

Quality Assurance Project Plan

for

Nutrient and Chlorophyll Analyses for Outfall Monitoring

**Massachusetts Water Resources Authority
Environmental Quality Department
Report 2010-09**



Leo WS, Prasse J, Delaney MF, Epelman P, Rhode S, Lao Y. 2010. Combined Work/Quality Assurance Project Plan (QAPP) for Nutrient and Chlorophyll Analyses for Outfall Monitoring. Boston: Massachusetts Water Resources Authority. Report 2010-09. 40 p.

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

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March 2005
Revised January 2006
Revised January 2008
Revised June 2010

Environmental Quality Department
Technical Report 2010-09

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

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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 it 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.

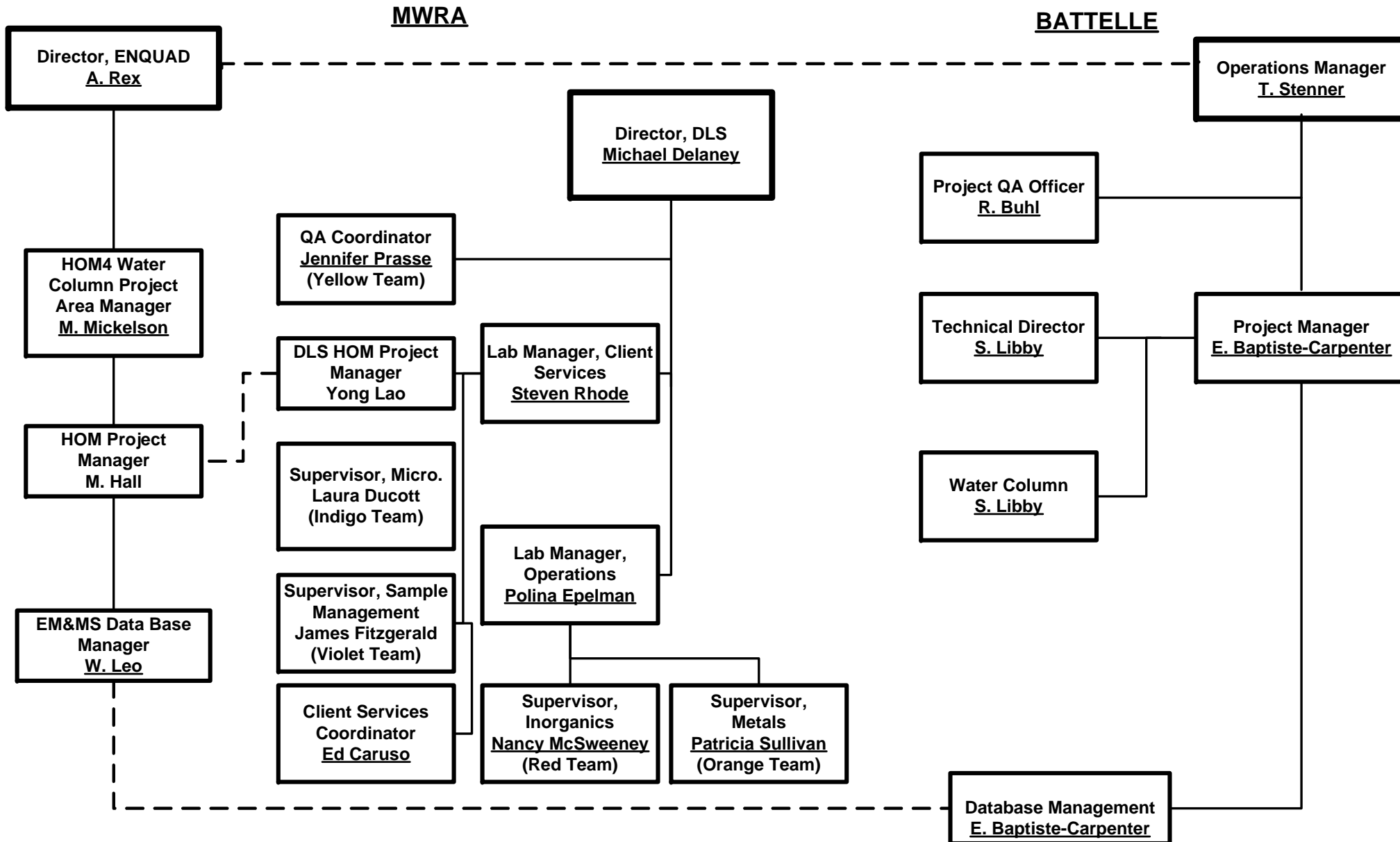
DLS Dr. Yong Lao is the Laboratory's Project Manager and will be DLS' primary point of contact for this project. Ms. Polina Epelman is the Section Manager responsible for the Red and Orange Teams. Ms. Nancy McSweeney is the Supervisor of the Red Team, responsible for nutrient analyses. Ms. Patricia Sullivan is the Supervisor of the Orange Team, responsible for DOC analyses. Mr. Steve Rhode is the Section Manager responsible for client services, the Violet Team, and the Indigo Team. Ms. Laura Ducott is supervisor of the Indigo Team, responsible for seawater TSS and chlorophyll analyses. Mr. James Fitzgerald is 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. Ms. Jennifer Prasse 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 | | | | |
|---|---|--|--|---|
| Michael Delaney, Director of Laboratory Services | | | | |
| Polina Epelman, Lab Manager (Operations) | | Steven Rhode, Lab Manager (Client Services) | | Jennifer Prasse QA Coordinator (Quality Assurance) |
| Nancy McSweeney Supervisor, Red Team | Patricia Sullivan Supervisor, Orange Team | James Fitzgerald Supervisor. Violet Team | Laura Ducott Supervisor, Indigo Team | |
| DIN, Particulate Carbon, Nitrogen and Phosphorous, Biogenic Silica | DOC | Sample Management | Chlorophyll, Phaeophytin, TSS | Performance Testing, QA/QC 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. Mr. Scott Libby 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. 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 ENQUAD and QA Statements submitted by DLS for completeness and adherence to the Water Column QAPP (Libby *et al.*, 2010).

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, DOC, and Chlorophyll Test for the Outfall Monitoring Program



| Table 2. | | Contact Information | | |
|--------------------------|-------------------------------------|----------------------------|---------------------------------------|--------------|
| Name | Title/Role | Location | email | Phone |
| Ellie Baptiste-Carpenter | HOM6 Project Manager | BOS ² | baptiste[at]battelle.org | 781-952-5361 |
| Mike Delaney | Laboratory Director | DLS ¹ | 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 |
| Matt Fitzpatrick | Field Manager/Sample Custodian | BOS | fitzpatrickm[at]battelle.org | 781-952-5351 |
| Doug Hersh | EM&MS Database Administrator | ENQUAD ³ | douglas.hersh[at]mwra.state.ma.us | 617-788-4945 |
| Maury Hall | ENQUAD Project Manager | ENQUAD | maurice.hall[at]mwra.state.ma.us | 617-788-4944 |
| Wendy Leo | EM&MS Manager | ENQUAD | 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 |
| Mike Mickelson | Outfall Monitoring Program Manager | ENQUAD | mike.mickelson[at]mwra.state.ma.us | 617-788-4951 |
| 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 |
| Jim Fitzgerald | Team Supervisor (Violet) | DLS | james.fitzgerald[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 |
| Rosanna Buhl | Quality Systems Manager | BOS | buhl[at]battelle.org | 781-952-5309 |

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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 (Table 3.)

Dr. Yong Lao will attend HOM project meetings, held quarterly at Battelle in Duxbury (March, June, September, and December) and in other months at MWRA in the Charlestown Navy Yard. Generally these meetings are held on the last Wednesday morning of the month. DLS holds an 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 | Matt Fitzpatrick, Jim Fitzgerald (Violet), Ed Caruso |
| data interpretation | Mike Mickelson, Scott Libby |
| laboratory technical issues | Relevant DLS Team Supervisor(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) |
| data management/database | Wendy Leo |
| cost/schedule | Ken Keay, Mike Delaney Ellie Baptiste-Carpenter (issues affecting cost/schedule of Battelle contract) |
| quality assurance | Jen Prasse, 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 HOM6 archive HOM6@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. Matt Fitzpatrick) 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.

1.3 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.* 2010). 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 2010. The water column QAPP (Libby *et al.* 2010) 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. Tables 4 and 5 identify 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 Analysis | Units | # Samples/survey (6 nearfield-only) | # Samples/survey (6 nearfield/farfield) | Total samples/year |
| Nitrate+Nitrite | DINOWAAN | μM | 7x5=35 | (7x5)+ [(24x5)+(2x3)]=161 | 1176 |
| Nitrite | DINOWAAN | μM | 35 | 161 | 1176 |
| Ammonium | DINOWAAN | μM | 35 | 161 | 1176 |
| Phosphate | DINOWAAN | μM | 35 | 161 | 1176 |
| Silicate | DINOWAAN | μM | 35 | 161 | 1176 |
| Total dissolved nitrogen | TNP-SWAAN | μM | 7x3=21 | (7x3)+(14x3) = 63 | 504 |
| Total dissolved phosphorus | TNP-SWAAN | μM | 21 | 63 | 504 |
| Dissolved organic carbon | DOC-OWCIR | μM | 21 | 63 | 504 |
| Particulate nitrogen | PCPNSWCHN | μM | 21 | 63 | 504 |
| Particulate phosphorus | PP--SWOXA | μM | 21 | 63 | 504 |
| Particulate carbon | PCPNSWCHN | μM | 21 | 63 | 504 |
| Biogenic silica | BSI-SWAAN | μM | 21 | 63 | 504 |
| Chlorophyll <i>a</i> | CHLAAQFLU | μg/L | 35 | 35+[(12x5)+(2x3)] = 101 | 816 |
| Phaeophytin | CHLAAQFLU | μg/L | 35 | 101 | 816 |
| Total suspended solids | TSS-SWGRV | 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. 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 (Libby *et al.* 2010), 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 was performed during 2004 and may be repeated 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. 2010). 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.

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.

| 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 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 _{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).

1.7 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.*, 2010), 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 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 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, 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 (2) years and every year-end a backup is done which is kept for a period of fifteen (15) 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.* 2010. It has been ongoing, with slight changes in sampling frequency and sampling locations, since 1992, thus including eighteen 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 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.* 2010). 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.* 2010. 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.* 2010.

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.* 2010.

^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 (SAMPLE_NUMBER) and barcode provided by MWRA prior to each survey. The QAPP for Water Column studies (Libby *et al* 2010.) 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. 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, and 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 SAMPLE_NUMBER from the barcoded label or otherwise entered 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.

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 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.

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

| 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) |
| Dissolved organic carbon | DOC-OWCIR | μM | Shimadzu TOC-Vcsh (Backup: Tekmar-Dorhmann, Apollo 9000) | SOP DCN 1126 (Sugimura and Suzuki (1988); SM 5310B) |
| Total dissolved nitrogen and Total dissolved phosphorus | TNP-SWAAN | μM | Skalar Autoanalyzer | SOP DCN 1072 (D'Elia <i>et al.</i> (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)) |
| Biogenic Silica | BSI-SWAAN | μM | Skalar Autoanalyzer | SOP DCN 1177 (Paasche (1973)) |
| 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) |
| Total suspended solids | TSS-SWGRV | mg/L | Mettler 5-place or Sartorius 6-place balance | SOP DCN 1104 (EPA 160.2) |

Figure 2

Battelle Chain-of-Custody Form

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

Today's Date : 2/28/2005 11:55:23

Laboratory : MWRA

Chain-of-Custody # : WF052-IN-0037

Survey ID : WF052

Analysis ID : IN

Analysis Description : Dissolved Inorganic Nutrients

Dept. Lab Services

190 Tafts Ave
















Winthrop

MA 02152

Mr. Yong Lao

617-660-7833 (Phone)

(Fax)

| Bottle ID : | Bottle ID : | Sampling Date : | Station ID : | Depth Code: | Ck 1 | Ck 2 | Ck 3 |
|---|-------------|--|--------------|-------------|-------------------------------------|-------------------------------------|--------------------------|
|  | WF052104IN1 | 2/26/2005 8:00:39 AM 05010901 ✓ | F25 | E | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052105IN1 | 2/26/2005 8:01:11 AM 05010900 ✓ | F25 | D | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052106IN1 | 2/26/2005 8:01:52 AM 05010899 ✓ | F25 | C | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052106IN2 | 2/26/2005 8:01:52 AM 05010979 ✓ | F25 | C | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052108IN1 | 2/26/2005 8:02:33 AM 05010898 ✓ | F25 | B | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052109IN1 | 2/26/2005 8:03:01 AM 05010897 ✓ | F25 | A | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052117IN1 | 2/26/2005 8:49:30 AM 05010841 ✓ | F10 | E | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052118IN1 | 2/26/2005 8:50:08 AM 05010845 ³⁹ ✓ | F10 | C | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF052119IN1 | 2/26/2005 8:50:45 AM 05010839 ⁴⁰ ✓ | F10 | D | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF05211AIN1 | 2/26/2005 8:51:13 AM 05010838 ✓ | F10 | B | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF05211BIN1 | 2/26/2005 8:51:45 AM 05010837 ✓ | F10 | A | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF05212CIN1 | 2/26/2005 9:20:41 AM 05010826 ✓ | F05 | E | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF05212DIN1 | 2/26/2005 9:21:08 AM 05010825 ✓ | F05 | D | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF05212EIN1 | 2/26/2005 9:21:47 AM 05010824 ✓ | F05 | C | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
|  | WF05212FIN1 | 2/26/2005 9:22:15 AM 05010823 ✓ | F05 | B | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> |

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


| | |
|---|---|
| Relinquished By / Date / Time / Company / Transport-Airbill #  2/28/05 1200 B20 | Received By / Date / Time / Company Ed CARNO / 3/1/05 / 13:00 / MWRA |
|---|---|

Figure 3

DLS LIMS Internal Chain-of-Custody Form



Internal Chain of Custody Record

Data Date and Time: 12-Feb-2010 10:23

Sample: M2010-0003033-008

| | | | |
|------------------------|---------------------------|------------------|---------------------------|
| Field Name: | X_CUST_SET_C | New Field Value: | 2010-02-10 14:32:02 |
| Audit Timestamp (GMT): | 10-Feb-2010 19:32:13 | Old Field Value: | 2010-02-10 10:20:16 |
| Reason: | Internal Chain Of Custody | Changed By: | Charles Blodget |
| Field Name: | X_CUST_SET_I | New Field Value: | CBLODGET |
| Audit Timestamp (GMT): | 10-Feb-2010 19:32:13 | Old Field Value: | Z_LARISSA |
| Reason: | Internal Chain Of Custody | Changed By: | Charles Blodget |
| Field Name: | X_CUSTODY_C | New Field Value: | CBLODGET |
| Audit Timestamp (GMT): | 10-Feb-2010 19:32:13 | Old Field Value: | Z_LARISSA |
| Reason: | Internal Chain Of Custody | Changed By: | Charles Blodget |
| Field Name: | LOCATION | New Field Value: | 147-SAMPLE BANK |
| Audit Timestamp (GMT): | 10-Feb-2010 19:32:13 | Old Field Value: | 316A-WET CHEM NU |
| Reason: | Internal Chain Of Custody | Changed By: | Charles Blodget |
| Field Name: | X_CUST_SET_C | New Field Value: | 2010-02-10 10:20:16 |
| Audit Timestamp (GMT): | 10-Feb-2010 15:21:54 | Old Field Value: | |
| Reason: | Internal Chain Of Custody | Changed By: | Larissa M. Zilitinkevitch |
| Field Name: | X_CUST_SET_I | New Field Value: | Z_LARISSA |
| Audit Timestamp (GMT): | 10-Feb-2010 15:21:54 | Old Field Value: | |
| Reason: | Internal Chain Of Custody | Changed By: | Larissa M. Zilitinkevitch |
| Field Name: | X_CUSTODY_C | New Field Value: | Z_LARISSA |
| Audit Timestamp (GMT): | 10-Feb-2010 15:21:54 | Old Field Value: | |
| Reason: | Internal Chain Of Custody | Changed By: | Larissa M. Zilitinkevitch |
| Field Name: | LOCATION | New Field Value: | 316A-WET CHEM NU |
| Audit Timestamp (GMT): | 10-Feb-2010 15:21:54 | Old Field Value: | 147-SAMPLE BANK |
| Reason: | Internal Chain Of Custody | Changed By: | Larissa M. Zilitinkevitch |

| | | | |
|------------------------|----------------------|------------------|-------------|
| Field Name: | RECEIVED_BY | New Field Value: | CSEAMAN |
| Audit Timestamp (GMT): | 08-Feb-2010 12:49:30 | Old Field Value: | |
| Reason: | No reason specified | Changed By: | Cara Seaman |

| | | | |
|------------------------|----------------------|------------------|---------------------|
| Field Name: | RECD_DATE | New Field Value: | 2010-02-08 07:49:29 |
| Audit Timestamp (GMT): | 08-Feb-2010 12:49:30 | Old Field Value: | |
| Reason: | No reason specified | Changed By: | Cara Seaman |

| | | | |
|------------------------|----------------------|------------------|-----------------|
| Field Name: | LOCATION | New Field Value: | 147-SAMPLE BANK |
| Audit Timestamp (GMT): | 08-Feb-2010 12:49:30 | Old Field Value: | |
| Reason: | No reason specified | Changed By: | Cara Seaman |

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- μ m 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 is 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.*, 2010 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 reagents and chemicals are Analytical Reagent Grade or higher. Standards are purchased according to the requirements of the respective analysis SOP and all information concerning the standards (purchased or prepared) is kept in the Standards Logbook. Certifications are kept in the team's Standards Certificate File. Expiration dates are assigned by the analyst either according to the manufacturer's specification or according to the requirements given in the respective analysis SOP. Additional information concerning standards and reagents can be found in Section 6.0 of DLS' QAMP (DCN: 5000).

| Table 10. Quality Control Samples | | | |
|--|---|----------------------------------|--|
| Quality Control Sample Type | Frequency | Quality Acceptance Limits | Corrective Action⁶ |
| 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. |
| TSS | 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 | |
| TSS | 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 TN/TP | 3 per survey | ≤5 x MDL | Flag with 'W' (use with caution) |
| Prepared Standards (LCS) | | | |
| DIN | 1 per batch of 20 | 85%-115% recovery ² | As for Method Procedural Blanks |
| DOC, and TN/ TP | 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 '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) | | | |
| TSS | 1 per batch of 20 | ≤20% RPD | Flag with 'R' (precision does not meet DQO) |
| TN/TP | 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, TN/ TP | 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.

⁷ SOP DCN #5005

| 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) | Sartorius 6-place Balance or Mettler 5-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% |

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

²Percent 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 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 12 and 13. 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).

| 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 |

| Table 12. Station Identifiers | |
|--------------------------------------|--|
| EM&MS STAT_ID | Location Description |
| N04 | 42-26.64, 70-44.22, NORTHEASTERN CORNER OF NEARFIELD |
| 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 or automatically 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 14.

2.8.3.2 Comment Types

Comments are entered as either as predefined text (Table 14) 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: LIMS Data Entry Screen

| Result Entry by Sample | | | | | | | |
|---|---------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| File Edit Direction Function MWRA | | | | | | | |
| <input type="checkbox"/> Show Attributes <input checked="" type="radio"/> Entry | | | | | | | |
| Test | | Instrument | | Units MG_P_L | | | |
| | Sample Number: | 2061001 /1 | 2061002 /1 | 2061006 /1 | 2061014 /1 | 2061024 /1 | 2061027 /1 |
| | X Test Location: | | | | | | |
| | X Sch Collect Date: | 02/10/2010 01:05:14 | 02/10/2010 01:05:14 | 02/10/2010 01:05:14 | 02/10/2010 01:05:14 | 02/10/2010 01:05:14 | 02/10/2010 01:05:14 |
| | X Gce Time: | 08:56:44 | 08:56:44 | 08:55:52 | 08:55:09 | 11:14:34 | 11:13:52 |
| | Description: | reason | reason | reason | reason | reason | reason |
| | Text Id: | M2010-0003035-009 | M2010-0003035-010 | M2010-0003036-001 | M2010-0003037-008 | M2010-0003038-008 | M2010-0003039-001 |
| 1 | DIN-QWAAN: NH3 Raw | | | | | | |
| 2 | DIN-QWAAN: DF-NH3 | | | | | | |
| 3 | DIN-QWAAN: NH3-N | | | | | | |
| 4 | DIN-QWAAN: NH3-N (uM) | | | | | | |
| 5 | DIN-QWAAN: NO32instrValue | | | | | | |
| 6 | DIN-QWAAN: DF-NO32 | | | | | | |
| 7 | DIN-QWAAN: NO32-N | | | | | | |
| 8 | DIN-QWAAN: NO32-N (uM) | | | | | | |
| 9 | DIN-QWAAN: NO2instrValue | | | | | | |
| 10 | DIN-QWAAN: DF-NO2 | | | | | | |
| 11 | DIN-QWAAN: NO2-N | | | | | | |
| 12 | DIN-QWAAN: NO2-N (uM) | | | | | | |
| 13 | DIN-QWAAN: PO4instrValue | | | | | | |
| 14 | DIN-QWAAN: DF-PO4 | | | | | | |
| 15 | DIN-QWAAN: PO4-P | | | | | | |
| 16 | DIN-QWAAN: PO4-P (uM) | | | | | | |
| 17 | DIN-QWAAN: SiO4instrValue | | | | | | |
| 18 | DIN-QWAAN: DF-SiO4 | | | | | | |
| 19 | DIN-QWAAN: SiO4-Si | | | | | | |
| 20 | DIN-QWAAN: SiO4-Si (uM) | | | | | | |

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 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 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 ENQUAD 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.

| LIMS Sample, Test or Result | 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 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 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 ENQUAD 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 are 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 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 (Test Review):** 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 (Sample Review):** 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 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 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 exceedance 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 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.

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.

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> , 2008) 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:

- | | |
|---|--------------------------------|
| <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.

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.

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.

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, 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.* 2010), 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.* 2010), “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.”

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 C.1.1 of the Water Column QAPP (Libby *et al.* 2010.)

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 quarterly to DLS managers and supervisors as part of DLS' quarterly QA Report and Rolling Audit Report. The QA Coordinator prepares these reports. 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 the WWQ data warehouse by tested automated routines. Transfer of data from WWQ to EM&MS work tables will be done by ENQUAD 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 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 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 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, pertinent information from the test comments, sample notepad comments, and ENQUAD Project Manager.
- Produce a data report incorporating the results.

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 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.* 2010, 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.* 2010).

4.1.4.4 Data Transmittal to Battelle

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

ENQUAD 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.* 2010).

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