Quality Assurance
Project Plan

for

Nutrient and Chlorophyll Analyses for Outfall Monitoring

Massachusetts Water Resources Authority
Environmental Quality Department
Report 2017-05

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Quality Assurance Project Plan (QAPP)

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Nutrient and Chlorophyll Analyses for Outfall Monitoring

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Quality Assurance Project Plan (QAPP)
for
Nutrients and Chlorophyll Analyses for Outfall Monitoring

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[1] DLS = Department of Laboratory Services
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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 (ENQUAL). It includes onshore sample handling, sample analysis, and data loading for the nutrients and chlorophyll analyses that are part of the water column study in the MWRA's outfall ambient monitoring program (bay water quality monitoring study, or BWQM.)

ENQUAL Mr. Ken Keay is the Outfall Monitoring Program Manager. Dr. Daniel Codiga, Project Manager, is responsible for general coordination of monitoring activities and Dr. David Taylor, Project Manager, is 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. Dr. Doug Hersh leads the data management group and serves as ENQUAL's quality assurance manager. He will be responsible for assigning staff to transfer data from the DLS laboratory information management system (LIMS) into the ENQUAL environmental monitoring and management database (EM&MS) and transmitting it to Battelle. Dr. Betsy Reilley 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. Mr. Mark Lambert is the Section Manager responsible for the Red Team. Ms. Nancy McSweeney is the Supervisor of the Red Team, responsible for nutrient and solids analyses. Mr. Steve Rhode is the Section Manager responsible for Client Services, the Violet Team, and the Indigo Team. Ms. Laura Ducott is supervisor of the Indigo Team, responsible for seawater chlorophyll analyses. Mr. James Fitzgerald is Supervisor of the Violet team, responsible for Sample Management. Ms Corinna Standring is Client Services Coordinator. She is responsible for providing Battelle with sample identification numbers and assisting with sample management. Ms. Jennifer Constantino is the QA Coordinator and is responsible for the laboratory's Proficiency Testing programs and laboratory QA/QC oversight/audits programs. Dr. Michael Delaney is the Director of Laboratory Services. The DLS reporting relationships and functional responsibilities are shown in the Table 1.

Table 1. DLS Reporting Relationships

<table>
<tr><td colspan="5">Michael Delaney, Director of Laboratory Services</td></tr>
<tr><td colspan="3">Steven Rhode
Lab Manager
(Client Services)</td><td>Mark Lambert
Lab Manager
(Operations)</td><td>Jennifer Constantino
QA Coordinator
(Quality Assurance)</td></tr>
<tr><td>Yong Lao
HOM Project Manager,
Corinna Standring Client Services Coordinator</td><td>James Fitzgerald
Violet Team Supervisor,
Sample Management</td><td>Laura Ducott
Indigo Team Supervisor,
Chlorophyll, Phaeophytin</td><td>Nancy McSweeney
Red Team Supervisor,
DIN, Particulate Carbon, Nitrogen and Phosphorous</td><td>Performance Testing, QA/QC Oversight and Document Control</td></tr>
</table>

Battelle Ocean Sciences (BOS) Ms. Ellen Baptiste-Carpenter is the HOM project manager for BOS, and also leads the BOS data management group. She is responsible for the overall performance of the HOM project. Mr. Scott Libby is the Battelle Technical Manager and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise. He is also the BOS Task Area Manager for the water column study, and thus will be the first and principal user of the data. The Battelle Quality Assurance Officer for the project is Ms. Rosanna Buhl. For this task, Ms. Buhl is responsible for reviewing data submitted by ENQUAL and QA Statements submitted by DLS for completeness and adherence to the Water Column QAPP (Libby *et al.*, 2017).

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

Figure 1 Organizational Chart for Nutrients and Chlorophyll Tests for the Outfall Monitoring Program

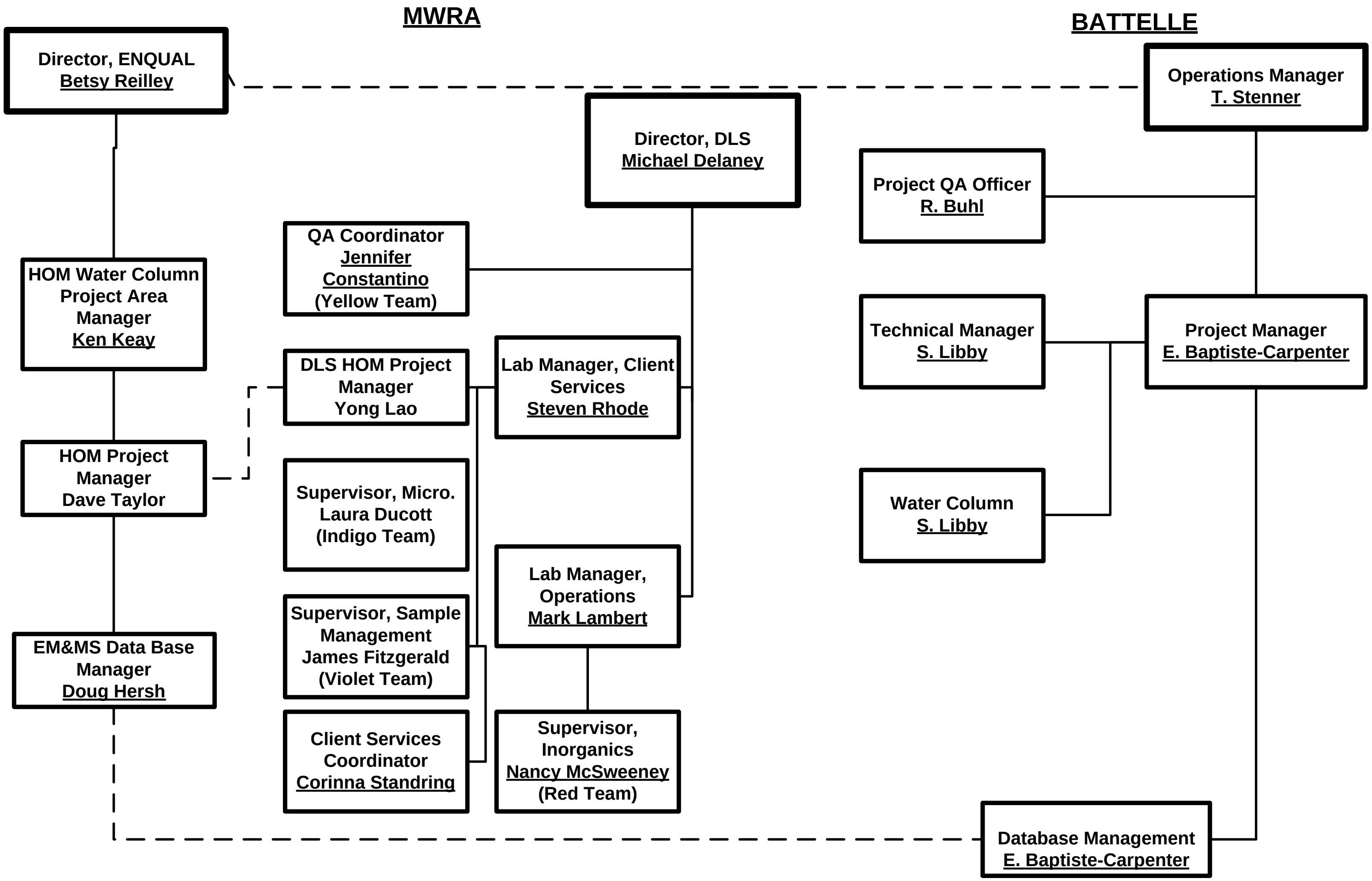

Table 2.	**Contact Information**			
Name	Title/Role	Location	Email	Phone
Ellie Baptiste-Carpenter	HOM10 Project Manager	BOS[1]	baptiste[at]battelle.org	781-952-5361
Rosanna Buhl	Quality Systems Manager	BOS	buhl[at]battelle.org	781-952-5309
Jennifer Constantino	QA Coordinator (Yellow)	DLS[2]	jennifer.constantino[at]mwra.state.ma.us	617-660-7808
Daniel Codiga	Project Manager	ENQUAL[3]	Daniel.codiga[at]mwra.state.ma.us	617-788-4942
Mike Delaney	Laboratory Director	DLS	michael.delaney[at]mwra.state.ma.us	617-660-7801
Laura Ducott	Team Supervisor (Indigo)	DLS	laura.ducott[at]mwra.state.ma.us	617-660-7832
Jim Fitzgerald	Team Supervisor (Violet)	DLS	james.fitzgerald[at]mwra.state.ma.us	617-660-7851
Matt Fitzpatrick	Field Manager/Sample Custodian	BOS	fitzpatrickm[at]battelle.org	781-952-5351
Doug Hersh	Program Manager, Marine Data	ENQUAL	douglas.hersh[at]mwra.state.ma.us	617-788-4945
Ken Keay	Water Quality Program Manager	ENQUAL	kenneth.keay[at]mwra.state.ma.us	617-788-4947
Mark Lambert	Laboratory Manager	DLS	mark.lambert[at]mwra.state.ma.us	617-660-7817
Yong Lao	DLS Project Manager	DLS	yong.lao[at]mwra.state.ma.us	617-660-7841
Wendy Leo	Sr. Program Manager	ENQUAL	wendy.leo[at]mwra.state.ma.us	617-788-4948
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
Steve Rhode	Laboratory Manager	DLS	steve.rhode[at]mwra.state.ma.us	617-660-7803
Corinna Standring	Client Services Corodinator	DLS	corona.standring[at]mwra.state.ma.us	617-660-7859
Dave Taylor	Project Manager	ENQUAL	David.taylor[at]mwra.state.ma.us	617-788-4952

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[2] Department of Laboratory Services, MWRA, 190 Tafts Avenue, Winthrop, MA 02152, 617-660-7800
[3] Environmental Quality Department, MWRA, 100 First Avenue, Boston, MA 02129, 617-788-4941

1.2 Communication Plan

Dr. Dave Taylor will be the primary contact with Battelle on technical issues. Dr. Yong Lao will be DLS' primary contact with ENQUAL. Communication between DLS and Battelle staff at all levels of the team is encouraged; they should keep ENQUAL informed (Table 3.)
Dr. Yong Lao will attend monthly HOM project monthly meetings at MWRA in the Charlestown Navy Yard by conference call. 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 is attended by the DLS Lab Managers and Supervisors. 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 HOM10 archive bconorhom10@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.

Table 3.	**Email cc: List**
If the subject is…	*Copy the email to…*
Any	**Dave Taylor, Yong Lao**
transfer of samples	Matt Fitzpatrick, Jim Fitzgerald (Violet), Corinna Standring
data interpretation	Ken Keay, Scott Libby
laboratory technical issues	Relevant DLS Team Supervisor(s): ▪ L. Ducott (Indigo- chl), ▪ N. McSweeney (Red-nutrients), Mark Lambert, Steve Rhode Scott Libby (issues affecting data interpretation)
data management/database	Doug Hersh
cost/schedule	Ken Keay, Mike Delaney Ellie Baptiste-Carpenter (issues affecting cost/schedule of Battelle contract)
quality assurance	Jennifer Constantino, Doug Hersh Rosanna Buhl (issues affecting data quality not resolved internal to DLS)

If expected samples are missing, the DLS Violet Team will immediately notify the Battelle Field Manager (Mr. Matt Fitzpatrick) as well as Dr. Yong Lao and Dr. Doug Hersh.

Changes to the number of planned samples should be communicated to the Violet Team, Dr. Yong Lao and Dr. Doug Hersh in advance. It may occur that unusual environmental conditions lead to a decision during field sampling to collect extra samples. In this case, the field team should notify the Violet Team before delivering the samples if possible. If this is not possible, the fact that there are extra samples should be clearly indicated on the chain-of-custody forms to avoid sample mix-ups.

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

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

1.3 Project Definition and Background

The background of the HOM project can be found in the HOM Project Management Plan (Battelle 2009), and more comprehensive background for the water column monitoring in the QAPP for Water Column Monitoring (Libby *et al.* 2017.) A principal concern with the offshore outfall discharge is nutrients and their resultant eutrophication effects on the water column. Thus, water quality monitoring regularly 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 had been conducted by subcontractor laboratories to the HOM consultant (currently, Battelle Ocean Sciences.) This QAPP describes the quality system implemented for analytical procedures that are performed for the HOM project by the MWRA DLS.

1.4 Project Description and Schedule

The Harbor and Outfall Monitoring (HOM) Project water column surveys have been conducted since 1992 and are scheduled to continue at least through 2019. Revisions to the sampling scheme were made in 2004 and 2011. The water column QAPP (Libby *et al.* 2017) 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, particulate carbon and nitrogen, particulate phosphorous, chlorophyll *a* and phaeophytin. 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 eleven sampling locations in Massachusetts Bay sampled nine times per year. Nutrients samples will be collected at five depths at all stations. Chlorophyll samples will be collected at three depths at all stations.

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

Table 4. Samples Collected at Each Location

Stations	DIN[a]	Other Nutrients[b]	Chlorophyll[c]
F22, N04, N01, N21, N18, N07, F23, F15, F13, F10 and F06	5 depths	5 depths	3 depths[d]

[a] DIN = Dissolved Inorganic Nutrients = Nitrate, Nitrite, Ammonium, Orthophosphate, Silicate
[b] Other nutrients = particulate and dissolved organic nutrients [Total Dissolved Nitrogen (TDN), Total Dissolved Phosphorous (TDP), Particulate Carbon (PC), Particulate (PN), and Particulate Phosphorous (PP)]
[c] Laboratory analyses for chlorophyll and phaeophytin.

[d] Surface, chlorophyll maximum or mid-depth, bottom at stations F22, F23, N04 and N18; surface, mid-surface, and chlorophyll maximum at the other seven stations.

The nine surveys per year target weeks number 6, 12, 15, 20, 25, 30, 34, 36, and 43. Table 5 identifies the parameters, LIMS analysis codes, and sample numbers.

Table 5. Parameters Measured, Units and Number of Samples

Parameter	LIMS Analysis	Unit	# Samples/survey (9 surveys)	Total samples/yr
Nitrate+Nitrite	DINOWAAN	μM	11x5=55	495
Nitrite	DINOWAAN	μM	55	495
Amonium	DINOWAAN	μM	55	495
Phosphate	DINOWAAN	μM	55	495
Silicate	DINOWAAN	μM	55	495
Total dissolved nitrogen	TNP-SWAAN	μM	55	495
Total dissolved phosphorus	TNP-SWAAN	μM	55	495
Particulate carbon	PCPNSWCHN	μM	55	495
Particulate phosphorus	PP--SWOXA	μM	55	495
Particulate nitrogen	PCPNSWCHN	μM	55	495
Chlorophyll *a*	CHLAAQFLU	μγ/Λ	11x3=33	297
Phaeophytin	CHLAAQFLU	μγ/Λ	33	297

In addition to the measurements listed in Tables 4 and 5, there may also be a few late spring red tide sampling events that may generate nutrient or chlorophyll samples (Libby et al. 2013.) Chlorophyll and nutrient samples generated by red tide surveys are handled and analyzed in the same manner as routine survey samples.

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 5.

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 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 6 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 9. Method procedural blanks for parameters that use blank correction are the batch-average uncorrected method procedural blanks. To facilitate tracking blank adjustment in LIMS, for Particulate Carbon and Nitrogen the values entered in LIMS are in “instrument signal” units 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 (Libby *et al.* 2010, 2006, Costa et al. 2013), 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.

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 6) provide the sensitivity goals for the procedures. The MDLs listed in Table 6 are comparable to those listed in Libby, et al. 2002).

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 to the practical detection limit, 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 2.8.3 with the qualifiers listed in Table 13.

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.

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

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	0.025μM 0.013 μM 0.028 μM 0.010 μM 0.036 μM
Total dissolved nitrogen Total dissolved phosphorus	≤ 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
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

Chlorophyll *a* 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

[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 7. 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)% = │ (replicate 1 - replicate 2) x 2/(replicate 1 + replicate 2) │x 100.
[3] Percent Difference (PD) % = [(true concentration – measured concentration)/true concentration] x 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).

1.6 Special Training Requirements and Certification

Nutrient and chlorophyll measurements for the HOM study use routine laboratory analyses and 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 (Constantino, *et al.*, 2017), the DLS QAMP (DCN: 5000) and the analysis SOPs (See Table 7). The guidance for the control of DLS' documents 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 analytical SOP can be found on the shared network computer drive in the laboratory. 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 oversight is the responsibility of DLS Quality Assurance Coordinator.

1.7.2 Analytical 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 fifteen 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, monthly, and yearly by MWRA's MIS department. All backups are sent to an off-site secured facility where they are kept for the appropriate retention period. Daily backups are kept for a five week rotating cycle. Monthly backups are kept for a period of two years and every year-end a backup is done which is kept for a period of fifteen years.

1.7.5 Records Managed by ENQUAL

ENQUAL 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.* 2017. It has been ongoing, with slight changes in sampling frequency and sampling locations, since 1992, thus including eighteen years of monitoring. In 2011 and subsequent years, the BWQM study includes nine routine sampling events per year between February and October of each year. It may also include a few late spring red tide sampling events that may generate nutrient or chlorophyll samples (Libby et al. 2013).

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. Changes will be assessed through measurement of nutrient and chlorophyll concentrations, among others. Samples are collected near the outfall where outfall effects are most likely, as well as at more distant stations which serve as reference stations and document 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. It is 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 2010) and in the QAPP for Water Column monitoring (Libby *et al.* 2017). 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 2010).

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.* 2017. The sample bottles and the associated analytes are shown in Table 7, along with field preservation method and holding time. DLS provides the filters for the particulate carbon, particulate nitrogen, 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.* 2017.

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

2.3 Sample Handling and Custody Requirements

2.3.1 Sampling Equipment, Preservation and Holding Times Requirements

Samples collected for laboratory analysis will be stored on ice in coolers or frozen and holding times (Table 7) 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.

Table 7. Sample Collection and Storage

Parameter	Sample Volume (Target) (mL)[a]	Sample Containers[b, c]	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
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
Chlorophyll *a* 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

[a] Volume processed for analysis. Total volumes removed from Rosette sampling bottles are listed in Appendix A of Libby *et al.* 2017.
[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.

2.3.2 Sample Custody Procedure

All sample labels will include a printed and barcoded bottle identification (ID) number (SAMPLE_NUMBER) provided by MWRA to Battelle's field manager prior to each survey. The sample numbers are generated as follows: 1) Get the trip number. 2) Using HOM-TXT Stored Query Manager generate a list of samples using the trip number. 3) Export the samples into a CSV file in Excel and email it to Battelle. 4) Battelle will create barcodes based on the sample numbers.

The QAPP for Water Column studies (Libby *et* al 2017) 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 (sample_number) 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. If a survey lasts more than a day or two, 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, and are also communicated to the DLS HOM Project Manager who will notify the Battelle Field Manager within 24 hours of receipt. **Note:** The original COC forms will be sent to ENQUAL 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 SAMPLE_NUMBER from the barcoded label or otherwise entering it into LIMS. The LIMS SAMPLE_NUMBERs 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.

The Client Services Coordinator will:

- Copy into Labware the data in the "electronic COC" .csv file generated from Battelle's NavSam,and emailed to the Client Services Coordinator by Battelle's field manager. The following procedure is used:
  1) Batelle will create COCs using software that converts Excel spreadsheets into COCs.
  2) Batelle emails DLS completed COCs and electronic spreadsheets containing COC information.
  3) The Client Servies Coordinator formats the information to display sample IDs, sample collection date, and collection time.
  4) The Client Services Coordinator adds LabWare headers (Sample.SampleNumber, Sample.X_Grab_Comp_End_Date, Sample.X_GCE_Time, Sample.Sampled_by) to the columns in the spreadsheet.
  5) The spreadsheet is saved as a CSV file in Excel and saved to the desktop.
  6) After HOM samples are received in LabWare, the Client Services Coordinator imports the CSV file into LabWare (File> Import file).
  7) The Imported COC data then becomes associated with received samples. Labware matches Sample.SampleNumber with the other three parameters, Sample.X_Grab_Comp_End_Date, Sample.X_GCE_Time, and Sample.Sampled_by.)

After the samples are received by the DLS laboratory:

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

- Samples that are stored in the secure Sample Bank or freezer are in the custody of the Violet Team member who checked-in the samples until they are transferred from the Sample Bank to a member of laboratory staff for analysis. The receipt of samples by the analyst is documented in LIMS.

- 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 8).

- When the results are transferred to the EM&MS database (see section 4.1.2), ENQUAL automated routines will map the NavSam© sample ID into the SAMPLE_ID field and the LIMS SAMPLE_NUMBER into the BOTTLE_ID field and the LAB_SAMPLE_ID field.

Figure 2 Battelle Chain-of-Custody Form

MWRA Harbor and Outfall Monitoring Program
Project No. N007559
Sample Custody Form

Today's Date : 11/17/2010 8:17:40 AM

Chain-of-Custody # : WN10F-BS-0034
Survey ID : WN10P
Analysis ID : BS
Analysis Description : Biogenic silica

Laboratory : MWRA
Dept. Lab Services
190 Tafts Ave
Winthrop MA 02152
Yong Lau
617-660-7841 (Phone) (Fax)

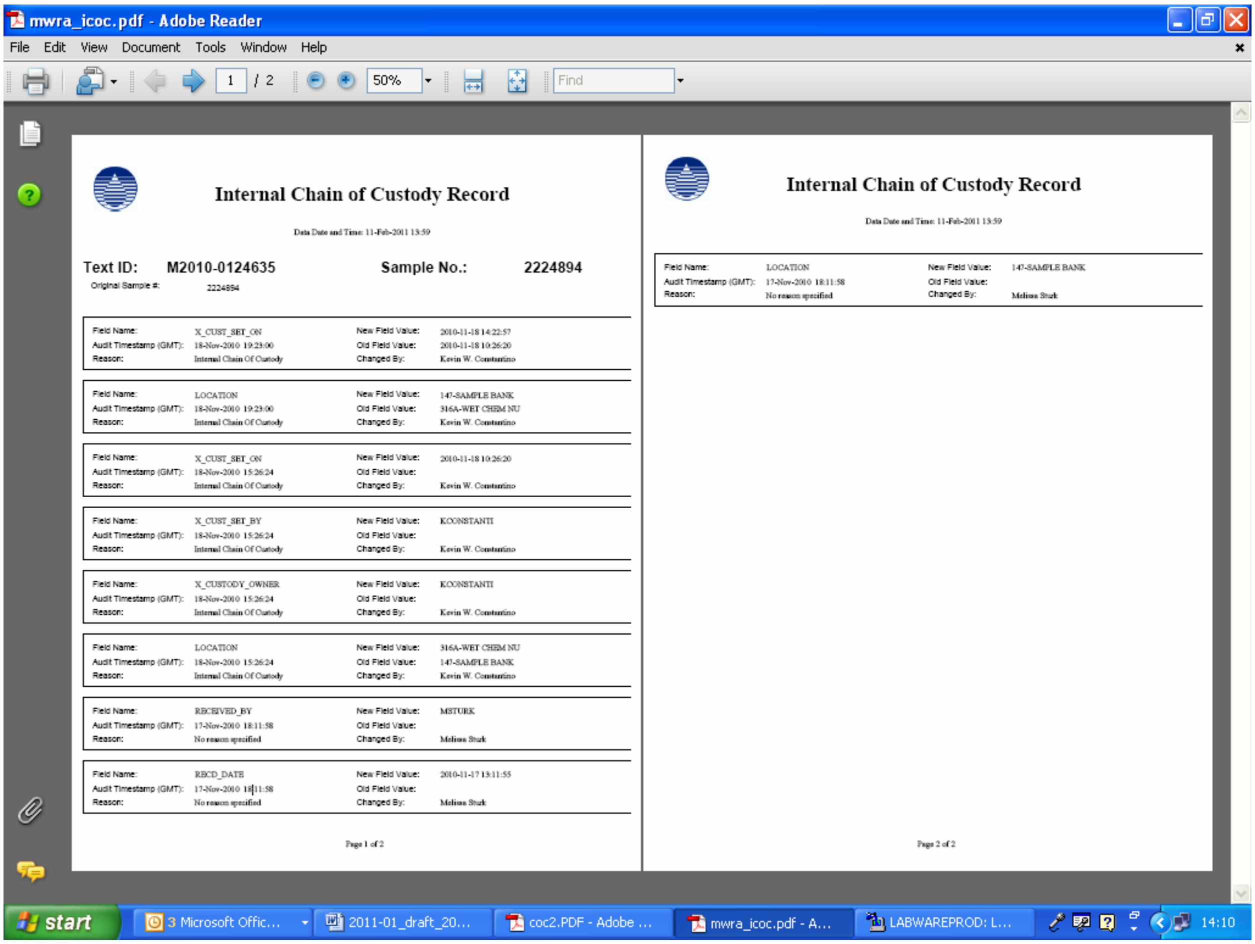
Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	2224694	11/15/2010 12:28:43 PM	BF2		✓	✓	
	2224695	11/15/2010 7:19:30 AM	BF1		✓	✓	
	2225321	11/15/2010 8:44:56 AM	N01	A	✓	✓	
	2225322	11/15/2010 8:44:56 AM	N01	A	✓	✓	
	2225333	11/15/2010 8:44:01 AM	N01	C	✓	✓	
	2225334	11/16/2010 8:44:01 AM	N01	C	✓	✓	
	2225348	11/15/2010 8:42:32 AM	N01	E	✓	✓	
	2225347	11/15/2010 8:42:32 AM	N01	E	✓	✓	
	2225356	11/15/2010 11:19:55 AM	N04	A	✓	✓	
	2225357	11/15/2010 11:19:55 AM	N04	A	✓	✓	
	2225368	11/15/2010 11:19:26 AM	N04	C	✓	✓	
	2225369	11/15/2010 11:19:26 AM	N04	C	✓	✓	
	2225380	11/15/2010 11:16:53 AM	N04	E	✓	✓	
	2225381	11/15/2010 11:16:53 AM	N04	E	✓	✓	
	2225390	11/15/2010 10:42:29 AM	N07	A	✓	✓	
	2225391	11/15/2010 10:42:29 AM	N07	A	✓	✓	

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

Relinquished By / Date / Time / Company / Transport-Airbill #	Received By / Date / Time / Company
[signature] 11/17/10 1045 BDO	[signature] 11/17/10 1045 BDO
[signature] 11/17/10 1230 BDO	[signature] 11/17/10 1300 MWRA

Page 1 of 3

Figure 3 **DLS LIMS Internal Chain-of-Custody Form**



Internal Chain of Custody Record

Data Date and Time: 11-Feb-2011 13:59

Text ID: M2010-0124635 **Sample No.:** 2224894

Original Sample #: 2224894

Field Name:	X_CUST_SET_ON	New Field Value:	2010-11-18 14:22:57
Audit Timestamp (GMT):	18-Nov-2010 19:23:00	Old Field Value:	2010-11-18 10:26:20
Reason:	Internal Chain Of Custody	Changed By:	Kevin W. Constantino

Field Name:	LOCATION	New Field Value:	147-SAMPLE BANK
Audit Timestamp (GMT):	18-Nov-2010 19:23:00	Old Field Value:	316A-WET CHEM NU
Reason:	Internal Chain Of Custody	Changed By:	Kevin W. Constantino

Field Name:	X_CUST_SET_ON	New Field Value:	2010-11-18 10:26:20
Audit Timestamp (GMT):	18-Nov-2010 15:26:24	Old Field Value:	
Reason:	Internal Chain Of Custody	Changed By:	Kevin W. Constantino

Field Name:	X_CUST_SET_BY	New Field Value:	KCONSTANTI
Audit Timestamp (GMT):	18-Nov-2010 15:26:24	Old Field Value:	
Reason:	Internal Chain Of Custody	Changed By:	Kevin W. Constantino

Field Name:	X_CUSTODY_OWNER	New Field Value:	KCONSTANTI
Audit Timestamp (GMT):	18-Nov-2010 15:26:24	Old Field Value:	
Reason:	Internal Chain Of Custody	Changed By:	Kevin W. Constantino

Field Name:	LOCATION	New Field Value:	316A-WET CHEM NU
Audit Timestamp (GMT):	18-Nov-2010 15:26:24	Old Field Value:	147-SAMPLE BANK
Reason:	Internal Chain Of Custody	Changed By:	Kevin W. Constantino

Field Name:	RECEIVED_BY	New Field Value:	MSTURK
Audit Timestamp (GMT):	17-Nov-2010 18:11:58	Old Field Value:	
Reason:	No reason specified	Changed By:	Melissa Sturk

Field Name:	RECD_DATE	New Field Value:	2010-11-17 13:11:55
Audit Timestamp (GMT):	17-Nov-2010 18:11:58	Old Field Value:	
Reason:	No reason specified	Changed By:	Melissa Sturk

Page 1 of 2

Internal Chain of Custody Record

Data Date and Time: 11-Feb-2011 13:59

Field Name:	LOCATION	New Field Value:	147-SAMPLE BANK
Audit Timestamp (GMT):	17-Nov-2010 18:11:58	Old Field Value:	
Reason:	No reason specified	Changed By:	Melissa Sturk

Page 2 of 2

2.4 Analytical Requirements

2.4.1 Analytical Methods

Table 8 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 8. 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. The DLS LIMS keeps track of specific instruments in use.

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

Parameter	LIMS test code	Units	Instrument	DLS SOP (Based on Reference)
Dissolved ammonium	DIN-OWAAN	μM	Skalar Autoanalyzer	SOP DCN 1184 (Oviatt and Hindle (1994); Solorzano (1969); USEPA NERL, 349.0
Dissolved inorganic nitrate/ nitrite and inorganic nitrite	DIN-OWAAN	μM	Skalar Autoanalyzer	SOP DCN 1183 (Bendschneider and Robinson (1952), and Morris and Riley (1963); USEPA NERL, 353.4)
Dissolved inorganic phosphate	DIN-OWAAN	μM	Skalar Autoanalyzer	SOP DCN 1180 (Murphy and Riley (1962); USEPA NERL 365.5)
Dissolved inorganic silicate	DIN-OWAAN	μM	Skalar Autoanalyzer	SOP DCN 1017 (Brewer and Riley (1966); Oviatt and Hindle (1994); USEPA NERL 366.0)
Total dissolved nitrogen and Total dissolved phosphorus	TNP-SWAAN	μM	Skalar Autoanalyzer	SOP DCN 1072 (D'Elia *et al.* (1997); Valderrama (1981))
Particulate carbon and Particulate nitrogen	PCPNSWCHN	μM	Perkin Elmer CHN Elemental Analyzer II	SOP DCN 1156 (Menzel and Vaccaro (1964); USEPA NERL 440.0)
Particulate phosphorus	PP--SWOXA	μM	Skalar Autoanalyzer	SOP DCN 1102 (Solorzano and Sharp (1980))
Chlorophyll Phaeophytin	CHLAAQFLU	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)

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 9. 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 Total Dissolved Nitrogen and Phosphorus

DLS uses the Skalar Autoanalyzer to perform this analysis based on the Valderrama (1981) method. The TDN and TDP samples are filtered in the field and undergo 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 measured on the Skalar Autoanalyzer are blank corrected using the batch-average method procedural blank. The reported name in LIMS is “TDN/TDP” to indicate that the samples have been filtered.

2.4.1.3 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.

2.4.1.4 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.

2.4.1.5 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 -10ºC. 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 4ºC. 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 is remeasured after 90 seconds to determine phaeophytin concentrations. Chlorophyll a and phaeophytin are collected at surface and chlorophyll maximum depths at all stations, and at either mid-surface or bottom depths for specific station sets described in footnotes of tables 4 and 12. Results of analyses of these samples will be used to calibrate the fluorescence measurements.

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 9 lists the quality control samples and data quality acceptance limits for each measurement according to the particular parameter(s) being analyzed. Other QC samples (e.g., instrument QC) may be dictated by the analytical method and are described in Section 8 of DLS' QAMP (DCN: 5000.0, 2003) and the specific SOP. The definitions of particular QC samples are 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.*, 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 10. 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.

Table 9.		**Quality Control Samples**		
Quality Control Sample Type		**Frequency**	**Quality Acceptance Limits**	**Corrective Action**[5]
Method Procedural Blanks				
	DIN	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.
Method Procedural Filter Blanks				
	Particulate nutrients	1 per batch of 20	≤5 x MDL	As above
	Chlorophyll *a*/phaeophytin	1 per batch of 20	≤5 x MDL	
Field Filter Blanks				
	Particulate nutrients	(See note 4, below)	≤5 x MDL	As above
	Chlorophyll *a*/phaeophytin	(See note 4, below)	≤5 x MDL	
Field Blanks (Sample container containing field filtered reagent water)				
	DIN and TN/TP	3 per survey	≤5 x MDL	As above
Prepared Standards (LCS)				
	DIN	1 per batch of 20	85%-115% recovery[2]	As for Method Procedural Blanks
	TN/ TP	1 per batch of 20	85%-115% recovery	
	Particulate nutrients	1 per batch of 20	85%-115% recovery	
	Chlorophyll *a*	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
Laboratory Duplicates (Instrument duplicates)				
	DIN	1 per batch of 20	≤10%RPD[3]	Flag with 'R' (precision does not meet DQO), unless native or duplicate < RL.
	Chlorophyll *a*/phaeophytin	1 per batch of 20	≤15% RPD	
Laboratory Duplicates (Processing Duplicates)				
	TN/TP	1 per batch of 20	≤10% RPD	Flag with 'R' (precision does not meet DQO), unless native or duplicate < RL.
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	ENQUAL will flag with value qualifier 'R' (precision does not meet DQO)
	TN/ TP	mid-depth at station N16	≤30% RPD	
	Particulate Nutrient	1 per batch of 20	≤30% RPD	
	Chlorophyll a/phaeophytin	Each mid-depth	≤50% RPD	

1 MDL = method detection limit, SOP DCN #5005

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 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.

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

Table 10. Calibration Procedures for Laboratory Instruments

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 ≥ 0.995	Prior to analytical run	PR[1] ±15%	Every 20 samples	Investigate, recalibrate
Total dissolved nitrogen and phosphorus	Skalar Autoanalyzer	4-5	r>0.995	Prior to analytical run	PR ±15%	Every 20 samples	Investigate, recalibrate
Particulate carbon and nitrogen	Perkin Elmer CHN Elemental Analyzer II	1	NA	Prior to analytical run	PR ±15%	Every 20 samples	Investigate, recalibrate
Particulate phosphorus	Skalar Autoanalyzer	4-5	r ≥0.995	Prior to analytical run	PR ±15%	Every 20 samples	Investigate, recalibrate
Chlorophyll *a* and phaeophytin	Turner Fluorometer, TD-700 (Backup: Model 450-003)	5	r ≥ 0.995	Annually or if continuing calibration fails	PD[2] from gel standard baseline ≤5%	Every 20 samples	Investigate, recalibrate

[1]Percent Recovery. So ±15% is 85% to 115%.
[2] Percent difference

Table 11. Station Identifiers

EM&MS STAT_ID	Location Description
F06	42-10.26, 70-34.62, MASS. BAY SOUTH OF OUTFALL SITE
F10	42-14.52, 70-38.22, MASS. BAY SOUTH OF OUTFALL SITE
F13	42-16.08, 70-44.10, MASS. BAY SOUTH OF OUTFALL SITE
F15	42-18.96, 70-43.68, MASS. BAY SOUTH OF NEARFIELD
F22	42-28.80, 70-37.08, MASS. BAY NEAR SALEM SOUND
F23	42-20.34, 70-56.52, PRESIDENT ROADS NEAR DEER ISLAND
N01	42-25.14, 70-51.90, NORTHWEST CORNER OF NEARFIELD
N04	42-26.64, 70-44.22, NORTHEASTERN CORNER OF NEARFIELD
N07	42-21.36, 70-42.36, SOUTHEASTERN CORNER OF NEARFIELD

Table 11.	**Station Identifiers**
EM&MS STAT_ID	**Location Description**
N18	42-21.96, 70-46.68, SOUTH OF OUTFALL SITE
N21	42-23.27,70-47.12, MIDDLE OF OUTFALL

Table 12.	**Sample Depth Codes**		
EM&MS SAMPLE_ DEPTH_ CODE	**Label Color**	**Description**	**Analyses (EM&MS Parameter Codes)**
A	Black	Surface	NH3, NO2, NO3, PO4, SIO4, TDN, TDP, POC, PON, PARTP. CHLA
B	Light Blue	Mid-surface	NH3, NO2, NO3, PO4, SIO4, TDN, TDP, POC, PON, PARTP, CHLA[1]
C	Green	Chlorophyll maximum	NH3, NO2, NO3, PO4, SIO4, TDN, TDP, POC, PON, PARTP, CHLA
D	Yellow	Mid-bottom	NH3, NO2, NO3, PO4, SIO4, TDN, TDP, POC, PON, PARTP
E	Red	Bottom	NH3, NO2, NO3, PO4, SIO4, TDN, TDP, POC, PON, PARTP, CHLA[2]

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.

[1] Mid-surface samples are analyzed for CHLA at stations F22, F23, N04 and N18.

[2] Bottom samples are analyzed for CHLA at stations F06, F10, F13, F15, N01, N07, and N21.

2.7 Tracking and Quality Verification of Supplies and Consumables

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

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 SAMPLE_NUMBER. Except for date and time, no Battelle field measurements will be entered in LIMS. Station Ids and depth codes are given in Tables 11 and 12. The LIMS sampling_point is a concatenation of the city code (facility, MASSBAYN or MASSBAYF), the station_id (EM&MS STAT_ID) and the depth code (EM&MS SAMPLE_DEPTH_CODE).

2.8.2 Data Recording

All documentation will conform to the DLS QAMP (DCN: 5000.0, MWRA 2003), 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, test results will either be manually entered into LIMS from laboratory logbooks, spreadsheets, or instrument data system printouts, or automatically entered from instrument data systems. The LIMS Batch Manager 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 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 control limit. This allows gross typographical errors to be detected and as an early notification of any limit exceedance. LIMS tests have been programmed to automatically convert results in mg/L to μM for tests reported in μM, where appropriate, and also take 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 2.8.5. 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

Flags and comments, where necessary, 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 flags and comments associated with a sample/test/result are part of the LIMS database record for the analysis of the respective sample.

2.8.3.1 Flag Types

Flags are the preferred type of annotation. Flags can be applied at the sample, test, and result levels using a pre-defined list of flags, including those in Table 13.

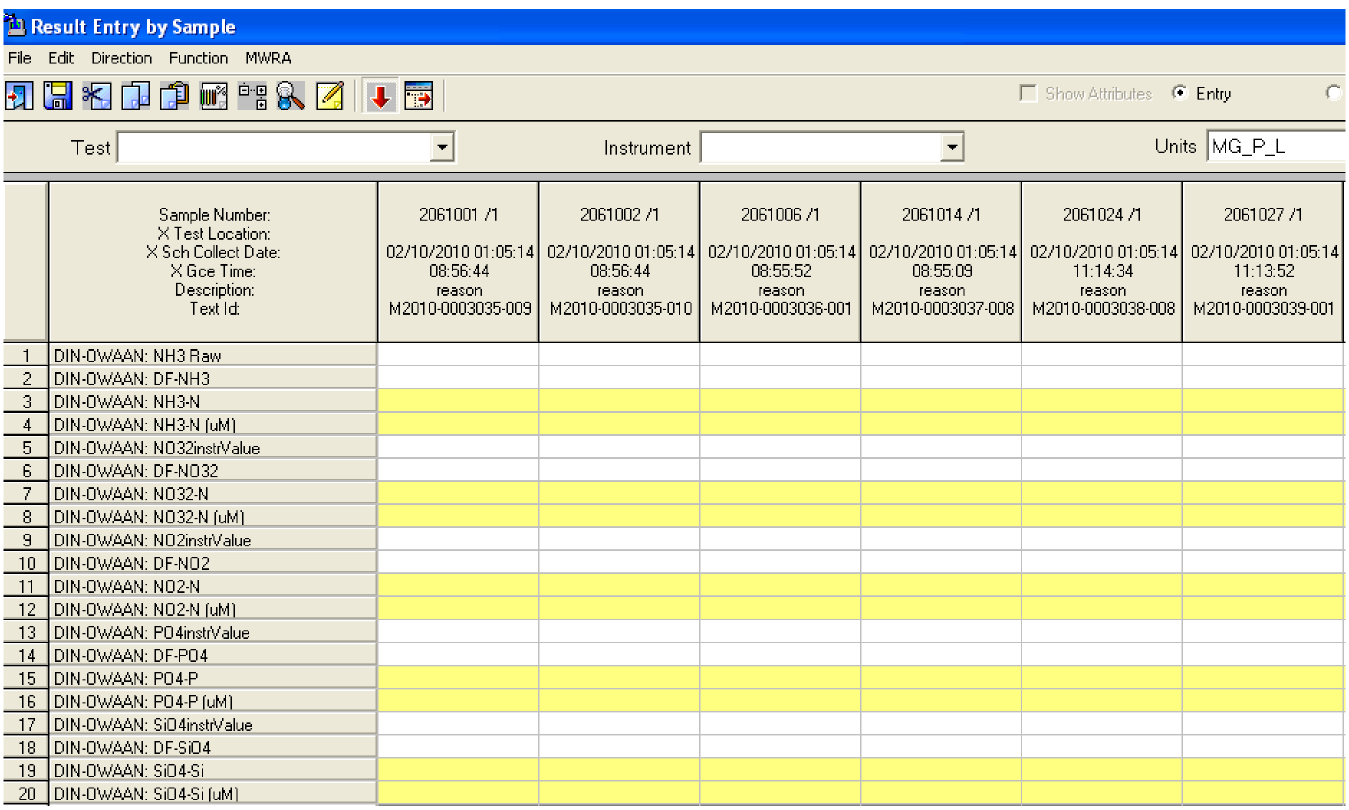
2.8.3.2 Comment Types

Comments are entered as either as predefined text (Table 13) or free-flowing text. Comments can be applied at the sample, test, and result levels. When pre-defined text is used, it should not be altered. Comments should be used to augment the pre-defined text or as a substitute to pre-defined text when there is no appropriate existing flag. Further, TEST COMMENTS for HOM analyses are only used to qualify data and are entered either by the analyst or validator, or to document a DAIR.

2.8.3.3 Sample Notepad Comments

If there is a situation for which flags or comments are inappropriate, the Sample Notepad is available for entry of free-flowing text. The Sample Notepad should not be needed routinely and should be regarded as a last resort.

Figure 4: <u>LIMS Data Entry Screen</u>



2.8.3.4 Test and Result Flags

From time to time, a test or result will be rejected (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 using an appropriate sample, test, or result flag. The pre-defined flags are listed in Table 13, 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 tests and QC in the batch are flagged with "B". Note that tests 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 tests in a batch when the LCS recovery is outside limits.
- "R", precision does not meet data quality objectives, is used only on a test 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.

LabWare LIMS allows multiple result flags (or test flags) to be used; these will be concatenated in the data warehouse and parsed into multiple value qualifiers by ENQUAL automated routines.

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

Table 13. Test Comments Qualifiers for Qualifying/Annotating Sample Test Results

LIMS Sample, Test or Result Flag	Description
A	Not detected - value reported as negative or missing
B	Not blank corrected, blank ≥5x MDL
B2	Blank corrected, blank ≥ 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

[1]A 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 a rejected (invalid) result is not superseded by a retest, it must include a flag or comment indicating why the result was rejected and could not be retested. A rejected sample will appear to the LIMS user on the screen in italics not bold and not red.

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 9) and the quality standards in section 7.0 of DLS' QAMP (DCN: 5000). The completion of the validation process and the approval process is documented in LIMS. Until a sample is approved, the results are regarded as preliminary. Subsequent to the approval of a sample test result, data can only be changed through the DAIR process described in section 2.8.7, below.

The ENQUAL HOM Project Manager has provided concentration ranges for each test based on historical data. These ranges have been included in LIMS to flag out-of-range results. During data entry and validation out-of-range results will appear red to the LIMS user . All out-of-range results need to be double checked by the analyst to ensure that calculation or data entry mistakes have not been made. If the result is still out-of-range, confer with the supervisor for additional guidance and consider retesting the sample if possible. In particular, duplicate filters are collected for all particulate parameters, so additional filters are likely to be available for retesting.

The second step in the process is the review of the results by the ENQUAL 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;

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

- **<u>Approval (Sample Review)</u>:** 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 rejected (invalid) in LIMS unless the data validator has provided an explanation with a flag or 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 ENQUAL Project Manager and Data Management group.

2.8.6 Reporting of Results

All data are reported electronically to the ENQUAL Project Manager as approved results in LIMS. Also, a QA Package (see 2.8.6.4, below) is to be forwarded to the ENQUAL HOM Project Manager by the requested due date after 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 6. 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 9.

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 ENQUAL.

2.8.6.4 QA Package

Immediately after the approval of all survey data, DLS will forward to the ENQUAL Project Manager a QA Package consisting of:

- **Deviations from the CW/QAPP:** Document any deviations from the CW/QAPP. Include these deviations in each subsequent QA Statement until they are rectified, or until the CW/QAPP is amended.

- **Audit Reports:** Copies of the quarterly rolling compliance audit including any audits they may have been specifically performed on HOM items.

- **Control Charts:** LIMS automatically reviews LCS and Method Blank results against control limits and Corrective Actions are automatically initiated when there is an exceedence or a violation of a trend or pattern rule. All batch QC results are transferred to the client's data warehouse so the preparation of control charts is no longer necessary.

- **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 ENQUAL 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 ENQUAL HOM Project Manager.

Figure 5: Quality Assurance Statement

MWRA DEPARTMENT OF LABORATORY SERVICES

MWRA Harbor and Outfall Monitoring Project

Quality Assurance Statement

Description of Data Set or Deliverable:____________________________________

1.0 Sample Analyses

All samples were handled, analyzed and reported according to the procedures and requirements specified in the QAPP (Constantino *et al*., 2017), 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 (Constantino *et al.*, 2017) were met. **Yes No**
- 100% of the data entry and 20% of manually-calculated data were checked for accuracy. **Yes No**
- Sample/Test/Result Flags and Comments were assigned properly. **Yes No**
- All samples/tests/results were validated and approved. **Yes No**

2.0 Attached Documentation

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

- ❑ Audit Reports
- ❑ Control Charts
- ❑ Corrective Actions
- ❑ DAIRs

Battelle COC Forms (Originals)

Comments:

____
____
____
____

3.0 CERTIFICATION

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

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

2.8.7 Changes to Approved Data

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

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

In LabWare LIMS, all DAIRs are processed electronically. Client-initiated DAIRs should be communicated via email to the QA Coordinator. She will initiate the electronic DAIR or designate to the appropriate personnel. The initiator is to include any comments or information received from the client. The results of a completed DAIR will be communicated back to the client.

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, and ammonia. Acceptable performance on these PT samples is required for NPDES self-monitoring analyses and Massachusetts DEP Certification, respectively.

In addition, the DLS participates in two seawater PT programs. The Chesapeake Biological Laboratories (CBL) PT program takes place biannually and includes samples to be tested for TDN, TDP, ammonia, nitrate+nitrite, phosphate, PC, PN, PP, Chlorophyll, and TSS. Starting in 2011 the Red Team also participates in the USGS Standard Reference Sample Project which will take place twice a year. Applicable parameters for this study include low level ammonia,

nitrate, nitrate+nitrite and phosphate. Participation in these programs allows for interlaboratory comparison with other organizations performing the same analyses.
Also, 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.

Quarterly 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 quarter different aspects of the laboratory operation are 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.

All data must be reviewed by the ENQUAL 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.

Upon the initiation of a corrective action, the problem is documented, and a corrective action plan is developed. After required corrective action has been taken, the information is documented by the initiator and reviewed by the QA Manager. If the action taken is determined to be effective and sufficient, the corrective action is approved and closed. All information is maintained in the Investigation Manager in LIMS. The ENQUAL Project Manager is notified of the corrective action taken.

In LabWare LIMS all corrective actions are processed electronically. Client-initiated corrective actions should be communicated via email to the QA Coordinator. She will initiate the electronic corrective action, or designate to the appropriate personnel. The initiator is to include any comments or information received from the client. The results of a completed corrective action will be communicated back to the client.

3.2 Battelle Ocean Sciences

3.2.1 Performance and system audits

The Battelle QA Officer for the Harbor and Outfall Monitoring Project conducted an initial systems audit to ensure that nutrient 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.* 2017), 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.* 2017), "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 HOM10 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."

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 ENQUAL 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 ENQUAL 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 C.1.2 of the Water Column QAPP (Libby *et al*. 2017)

3.3 Work Stoppage for Cause

The ENQUAL 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 quarterly to DLS managers and supervisors as part of DLS' quarterly QA Report. Specific information resulting from any oversight activities is included in the QA Package (2.8.6.4) accompanying the survey results. . The QA Coordinator prepares these reports. Guidance for QA reporting can be found in Section 13.0 of DLS' QAMP (DCN: 5000).

4.0 DATA VALIDATION AND USABILITY BY ENQUAL

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 the WWQ data warehouse by tested automated routines. Transfer of data from WWQ to EM&MS work tables will be done by ENQUAL using 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 ENQUAL 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 ENQUAL 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 ENQUAL 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 correcting 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 ENQUAL Project Manager will use the data preview application HOM Review, written by ENQUAL using Microsoft Excel and Oracle, to review the analytical results, flags, 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 ENQUAL 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 ENQUAL 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 ENQUAL Database Manager will:

- Make available for the ENQUAL 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 WWQ.

- 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, pertinent information from the test comments, sample notepad comments, and notes from the review by the ENQUAL Project Manager.

- Produce a data report incorporating the results.

4.1.4.2 Data Validation/Fitness-for-Use

The ENQUAL 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 synthesis reports.

The data validation procedures for this project are consistent with those defined in the HOM 4 Quality Management Plan (Battelle 2009), 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.* 2017, 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 ENQUAL 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.* 2017).

4.1.4.4 Data Transmittal to Battelle

The ENQUAL EM&MS Manager will forward the original Battelle COCs, and will also forward the QA statement from DLS for their information. The ENQUAL Project Manager will communicate any information resulting from his data review, which is relevant to sampling procedures for the upcoming surveys.

ENQUAL will send the data to Battelle as part of a Nutrients Data Report after the end of each season (January-April, May-June, July-August, September-December).

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.* 2017).

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.

Battelle, 2009. Environmental Product Line Quality Management Plan. Revision 0. October 2009

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.

Costa A, Larson E, Stamieszkin K. 2013. Quality Assurance Project Plan (QAPP) for water column monitoring in Cape Cod Bay 2014-2016. Boston: Massachusetts Water Resources Authority. Report 2014-07. 97 p.

D'Elia, CF, Connor, EE, Kaumeyer, NL, Keefe, Wood, 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 S, Rex AC, Keay KE, Mickelson MJ. 2013. Alexandrium Rapid Response Study Survey Plan. Revision 1. Boston: Massachusetts Water Resources Authority. Report 2013-06. 13 p.

Libby PS, Mansfield A, Buhl R, Lescarbeau G, Leo W, Keller AA, Borkman DG, Turner JT, Oviatt CA. 2006. Combined work/quality assurance project plan (QAPP) for water column monitoring 2006 - 2007, tasks 4, 5, 6, 7, 8, 11. Boston: Massachusetts Water Resources Authority. Report 2006-03. 119 p..

Libby PS, Fitzpatrick MR, Buhl RL, Lescarbeau GR, Leo WS, Borkman DG, Turner JT, Oviatt CA.2010. Quality assurance project plan (QAPP) for water column monitoring 2010: Tasks 4-9 and 13. Boston: Massachusetts Water Resources Authority. Report 2010-02. 105 p.

Libby PS, Fitzpatrick MR, Buhl RL, Lescarbeau GR, Borkman DG, Turner JT. 2017. Quality assurance project plan (QAPP) for water column monitoring 2017-2019: Tasks 4,5,6,7,10. Boston: Massachusetts Water Resources Authority. Report 2017-02. 67p. + appendices.

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. 2010. Ambient monitoring plan for the Massachusetts Water Resources Authority effluent outfall revision 2. July 2010. Boston: Massachusetts Water Resources Authority. Report 2010-04. 107p.

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.

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.

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.

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