

**COMBINED WORK/QUALITY
ASSURANCE PROJECT PLAN
(QAPP)**

for

**Nutrient and Chlorophyll Analyses for
Outfall Monitoring
Revision 1**

Massachusetts Water Resources Authority

**Environmental Quality Department
Report ENQUAD 2005-04**



Citation: Leo, W, W Andruchow, MF Delaney, and P Epelman. 2006. **Combined Work/Quality Assurance Project Plan (QAPP) for Nutrient and Chlorophyll Analyses for Outfall Monitoring, Revision 1**. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2005-04. 41 p.

Combined Work/Quality Assurance Project Plan (QAPP)

for

**Nutrient and Chlorophyll Analyses for Outfall Monitoring
Revision 1**

Prepared by

Wendy Leo¹
William Andruchow²
Michael F. Delaney²
Polina Epelman²
Yong Lao²

¹Environmental Quality Department
Massachusetts Water Resources Authority
100 First Avenue
Boston, MA 02129
(617) 788 - 4601

²Department of Laboratory Services
Massachusetts Water Resources Authority
190 Tafts Avenue
Winthrop, MA 02152
(617) 660-7800

March, 2005
Revised January 2006

Environmental Quality Department
Technical Report 2005-04

Combined Work/Quality Assurance Project Plan (QAPP)
for
Nutrient and Chlorophyll Analyses for Outfall Monitoring
Revision 1

ENQUAD Project Manager:

Mr. Maurice Hall, Project Manager
Massachusetts Water Resources Authority
(617) 788-4721

Date

Laboratory Project Manager:

Dr. Yong Lao, Project Manager
Massachusetts Water Resources Authority
(617) 660-7841

Date

Environmental Monitoring and Management Database Manager:

Ms. Wendy Leo, Project Manager Marine Studies
Massachusetts Water Resources Authority
(617) 788-4743

Date

Laboratory Quality Assurance Officer:

Dr. William Andruchow, QA Manager
Massachusetts Water Resources Authority
(617) 660-7804

Date

Distribution List

William Andruchow, MWRA (QA Manager, DLS¹)
Michael Delaney, MWRA (Director, DLS)
Polina Epelman, MWRA (Section Manager, DLS)
Maurice Hall, MWRA (Project Manager)
Wendy Leo, MWRA (Project Manager, Marine Studies)
Nancy McSweeney, MWRA (Supervisor, DLS)
Michael Mickelson, MWRA (Outfall Monitoring Program Manager)
Laura Ducott, MWRA (Supervisor, Laboratory Services)
Jennifer Prasse, MWRA (QA Coordinator, DLS)
Steven Rhode, MWRA (Section Manager, DLS)
Patricia Sullivan, MWRA (Supervisor, DLS)
Edward Caruso, Jr., MWRA (Client Services Coordinator, DLS)
Cara Seaman, MWRA (Acting Supervisor, DLS)
Yong Lao, MWRA (HOM Project Manager, DLS)
Ellen Baptiste-Carpenter, Battelle (Project Manager and Senior Scientist)
Rosanna Buhl, Battelle (QA Officer)
Carlton Hunt, Battelle (Technical Director)
Scott Libby, Battelle (Senior Scientist. Water Column Monitoring)

¹ DLS = Department of Laboratory Services

TABLE OF CONTENTS

1.0 PROJECT MANAGEMENT 1

- 1.1 Project Organization 1
- 1.2 Communication Plan 4
- 1.3 Project Definition and Background 6
- 1.4 Project Description and Schedule 6
- 1.5 Quality Objectives and Criteria for Measurement Data 8
 - 1.5.1 Quality Objectives 8
 - 1.5.2 Measurement Performance Criteria 9
- 1.6 Special Training Requirements and Certification 11
- 1.7 Documentation and Records 11
 - 1.7.1 Document Control 11
 - 1.7.2 Analyses Records 12
 - 1.7.3 Records Retention and Storage 12
 - 1.7.4 LIMS Electronic Records 12
 - 1.7.5 Records Managed by ENQUAD 12

2.0 MEASUREMENT/DATA ACQUISITION 12

- 2.1 Sampling Process Design (Experimental Design) 12
 - 2.1.1 Scheduled Project Activities, Including Measurement Activities 12
 - 2.1.2 Design Rational 12
 - 2.1.3 Design Assumptions 13
 - 2.1.4 Procedures for Locating and Selecting Environmental Samples 13
 - 2.1.5 Classification of Measurement as Critical or Non-Critical 13
- 2.2 Sampling Methods Requirements 13
 - 2.2.1 Sample Collection, Preparation, Documentation Procedures 13
 - 2.2.2 Sampling/Measurement System Failure Response 13
- 2.3 Sample Handling and Custody Procedures 14
 - 2.3.1 Sampling Equipment, Preservation and Holding Time Requirements 14
 - 2.3.2 Sample Custody Procedures 14
 - 2.3.3 Sample Receipt and Check-In 15
- 2.4 Analytical Requirements 16
 - 2.4.1 Analytical Methods 16
 - 2.4.2 Quality Control Requirements 20
- 2.5 Instrument/Equipment Testing, Inspection and Maintenance 22
- 2.6 Instrument Calibration and Frequency 22
- 2.7 Tracking and Quality Verification of Supplies and Consumables 22
- 2.8 Data Management 26
 - 2.8.1 Acquisition of Non-Direct Measurement Data 26
 - 2.8.2 Data Recording 27
 - 2.8.3 Analyses Comments 27
 - 2.8.4 Data Reduction 30
 - 2.8.5 Data Validation 30
 - 2.8.6 Reporting of Results 30
 - 2.8.7 Changes to Approved Data 30

3.0 ASSESSMENT AND OVERSIGHT	35
3.1 Department of Laboratory Services	35
3.1.1 Performance and System Audits	35
3.1.2 Corrective Actions	35
3.2 Battelle Ocean Sciences	36
3.2.1 Performance and System Audits.....	36
3.2.2 Corrective Action	36
3.3 Work Stoppage for Cause	37
3.4 Reports to Management	37
4.0 DATA VALIDATION AND USABILITY BY ENQUAD	37
4.1 Data Reduction and Transfer	37
4.1.1 Data Reduction and Processing	37
4.1.2 Data Transfer	37
4.1.3 Change and Corrections in the EM&MS Database.....	38
4.1.4 Data Review, Validation and Fitness-for-Use	38
5.0 REFERENCES	40

LIST OF FIGURES

Figure 1	Organizational Chart for Nutrient, DOC, TSS and Chlorophyll Tests for the Outfall Monitoring Program	3
Figure 2	Battelle Chain-of-Custody Form	18
Figure 3	DLS LIMS Internal Chain-of-Custody	19
Figure 4	LIMS Data Entry Screen	29
Figure 5	Quality Assurance Statement	34

LIST OF TABLES

Table 1	DLS Reporting Relationships	2
Table 2	Contact Information	4
Table 3	Email cc: List	5
Table 4	Nearfield DLS Nutrient Sample Analyses	7
Table 5	Farfield DLS Nutrient Sample Analyses	7
Table 6	Parameter Measured, Units and Number of Samples	8
Table 7	Desired Precision, Accuracy and MDL for Each Parameter Based on Quality Objectives	10
Table 8	Sample Collection and Storage	14
Table 9	Methods for Water Column Sample Analyses to be Conducted by DLS	16
Table 10	Quality Control Samples	24
Table 11	Calibration Procedures for Laboratory Instruments	25
Table 12	Station Identifiers	26
Table 13	Sample Depth Codes	27
Table 14	Test Comments for Qualifying/Annotating Sample Test Results	30

1.0 PROJECT MANAGEMENT

1.1 Project Organization

Figure 1 presents the project management structure for nutrient and chlorophyll 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 nutrients, chlorophyll, and oxygen analyses that are part of the water column study in the MWRA's outfall ambient monitoring program (bay water quality monitoring study, or BWQM.)

ENQUAD Dr. Michael Mickelson is the Outfall Monitoring Program Manager for ENQUAD and is also primarily responsible for water column studies within that program. Mr. Maurice Hall, Project Manager, 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 insure that the data collected as part of the monitoring project satisfies the quality objectives set forth in this QAPP. Ms. Wendy Leo leads the data management group and serves as ENQUAD's quality assurance manager. She will be 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 Dr. Yong Lao is the Laboratory's Project Manager and will be DLS' primary point of contact for this project. Ms. Polina Epelman is the Section Manager responsible for the Red and Orange Teams. Ms. Nancy McSweeney is the Supervisor of the Red Team, responsible for nutrient analyses. Ms. Patricia Sullivan is the Supervisor of the Orange Team, responsible for DOC analyses. Mr. Steve Rhode is the Section Manager responsible for client services, sample management (Violet Team), and the Indigo Team. Ms. Laura Ducott is supervisor of the Indigo Team, responsible for seawater TSS and chlorophyll analyses. Ms. Cara Seaman. is acting supervisor of the Violet team, responsible for sample management. Mr. Edward Caruso, Jr. is Client Services Coordinator. He is responsible for providing Battelle with sample identification numbers and assisting with sample management. Dr. William Andruchow is the Quality Assurance manager for Laboratory Services and oversees the QA/QC and Supervisor of the Yellow Team. Ms. Jennifer Prasse is the QA Coordinator and is responsible for the laboratory's Proficiency Testing programs and laboratory oversight/audits programs. Dr. Michael Delaney is the Director of Laboratory Services. The DLS reporting relationships and functional responsibilities are shown in the table below.

Table 1. DLS Reporting Relationships				
Michael Delaney, Director of Laboratory Services				
Polina Epelman, Lab Manager (Operations)		Steven Rhode, Lab Manager (Client Services)		William Andruchow, Lab Manager (Quality Assurance)
Nancy McSweeney Supervisor, Red Team	Patricia Sullivan Supervisor, Orange Team	Cara Seaman Acting Supervisor. Violet Team	Laura Ducott Supervisor, Indigo Team	Jennifer Prasse QA Coordinator
DIN, Particulate Carbon, Nitrogen and Phosphorous, Biogenic Silica	DOC	Sample Management	Chlorophyll, Phaeophytin, TSS	Performance Testing, Oversight and Document Control

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 ensuring that Battelle's reviews of data reports, produced by ENQUAD using DLS data, adhere to the Water Column QAPP (Libby *et al.* 2006 in prep.) Mr. Scott Libby is the BOS Task Area Manager for the water column study, and thus will be the first and principal user of the data.

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 Nutrients, DOC and Chlorophyll Test for the Outfall Monitoring Program

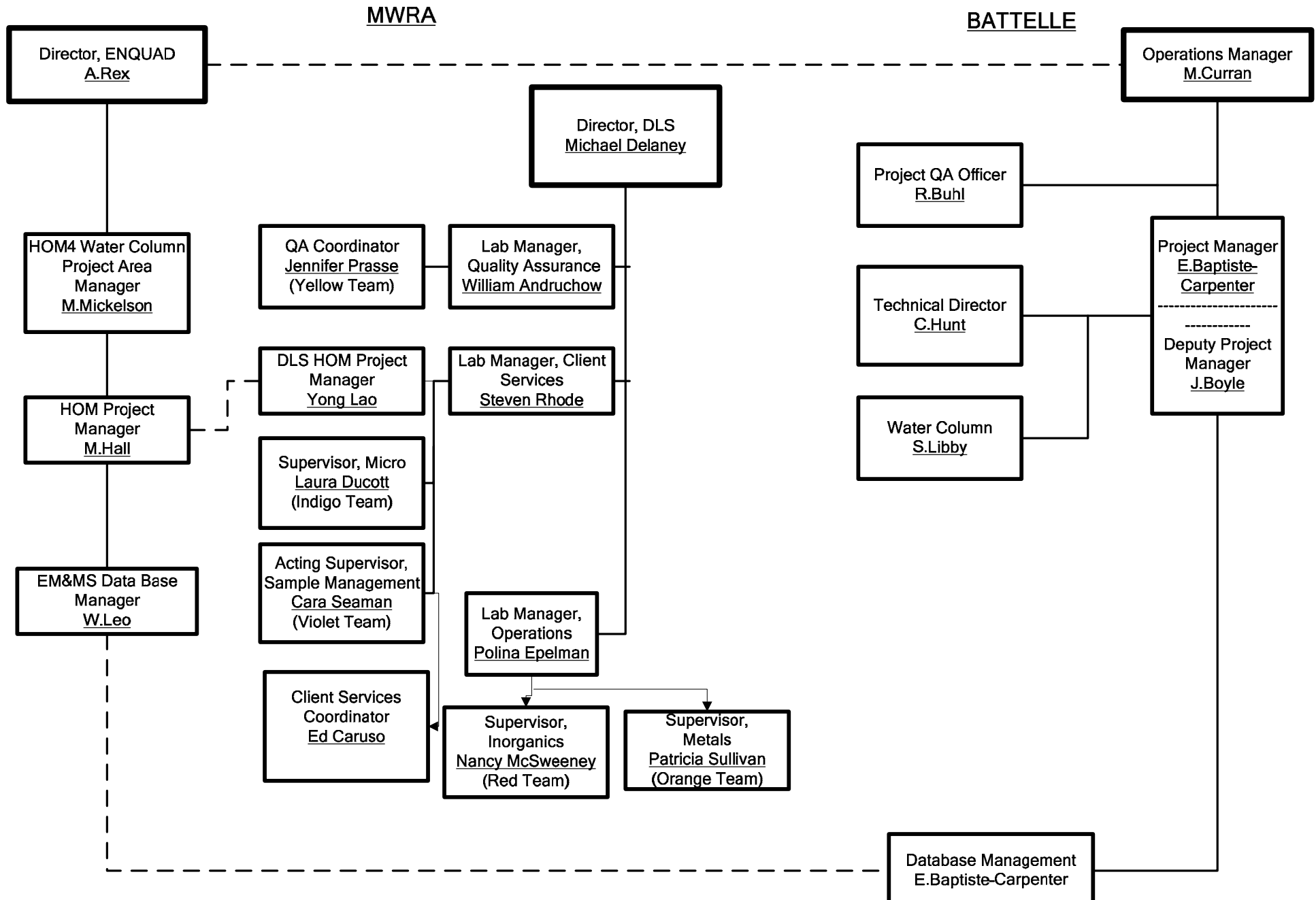


Table 2.		Contact Information		
Name	Title/Role	Location	email	Phone
Bill Andruchow	Laboratory QA Manager (Yellow)	DLS ¹	william.andruchow[at]mwra.state.ma.us	617-660-7804
Ellie Baptiste-Carpenter	HOM4 Project Manager	BOS ²	baptiste[at]battelle.org	781-952-5361
Mike Delaney	Laboratory Director	DLS	Michael.delaney[at]mwra.state.ma.us	617-660-7801
Polina Epelman	Laboratory Manager (Red, Orange)	DLS	polina.epelman[at]mwra.state.ma.us	617-660-7802
Alex Mansfield	Field Manager	BOS	mansfielda[at]battelle.org	781-934-0571
Doug Hersh	EM&MS Database Administrator	ENQUAD ³	douglas.hersh[at]mwra.state.ma.us	617-788-4738
Maury Hall	ENQUAD Project Manager	ENQUAD	maurice.hall[at]mwra.state.ma.us	617-788-4721
Wendy Leo	EM&MS Manager	ENQUAD	wendy.leo[at]mwra.state.ma.us	617-788-4743
Scott Libby	Water Column Task Area Manager	BOS	libby[at]battelle.org	781-952-5375
Nancy McSweeney	Team Supervisor (Red)	DLS	nancy.mcsweeney[at]mwra.state.ma.us	617-660-7846
Mike Mickelson	Outfall Monitoring Program Manager	ENQUAD	mike.mickelson[at]mwra.state.ma.us	617-788-4746
Laura Ducott	Team Supervisor (Indigo)	DLS	laura.ducott[at]mwra.state.ma.us	617-660-7832
Jennifer Prasse	QA Coordinator (Yellow)	DLS	jprasse[at]mwra.state.ma.us	617-660-7808
Steve Rhode	Laboratory Manager (Violet, Indigo)	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
Cara Seaman	Acting Team Supervisor (Violet)	DLS	cara.seaman[at]mwra.state.ma.us	617-660-7851
Ed Caruso	Client Services Coordinator	DLS	edward.carusojr[at]mwra.state.ma.us	617-660-7807
Yong Lao	DLS Project Manager	DLS	yong.lao[at]mwra.state.ma.us	617-660-7841

¹ Department of Laboratory Services, MWRA, 190 Tafts Avenue, Winthrop, MA 02152, 617-660-7800

² Battelle Ocean Sciences, 397 Washington Street, Duxbury, MA 02332, 781-934-0571

³ Environmental Quality Department, MWRA, 100 First Avenue, Boston, MA 02129, 617-788-4601

1.2 Communication Plan

Mr. Maury Hall will be the primary contact with Battelle on technical issues. Dr. Yong Lao will be DLS' primary contact with ENQUAD. Communication between DLS and Battelle staff at all levels of the team is encouraged; they should keep ENQUAD informed (see "email" below.)

Dr. Yong Lao will attend HOM project meetings, held quarterly at Battelle in Duxbury (March, June, September, 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 internal weekly scheduling and coordination meeting on Tuesdays, which are attended by the DLS Lab Managers and Supervisors.

Table 3. Email cc: List	
<i>If the subject is...</i>	<i>Copy the email to...</i>
Any	Maury Hall, Yong Lao
transfer of samples	Alex Mansfield, Cara Seaman (Violet), Ed Caruso
data interpretation	Mike Mickelson, Scott Libby
laboratory technical issues	Relevant DLS Team Manager(s): <ul style="list-style-type: none"> ▪ L. Ducott (Indigo-TSS/chl), ▪ N. McSweeney (Red-nutrients), ▪ P. Sullivan (Orange-DOC), Polina Epelman, Steve Rhode Scott Libby (issues affecting data interpretation) Deirdre Dahlen (issues affecting data quality)
data management/database	Wendy Leo
cost/schedule	Ken Keay, Mike Delaney Ellie 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)

Email will be the primary day-to-day communication method.

The individuals listed in Table 3 will 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 HOM5 archive HOM5@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, the DLS Violet Team will immediately notify the Battelle Field Manager (Mr. Alex Mansfield) as well as Dr. Yong Lao and Mr. Maury Hall.

Changes to the number of planned samples should be communicated to the Violet Team, Dr. Yong Lao and Mr. Maury Hall 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.

1.3 Project Definition and Background

The background of the HOM project can be found in the HOM Project Management Plan (Battelle, 2002), and more comprehensive background for the water column monitoring in the QAPP for Water Column Monitoring (Libby *et al.* 2005, Libby *et al.* 2006 in prep.) A principal concern with the offshore outfall discharge is nutrients and their resultant eutrophication effects on the water column. Thus, water quality monitoring includes measurements of nutrient concentrations (particulate and dissolved forms), phytoplankton biomass in the form of chlorophyll, and dissolved oxygen.

From 1992-2003 the nutrient and chlorophyll analyses have been conducted by subcontractor laboratories to the HOM consultant (currently, Battelle Ocean Sciences.) This QAPP reflects a change in analytical laboratories and describes the quality system implemented for analytical procedures that will be performed for the HOM project by the MWRA DLS.

1.4 Project Description and Schedule

The Harbor and Outfall Monitoring (HOM) Project water column surveys have been conducted since 1992 and are scheduled to continue at least through 2007. The water column QAPP (Libby *et al.*, 2006 in prep.) describes activities specific to the water column surveys of Massachusetts Bay and Cape Cod Bay conducted several times per year.

The nutrient and chlorophyll analyses are intended to describe the water quality by measuring concentrations of dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate), total dissolved organic nitrogen and phosphorous, dissolved organic carbon, particulate carbon and nitrogen, particulate phosphorous, biogenic silica, chlorophyll *a* and phaeophytin, and total suspended solids (TSS). Chlorophyll measurements are used to calibrate *in situ* probes.

The water column monitoring data are used to verify that the impact of the discharge on the environment is within the bounds predicted (USEPA, 1988); and to test whether change within the system exceeds the MWRA Contingency Plan (MWRA, 2001) thresholds.

The study includes seven sampling locations in the nearfield sampled twelve times per year, and 26 stations in the farfield, sampled six times per year. "Nearfield" refers to a 10 km x 11km rectangle area centered on the outfall. "Farfield" refers to the rest of Massachusetts and Cape Cod Bays and Boston Harbor.

Samples collected at each location (relevant to this QAPP) are listed in Tables 4 and 5.

Table 4. Nearfield DLS Nutrient Sample Analyses			
Stations	DIN ^a	Other Nutrients ^b	Chlorophyll ^c
N01, N20, N16, N10, N07, N04, N18	5 depths	3 depths ^d	5 depths

^a DIN = Dissolved Inorganic Nutrients = Nitrate, Nitrite, Ammonium, Orthophosphate, Silicate

^b Other nutrients = particulate and dissolved organic nutrients [Dissolved Organic Carbon (DOC), Total Dissolved Nitrogen (TDN), Total Dissolved Phosphorous (TDP), Particulate Carbon (PC), Particulate (PN), Particulate Phosphorous (PP), Biogenic Silica (Bsi) and Total Suspended Solids (TSS)]

^c Laboratory analyses for chlorophyll and phaeophytin. The number of chlorophyll analyses may be reduced.

^d Surface, chlorophyll maximum or mid-depth, bottom

Table 5. Farfield DLS Nutrient Sample Analyses			
Stations	DIN ^a	Other Nutrients ^b	Chlorophyll ^c
F03, F05, F07, F10, F12, F14, F15, F16, F17, F18, F28, F29	5 depths		
F01, F02, F06, F13, F19, F22, F23, F24, F25, F26, F27, N16	5 depths	3 depths ^d	5 depths
F30, F31 (harbor stations)	3 depths	3 depths ^d	3 depths

^a DIN = Dissolved Inorganic Nutrients = nitrate, nitrite, ammonium, orthophosphate, silicate

^b Other nutrients = particulate and dissolved organic nutrients [Dissolved Organic Carbon (DOC), Total Dissolved Nitrogen (TDN), Total Dissolved Phosphorous (TDP), Particulate Carbon (PC), Particulate (PN), Particulate Phosphorous (PP), Biogenic Silica (Bsi) and Total Suspended Solids (TSS)]

^c Laboratory analyses for chlorophyll, and phaeophytin. The number of chlorophyll analyses may be reduced.

^d Surface, chlorophyll maximum or mid-depth, bottom

The twelve nearfield surveys per year target weeks number 6, 9, 12, 15, 20, 25, 30, 34, 36, 40, 43, and 46. The six farfield surveys per year target weeks number 6, 9, 15, 25, 34, and 43. Table 5 identifies the parameters, LIMS codes, and sample numbers planned for the nearfield and farfield surveys.

Table 6. Parameters Measured, Units and Number of Samples					
Parameter	LIMS code	Units	# Samples/survey (6 nearfield-only)	# Samples/survey (6 nearfield/farfield)	Total samples/year
Nitrate+Nitrite	NO32OWAAN	μM	7x5=35	(7x5)+ [(24x5)+(2x3)]=161	1176
Nitrite	NO2-OWAAN	μM	35	161	1176
Ammonium	NH3-OWAAN	μM	35	161	1176
Phosphate	PO4-OWAAN	μM	35	161	1176
Silicate	SIO4OWAAN	μM	35	161	1176
Total dissolved nitrogen	TDN-OWAAN	μM	7x3=21	(7x3)+(14x3) = 63	504
Total dissolved phosphorus	TDP-OWAAN	μM	21	63	504
Dissolved organic carbon	DOC-OWCIR	μM	21	63	504
Particulate nitrogen	PN--OWCHN	μM	21	63	504
Particulate phosphorus	PP--OWOXA	μM	21	63	504
Particulate carbon	PC--OWCHN	μM	21	63	504
Biogenic silica	BS--OWAAN	μM	21	63	504
Chlorophyll <i>a</i>	CHLAOWFLU	μg/L	35	35+[(12x5)+(2x3)] = 101	816
Phaeophytin	PHAEOWFLU	μg/L	35	101	816
Total suspended solids	TSS-OWGRV	mg/L	21	63	504

1.5 Quality Objectives and Criteria for Measurement Data

The parameters measured, the concentration reporting units and the number of samples are listed in Table 6.

1.5.1 Quality Objectives

Data quality objectives are as follows:

- To ensure that parameters measured will adequately describe the effects of effluent discharge on eutrophication status of Massachusetts Bay,
- To ensure that sample results are representative of the location sampled and are accurate.

1.5.2 Measurement Performance Criteria

The objectives will be met by examining data collected on BWQM surveys to quantify nutrient, TSS and/or chlorophyll concentrations in the receiving waters of interest, 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/filter blanks, prepared standards, standard reference materials (SRMs), where available, laboratory control samples (LCS), laboratory replicates and field replicates, as applicable. Table 7 lists the desired precision, accuracy, and detection limit goals for each parameter to be measured. QC samples to be analyzed in the laboratory to assess precision and accuracy are listed in Table 10 in section 2.4.2. Method procedural blanks for parameters that use blank correction are the batch-average uncorrected method procedural blanks. To facilitate tracking blank adjustment in LIMS, the values entered in LIMS are in “instrument signal” units for Particulate Carbon and Nitrogen and for Particulate Phosphorus the value entered in LIMS is the raw blank results uncorrected for sample volume.

There is no SRM for particulate nutrients, but marine sediment SRM (BCSS sediment from Canada) is analyzed by DLS on a quarterly basis for particulate carbon and nitrogen. This sediment SRM is certified for total carbon and there is a reference value for total nitrogen. Analytical results are compared to those C and N values (certified and reference, respectively) and the data quality objective is 85%-115% recovery. Duplicate filter samples are collected for all particulate nutrients and 5% of the duplicate samples will be analyzed as a measure of precision. For particulate nutrients, analysis of duplicate filters is a measure of both laboratory and field precision as it is impossible to separate the effects of sample processing and instrumental analysis.

1.5.2.2 Comparability

Data will be directly comparable to results obtained previously at the same or similar sites in Massachusetts Bay and to those of similar studies conducted in Cape Cod Bay (see Libby *et al.* 2005), 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 will be 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.

To verify that data generated for the HOM study are comparable to data generated for harbor monitoring studies, an inter-comparison study will be performed during 2004 and occasionally thereafter (at dates to be defined.) Samples from either HOM or Harbor (BHWQM) surveys or MWRA sampling activities will be split analyzed under both projects to establish comparability between projects.

Reporting units for concentrations will follow standard convention for most oceanographic studies.

1.5.2.3 Representativeness

Representativeness is addressed primarily in sampling design. The sampling practices and laboratory measurements that will be performed during the water quality monitoring have already been used in many systems to characterize eutrophication effects on the water column and are, therefore, considered to yield data representative of the study area. Representativeness will also be 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 QAPP will be 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 7) provide the sensitivity goals for the procedures. The MDLs listed in Table 7 are comparable to those listed in Libby, et al. (2002). For DOC, a Practical Detection Limit (PDL) is listed because the method's precision and accuracy are too poor at the measured MDL.

Data users should be aware that precision and accuracy generally degrade as analyte concentrations decrease. While numerical results are being reported down to the MDL (or PDL), results below the lowest calibration standard will often have precision and accuracy that doesn't meet the projects data quality objectives. Results will be qualified as described in 2.3.3 with the qualifiers listed in Table 14.

Parameter	Field Precision	Lab Precision	Accuracy	Blank Cleanliness	Current MDL (or PDL) ¹
Nitrate/Nitrite Nitrite Ammonium Phosphate Silicate	≤ 30% RPD for field duplicates	≤ 10% RPD ² for instrument duplicates	±15% PD ³ based on recovery of standards	Method procedural blank ≤5 x MDL Field Blank ≤5 x MDL	0.025 μM 0.013 μM 0.028 μM 0.010 μM 0.036 μM
Total dissolved nitrogen Total dissolved phosphorus Dissolved organic carbon	≤ 30% RPD for field duplicates	≤ 10%RPD for laboratory (instrument) duplicates	±15% PD based on recovery of standards	Field Blank ≤5 x MDL	1.61 μM 0.11 μM (25 μM)
Particulate nitrogen Particulate phosphorus Particulate carbon	≤ 30% RPD for field duplicates		±15% PD based on recovery of standard reference material ⁴	Method filter procedural blank ≤5 x MDL	0.12 μM 0.006 μM 0.78 μM
Biogenic silica	≤ 30% RPD for field duplicates		±15% based on recovery of standards	Method filter procedural blank <5 x MDL	0.003 μM
Chlorophyll <i>a</i> and phaeophytin	≤ 50% RPD for field duplicates	≤15% RPD for laboratory (instrument) duplicates	±15% PD based on recovery of standards	Filter blank ≤5 x MDL	0.1 μg/L and 0.1 μg/L

Total suspended solids		≤ 20% RPD for laboratory duplicates (processing duplicates)	±20% PD ³ based on recovery of standards	Method Procedural blank and Method filter blank ≤ 5 x MDL	0.24 mg/L
------------------------	--	---	---	--	-----------

¹ MDL = method detection limit. PDL = practical detection limit. The actual MDL may be updated periodically. MDLs are based on the target sample volumes shown in Table 8. PDLs are used when the MDL is too low to be verified. PDLs are based on either the lowest concentration that gives reasonable precision and accuracy or the lowest calibration standard, whichever is lower. Note that most of the DIN MDLs are too low to be verified using the normal DLS procedure, but they have been retained as the lower reporting limit for historical reasons. Accuracy and precision decrease below the lowest calibration standard.

² Relative Percent Difference (RPD)% = $\left| \frac{\text{replicate 1} - \text{replicate 2}}{\text{replicate 1} + \text{replicate 2}} \right| \times 100$.

³ Percent Difference (PD) % = $\left[\frac{\text{true concentration} - \text{measured concentration}}{\text{true concentration}} \right] \times 100$.

⁴ There is no SRM for particulate nutrients, but marine sediment SRM (BCSS sediment from Canada) is analyzed on a quarterly basis. This sediment SRM is certified for total carbon and there is a reference value for total nitrogen. Analytical results are compared to those C and N values (certified and reference, respectively).

1.5.2.5 Completeness

It is expected that 100% of the samples collected and intended for analysis will be analyzed. However, a sample loss of <10% for the entire project will not compromise the objectives of the project.

1.6 Special Training Requirements and Certification

Nutrient and chlorophyll measurements for the HOM study use routine laboratory analyses, or data validation, therefore specialized training is not required. Each analyst's test specific training is documented in their training files maintained by the DLS QA Team (Yellow) Also, all DLS analysts and supervisors are experienced in standard protocols specified in MWRA's Department of Laboratory Services Quality Assurance Management Plan (QAMP, DCN 5000, section 3.0) for handling, storing, and preparing samples for analysis. Laboratory personnel are also experienced in using the equipment identified within this QAPP. DLS analysts are certified in the analyses that they perform according to the requirements detailed in Section 3.0 of DLS' QAMP (DCN: 5000). Certifications relevant to implementing this plan are not required.

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 will maintain documents relevant to laboratory analysis activities and entry of data into the 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 QAPP (Leo, *et al.*, 2006), the DLS QAMP (DCN: 5000) and the analysis SOPs (See Table 8). The guidance for the control of DLS' document is set forth in the DLS SOP DCN: 5006. "Guidance for Writing, Revising and Approving

Standard Operating Procedures”. After revision and approval, all documents are immediately distributed to the respective Team/Supervisor/analyst. A copy of the most current analyses SOP is kept in the lab area where the analysis is being performed. This document references the SOP number without the revision number. Significant SOP revisions will be brought to the attention of the project management.

Document Control is the responsibility of DLS’ Laboratory Manager, Quality Assurance.

1.7.2 Analyses Records

All data will be recorded initially into bound laboratory logbooks, onto established data forms or onto electronic file, where applicable. Sampling logs associated with custody and tracking will be held in the custody of the Violet Team Supervisor responsible for sample management. Field measurements and laboratory analytical results will subsequently be 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. All records are kept for a period of ten (10) 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 (10) years.

1.7.5 Records Managed by ENQUAD

ENQUAD will maintain 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 BWQM study is performed on an ongoing basis as specified in Libby *et al.* 2006 in prep. It has been ongoing, with slight changes in sampling frequency and sampling locations, since 1992, thus including twelve years of monitoring. The BWQM study will include, on average, 12 sampling events per year (6 farfield and 6 combined nearfield/farfield) between February and November of each year.

2.1.2 Design Rationale

The objective of the BWQM study is to measure water quality changes after wastewater discharges were transferred offshore to Massachusetts Bay. The evaluation of water quality changes due to the transfer of discharges offshore will be assessed through measurement of nutrient and chlorophyll concentrations, among others. The most frequent samples are collected at the nearfield stations, where outfall effects are most likely. Farfield stations serve as reference stations as well as documenting the spatial extent of any change due to the outfall.

2.1.3 Design Assumptions

It is assumed that the water properties change only gradually with depth so that five sampling depths can characterize the vertical variation of nutrients (three depths at the two shallow Boston Harbor stations.) It is also assumed that the spatial scales of variation are large enough that the sampling locations selected for each region are representative of water quality for that region. It is also assumed that, since surveys are conducted independent of tidal influence and weather that the annual survey frequency is high enough that fluctuations in conditions due to weather or tide will not result in biased results.

2.1.4 Procedures for Locating and Selecting Environmental Samples

The choice of sampling locations is discussed in the Ambient Monitoring Plan (MWRA 2003a) and in the QAPP for Water Column monitoring (Libby et al. 2005, Libby *et al.* 2006 in prep.) This QAPP 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 2003a).

2.2 Sampling Methods Requirements

2.2.1 Sample Collection, Preparation, Decontamination Procedures

Samples for each suite of analytes are collected in PVC rosette bottles at various depths as described in Libby *et al.* 2006 in prep. The sample bottles and the associated analytes are shown in Table 8, along with field preservation method and holding time. DLS provides the filters for the particulate carbon, particulate nitrogen, biogenic silica and dissolved inorganic nutrient samples, as well as all sample containers. All other field supplies and filters are provided by BOS.

2.2.2 Sampling/Measurement System Failure Response and Corrective Action Process

Corrective action in the field is covered in Libby *et al.* 2006 in prep.

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.

Parameter	Sample Volume (Target) (mL)^a	Sample Containers^b	Shipboard Processing/ Preservation^b	Maximum Holding Time to Analysis
Dissolved inorganic nutrients	40	125-mL polyethylene bottle	Pass through a Nucleopore membrane filter. Freeze filtrate until analysis.	28 days
Dissolved organic carbon	25	40-mL borosilicate glass vial (or Teflon)	Pass sample through a GF/F ^c . Freeze filtrate until analysis.	28 days
Total dissolved phosphorus and nitrogen	20	125-mL polyethylene bottle or 30- mL borosilicate glass test tube	Pass sample through a GF/F. Freeze filtrate until analysis.	28 days
Particulate organic carbon and nitrogen	10 – 500 (500)	Whatman GF/F in foil	Pass through a GF/F. Freeze filter until analysis.	28 days
Particulate phosphorus	25 – 500 (400)	Whatman GF/F in foil	Pass sample through a GF/F. Freeze filter until analysis.	28 days
Biogenic silica	25 – 500 (400)	Nucleopore filter in foil	Pass sample through Nucleopore filter. Freeze filter until analysis.	90 days
Chlorophyll <i>a</i> and phaeophytin	25 – 400 (400)	Whatman GF/F in foil	Pass through GF/F. Fix with a saturated MgCO ₃ solution. Freeze filter until analysis.	28 days
Total suspended solids	100 – 500 (300)	1-L dark bottle	Store water in 1-L dark bottle at 4°C up to and during transport to DLS for filtration.	7 days

^a Volume processed for analysis. Total volumes removed from Rosette sampling bottles are listed in Appendix A of Libby *et al.* 2005.

^b Name brand items (*e.g.*, Nucleopore, Whatman) may be substituted with comparable items from a different manufacturer.

^c GF/F: glass fiber filter. Particulate carbon/nitrogen GF/F are pre-ashed by DLS. Other GF/F are provided by Battelle.

2.3 Sample Handling and Custody Requirements

2.3.1 Sampling Equipment, Preservation and Holding Times Requirements

Samples collected for laboratory analysis will be stored on ice in coolers or frozen and holding times (Table 8) will be met to ensure the accuracy of results. The temperatures of sample storage units will be monitored to verify that holding temperatures are met.

2.3.2 Sample Custody Procedure

All sample labels will include a bottle identification (ID) number (CONTAINER_ID) and barcode provided by MWRA prior to each survey. The QAPP for Water Column studies (Libby *et al.* 2006 in prep.) 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 container (bottle), the data recorded on the chain form, and the sample collection information stored within NavSam[®] (*i.e.* location, depth, and time.) The COC forms will 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 bottle ID vs. the COC forms generated by NavSam[®] prior to delivering the samples to the laboratory. All samples will be delivered to the Battelle Field Sample Custodian, who will distribute 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 will be placed on dry ice with protective layers of foam or bubble wrap to ensure samples remain intact and frozen during shipment.

Battelle field staff will generally drive the samples up to Deer Island a day or two after the survey. On rare occasions they will ship via FedEx. During farfield surveys the samples will be transferred from Battelle to DLS once or twice sometime in the middle of the survey to meet the 7-day holding time. Coordinating with the DLS HOM Project Manager, the samples can be dropped off or picked up first thing in the morning (0700), for example on day 3 of the survey.

2.3.3 Sample Receipt and Check-in

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

- Inspect the samples to verify that (1) integrity is intact (containers are sealed and intact), (2) the sample container label and custody forms agree, (3) all shipped sample containers have been received, and (4) holding temperatures were maintained. Items (1) and (4) are performed immediately upon receipt and the other items are performed when the containers are checked into LIMS.
- Complete the Battelle COC forms, and sign 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 QAPP will be documented in detail on the COC, which are also communicated to the DLS Project Manager who will notify the Battelle Field Manager within 24 hours of receipt. **Note:** The original COC forms will be sent to ENQUAD to be forwarded to Battelle along with the data set and other associated documentation; copies will be kept at the DLS Laboratory.
- Check the samples into LIMS to provide a permanent laboratory record. This is accomplished by scanning the LIMS CONTAINER_ID from the barcoded label or otherwise entered into LIMS. The LIMS CONTAINER_IDS are used throughout the laboratory analysis. If samples are checked into LIMS after the date they are physically received by DLS, the received dates are manually corrected in LIMS. After sample receipt, manual and automated checking is performed to screen for typographical errors and missing, duplicate, or mislabeled samples or tests.

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 8. 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.
- 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 QAPP will be analyzed by the DLS Central Laboratory following the various DLS SOPs (Table 9).
- When the results are transferred to the EM&MS database (see section 4.1.2), ENQUAD EM&MS personnel will map the NavSam[©] sample ID into the SAMPLE_ID field, the LIMS CONTAINER_ID into the BOTTLE_ID field, and the LIMS SAMPLE_ID into the LAB_SAMPLE_ID field.

2.4 Analytical Requirements

2.4.1 Analytical Methods

Table 9 summarizes the methods used for sample analysis. The analyses will be conducted as described in the DLS SOPs listed, which are based on literature references or EPA methods as detailed in Table 9. DLS SOPs include a revision number as part of the Document Control Number (e.g. DCN 1005.2 would be the second revision of SOP 1005.) There is a formal review and approval process for revising SOPs and archival copies of all SOP revisions are maintained by the DLS Quality Assurance team. Generally, LIMS test codes are not changed when SOPs are revised and the specific SOP revision is not documented in the DLS LIMS. Also, the DLS LIMS does not keep track of specific instrument in use. However, the specific instrument in use is documented in the raw data for that test.

Parameter	LIMS test code	Units	Instrument	DLS SOP (Based on Reference)
Dissolved ammonium	NH3-OWAAN	µM	Skalar Autoanalyzer	SOP DCN 1005 (Oviatt and Hindle (1994); Solorzano (1969); USEPA NERL, 349.0)
Dissolved inorganic nitrate/nitrite and inorganic nitrite	NO32OWAAN NO2-OWAAN	µM	Skalar Autoanalyzer	SOP DCN 1007 (Bendschneider and Robinson (1952), and Morris and Riley (1963); USEPA NERL, 353.4)
Dissolved inorganic phosphate	PO4-OWAAN	µM	Skalar Autoanalyzer	SOP DCN 1006 (Murphy and Riley (1962); USEPA NERL 365.5)
Dissolved inorganic silicate	SIO4OWAAN	µM	Skalar Autoanalyzer	SOP DCN 1017 (Brewer and Riley (1966); Oviatt and Hindle (1994); USEPA NERL 366.0)

Table 9. Methods for Water Column Sample Analyses to be Conducted by DLS				
Parameter	LIMS test code	Units	Instrument	DLS SOP (Based on Reference)
Dissolved organic carbon	DOC-OWCIR	µM	Shimadzu TOC-Vcsh (Backup: Tekmar-Dorhmann, Apollo 9000)	SOP DCN 1126 (Sugimura and Suzuki (1988); USEPA 415.1)
Total dissolved nitrogen and Total dissolved phosphorus	TDN-OWAAN and TDP-OWAAN	µM	Skalar Autoanalyzer	SOP DCN 1072 (D'Elia <i>et al.</i> (1997); Valderrama (1981))
Particulate carbon and Particulate nitrogen	PC--OWCHN PN--OWCHN	µM	Perkin Elmer CHN Elemental Analyzer II	SOP DCN 1156 (Menzel and Vaccaro (1964); USEPA NERL 440.0)
Particulate phosphorus	PP--OWOXA	µM	Skalar Autoanalyzer	SOP DCN 1102 (Solorzano and Sharp (1980))
Biogenic Silica	BSI-OWAAN	µM	Skalar Autoanalyzer	SOP DCN 1177 (Paasche (1973))
Chlorophyll Phaeophytin	CHLAOWFLU PHAEOWFLU	µg/L	Turner Fluorometer, Model TD-700 (450-003 is a backup)	SOP DCN 1108 (Arar and Collins (1992); USEPA NERL 445.0, V. 1.1, 1992)
Total suspended solids	TSS-OWGRV	mg/L	Mettler 5-place or Sartorius 6-place balance	SOP DCN 1104 (EPA 160.2)

MWRA Harbor and Outfall Monitoring Program

Contract No. S366















Sample Custody Form

Today's Date : 2/14/2006 9:00:03 A

Laboratory : MWRA

Chain-of-Custody # : WF061-BS-0051
 Survey ID : WF061
 Analysis ID : BS
 Analysis Description : Biogenic silica

Dept. Lab Services
 190 Tafts Ave
 Winthrop MA 02152
 Yong Lao
 617-660-7841 (Phone) (Fax)

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	06002302-02	2/10/2006 7:06:04 AM	BF11		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
 *06011818-01*	06002303-02 06011818-01	2/11/2006 6:45:34 AM	BF12		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002309-01	2/13/2006 8:00:11 AM	BF13		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002311-01	2/10/2006 5:49:56 PM	BF21		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002321-01	2/11/2006 4:44:16 PM	BF22		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002322-01	2/13/2006 11:41:31 AM	BF23		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002330-04	2/13/2006 8:37:14 AM	F01	A	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002331-01	2/13/2006 8:37:14 AM	F01	A	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002335-04	2/13/2006 8:35:46 AM	F01	C	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002337-01	2/13/2006 8:35:46 AM	F01	C	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002341-04	2/13/2006 8:34:16 AM	F01	E	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002342-01	2/13/2006 8:34:16 AM	F01	E	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002345-04	2/13/2006 9:46:11 AM	F02	A	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
	06002346-01	2/13/2006 9:46:11 AM	F02	A	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

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

Relinquished By / Date / Time / Company / Transport-Airbill # <i>Matthew R. Fitzpatrick</i> 2/16/06 0800 BDO	Received By / Date / Time / Company <i>Michael Walsh</i> 2/16/06 0800 BDO <i>(Joanna)</i> 2/16/06 1300 MWRA
---	---

Figure 2: Battelle Chain-of-Custody Form

Figure 3: DLS LIMS Internal Chain-of-Custody

3/01/2004		MWRA -LIMS Internal Chain of Custody			11:03:41	
ENTRY	Container #	Type	Current Storage L.	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	13:46:21	2/09/2004
1	04006748-01	FGF-CH	141-SAMPLE RECVG	SEAMAN=C	13:44:33	2/09/2004

List of Revisions, Highlighted Fields have Changed

(RETURN)	(RETURN)	(RETURN)	(RETURN)
Next Page	Previous Page	(RETURN)	RETURN

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 will be reviewed by analysts and maintained in the laboratory document retention system.

2.4.1.1 Dissolved Inorganic Nutrients

The analysis of dissolved inorganic nutrients is based on the cited EPA methods. Dissolved inorganic nutrient concentrations are determined for samples that have been passed through a 0.4-µm pore size membrane filter in the field. The concentrations of ammonium, nitrate, nitrite, silicate, and phosphate are measured colorimetrically on a Skalar Autoanalyzer. This instrument automates standard manual techniques for the analysis of nutrients. The ammonium analysis is based on the technique of Solorzano (1969) whereby absorbance of an indophenol blue complex is measured at 660 nm. Nitrite is measured by the method of Bendschneider and Robinson (1952). The total of nitrate and nitrite is determined by reducing all nitrate in the sample to nitrite and analyzing for nitrite as above. The concentration of nitrate is obtained by difference. The reduction is accomplished using a cadmium column (Morris and Riley, 1963). The analysis of phosphate is based on the molybdate blue procedure of Murphy and Riley (1962). The colorimetric analysis of silicate is based on that of Brewer and Riley (1966).

2.4.1.2 Dissolved Organic Carbon

A Shimadzu TOC-Vcsh Carbon Analyzer (Tekmar-Dorhmann, Apollo 9000 is a backup.) is used to perform this analysis, based on EPA method 415.1. This instrument uses an automated, high-temperature combustion technique where an exact volume of sample is injected into the instrument and oxidized into carbon dioxide. A platinum catalyst greatly enhances this reaction. Inorganic carbon is removed by acidification and sparging prior to analysis. The carbon dioxide content is measured via a non-dispersive infrared detector (Sugimura and Suzuki, 1988).

2.4.1.3 Total Dissolved Nitrogen and Phosphorus

DLS uses the Skalar Autoanalyzer to perform this analysis based on the Valderrama (1981) method. This method is a persulfate oxidation technique for nitrogen and phosphorus where, under alkaline conditions, nitrate is the sole nitrogen product and phosphate is the sole phosphorus product. Then the concentrations of nitrate and phosphate are measured on the Skalar Autoanalyzer. Dissolved organic P is the difference between total dissolved P and phosphate. Dissolved organic N is the difference between total dissolved N and dissolved inorganic nitrogen components. TDN and TDP results are blank corrected using the batch-average method procedural blank.

2.4.1.4 Particulate Carbon and Nitrogen

The analysis, performed on a Perkin-Elmer CHN Elemental Analyzer II, is a high temperature combustion where the combustion products - water vapor, carbon dioxide and nitrogen gas are separated, quantitated with a thermal conductivity detector and compared to a known standard (EPA Method 440.0 [March 1997]). This analysis does not distinguish between particulate organic and particulate inorganic components of a sample. The results are corrected by subtracting the procedural filter blank result from the unadjusted sample result.

2.4.1.5 Particulate Phosphorus

The filters are placed in aluminum foil packets and frozen at -20 degrees C. To convert the phosphorus to phosphates, filters are transferred to aluminum weighing dishes and placed in 550 degree oven for 1 hour. Cooled filters are placed in centrifuge tubes and 1mL of 10% HCl is added. The filters are digested overnight. The next day 19 mL of DI water is added, centrifuge tubes are shaken. The tubes are covered and precipitate is settled overnight. The unturbid portion of the sample is analyzed. PP results are blank corrected using the batch-average procedural filter blank.

2.4.1.6 Biogenic Silica

Biogenic silica is analyzed according to the method outlined in Paasche (1973). This is an extraction/digestion technique using NaOH in a 100°C water bath followed by analysis of silicate in the extract by a Skalar Autoanalyzer. The results are corrected by subtracting the procedural filter blank result from the unadjusted sample result.

2.4.1.7 Chlorophyll a and Phaeophytin

Samples for chlorophyll a/phaeophytin are processed according to EPA method 445.0 using a Turner Fluorometer, Model TD-700 (Model 450-003 is a backup.). Samples are filtered in the field as soon as possible after collection and the filters stored at -10°C. All handling steps are performed in subdued light. The chlorophyll a/phaeophytin is extracted from the cells retained on the GF/F filter by a 16-24 hour steep in 90% buffered acetone at 4°C. The sample is then centrifuged and the extract analyzed using a fluorometer. 150 µL of 0.1 N HCl is added to the extract and the extract remeasured after 90 seconds to determine phaeophytin concentrations.

2.4.1.8 Total Suspended Solids

Samples for total suspended solids (TSS) determination are processed in a particulate free area within 7 days (stored in an amber bottle at 4°C). Using a vacuum-filter system, aliquots are vacuum filtered (<300 mm Hg) through a tared 0.4-µm pore size polycarbonate (i.e. Nucleopore) 47-mm-diameter membrane filter. The volume filtered is determined by the analyst based on the rate of flow through the filter. When the entire aliquot has passed through the filter, the filtration apparatus is washed down with 20 mL of pH 8 deionized water three separate times, waiting for all the water to pass through the filter between rinses. Following filtration, the filters are folded in quarters, stored in a plastic petri dish, partially covered, labeled, and placed in a desiccator for at least 48 hours. Upon removal from the desiccator, the filter is weighed on a microbalance. TSS is calculated as the net filter weight relative to the sample volume.

2.4.2 Quality Control Requirements

Quality Control (QC) samples will be run with every analytical batch of 20 samples or fewer. The suite of QC samples specified for a particular analytical batch will depend on the parameters being analyzed. Table 10 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 of DLS' QAMP (DCN: 5000.0, 2003) and the specific SOP. The definitions of particular QC samples is as follows:

- **Laboratory Control Sample:** A sample matrix, free from the analytes of interest and interferences, spiked with verified known amounts of analytes. It is generally used to establish intra-laboratory or analyst specific 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 material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.
- **Laboratory Duplicate (Instrument):** The sample analyzed (aspirated) twice by an instrument from the same cup.
- **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 analytical procedures. The purpose of the Method Blank is to demonstrate that the analytical system is free of target analytes and interferences.
- **Filter Blanks:** An unused method prescribed filter taken from the same lot as filters used in the analyses and processed simultaneously with and under the same conditions as samples through all steps of the analytical process. The purpose of the filter blank is to demonstrate that the filter material is free of target analytes and interferences.
- **Field Duplicates:** Two aliquots of water taken from one field sample and filtered in the field as two separate samples, resulting in two filters or two filtrates.
- **Field Filter Blank:** An unused prescribed filter taken from the same lot as filters used in the field to filter water column samples as described in Libby *et al.*, (2006 in prep.) and processed simultaneously with and under the same conditions as samples through all steps of the analytical process. The purpose of the field filter blank is to demonstrate that the filter material is free of target analytes and interferences that may have been picked up in the field.
- **Field Blank:** A sample container is handled in the field along with the other sample containers. To it is added a volume of field reagent water equivalent to the volume of water used for that parameter. The purpose of the field blank is to demonstrate that the sample containers, field reagent water, field filtration, and field handling are free of, or do not introduce, target analytes or interferences.

2.5 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

All equipment associated with nutrient, and chlorophyll analyses (autoanalyzers, elemental analyzers, analytical balances, thermometers, and incubators) will be calibrated and maintained according to manufacturer's specifications. These are done or checked on each day of use as described in Section 10 of DLS' QAMP (DCN: 5000) or the pertinent SOP. An equipment logbook will be maintained to document periodic maintenance of major equipment.

2.6 Instrumentation Calibration and Frequency

Calibration procedures for laboratory instruments are summarized in Table 11. All laboratory calibration records will be reviewed by the Team Supervisor and maintained in laboratory notebooks.

DLS policy on calibration standards is described in Section 6 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 reagent 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) are 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 reagent can be found in Section 6.0 of DLS' QAMP (DCN: 5000).

Table 10. Quality Control Samples			
Quality Control Sample Type	Frequency	Quality Acceptance Limits	Corrective Action⁶
Method Procedural Blanks			
Dissolved nutrients	1 per batch of 20	≤5 x MDL ¹	Results examined by DLS supervisor, laboratory manager, or project manager. Corrective action (e.g., re-extraction, reanalysis, data qualifier) is documented in LIMS sample notepad and/or test comments.
Total suspended solids	1 per batch of 20	≤5 x MDL	
Method Procedural Filter Blanks			
Particulate nutrients, BSI	1 per batch of 20	≤5 x MDL	As above
Chlorophyll <i>a</i> /phaeophytin	1 per batch of 20	≤5 x MDL	
Total suspended solids	1 per batch of 20	≤5 x MDL	
Field Filter Blanks			
Particulate nutrients, BSI	(See note 5, below)	≤5 x MDL	As above
Chlorophyll <i>a</i> /phaeophytin	(See note 5, below)	≤5 x MDL	
Field Blanks (Sample container containing field filtered reagent water)			
DIN, DOC, and TDN/TDP	3 per survey	≤5 x MDL	Flag with test_comment 'W' (use with caution)
Prepared Standards (LCS)			
DIN	1 per batch of 20	85%-115% recovery ²	As for Method Procedural Blanks
DOC, TDN, and TDP	1 per batch of 20	85%-115% recovery	
Particulate nutrients, BSI	1 per batch of 20	85%-115% recovery	
Chlorophyll <i>a</i>	1 per batch of 20	85%-115% recovery	As for Method Procedural Blanks
Phaeophytin	None. There is no commercially available phaeophytin standard.	Not Applicable	Not applicable
TSS ⁴	1 per batch of 20	80-120% recovery	As for Method Procedural Blanks
Laboratory Duplicates (Instrument duplicates)			
DIN	1 per batch of 20	≤10%RPD ³	Flag with test_comment 'R' (precision does not meet DQO)
DOC	1 per batch of 20	≤10% RPD	
Chlorophyll <i>a</i> /phaeophytin	1 per batch of 20	≤15% RPD	
Laboratory Duplicates (Processing Duplicates)			
Total suspended solids	1 per batch of 20	≤20% RPD	Flag with test_comment 'R' (precision does not meet DQO)
TDN, TDP	1 per batch of 20	≤10% RPD	
Field Duplicates (2 aliquots filtered in the field from one sample)			
DIN	6 mid-depths (nearfield stations) and 7 mid-depths (farfield stations, farfield surveys only)	≤30% RPD	ENQUAD will flag with value qualifier 'r' (precision does not meet DQO)
DOC, TDN, and TDP	mid-depth at station N16	≤30% RPD	
Particulate Nutrients, BSI	1 per batch of 20	≤30% RPD	
Chlorophyll <i>a</i> /phaeophytin	Each mid-depth	≤50% RPD	

¹ MDL = method detection limit

² Percent Recovery = [(measured concentration)/true or nominal concentration] x 100%.

³ Relative Percent Difference (RPD) = |(replicate 1 - replicate 2) x 2/(replicate 1 + replicate 2)| x 100%.

⁴ The QC sample used to assess the accuracy of the TSS method is an SRM purchased from ERA, Arvada, CO.

⁵ Generally, 2 Field Filter Blanks are collected every survey day and are to be analyzed as samples. From time to time, depending on the number of stations surveyed, only one per day will be collected.

⁶ Note that not all tests can be retested, for example, when the entire filter is consumed in the original test.

Parameter	Instrument Type	Initial Calibration			Continuing Calibration		Corrective Action
		No. Stds	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	
Dissolved inorganic nutrients	Skalar Autoanalyzer	4-5	$r \geq 0.995$	Prior to analytical run	PR ¹ $\pm 15\%$	Every 20 samples	Investigate, recalibrate
Dissolved organic carbon	Shimadzu TOC-Vcsh (Backup: Tekmar-Dorhmann Apollo 9000 Analyzer)	4-5	$r \geq 0.995$	Monthly or if continuing calibration fails	PR $\pm 15\%$	Every 20 samples	Investigate, recalibrate
Total dissolved nitrogen and phosphorus	Skalar Autoanalyzer	4-5	$r > 0.995$	Prior to analytical run	PR $\pm 15\%$	Every 20 samples	Investigate, recalibrate
Particulate carbon and nitrogen	Perkin Elmer CHN Elemental Analyzer II	1	NA	Prior to analytical run	PR $\pm 15\%$	Every 20 samples	Investigate, recalibrate
Particulate phosphorus	Skalar Autoanalyzer	4-5	$r \geq 0.995$	Prior to analytical run	PR $\pm 15\%$	Every 20 samples	Investigate, recalibrate
Biogenic silica	Skalar Autoanalyzer	4-5	$r \geq 0.995$	Prior to analytical run	PR $\pm 15\%$	Every 20 samples	Investigate, recalibrate
Chlorophyll <i>a</i> and phaeophytin	Turner Fluorometer, TD-700 (Backup: Model 450-003)	5	$r \geq 0.995$	Annually or if continuing calibration fails	PD ² from gel standard baseline $\leq 5\%$	Every 20 samples	Investigate, recalibrate
Total Suspended Solids (TSS)	Mettler 5-place Balance or Sartorius 6-place Balance	NA	Professionally calibrated to agree with NIST traceable Calibration Weights	Annually	PD less than 1% from reference weights	Each day of use and reweigh every 10 samples	Professional Service requested for PD over 5%

¹ Percent Recovery. So $\pm 15\%$ is 85% to 115%.

² Percent difference

2.8 Data Management

2.8.1 Acquisition of Non-Direct Measurement Data

Field sample locations and depths are pre-loaded in LIMS as Station IDs and sample depth code (e.g. N01C for station N01, chlorophyll maximum or mid-depth). Samples are checked into LIMS using the LIMS container_ID. Except for date and time, no Battelle field measurements will be entered in LIMS. Station IDs and depth codes are given in Tables 12 and 13. The LIMS location_ID is a concatenation of the station_id (EM&MS STAT_ID) and the depth code (EM&MS SAMPLE_DEPTH_CODE).

Table 12. Station Identifiers	
EM&MS STAT_ID	Location Description
F01	41-51.06, 70-27.18, WESTERN CAPE COD BAY
F02	41-54.48, 70-13.68, EASTERN CAPE COD BAY
F03	41-57.00, 70-32.88, NORTH OF MANOMET POINT
F04	42-04.80, 70-16.86, NORTHWEST OF PROVINCETOWN
F05	42-08.34, 70-39.00, MASS. BAY NEAR HUMAROCK
F06	42-10.26, 70-34.62, MASS. BAY SOUTH OF OUTFALL SITE
F07	42-11.82, 70-30.96, MASS. BAY SOUTH OF OUTFALL SITE
F08	42-16.68, 70-26.88, MASS. BAY SOUTH OF OUTFALL SITE
F09	42-13.32, 70-41.22, MASS. BAY SOUTH OF OUTFALL SITE
F10	42-14.52, 70-38.22, MASS. BAY SOUTH OF OUTFALL SITE
F11	42-16.26, 70-35.10, MASS. BAY SOUTH OF OUTFALL SITE
F12	42-19.80, 70-25.38, MASS. BAY SOUTH OF OUTFALL SITE
F13	42-16.08, 70-44.10, MASS. BAY SOUTH OF OUTFALL SITE
F14	42-18.00, 70-48.48, MASS. BAY SOUTH OF NEARFIELD
F15	42-18.96, 70-43.68, MASS. BAY SOUTH OF NEARFIELD
F16	42-19.86, 70-39.00, MASS. BAY SOUTHEAST OF NEARFIELD
F17	42-20.76, 70-34.26, MASS. BAY SOUTHEAST OF NEARFIELD
F18	42-26.52, 70-53.28, NAHANT BAY
F19	42-24.90, 70-38.22, MASS. BAY EAST OF NEARFIELD
F20	42-29.64, 70-46.44, MASS. BAY NEAR SALEM SOUND
F21	42-29.76, 70-42.54, MASS. BAY NEAR SALEM SOUND
F22	42-28.80, 70-37.08, MASS. BAY NEAR SALEM SOUND
F23	42-20.34, 70-56.52, PRESIDENT ROADS NEAR DEER ISLAND
F24	42-22.50, 70-53.76, BROAD SOUND
F25	42-19.32, 70-52.56, OFF POINT ALLERTON
F26	42-36.12, 70-33.90, EAST IF CAPE ANN
F27	42-33.00, 70-26.82, NORTH OF STELLWAGEN BANK
F28	42-24.60, 70-25.98, WITHIN STELLWAGEN BANK
F29	42-07.02, 70-17.40, NORTH OF PROVINCETOWN
F30	42-20.46, 71-00.48, ENTRANCE TO INNER HARBOR
F31	42-18.36, 70-56.40, NANTASKET ROADS
F32	41-52.80, 70-20.46, MIDDLE CAPE COD BAY
F33	42-00.78, 70-15.54, CAPE COD BAY APPROX 5KM SW OF PROVINCETOWN
N01	42-25.14, 70-51.90, NORTHWEST CORNER OF NEARFIELD
N04	42-26.64, 70-44.22, NORTHEASTERN CORNER OF NEARFIELD

Table 12. Station Identifiers	
EM&MS STAT_ID	Location Description
N07	42-21.36, 70-42.36, SOUTHEASTERN CORNER OF NEARFIELD
N10	42-19.92, 70-50.04, SOUTHWESTERN CORNER OF NEARFIELD
N16	42-23.64, 70-45.18, EAST OF OUTFALL SITE
N18	42-21.96, 70-46.68, SOUTH OF OUTFALL SITE
N20	42-22.92, 70-49.02, WEST OF OUTFALL SITE

Table 13. Sample Depth Codes			
EM&MS SAMPLE_DEPTH_CODE	Label Color	Description	Analyses (EM&MS Parameter Codes)
A	Black	Surface	NH3, NO2, NO3, PO4, SIO4, CHLA, DOC, TDN, TDP, POC, PON, PP, BIOSI, TSS
B	Light Blue	Mid-surface	NH3, NO2, NO3, PO4, SIO4, CHLA
C	Green	Chlorophyll maximum	NH3, NO2, NO3, PO4, SIO4, CHLA, DOC, TDN, TDP, POC, PON, PARTP, BIOSI, TSS
D	Yellow	Mid-bottom	NH3, NO2, NO3, PO4, SIO4, CHLA
E	Red	Bottom	NH3, NO2, NO3, PO4, SIO4, CHLA, DOC, TDN, TDP, POC, PON, PARTP, BIOSI, TSS

Note: The depths are not always in order, since the chlorophyll maximum depth can be above or below the mid-water. The samples can be collected in any of the following orders (from the bottom): E-D-C-B-A, E-D-B-C-A, or E-C-D-B-A. Shallow harbor stations F30 and F31 have samples collected only at A, C, and E depths.

2.8.2 Data Recording

All documentation will conform to the DLS QAMP (DCN: 5000.0, MWRA 2003b), 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) will be recorded in laboratory notebooks.

For this project, all test results will be manually entered into LIMS from laboratory logbooks, spreadsheets, or instrument data system printouts. The LIMS worklist module (WKLIST) will be 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. A LIMS program automatically converts results in mg/L to μM for tests reported in μM and also takes into account dilutions, reporting limits, and significant figures. All LIMS tests are configured to store final results with three significant figures.

Completed data forms or other types of hand-entered data will be signed and dated by the individual entering the data. Direct-entry and electronic data entries will indicate the person collecting or entering the data. An example LIMS data entry screen for this project is shown in Figure 4. It will be the responsibility of the team Supervisor to ensure that all data entries and hand calculations are verified in accordance with procedures described in Section 2.8.4. When a test is repeated and both the original test and the reanalysis are going to be reported through LIMS, a second occurrence of the same test code is added to that sample.

2.8.3 Analyses 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.

2.8.3.2 Sample Notepad Comments

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

Figure 4: LIMS Data Entry Screen

```
VALDSA                      MWRA -LIMS                      DATE: 3/01/2004
                           DATA ENTRY BY SAMPLE          TIME: 11:01:22
Sample ID: 04006748 Notepad(*) ,
Vald Stat: (V/I) Vald Cmts:

CHLAOWFLU      Instrument: Status: P      Units of Measure: UG/L
Sample ID : 04006748 Client: NPDES   Project: HOM-WC      Location: F27D
Container: 04006748-01 Lab: CENTRAL   Worklist   Position: 3 Y/C/D:
Collected: 14:44:00 2/04/2004 Analysis Due Date: 2/28/2004 Notepad: ( )
                           Analyst: BERGER_K Analyzed: 0:00:00 2/17/2004

Comment:
CHLOROPHYLL A-OCEAN H2O-FLUOR >= 0.0100 <= 15.0 >= 0.210 <= 10.7
CHLOROPHYLL A      RES      0.310 RAW      DIL

Ready, Waiting for input!                                Page ( 1 ) of ( 4 )
      Search      Validate All      Save Results      Validate Test
CTRL LOC SPCFIC      Edit Notepad      (Help/ More)      Exit
```

2.8.3.3 Test Comments

From time to time, a test result will be reported as invalid or will be qualified by the DLS. When such a situation occurs, the analyst/validator/approver will annotate 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 14, below.

To alert the data user to results that may be affected by low-level laboratory bias, the following flagging procedure is used with regard to method procedural blanks. If the method procedural blank is >5 times the MDL, all samples and QC in the batch are flagged with “B”. Note that samples are also flagged with “J” (“estimated value”) when the result is below the lowest calibration standard. However, when a J flag is used, no other flags are needed on that test because the J flag already indicates that the result is an “estimated value”.

Also, note the following:

- “Q”, accuracy does not meet data quality objectives, is used for all samples in a batch when the LCS recovery is outside limits.

- “R”, precision does not meet data quality objectives, is used only on a sample used for duplicate analysis when the duplicate RPD is outside limits.
- “W”, use with caution, is only used for exceptional situations. It will no longer be routinely used when a blank is >MDL and the sample is <5x the blank.

If more than one test comment (qualifier) needs to be annotated, use a predefined multiple test qualifier (e.g. JW), or if the multiple test qualifier is not defined, use the pre-defined qualifier = X (See Sample Notepad) will be used. The entry into the Sample Notepad will contain 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:

NH3-OWAAN L, Analytical concentration reported from dilution; Q, Accuracy 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.

LIMS Test Comment	Description
A	Not detected - value reported as negative or missing
B	Not blank corrected, blank $\geq 5x$ MDL
B2	Blank corrected, blank $\geq 5x$ MDL
E1	Calibration level exceeded
E2	Results not reported, value given is NULL, see comments field
J	Estimated value ¹
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

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

In order to ensure that all samples are accounted for when transferring the results from LIMS to EM&MS, if an invalid result is not superseded by a retest, it will be given a validation_status of ‘VALID’ but flagged as missing (test_comment = E2) with an explanation in the notepad that the result was invalidated and couldn't be retested.

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 will be performed electronically either by the instrument software or in a spreadsheet and will be validated according to procedures described in Section 2.8.5. All individual laboratory replicates and all field replicates will be reported as individual sample values.

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 10) 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.

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 will not 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 Objectives of this plan will be annotated (See Section 2.8.3, above). When all samples from a survey are approved in LIMS, the DLS HOM Project Manager will notify 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 turnaround time for all tests is 28 calendar days.

2.8.6.2 Results Data Entry

All results will be entered into the DLS' Laboratory Information management System (LIMS), reported down to the Method Detection Limit (MDL) and in the units described in Table 7. Results between the MDL and, where applicable, the lowest calibration standard will be reported as an estimated value and flagged with the qualifier, "J".

Every sample will have its respective batch QC results reported as defined in Table 10.

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 Structured 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 will forward to the ENQUAD Project Manager a QA Package consisting of:

- **Deviations from the QAPP:** Document any deviations from the QAPP. Include these deviations in each subsequent QA Statement until they are rectified, or until the QAPP is amended.
- **Audit Reports:** Copies of the monthly rolling compliance audit including any audits they may have been specifically performed on HOM items.
- **Control Charts:** Control charts for all parameters for both LCS and Method Blanks.
- **Missing Samples Report:** A missing Samples report will be 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 survey sample analyses.
- **DAIR (Data Anomaly Investigation Report) Report:** Photocopies of DAIRs associated with HOM 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 will be 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, will be forwarded by inter-office mail to the ENQUAD HOM Project Manager.

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 be reviewed and, if necessary, changed after approval but before it is released by ENQUAD, the "Fast Track" DAIR process should be used.

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 QAPP (Leo *et al.*, 2005), 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: 5000.0, 2003) and the QAPP (Leo, <i>et al.</i> , 2006) 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:

- | | |
|---|--------------------------------|
| <input type="checkbox"/> Audit Reports | Battelle COC Forms (Originals) |
| <input type="checkbox"/> Control Charts | |
| <input type="checkbox"/> Corrective Actions | |
| <input type="checkbox"/> DAIRs | |

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*)

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 its 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: nitrate, nitrite, phosphate, ammonia and TSS. 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. Further, the DLS participates in the Chesapeake Bay Laboratories Seawater PT program.

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 will be 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 will be 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 conducted of an initial systems audit to ensure that nutrient, TSS and chlorophyll analyses were carried out in accordance with this QAPP. In addition, the Battelle QA Officer will review 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 Water Column Monitoring QAPP (Libby *et al.* 2006 in prep.), tabular data reported in deliverables will be 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 QAPP-prescribed formats; no other will be acceptable.

3.2.2 Corrective action

As defined in Battelle’s QAPP (Libby *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, will be 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 QAPP, 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) will be resolved by DLS staff and/or by ENQUAD staff. Issues that affect schedule, cost, or performance of the water-column monitoring tasks will be reported to the MWRA Outfall Monitoring Program Manager and to the Battelle Project Manager. Battelle’s Technical Director will be notified of any issues affecting data quality. The DLS HOM Project Manager, the ENQUAD HOM Project Manager, and the MWRA Outfall Monitoring Program Manager will be 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 will be reported and corrected as described in Section 17.0 of the Water Column QAPP (Libby *et al.* 2005.)

3.3 Work Stoppage for Cause

The ENQUAD Outfall Monitoring Program 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 will be transferred to EM&MS, including those marked as invalid by DLS. The data will be transferred after the QA Package is received. Following LIMS approval data will be 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 will be done by tested automated routines.
- Application of qualifiers in EM&MS will be 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 will be 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 will be 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 correction data in the EM&MS database is as follows:

- Corrections to data in EM&MS work or production tables will be 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 will use the data preview application HOM Review, written by ENQUAD using Oracle 9i Forms, to review the analytical results, test comments and LIMS notepad entries. Standard LIMS test comments will be parsed into EM&MS qualifiers. In order to review and assess the HOM results, the ENQUAD Project Manager will:

- Review all data for technical reasonableness and completeness. Review will include all rejected samples, deleted and invalid tests, and out of range results. The ENQUAD Project Manager will review documentation in LIMS and the QA Package, and compare results to historical data distributions to check for reasonableness.
- Correct or add to qualifiers and comments as appropriate based on review of the data (see section 4.2.1 below). If there are questions that cannot be resolved by examining the comments, he will initiate a DAIR (see 2.8.7).

The ENQUAD Database Manager will:

- Make available for the ENQUAD Project Manager's review: the Survey Samples Results Report, the Notepad comments Report and the Test Comments Report.
- Calculate 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.
- Ensure that the data, which will be sent to Battelle, meet all applicable constraints (*i.e.* on the BOTTLE, ANALYTICAL_RESULTS and QC_RESULTS tables.)

- Forward 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 will deem 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 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 Libby *et al.* 2006 in prep., data from the laboratories receive a quality assurance review before the data are incorporated into the database. Any issues identified in production of the database are corrected in the database and documented in scripts and list files maintained by MWRA ENQUAD data management.

4.1.4.3 Sampling Design

All sampling is performed by Battelle Ocean Sciences. This QAPP does not address sampling design, which is described in the Water Column Monitoring QAPP (Libby *et al.* 2006 in prep.)

4.1.4.4 Data Transmittal to Battelle

The ENQUAD EM&MS Database Manager will send the data to Battelle as an Oracle export file of the BOTTLE, ANALYTICAL_RESULTS and QC_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 will accompany the data.

Further processing of laboratory data at Battelle is described in MWRA SOP 004, *Loading and Reporting Water Column Data*.

4.1.4.5 Data Analysis

Data will be analyzed and reported by Battelle as part of the synthesis reporting under the HOM contract (see Libby *et al.* 2006 in prep.)

5.0 REFERENCES

- Arar, EJ and Collins, GB. 1992. *In Vitro* Determination of Chlorophyll *a* and Phaeophytin *a* in Marine and Freshwater Phytoplankton by Fluorescence. Method 445.0 Version 1.1 (November 1992). U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, OH.
- 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.
- Bendschneider, K and Robinson, RJ. 1952. A New Spectrophotometric Determination of Nitrite in Seawater. *J. Mar. Res.* 11:87-96.
- Brewer, PG and Riley, JP. 1966. The Automatic Determination of Silicate Silicon in Natural Waters with Special Reference to Seawater. *Anal. Chim. Acta.* 35:514-519.
- D'Elia, CF, Connor, EE, Kaumeyer, NL, Keefe, CWWood, KV and Zimmermann, CF. 1997. Nutrient Analytical Services Laboratory: Standard Operating Procedures. Technical Report Series No. 158-97. May 1997. Chesapeake Biological Laboratory Center for Environmental Science, Solomons, MD. 77 pp.
- Libby PS, Gagnon C, Albro CS, Mickelson MJ, Keller AA, Borkman D, Turner JT and Oviatt CA. 2002. Combined work/quality assurance plan (QAPP) for water column monitoring 2002 - 2005 - tasks 9, 10, 12, 13, 14, 15. Boston: Massachusetts Water Resources Authority. Report ms-074. 79 p.
- Libby PS, Gagnon C, Albro CS, Mickelson MJ, Keller AA, Borkman DG, Turner JT and Oviatt CA. 2005. Combined work/quality assurance plan (QAPP) for water column monitoring 2002 - 2005 - tasks 9, 10, 12, 13, 14, 15. Boston: Massachusetts Water Resources Authority. Report 2005-09. 115 p.
- Libby PS *et al.* 2006 in prep. Combined work/quality assurance plan (QAPP) for water column monitoring 2006 - 2007 - tasks 4, 5, 6, 7, 8. Boston: Massachusetts Water Resources Authority. Report 2006-x. x p. [Check reference]
- Loder, T, unpublished, 6/14/95.
- Menzel, DW and Vaccaro, RF. 1964. The Measurement of Dissolved Organic and Particulate Carbon in Seawater. *Limnol. Oceanogr.* 9:138-142.
- Morris, AW and Riley, JP. 1963. The Determination of Nitrate in Seawater. *Anal. Chim. Acta.* 29:272-279.
- Murphy, J and Riley, JP. 1962. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. *Anal. Chim. Acta.* 27:31-36.

- MWRA. 2001. Massachusetts Water Resources Authority Contingency Plan Revision 1. Boston: Massachusetts Water Resources Authority. Report ms-071. 47 p.
- MWRA. 2003a. Massachusetts Water Resources Authority effluent outfall ambient monitoring plan Revision 1, November 2003. Boston: Massachusetts Water Resources Authority. Report ms-087. 53 p.
- MWRA. 2003b. (DCN 5000.0). Department of Laboratory Services Quality Assurance Management Plan, Revision 2.0. Massachusetts Water Resources Authority, Boston, MA.
- Oviatt, CA and Hindle, KM. 1994. Manual of Biological and Geochemical Techniques in Coastal Areas. MERL Series, Report No. 1. Third Edition. The University of Rhode Island, Kingston, Rhode Island. Marine Technical Report No. 85. 281 pp.
- Paasche, E. 1973. Silicon and the Ecology of Marine Plankton Diatoms *Thalassiosira pseudonana* (*Cyclotella nana*) Grown in Chemostat with Silicate as the Limiting Nutrient. *Mar. Biol.* 19:117-126.
- Solorzano, L. 1969. Determination of Ammonia in Natural Waters by the Phenol Hypochlorite Method. *Limnol. Oceanogr.* 14:799-801.
- Solorzano, L. and Sharp, JH. 1980. Determination of Total Dissolved Phosphorus and Particulate Phosphorus in Natural Waters. *Limnol. Oceanogr.* 25:758-760.
- Sugimura, Y and Suzuki, Y. 1988. A High Temperature Catalytic Oxidation Method for the Determination of Non-Volatile Dissolved Organic Carbon in Seawater by Direct Injection of a Liquid Sample. *Mar. Chem.* 24:105-131.
- USEPA. 1988. Boston Harbor Wastewater Conveyance System. Supplemental Environmental Impact Statement (SEIS). Environmental Protection Agency Region I, 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.
- Valderrama, JC. 1981. The Simultaneous Analysis of Total Nitrogen and Total Phosphorus in Natural Waters. *Mar. Chem.* 10:109-122.



Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA 02129
(617) 242-6000
<http://www.mwra.state.ma.us>