time exceeded
W	This datum should be used with caution, see comment field
X	See Sample Notepad for multiple qualifiers

[1]A value reported between the MDL and the lowest calibration standard is considered to be estimated.

2.8.4 Data Reduction

Data reduction procedures and formulae are defined in laboratory SOPs and in Section 7.0 of the QAMP (DCN #5000). This is performed electronically either by the instrument software or in a spreadsheet and is validated according to procedures described in Section 2.8.5.

2.8.5 Data Validation

Data validation, a two-step process, is a standardized process for judging the quality and usefulness of a discrete set of chemical data. The first data validation step for HOM data produced by the DLS involves the review of analytical results of both HOM samples and QC samples against the Data Quality Objectives (Table 9) and the quality standards in Section 7.0 of DLS' QAMP (DCN #5000). The completion of the validation process and the approval process is documented in LIMS. Until a sample is approved, the results are regarded as preliminary. Subsequent to the approval of a sample test results, data can only be changed through the DAIR process described in Section 2.8.7, below.

The second step in the process is the review of the results by the ENQUAD HOM Project Manager and is detailed in Section 4.0 below**.**

2.8.5.1 Validation of Analytical Results

The veracity and validity of analytical results are assessed throughout the analytical data result Analyst Review, Validation and Approval process, which includes, but is not limited to:

- **Analyst Review:** An assessment of the components of the analytical method (reagents, glassware cleanliness, standard expiration dates, instrument operation, etc.), QC, calculations, and data entry by the analyst;

- **Validation:** Performance of QC sample results against established limits, holding times calculation cross-checking, etc. by the Team Supervisor or his/her delegated Validator; and;

- **Approval:** Comparability and test consistency of the sample, etc. by a Lab Manager or his/her delegated Approver.

Data specified in the QAMP or specified in this plan is not to be marked as invalid in LIMS unless the data validator has provided an explanation with a Validation Comment and a Sample Notepad Comment. Data that do not meet the Data Quality Objective of this plan is annotated (See Section 2.8.3, above). When all samples from a survey are approved in LIMS, the DLS HOM Project Manager notifies the ENQUAD Project Manager and Data Management group.

2.8.6 Reporting of Results

All data are reported electronically to the ENQUAD HOM Project Manager as approved results in LIMS. Also, a QA Package (see 2.8.6.4, below) is to be forwarded to the ENQUAD HOM Project Manager immediately subsequent to the completion of the analyses of all survey samples.

2.8.6.1 Turnaround Times

In order to meet the reporting deadlines to Battelle, the sample turnaround time for benthic parameters is 42 calendar days.

2.8.6.2 Results Data Entry

Organics: For organics, "non-detects" are reported as <RL, where the RL is based on the concentration of the low standard in the ICAL (see table 6). However, all "detects" are reported, regardless of the RL or MDL, as long as they meet the following identification criteria:

- The peak must be at the correct retention time.
- The signal-to-noise ratio of the quantitation ion must be ≥ 3.
- The secondary ion ration criteria must be met.

If the ion ratio criteria are not met but it is the analyst's professional judgment that the compound is present, the compound can be reported with an "S" flag. The reasons for including a compound that fails the ion ratio criteria include: suspected interferences, if its presence is consistent with other compounds (such as Fluoranthene/Pyrene, DDE/DDT, etc.), or based on historical data.

Whenever a compound is reported at a concentration below either the MDL or RL, the data must be flagged using the TEST_COMMENTS in LIMS and the Sample Notepad (where necessary) to provide information regarding component-specific qualifiers. All sample data must be clearly marked on the data summary sheet, so that the appropriate comments can be added by the data validator.

Metals, TOC, and Solids: Results for metals and TOC are reported down to the Instrument Blank. In most cases, the Instrument Blank is equal to the MDL. In instances when the Instrument Blank exceeds the MDL, blank and sample results are reported down to the RL. For solids, results are reported down to 0.0125%. Results are expressed in the units listed in Table 8.

2.8.6.3 Traceability

Reported results must be traceable. Traceability is the characteristic of data that allows a final result to be verified by review of its associated documentation. All laboratory results for a given sample must be traceable throughout the entire analytical process applied to the sample. Traceability is maintained through LIMS (which stores all of the pertinent data associated with the sample and keeps an audit trail of all record transactions) and by the utilization of various

logbooks (preparation, analytical, and instrumental), instrument raw data printouts, electronic files, and spreadsheets. Traceability in EM&MS is documented through the use of Standard Query Language (SQL) scripts to make any corrections to the data; electronic records of scripts and their output files are maintained by ENQUAD.

2.8.6.4 QA Package

Immediately after the approval of all survey data, DLS forwards to the ENQUAD Project Manager a QA Package consisting of:

- QA results vs. acceptance ranges.
- Any descriptive QA information relevant to the delivered data (i.e. sample notepad comments).
- **Audit Reports:** Copies of the monthly rolling compliance audit and any audits that may have been specifically performed on HOM items.
- **Missing Samples Report:** A Missing Samples Report is generated by DLS and forwarded as part of the QA Package along with an explanation of why the samples are missing.
- **Corrective Action Report:** Photocopies of corrective actions associated with HOM benthic survey sample analyses.
- **DAIR (Data Anomaly Investigation Report) Report:** Photocopies of DAIRs associated with HOM benthic survey sample analyses.
- **Battelle Chain-of-Custody forms:** All signed originals.
- **QA Statement:** A QA Statement (see Figure 5) based on the Precision, Accuracy, and Representativeness (where applicable), Custody, and Comparability is compiled and forwarded to the ENQUAD Project Manager. The QA Statement is signed by the DLS HOM Project Manager and Lab Manager.

All information, including the signed QA Statement, is forwarded by inter-office mail to the ENQUAD HOM Project Manager.

Figure 5: Quality Assurance Statement

MWRA DEPARTMENT OF LABORATORY SERVICES

MWRA Harbor and Outfall Monitoring Project

Quality Assurance Statement

Description of Data Set or Deliverable:_____

1.0 Sample Analyses

All samples were handled, analyzed and reported according to the procedures and requirements specified in the CWQAPP (Leo *et al*., 2004), except as noted in the comments. Specifically:

- The custody of all samples were transferred properly and maintained. □ **Yes** □ **No**
- All of the samples on the COC were received and all required tests performed. □ **Yes** □ **No**
- QC samples were analyzed and all acceptance criteria in accordance with the DLS QAMP (DCN #5000) and the CWQAPP (Leo, *et al.,* 2004) were met. □ **Yes** □ **No**
- 100% of the data entry and 20% of manually-calculated data were checked for accuracy. □ **Yes** □ **No**
- Test/Sample Comments were assigned properly. □ **Yes** □ **No**
- All tests were validated and approved. □ **Yes** □ **No**

2.0 Attached Documentation

The following documentation, when applicable, is included in the QA Package:

- ❑ Audit Reports
- ❑ Control Charts
- ❑ Corrective Actions
- ❑ DAIRs
- □ Battelle COC Forms (Originals)

Comments:

_____
_____
_____
_____
_____

3.0 CERTIFICATION

We, the undersigned, attest that the material contained in this analytical report is, to the best of our knowledge and belief, accurate and complete.

_____ _____

DLS Project Manager *(date)* DLS Section Manager *(date)*

2.8.7 Changes to Approved Data

Once a LIMS result has been approved and released to the client, it can only be modified through the DAIR (Data Anomaly Investigation Report) process. The DAIR process is detailed in the DLS SOP DCN: 5004, "Procedures for the Response to Discoveries of Anomalies in the Department of Laboratory Services' Data Records". A DAIR is initiated by anyone who wants a data anomaly to be researched and, if possible, rectified. For example, this may result from a discovery that wasn't known when the samples were being processed (e.g. a sample was collected at the wrong location) or when results appear suspect (e.g. significantly higher or lower than previous results). The DAIR process documents the review of the suspect results, the decisions that were reached, and any changes that were made to the LIMS results. Ultimately, the client's approval (ENQUAD) is obtained before results are changed in LIMS.

In the event that apparently anomalous data needs to reviewed and, if necessary, changed after approval but before it is released by ENQUAD, the "Fast Track" DAIR process should be used.

3.0 ASSESSMENT/OVERSIGHT

3.1 Department of Laboratory Services

3.1.1 Performance and system audits

The DLS' audit procedures are documented in Section 9.0 of the QAMP (DCN #5000). A performance audit provides a quantitative assessment of the analytical measurement process. It provides a direct and independent, point-in-time evaluation of the accuracy of the various measurements systems and methods. This is accomplished by challenging each analytical system (method/procedure) with an accepted reference standard for the analyte(s) of interest. The DLS annually participates in Discharge Monitoring Report (DMR) Performance Testing (PT) studies and in the Water Pollution (WP) and Water Supply (WS) Performance Testing studies. The applicable parameters found in the PT samples are: TOC, Pesticides, PCBs, and metals. Acceptable performance on these PT samples is required for NPDES self-monitoring analyses and Massachusetts DEP Certification, respectively.

In addition, internally administered performance evaluation samples may be submitted to the laboratory sections on a random, as required, basis and for those analytes not present in the PT samples.

Monthly rolling compliance audits are performed to review laboratory operations to verify that the laboratory has the necessary facilities, equipment, staff, and procedures in place to generate acceptable data. Each month a different aspect of the laboratory operation is audited. This process identifies the strengths and weaknesses of the DLS Laboratory and areas that need improvement. Rolling audits are performed by the QA Coordinator. Any significant deviations from accepted practices result in Corrective Actions.

During the time that work is in progress, an inspection is conducted by either the DLS QA Manager or QA Coordinator in order to evaluate the laboratory data-production process. All data must be reviewed by the ENQUAD Project Manager prior to submission to the Battelle Database Manager and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality and a QC narrative of activities, as described in Section 2.8.6.4, above.

Performance audits, procedures used to determine quantitatively the accuracy of the total measurement system, or its components, are the responsibility of DLS as described above.

3.1.2 Corrective Action

Section 11.0 of DLS' QAMP (DCN #5000) details the situations that require corrective action, how corrective actions are initiated, investigated, resolved and documented to ensure a complete and systematic response to each corrective action request. Examples of situations requiring initiation of the corrective action process include mishandling of a sample or its documentation, deficiencies discovered during an internal audit, or use of unapproved modifications to an analytical method. The occurrence of a practice or incident that is inconsistent with the established quality assurance and quality control procedures of the laboratory must be formally addressed with a corrective action response. Any laboratory employee may request corrective actions when necessary. Requests for corrective action are reviewed and approved by the DLS QA Manager.

Upon the initiation of a corrective action, the problem is documented, and a corrective action plan is developed and then approved by the appropriate Laboratory Manager and QA Manager. After required corrective action has been taken, the information is documented and verified to be effective and sufficient by the appropriate Laboratory Manager and QA Manager. All information is maintained in the Corrective Action QA files. The ENQUAD Project Manager is notified of the corrective action taken.

3.2 Battelle Ocean Sciences

3.2.1 Performance and System Audits

The Battelle QA Officer for the Harbor and Outfall Monitoring Project directs an initial systems audit to ensure that analyses are carried out in accordance with this CWQAPP. In addition, the Battelle QA Officer reviews the QA Statements provided with the DLS data to ensure that they are complete, and that quality control exceedances and corrective actions have been documented.

As described in the Benthic Monitoring CWQAPP (Williams *et al.* 2002), tabular data reported in deliverables is audited under the direction of the Battelle Project QA Officer. Like other "subcontractor" laboratories on the HOM project, DLS is fully responsible for the QA of the data it submits. Data must be submitted in CWQAPP-prescribed formats; no other is acceptable.

3.2.2 Corrective Action

As defined in Battelle's CWQAPP (Williams *et al*, 2002), "All technical personnel share responsibility for identifying and resolving problems encountered in the routine performance of their duties. Ms. Ellen Baptiste-Carpenter, Battelle's Project Manager, is accountable to MWRA and to Battelle management for overall conduct of the Harbor and Outfall Monitoring Project, including the schedule, costs, and technical performance. She is responsible for identifying and resolving problems that (1) have not been addressed timely or successfully at a lower level, (2) influence multiple components of the project, (3) necessitate changes in this CWQAPP, or (4) require consultation with Battelle management or with MWRA. Dr. Carlton Hunt is the Battelle Technical Director and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise."

Identification of problems and corrective action at the laboratory level (such as meeting data quality requirements) is resolved by DLS staff and/or by ENQUAD staff. Issues that affect schedule, cost, or performance of the sediment monitoring tasks are reported to the MWRA Outfall Monitoring Program Manager and to the Battelle Project Manager. Battelle's Technical Director is notified of any issues affecting data quality. The DLS HOM Project Manager, the ENQUAD HOM Project Manager, and the MWRA Outfall Monitoring Program Manager is responsible for addressing these issues and for evaluating the overall impact of the problem on the project and for discussing corrective actions with Battelle Project Management. Problems identified by the Battelle QA Officer are reported and corrected as described in Section 17.0 of the Benthic CWQAPP (Williams *et al.* 2002.)

3.3 Work Stoppage for Cause

The ENQUAD Outfall Monitoring Manager, in consultation and conjunction with the Director of DLS, has the authority to stop any and all work for cause.

3.4 Reports to Management

Information concerning any activity or situation relating to the QA of this project is reported monthly to DLS managers and supervisors as part of DLS' monthly QA/IS (Quality Assurance/Information Systems) Report and Rolling Audit Report. The QA Coordinator prepares the monthly QA/IS Report and the Rolling Audit Report. Specific information resulting from any oversight activities is included in the QA Package (2.8.6.4) accompanying the survey results. Guidance for QA reporting can be found in Section 13.0 of DLS' QAMP (DCN #5000).

4.0 DATA VALIDATION AND USABILITY BY ENQUAD

This section addresses the review of data for fitness-for-use prior to transfer to Battelle subsequent to their being approved and validated by DLS.

4.1 Data Reduction and Transfer

4.1.1 Data Reduction and Processing

The requirements for data reduction and processing are described in the DLS QAMP (DCN # 5000), applicable laboratory SOPs, and Section 2.8 above.

4.1.2 Data Transfer

- Only approved data is transferred to EM&MS, including those marked as invalid by DLS. The data is transferred after the QA Package is received. Following LIMS approval, data is transferred overnight from LIMS automatically to Plant Operations Management System (OMS) by tested automated routines. Transfer of data from OMS to EM&MS work tables is done by tested automated routines.

- Application of qualifiers in EM&MS is done by automated routines that parse test comments applied by the laboratory, or by the ENQUAD Project Manager based on review of the data and associated comments.

- Generally, invalid data is given an EM&MS qualifier of 's'. Invalid data may be accepted into EM&MS with a qualifier other than 's' at the discretion of the ENQUAD Project Manager, provided another appropriate qualifier is used and an explanatory comment is included in the database record.

- Any manual additions or changes to qualifiers and comments by the ENQUAD Project Manager are documented in an Oracle table in the HOM Review application.

4.1.3 Change and Corrections in the EM&MS Database

The guidance for changing and correcting data in the EM&MS database is as follows:

- Corrections to data in EM&MS work or production tables is done only through the use of SQL scripts, which must include the following:

    - Indication of whether the script is to be run on work or production tables
    - Comments including the name of script, author, date, and purpose of script
    - Record of date run in spool file
    - List out records to be changed
    - Demonstrate that problem has been fixed (*e.g.* by listing changed records.)

- Changes may be made only by the EM&MS Database Administrator (Dr. Douglas Hersh) or his designee. These changes are also documented in the DB_TASKS table within the EM&MS database.

4.1.4 Data Review, Validation, and Fitness-for-Use

4.1.4.1 Data Review

The ENQUAD Project Manager uses the data preview application HOM Review, written by ENQUAD using Oracle SQL*Forms, to review the analytical results, test comments, and LIMS notepad entries. Standard LIMS test comments are parsed into EM&MS qualifiers. In order to review and assess the HOM results, the ENQUAD Project Manager:

- Reviews all data for technical reasonableness and completeness. Reviews include all rejected samples, deleted and invalid tests, and out of range results. The ENQUAD Project Manager reviews documentation in LIMS and the QA Package, and compares results to historical data distributions to check for reasonableness.

- Corrects or adds to qualifiers and comments as appropriate based on review of the data. If there are questions that cannot be resolved by examining the comments, he initiates a DAIR (see 2.8.7).

The ENQUAD Database Manager:

- Makes available for the ENQUAD Project Manager's review: the Survey Samples Results Report, the Notepad comments Report, and the Test Comments Report.

- Calculates descriptive statistics such as sample size, mean, standard deviation, minimum, and maximum after the survey results are transferred from LIMS to EM&MS via OMS.

- Ensures that the data, which is sent to Battelle, meet all applicable constraints (*i.e.* on the BOTTLE and ANALYTICAL_RESULTS tables.)

- Forwards to Battelle the QA Statement, the statistics, a list of non-detects, and pertinent information from the test comments, sample notepad comments and ENQUAD Project Manager along with the data.

4.1.4.2 Data Validation/Fitness-for-Use

The ENQUAD Project Manager determines whether the survey results are Fit-for-Use and can be transferred to Battelle for further assessment and incorporation into the respective data and synthesis reports.

The data validation procedures for this project are consistent with what is defined in the HOM 4 Quality Management Plan (Battelle 2002), except that in accordance with the DLS' QAMP

(DCN #5000) 20% of manual calculations are performed by a second staff member to verify that calculations are accurate and appropriate.

As described in Williams *et al.* 2002, data from the laboratories receive a quality assurance review after the data has been synthesized into a data report. Any issues are corrected in the database and documented in scripts and list files maintained by Battelle and MWRA data management.

4.1.4.3 Sampling Design

All sampling is performed by Battelle Ocean Sciences. This CWQAPP does not address sampling design, which is described in the Benthic Monitoring CWQAPP (Williams *et al.* 2002.)

4.1.4.4 Data Transmittal to Battelle

The ENQUAD EM&MS Database Manager sends the data to Battelle as an Oracle export file of the BOTTLE and ANALYTICAL_RESULTS work tables within one month of sampling. The QA statement from DLS, the original Battelle COCs and a cover letter describing the results of data review by ENQUAD Project Manager accompanies the data.

Further processing of laboratory data at Battelle is described in MWRA SOP 005, *Loading and Reporting Benthic Monitoring Data.*

4.1.4.5 Data Analysis

Data is analyzed and reported by Battelle as part of the synthesis reporting under the HOM contract (see Williams *et al.* 2002).

5.0 REFERENCES

Battelle. 2002. Project Management Plan for Professional Services on Harbor and Outfall Monitoring Project (Contract 366). Massachusetts Water Resources Authority Environmental Quality Department, Boston, MA 29 pp + apps.

MWRA. 2004a. Massachusetts Water Resources Authority effluent outfall ambient monitoring plan Revision 1, March 2004. Boston: Massachusetts Water Resources Authority. Report ms-092. 65 p.

MWRA 2004b. (DCN 1193.0). Department of Laboratory Services Standard Operating Procedure. "Preparation for Analysis of Total Elements in Sediment Samples by Microwave Digestion". June, 2004. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2004c. (DCN 1188.0). Department of Laboratory Services Standard Operating Procedure. "Combined Sediment Sample Extraction by Sonication for PAH, Pesticides,

and PCB Congener Analyses". June, 2004. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2004d. (DCN 1173.2). Department of Laboratory Services Standard Operating Procedure. "Trace Level PBC Congener and Pesticide Analysis by Gas Chromatography/Mass Spectrometry Using Selected Ion Monitoring." June, 2004. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2004e. (DCN 1030.3). Department of Laboratory Services Standard Operating Procedure. "Trace Level Polynuclear Aromatic Hydrocarbon Analysis by Gas Chromatograph/Mass Spectrometry using Selected Ion Monitoring (GC/MS SIM)". March, 2004. Massachusetts Water Resources Authority, Boston, MA.

MWRA. 2003a. (DCN 5000.0). Department of Laboratory Services Quality Assurance Management Plan, Revision 2.0. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2003b. (DCN 1168.0). Department of Laboratory Services Standard Operating Procedure. "Total Organic Carbon in Sediment by Combustion with Infrared Detection (Tekmar-Dorhmann, DC-190)". October, 2003. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2003c. (DCN 1150.0). Department of Laboratory Services Standard Operating Procedure. "Graphite Furnace Atomic Absorption Spectroscopy". April, 2003. Massachusetts Water Resources Authority, Boston, MA.

MWRA. 2001a. Massachusetts Water Resources Authority Contingency Plan Revision 1. Boston: Massachusetts Water Resources Authority. Report ms-071. 47 p.

MWRA 2001b. (DCN 1094.0). Department of Laboratory Services Standard Operating Procedure. "Percent Total, Volatile, and Fixed Solids in Solid and Semisolid Samples". September, 2001. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2001c. (DCN 1073.0). Department of Laboratory Services Standard Operating Procedure. "Pesticides/PCB's Soils by Sonication". June, 2001. Massachusetts Water Resources Authority, Boston, MA.

MWRA 2000. (DCN 1008.2). Department of Laboratory Services Standard Operating Procedure. "Metals Analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy". April, 2000. Massachusetts Water Resources Authority, Boston, MA.

MWRA 1999a. (DCN 1049.0). Department of Laboratory Services Standard Operating Procedure. "Mercury Analysis by Cold Vapor Atomic Absorption Spectroscopy (CETAC M6000A)". November, 1999. Massachusetts Water Resources Authority, Boston, MA.

MWRA 1999b. (DCN 1027.0). Department of Laboratory Services Standard Operating Procedure. "Digestion of Solid Samples for Mercury Analysis". March, 1999. Massachusetts Water Resources Authority, Boston, MA.

USEPA. 1997. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory (NERL) EPA/600/R-97/072.

Williams IP, Maciolek NJ, Boyle JD, Dahlen DT and Baptiste-Carpenter EM. 2002. Combined work/quality assurance plan for benthic monitoring: 2002-2005. Boston: Massachusetts Water Resources Authority. Report ms-076. 109 p.

Williams IP, et al. 2004, in prep. Combined work/quality assurance plan for benthic monitoring: 2004-2005. Boston: Massachusetts Water Resources Authority. Report ms-x. x p.