

**QUALITY ASSURANCE PROJECT PLAN
(QAPP)**

for

**WATER COLUMN MONITORING 2014-2016
Tasks 4, 5, 6, 7, 10**

MWRA Harbor and Outfall Monitoring Project

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**A PROJECT MANAGEMENT
VERSION 1.0**

A.1 TITLE AND APPROVALS

**FINAL QUALITY ASSURANCE PROJECT PLAN
(QAPP)
*for***

**WATER COLUMN MONITORING 2014-16
Tasks 4, 5, 6, 7, 10**

**MWRA Harbor and Outfall Monitoring Project
*Prepared by:***

Battelle
Massachusetts Water Resources Authority
Pausacaco Plankton
University of Massachusetts at Dartmouth

February 11, 2014

REVIEW AND APPROVALS

<u>Signature on file</u> Ms. Ellen Baptiste-Carpenter Battelle Project Manager	<u>2/12/2014</u> Date
<u>Signature on file</u> Mr. Scott Libby Battelle Technical Manager	<u>2/11/2014</u> Date
<u>Signature on file</u> Ms. Rosanna Buhl Battelle Project QA Officer	<u>2/11/2014</u> Date
<u>Signature on file</u> Mr. Kenneth Keay MWRA Project Manager	<u>2/14/2014</u> Date
<u>Signature on file</u> Dr. Michael Mickelson MWRA Technical Manager	<u>2/14/2014</u> Date
<u>Signature on file</u> Ms. Wendy Leo MWRA EM & MS Manager	<u>2/14/2014</u> Date

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APPENDICES

Appendix I	MWRA Standard Operating Procedures
Appendix II	Battelle Standard Operating Procedures
Appendix III	Water Column Sample Collection Requirements
Appendix IV	QA Statements

A.3 DISTRIBUTION LIST

This document will be distributed to the following project participants once all approval signatures have been received:

NAME	DATE SENT
Betsy Reilley (MWRA)	
Ken Key (MWRA)	
Michael Mickelson (MWRA)	
Maury Hall (MWRA)	
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Yong Lao (MWRA)	
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Carlton Hunt (Battelle)	
Jessica Tenzar (Battelle)	
Jeff Turner (University of Massachusetts Dartmouth Campus; UMD)	
David Borkman (Pausacaco Plankton)	
Don Anderson (Woods Hole Oceanographic Institution; WHOI)	

A.4 PROJECT AND TASK ORGANIZATION

The Water Column Monitoring tasks will be accomplished through the coordinated efforts of several organizations. Figure A-1 presents the Project Management structure and the major tasks necessary to complete the scope of work. Each element of the tasks has been assigned a separate sub-account with budget and milestones, and these accounts will be used to track costs against progress.

Dr. Betsy Reilley is the Director of the MWRA Environmental Quality Department.

Mr. Ken Keay is the MWRA Harbor and Outfall Monitoring (HOM) Project Manager. He has primary administrative and budgetary oversight of the program. He also serves as backup to the MWRA Water Column Monitoring Technical Manager.

Dr. Mike Mickelson is the MWRA Water Column Monitoring Technical Manager. He will be informed of all technical matters pertaining to work described in this Quality Assurance Project Plan (QAPP). He also serves as backup to the MWRA HOM Project Manager.

Ms. Wendy Leo is the MWRA Environmental Monitoring and Management System (EM&MS) Database Manager.

Ms. Ellen Baptiste-Carpenter is the Battelle Project Manager. She is responsible for ensuring that products and services are delivered in a timely and cost-effective manner that meet MWRA's expectation, and for the overall performance of this project. She is supported by Battelle Deputy General Manager Tracy Stenner who oversees operations at the Duxbury site.

Mr. Scott Libby is the Battelle Technical Manager overseeing all aspects of the sampling, analysis, and reporting of data from the water column monitoring.

Dr. Carlton Hunt is the Battelle Technical Advisor and will assist in ensuring that all technical aspects of Battelle's support to MWRA are provided at the same standards as previous HOM programs.

Mr. Matt Fitzpatrick is the Battelle Field Manager and is responsible for the overall field program and for all day-to-day field and laboratory activities conducted by Battelle for the project.

Ms. Rosanna Buhl is the Battelle Quality Assurance Officer. Ms. Buhl is responsible for reviewing data reports and QA Statements submitted by members of Battelle's water column monitoring team for completeness and adherence to the QAPP. She is also responsible for reviewing the synthesis reports for accuracy and completeness.

Ms. Jessica Tenzar is the Battelle Deputy Project Manager and is responsible for the PMPlan database and generating project management reports. She is assisted by Ms. Liz Ferson who supports the corporate business office.

The key contacts at each of the supporting organizations are shown in Figure A-1.

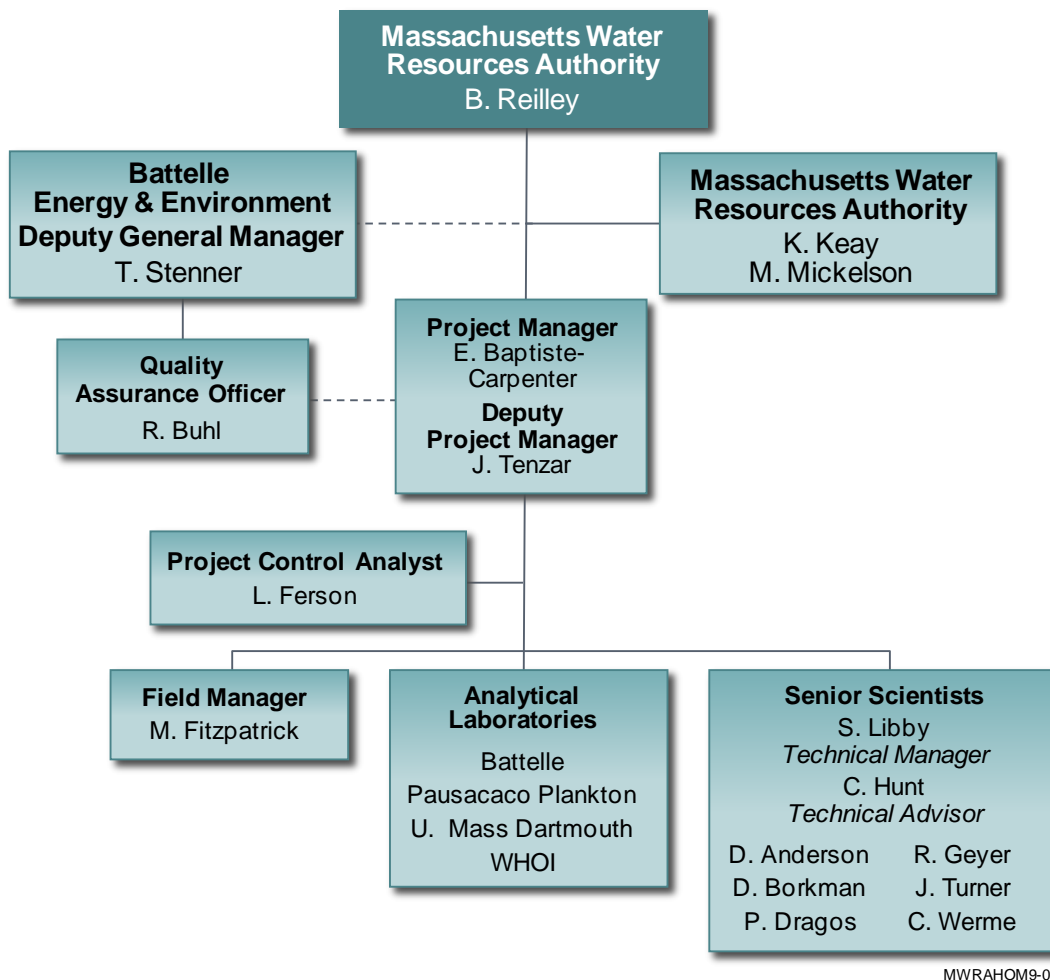


Figure A-1. Project Management Structure and Water Column Study Organization

A.5 PROBLEM DEFINITION/BACKGROUND

The MWRA has implemented a long-term marine environmental monitoring plan (MWRA 1991, 1997, 2004, 2010) for the MWRA effluent outfall located in Massachusetts Bay (Figure A-2). The outfall is regulated under a National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MassDEP 2000). The EPA Supplemental Environmental Impact Statement (SEIS) for the outfall (EPA 1988) determined that there would be no significant water quality or biological impacts associated with the outfall. Even so, the SEIS recommended a monitoring program for assessing compliance with the NPDES permit, assessing unacceptable impacts, and collecting data useful for outfall management considerations (MWRA 1990) be implemented. In response, the MWRA committed to implementing “long-term biological and chemical monitoring to describe existing conditions and evaluate the impacts of the treatment facility discharge.” To develop the monitoring plan, public, scientific, and regulatory areas of concern were identified following guidance for coastal monitoring (*i.e.*, NRC 1990). The program is designed to assess potential environmental impact of the effluent discharge into Massachusetts Bay, and evaluate compliance with the discharge permit.

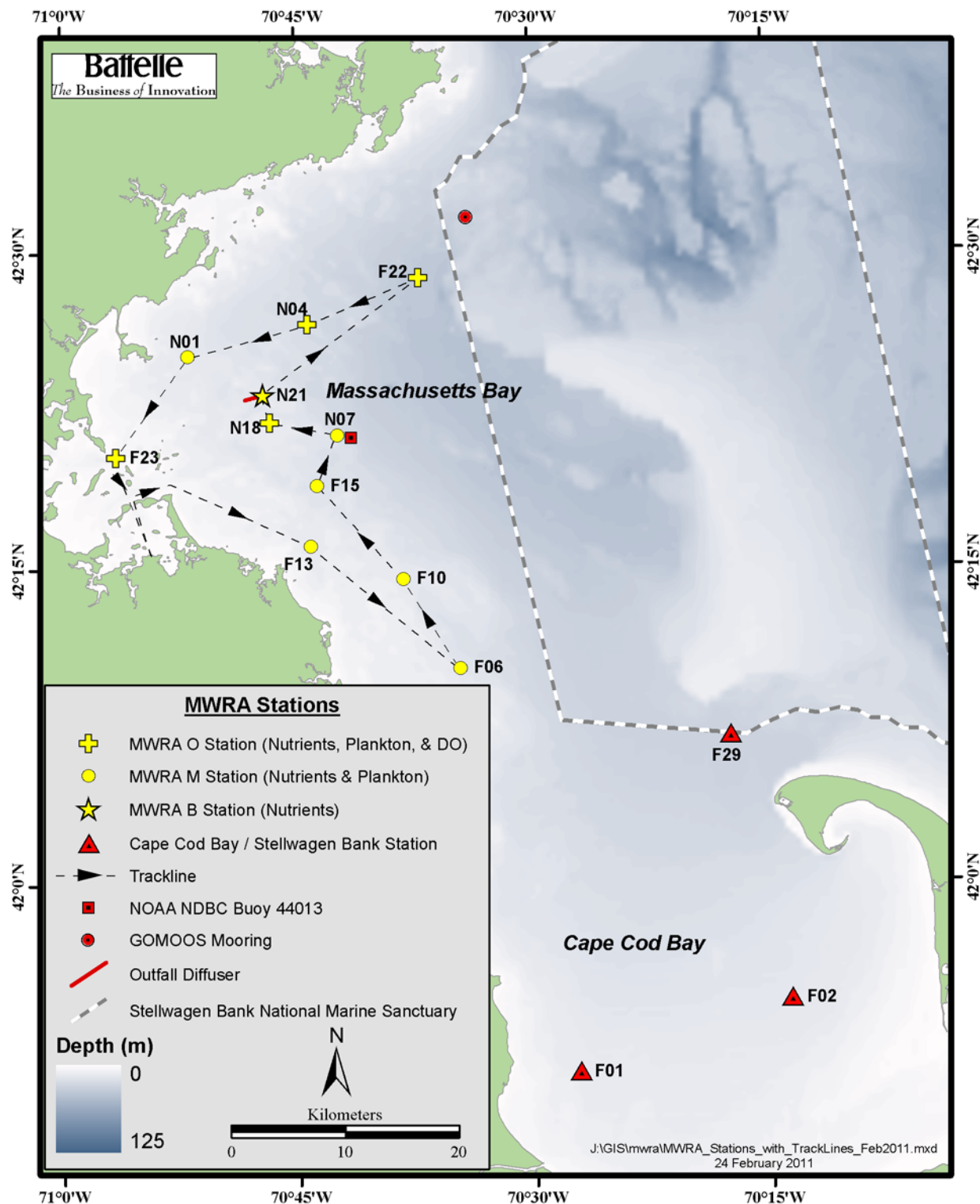


Figure A-2. Location of MWRA Effluent Outfall and monitoring stations in Massachusetts and Cape Cod Bays

The primary objective of water column monitoring is to detect changes in the water column of Massachusetts and Cape Cod Bays that may be caused by relocating the effluent outfall. The main concern is that discharged nutrients will be detrimental. The rationale for the work is discussed in the Outfall Monitoring Plan (MWRA 1991, 1997, 2004, 2010). The monitoring is focused on detecting changes in physical water properties, nutrient concentrations, dissolved oxygen, phytoplankton biomass, and phytoplankton and zooplankton community composition in Massachusetts Bay and Cape Cod Bay. To date no substantial change has been observed in the bays related to the outfall diversion (Libby *et al.* 2013).

During the baseline period (1992-September 2000), the monitoring plan was modified as data were evaluated and new questions were developed. Since the discharge was diverted to the bay outfall on September 6, 2000, there have been two major modifications to the water column monitoring plan. The first changes to the Ambient Monitoring Plan were implemented in 2004 following a comprehensive review of the data led to revisions and with concurrence from the Outfall Monitoring Science Advisory Panel and the EPA (MWRA 2004). The most substantial changes included reducing the number of nearfield surveys from 17 to 12 and reducing the number of nearfield stations from 21 to 7. These changes to the Ambient Monitoring Plan as well as other changes that were implemented in 2004 were captured in the revised QAPP for Water Column Monitoring: 2004 – 2005 and 2006 – 2007 (Libby *et al.* 2005, 2006). In 2009-2010, a second round of data evaluation and monitoring plan revisions was conducted.

The second revision to the Ambient Monitoring Plan (MWRA 2010) was submitted to EPA in July 2010 and officially approved by EPA on December 6, 2010. The changes were detailed in the QAPP for Water Column Monitoring: 2011-2013 (Libby *et al.* 2011) and include a reduction in surveys, stations, and analytical parameters. The number of surveys was reduced from six nearfield only and six combined nearfield/farfield surveys to nine Massachusetts Bay surveys per year. The number of water column stations was reduced from 32 to 14. A total 11 stations are sampled in Massachusetts Bay by Battelle and three additional stations in Cape Cod Bay/Stellwagen. Note that synoptic sampling in Cape Cod Bay and Stellwagen National Marine Sanctuary is being conducted under a separate contract by the Provincetown Center for Coastal Studies (PCCS). Biogenic silica, total suspended solids, dissolved organic carbon, primary production, and respiration analyses were dropped from the program based on diminished importance to the program or completion of associated special studies. The primary changes in this QAPP vs. Libby *et al.* (2011) are that buoy servicing and marine debris tow survey tasks have been dropped from the HOM9 program.

A.6 PROJECT/TASK DESCRIPTION

The HOM Project water column surveys have been conducted since 1992 and are scheduled to continue through 2016. This QAPP describes the HOM9 activities specific to the nine Massachusetts Bay water column surveys scheduled to be conducted each year from 2014 through 2016. Physical and meteorological data collected by stationary moorings and satellites may supplement data collected during the water column surveys. Under the water quality monitoring program, *in situ* hydrographic and water quality parameters, nutrient and biomass concentrations, and dissolved oxygen will be measured. Phytoplankton and zooplankton communities will also be described. The study objectives are described below.

- **Task 4 Data Quality Control and Data Set Submission:** Convert raw electronic data into useful data, load data generated by the project, including survey/sample collection data, into the database, and maintain data quality.
- **Task 5 Water Column Surveys:** Develop a three-dimensional picture of seasonal variability of water column properties in Massachusetts Bay; identify factors affecting the seasonal pattern of

plankton abundances and species composition and the seasonal decline of dissolved oxygen concentrations in Massachusetts Bay; describe the broad-scale interaction of water from Boston Harbor and the Gulf of Maine with Massachusetts Bay.

- **Task 6 Dissolved Oxygen (DO) Analysis:** Analyze water samples collected under Task 5 to determine DO concentrations. DO data will be used by MWRA to calibrate the high resolution, *in situ* DO data collected at all water column stations.
- **Task 7 Plankton Taxonomy:** Characterize the phytoplankton and zooplankton communities and describe changes in community structure.
- **Task 10 Synthesis Reports:** Report the results of the sampling and analytical tasks in survey reports, data reports, and synthesis reports.

A.7 QUALITY OBJECTIVES AND CRITERIA

A.7.1 DATA QUALITY OBJECTIVES

The data quality objectives for HOM9 are defined by the outfall discharge permit (EPA and MA DEP, 2000) and the Contingency Plan thresholds (MWRA, 2001). Threshold limits are described in a set of MWRA Standard Operating Procedures (SOPs; Appendix I). The method detection limits (MDLs) chosen are more than sufficient for distinguishing results from thresholds. Rather, the low MDLs are driven by the need to be sensitive enough to detect even subtle effects of the outfall. In addition, the general contract conditions further define the accuracy and sensitivity of geospatial (GPS) instrumentation to ensure that sampling locations are within $300\pm$ m of the defined station coordinates in order to enable intercomparison with previous sampling results and trends analysis.

A.7.2 MEASUREMENT QUALITY OBJECTIVES

Data will be examined in terms of precision, accuracy, completeness, comparability, and representativeness to ensure that all data generated during the conduct of surveys, analyses, and reporting are of the highest quality.

- **Precision** is the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.
- **Accuracy** is the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations.
- **Completeness** is the amount of data collected as compared to the amount needed to ensure that the uncertainty or error is within acceptable limits.
- **Comparability** is a measure of the confidence with which one data set can be compared to another.
- **Representativeness** is the degree to which data accurately and precisely represent a characteristic of a population.

The application of these data quality measures is described below.

A.7.3 NAVIGATIONAL AND HYDROGRAPHIC DATA

A.7.3.1 PRECISION AND ACCURACY

Manufacturer precision and accuracy objectives for navigation and hydrographic sampling are presented in Table A-1. Section B.5 provides details on sampling procedures established to ensure data quality.

Section B.6 and B.7 contain instrument calibration methods and specifications. Navigational accuracy of 10m is required for this program.

A.7.3.2 COMPLETENESS

Battelle's navigation software system outputs navigation positions at an interval of 1-second. The software system will display all position fixes and save these fixes in an electronic file during hydrocasts and sampling operations. The project time interval requirement for obtaining positions during sampling is one (1) minute. Thus, even if a few bad data streams from the dGPS navigation system to the computer are experienced, the software will provide enough position fixes within each 1-minute period for 100% data collection. During transit between stations, the software system will save vessel coordinates in an electronic file every five minutes.

Because hydrographic data are acquired electronically and monitored in real time, no loss of data is expected. With the sampling rates of the CTD (4 Hertz [Hz]) and navigation systems (1-second intervals), sufficient data will be acquired to locate the depth of the pycnocline. Stations will not be occupied if CTD measurements and navigation coordinates (at a minimum) cannot be obtained. If instrument malfunctions occur and operations are modified or suspended during any survey day, a decision on modification of activities for that survey will be made with consultation and agreement of MWRA, whenever possible. A 10% loss of hydrographic and navigation data over the entire program is not expected to compromise the objectives of the program.

Table A-1. Accuracy and Precision of Instrument Sensors

Sensor	Model	Units	Range	Accuracy	Precision
Pressure	Sea-Bird SBE-29	db	0 to 1000	0.1%	0.1
Temperature	Sea-Bird SBE-3	°C	-5 to +35	0.001	0.01
Conductivity	Sea-Bird SBE-4	mS/cm	0 to 70	0.03	0.01
Dissolved Oxygen	Sea-Bird SBE-43	mg/L	0 to 15	0.50	0.05
Fluorometer (Chl a)	WET Labs WETStar	µg/L	0.03 to 75	0.03	0.01
Transmissometer (20-cm)	WET Labs 25 cm C-star	m ⁻¹	0 to 40	0.20	0.01
<i>In situ</i> irradiance	Biospherical QSP-2200PD	µE m ⁻² s ⁻¹	0.14 to 5000	10	1
On-Deck irradiance	Biospherical QSR-240	µE m ⁻² s ⁻¹	0.14 to 5000	10	1
Altimeter	Data Sonic PSA-916	m	0-99.9	0.1	0.025
Echosounder (depth)	Furuno FCV-582	m	0 to 200	2	0.1
Navigation	Furuno GP33 Northstar 941XD	Degree	World	2 m	2 m

A.7.3.3 COMPARABILITY

All sampling positions will be comparable to positions obtained by previous MWRA monitoring activities as well as by other researchers that have used or are using differential GPS at these stations. The station locations are targets and sampling will be conducted within 300 m of the targets as visualized on the Battelle Ocean Sampling System (BOSS) navigation display.

The electronic measurement instruments that will be used during the water quality monitoring surveys are similar to the instruments that have been used by MWRA contractors since 1992 (Albro *et al.* 1993; Bowen *et al.* 1998; Albro *et al.* 1998; Libby *et al.* 2002, 2005, 2006, 2009, 2010, and 2011). Except for dissolved oxygen and chlorophyll fluorescence sensor values, the instrumentation data reduction methods are based on laboratory or vendor calibrations. To improve the representativeness of the electronic

dissolved oxygen and chlorophyll fluorescence values, the electronic data are post-calibrated by MWRA using the laboratory determined values for these parameters collected during each survey.

A.7.3.4 REPRESENTATIVENESS

The representativeness of the sampling program design is detailed in the Outfall Monitoring Plan (MWRA 1997) and defined by the results collected since 1992. Representativeness will also be ensured by proper handling, storage, and analysis of calibration samples so that the materials analyzed reflect the collected material. Deviations from the data collection procedures described in this QAPP will be documented in the survey logbook and described in the survey report.

A.7.4 WATER SAMPLING AND ANALYSIS

A.7.4.1 PRECISION AND ACCURACY

Precision and accuracy of water sampling procedures are quantified by the collection of field blanks and duplicates and are also ensured by the collection procedures. The sampling objective is to obtain uncontaminated samples representative of their location. Procedures will follow standard methods that can achieve this objective. Each sample will be clearly labeled with a unique sampling identifier (survey ID and sample number) that will allow the sample to be traced from collection through analysis to reporting. All samples will be handled and stored according to the appropriate protocols. Quality control (QC) procedures to assess precision and accuracy of laboratory data are detailed in Section B.5.

A.7.4.2 COMPLETENESS

The completeness criteria for sample collection are 100%: all water column stations must be sampled to be considered complete. At each station, discrete samples will be collected at five depths based on positions relative to a subsurface chlorophyll maximum usually associated with the presence of a pycnocline separating surface and bottom water layers. In the event of sample loss or equipment malfunction, the Chief Scientist will determine the need for appropriate corrective action (*e.g.*, resampling) and will record such action in the survey logbook. In all cases, the objectives of the project will not be compromised if representative surface and mid-depth ("chlorophyll maximum" if present) samples for nutrient and biological parameters, and measurements of bottom-water DO are successfully collected. The goal for water sample analysis is 100% completeness for zooplankton and phytoplankton. However, a 10% loss of sample data over the entire program is not expected to compromise the objectives of the program.

A.7.4.3 COMPARABILITY

Collection of samples for chlorophyll measurements coincidentally with *in situ* electronically captured data will allow for calibration of the electronic sensor data. Nutrient concentrations (dissolved and particulate) will be comparable to data from other recent surveys of the study area because standardized sampling procedures will be employed. This is also true for phaeophytin, phytoplankton and zooplankton. Concentration reporting units will follow standard convention for most oceanographic studies.

Comparability of the sampling and analysis procedures with previous studies will be achieved through adherence to procedures that are based on documented standard methods (*e.g.*, EPA or ASTM methods) or on methods previously described in the scientific literature or HOM program documents. Comparability throughout the project will be achieved through adherence to this QAPP.

A.7.4.4 REPRESENTATIVENESS

Water samples will be collected, handled, transported, and analyzed using procedures that will ensure the resulting data represent the sample material collected. Deviations from the sample collection procedures described in this QAPP will be documented in the survey logbook and described in the survey report.

A.8 SPECIAL TRAINING AND CERTIFICATION

It is Battelle policy that all management and technical personnel involved in conducting work must be qualified to perform their assigned activity and that training be documented. This objective is achieved by identifying personnel at all levels who have the education and/or experience needed to perform an assigned task, and by encouraging professional development through continual practical training and providing opportunities for professional growth. Battelle requirements for personnel qualifications and training are detailed in the Quality Management Plan (QMP), Battelle (2011). Specific requirements from this QMP which relate to HOM9 activities are summarized below.

A.8.1 TECHNICAL TRAINING

Technical training encompasses technical procedures and the associated QC requirements. All personnel that perform technical activities must be trained to perform their assigned activities prior to conducting those procedures independently. Where available, SOPs or manuals are used as the basis of technical training. Training for a technical activity is considered complete when a staff member can perform the technical operation independently and meet the criteria of the relevant SOP. All Battelle personnel conducting activities for HOM9 will have documented training in the appropriate SOPs. The training records for each staff member are maintained in Battelle training management database, Battelle University. The Battelle Project QA Officer is responsible for ensuring that the technical and management staff members are familiar with both the site and HOM9 specific procedures. All Battelle and subcontractor staff will receive training in QAPP requirements for documentation, version control, records management, and data review procedures.

A.8.2 SAFETY TRAINING

Basic safety training is provided to each employee during orientation sessions. Other specific safety training sessions are conducted with staff whose responsibilities expose him or her to potential risk or hazard (*e.g.*, boating safety). The Field Manager and the employee's resource manager are responsible for identifying the need for specific safety training. The resource managers are responsible for ensuring that safety training is conducted. Safety training is detailed in the Battelle Environmental, Safety, and Health Plan. A Job Hazard Analysis (JHA) has been prepared for the field program. It identifies potential hazards and mitigation and preventive actions to minimize injury. The JHA will be distributed to field staff at the beginning of the field season and used as part of the safety training for any personnel participating in the HOM9 field surveys.

A.8.3 RESPONSIBILITIES

The Project Manager is ultimately responsible for the overall quality of products produced and for ensuring that appropriately qualified personnel are assigned to the tasks.

The Quality Assurance Officer is responsible for ensuring that all staff are trained in Battelle quality systems and the requirements of the QMP and this QAPP. Each individual is responsible for ensuring that his/her training records are documented in Battelle University, any certificates are uploaded to the Battelle Field Team SharePoint site and for updating his/her curriculum vitae as needed. The ESH Officer is responsible for appropriate safety training.

A.9 DOCUMENTS AND RECORDS

A.9.1 DATA RECORDING

All data will be initially recorded either (1) electronically onto computer storage media from BOSS or other laboratory systems or (2) manually into bound logbooks or onto established data forms. All notes will be written in black ink. Corrections to hand-entered data will be initialed, dated, and justified. Corrections to electronically captured data (*e.g.*, electronic "spikes") will be documented on a hard-copy plot of the data. 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. It is the responsibility of the senior scientists or their delegates at Battelle, Pausacaco Plankton, UMD, and WHOI to ensure that all data entries and hand calculations are verified in accordance with procedures described in Sections D.1, D.2, and D.3 below. In addition to these documentation procedures, station logs associated with field and laboratory custody and tracking will be kept in the survey logbook for each survey. Survey logbooks will be stored at Battelle under the supervision of the Field Manager.

All field and laboratory data generated by Battelle must be reported to MWRA for incorporation into the EM&MS. Battelle data management staff will log in all data received for loading to maintain the data audit trail. These data are processed according to Section B.10 below. The ASCII data files are stored on the projects file server under the HOM9 project Task 4 deliverables. This server is backed up to tape nightly. All data submissions will include a data deliverable letter to MWRA sent via email and copied to the project archive mailbox (^BCO Dux HOM9; HOM9@battelle.org). Data submissions will be made through MWRA's Harbor and Outfall Monitoring Loading (HOML) application web site. Copies of the ASCII data files used for submission to the HOML web site are emailed to Battelle's Records Management Office.

A.9.2 DOCUMENTS

For each water column survey, one survey plan, one survey summary email, and one survey report will be prepared. A total of nine water column surveys will be conducted each year from 2014 to 2016. Details on the survey plans, email summaries and survey reports are provided below.

Collection data from water column surveys (Task 5), *in situ* data processing (Task 4), data loading and quality assurance (Task 4) and sample analysis (Tasks 6 and 7) are reported to MWRA in various forms as defined in the HOM9 contract. Task 5 collection data will be reported in survey reports while Tasks 6 (Dissolved Oxygen) and 7 (Plankton Taxonomy) will be reported in data sets used to generate data reports. Task 6 data will be used in Nutrient data reports and Task 7 data will be used in Plankton Data Reports (Section A.9.3). Data synthesis reports (Task 10) are described in Section A.9.4. Survey-related deliverables that will be generated under this QAPP include:

Task 5

- 27 Survey Plans (one for each of the water column surveys)
- 27 Email Survey Summaries (including the rapid phytoplankton and *Alexandrium* results)
- 27 Survey Reports (one for each of the water column surveys)
- Report any notable whale or floatables observations in the survey summary (Task 5.7) and survey report (Task 5.8).

Task 6

- 9 Hydrographic and Nutrient Data Report Review letters (three per year)

Task 7

- 9 Phytoplankton Data and Zooplankton Data report Review letters (three per year)

Draft and final reports will be submitted electronically as pdf and/or MS Word files. Cover letters will be submitted as a separate file. The final pdf documents should contain all text, tables, and figures suitable for loading onto the Internet. Documents greater than 3 megabytes should be submitted via the Battelle file exchange. All survey plans and reports will be submitted annually on CD after final acceptance by MWRA.

A.9.2.1 QUALITY ASSURANCE PROJECT PLAN

This QAPP describes the sampling and analysis activities of MWRA's water column monitoring program to be conducted under MWRA Contract OP216A in 2014, 2015, and 2016 with data analysis and interpretation continuing through 2017. This document is designed following EPA/QA R-5 and is based largely on water quality QAPPs of the MWRA monitoring program described in Libby *et al.* (2002, 2005, 2006, 2009, 2010, and 2011). The QAPP will be reviewed and revised annually by Battelle if directed to do so by MWRA based on significant changes to the procedures and requirements defined in this document. A history of QAPP modifications will be documented in the Revision History form located at the front of the document.

A.9.2.2 SURVEY PLANS

Survey plans will be prepared for each survey conducted. Each survey plan will follow Battelle SOP 6-043 *Preparation, Distribution, and Implementations of Field Survey Plans*¹ that is based on the guidelines established by EPA for use of their vessels. Each survey plan will be submitted electronically as a pdf file at least one week prior to the start of the survey and will include the following information:

- Purpose, background, and data use for survey
- Schedule of operations
- Specific location and coordinates of each station
- Survey/sampling methods
- Sample Handling and Custody
- Sequence of Tasks and Events
- Navigation and positioning control
- Vessel, equipment, and supplies
- QA/QC Procedures
- Documentation procedures
- Scientific party
- Reporting requirements
- Safety Procedures
- Documentation of any deviations from this QAPP

¹ Battelle SOPs are listed in Appendix II and were provided to MWRA electronic with the draft QAPP.

A.9.2.3 SURVEY EMAIL SUMMARY

A survey summary will be delivered to MWRA via email within 1 week of completion of each water column survey. This email will include a summary of the survey operational dates, weather conditions, stations not sampled and reason, summary of preliminary water quality observations, deviations from survey scope, results of the rapid phytoplankton and *Alexandrium* analyses (if available), observations from marine mammal sightings, notable anthropogenic debris seen, and identify technical problems encountered and resolutions. These summaries will also include satellite images of chlorophyll distribution from the day of the survey (if available) to make a comparison to the *in situ* observations. This summary will also highlight any potential exceedance of monitoring thresholds, or conditions, which if continued, might lead to exceedances.

A.9.2.4 SURVEY REPORTS

Survey reports will describe how the survey was conducted, stations occupied, measurements made, samples collected, problems experienced, and general observations from *in situ* sensor data, observations of visible anthropogenic debris, and summarize observations made by the certified whale observer. Unusual observations of environmental conditions, especially those with implications for the later testing of Contingency Plan thresholds, will be emphasized. Survey reports are expected to be 4-5 pages of text with accompanying station maps and survey tracklines, a complete sample collection table, a station data table, a floatables table, and a preliminary data summary table. The sample collection table will be a tabular summary of stations occupied, station locations, and samples collected versus planned. The station data table will be generated by MWRA data management staff and will include data on each station and depth sampled including arrival time, coordinates, depth, sample ID, and others. Any deviations from this QAPP, not known at the time of survey plan preparation, will also be incorporated into the survey reports. The survey report will be submitted to MWRA electronically as a pdf file no later than three weeks after the completion of each survey. MWRA's comments on the report will be due to Battelle two weeks after receipt of the report. The final electronic survey report in pdf format, addressing MWRA's comments, will be due to MWRA two weeks after receipt of the comments. If MWRA does not submit comments within the two-week period, the survey report will be considered final.

A.9.3 DATA REPORT REVIEW AND COMMENT

Three Hydrography/Nutrient and three Plankton data reports will be generated by MWRA for each monitoring year (2014-2016). The data reports are created directly from the EM&MS database. Battelle will perform a technical review and comment on the each of the data reports prepared by MWRA.

A.9.4 SYNTHESIS REPORTS (TASK 10)

The data delivered above will be used in the Water Column Summary Report prepared under Task 10. MWRA comments on the report will be provided to Battelle within 4 weeks of report receipt. The final report, addressing MWRA comments, will be due to MWRA within two weeks of comment receipt. Schedules for all activities, including this report, are provided in Table A-2.

A.9.4.1 WATER COLUMN SUMMARY REPORT (TASK 10.1)

All data for the annual Water Column Summary Report will come from the EM&MS database. Authors will request data extracts. The annual Water Column Summary Reports will provide a rapid synthesis of results from water column monitoring activities conducted under Tasks 5-7 during each monitoring year (2014-2016). The report will describe the status of the ecosystem, including spatial and temporal patterns within Massachusetts and Cape Cod Bays (e.g. the distribution of the MWRA effluent plume as described by NH₄ concentrations). It will have abbreviated introduction and method sections and primarily focus on

presenting the most noteworthy observations made during the year. The summary report will draw heavily upon the presentations at the Annual Technical Meeting (Task 9) and include both the presentations and the submitted abstracts as appendices.

A.9.4.2 OUTFALL MONITORING OVERVIEW (TASK 10.2)

This report will summarize key findings of the previous year’s monitoring findings and related findings about Massachusetts and Cape Cod Bays including any special studies and threshold violations. The overview will include data from other facets of the HOM9 program that are monitored under Contract II. The report will be written toward the general public, regulators, and interested scientists.

Table A-2. Schedule of Data Reports, Data Exports, and Synthesis Reports

Deliverable	Survey Period	Due Date
Task 4 Data Sets		
Water Column Data Sets	Each survey	1 week after survey
Hydrographic Data Sets (including laboratory DO concentrations)	Each survey	2 weeks after survey
Plankton Data Sets	Each survey	60 days after survey
Review Comments for Data Reports – Hydrographic/Nutrient	February – April	August 15
	May – August	December 15
	September – October	February 15 of following year
Review Comments for Data Reports – Plankton	February – April	August 15
	May – August	December 15
	September – October	March 15 of following year
Year’s electronic word processing files for the survey plans and final survey reports, including all graphics and tables	February – October	One month after field year
Task 5 Water Column Survey		
Survey Plans	Each survey	1 week prior to survey
Survey Email Summaries	Each survey	7 days after survey
Survey Reports – Draft	Each survey	3 weeks after survey
Survey Reports – Final	Each survey	14 days after receipt of comments
Task 10 Synthesis Reports		
Water Column Summary – Draft	February – October	April 2015, 2016, 2017
Water Column Summary – Final		May 2015, 2016, 2017
Outfall Monitoring Overview – Outline	February – October	May 2015, 2016, 2017
Outfall Monitoring Overview–Draft		August 2015, 2016, 2017
Outfall Monitoring Overview– Final		September 2015, 2016, 2017

B DATA GENERATION AND ACQUISITION

B.1 SAMPLING PROCESS DESIGN

B.1.1 WATER COLUMN SURVEYS (TASK 5)

Water column sampling will be conducted 9 times per year in 2014, 2015, and 2016 (Table B-1). Figure A-2 shows the location of the water column stations. Sampling under this contract will be conducted at the 11 stations in Massachusetts Bay. The stations include five nearfield stations and six farfield stations as designated based on distance from the bay outfall. Three additional stations are noted on Figure A-2 in Cape Cod Bay and Stellwagen National Marine Sanctuary that will be sampled concurrently by a different contractor (PCCS).

Table B-1. HOM9 Water Column Survey and Survey Related Deliverables Schedule

Survey ID	Target Date	Survey Plan	Survey Summary	Survey Report
WN141	2/4/2014	1/28/2014	2/11/2014	2/25/2014
WN142	3/18/2014	3/11/2014	3/25/2014	4/8/2014
WN143	4/8/2014	4/1/2014	4/15/2014	4/29/2014
WN144	5/13/2014	5/6/2014	5/20/2014	6/3/2014
WN145	6/17/2014	6/10/2014	6/24/2014	7/8/2014
WN146	7/22/2014	7/15/2014	7/29/2014	8/12/2014
WN147	8/19/2014	8/12/2014	8/26/2014	9/9/2014
WN148	9/2/2014	8/26/2014	9/9/2014	9/23/2014
WN149	10/21/2014	10/14/2014	10/28/2014	11/11/2014
WN151	2/3/2015	1/27/2015	2/10/2015	2/24/2015
WN152	3/17/2015	3/10/2015	3/24/2015	4/7/2015
WN153	4/7/2015	3/31/2015	4/14/2015	4/28/2015
WN154	5/12/2015	5/5/2015	5/19/2015	6/2/2015
WN155	6/16/2015	6/9/2015	6/23/2015	7/7/2015
WN156	7/21/2015	7/14/2015	7/28/2015	8/11/2015
WN157	8/18/2015	8/11/2015	8/25/2015	9/8/2015
WN158	9/1/2015	8/25/2015	9/8/2015	9/22/2015
WN159	10/20/2015	10/13/2015	10/27/2015	11/10/2015
WN161	2/9/2016	2/2/2016	2/16/2016	3/1/2016
WN162	3/22/2016	3/15/2016	3/29/2016	4/12/2016
WN163	4/12/2016	4/5/2016	4/19/2016	5/3/2016
WN164	5/17/2016	5/10/2016	5/24/2016	6/7/2016
WN165	6/21/2016	6/14/2016	6/28/2016	7/12/2016
WN166	7/26/2016	7/19/2016	8/2/2016	8/16/2016
WN167	8/23/2016	8/16/2016	8/30/2016	9/13/2016
WN168	9/6/2016	8/30/2016	9/13/2016	9/27/2016
WN169	10/25/2016	10/18/2016	11/1/2016	11/15/2016

*Note that survey WN1X8 must be conducted in September to meet threshold testing requirements.

B.1.2 SAMPLING LOCATIONS AND FREQUENCY

Table B-2 identifies the location, depth and station type for each of the water column monitoring stations. The five nearfield stations are located within five kilometers of the outfall. All three station types (B, M and O) are sampled in the nearfield. Table B-3 shows sub-sampling by station type and sample depth. The only differences in sample collection between stations is that no plankton samples will be collected at station N21, oxygen calibration samples will be collected from stations N04 and N18, and an additional sample for rapid phytoplankton analysis will be collected at station N18. The six farfield stations are located beyond the nearfield to (1) cover regional-scale oceanographic processes in Massachusetts Bay; (2) broadly characterize reference areas; and (3) to verify that impacts by the outfall plume are not found beyond the nearfield. Each water column survey will be conducted in a single day. Battelle will be in close communication with scientists at PCCS to coordinate sampling in Massachusetts and Cape Cod Bays. The water column surveys are scheduled to be conducted on a monthly basis (February through October) with target dates provided in Table B-1. Note that the early September surveys (WN148, WN158, and WN168) must fall in September so that they are within the autumn season as defined for seasonal threshold calculations (September-December).

Table B-2. Water Column Sampling Stations

Station	Station Type	Latitude	Longitude
F06	M	42.17067	-70.57667
F10	M	42.24233	-70.63733
F13	M	42.26833	-70.73500
F15	M	42.31550	-70.72767
F22	O	42.47983	-70.61767
F23	O	42.33917	-70.94200
N01	M	42.41933	-70.86450
N04	O	42.44383	-70.73650
N07	M	42.35633	-70.70617
N18	O	42.36583	-70.77767
N21	B	42.38783	-70.78533

B.1.3 HYDROCASTS AND SENSOR MEASUREMENTS

Hydrographic data will be collected at all water column stations. At each station, a hydrocast will be conducted with an underwater unit consisting of a conductivity–temperature–depth (CTD) system, various sensors (dissolved oxygen, chlorophyll fluorescence, optical beam transmittance, light irradiance (PAR), and altimeter), and a water-sampling system equipped with up to twelve 9-L Rosette sampling bottles.

Sensor measurements will be collected during the downcast from near surface (approximately 1-2 meters) to within approximately 3-5 m of the sea floor at each station. Salinity and density (as sigma-t) will be calculated in real time from the conductivity, temperature and depth data. Total incident photosynthetically active radiation at the sea surface (PAR), navigational position, and time will be recorded concurrently with the hydrocast measurements.

Table B-3. Subsamples by Station Type Code and Sample Depth Class

Station Type		B	M	O	Total
Number of Stations		1	6	4	11
Analysis Type (number of depths collected)	Sample Depth Codes	Number Depths Collected			Number Samples Collected
Dissolved inorganic nutrients (NH ₄ , NO ₃ , NO ₂ , PO ₄ , and SiO ₄)	ABCDE	5	5	5	55
Other nutrients (TDN, TDP, PC, PN, PP)	ABCDE	5	5	5	55
Chlorophyll	ACE	3	3	3	33
Zooplankton			1	1	10
Whole water phytoplankton	AC		2	2	20
<i>Alexandrium</i>	AC		2	2	20
Rapid analysis phytoplankton*	C			1	1
Dissolved oxygen	ACE			3	9

*Rapid sample collected at station N18 only.

B.1.4 WATER COLLECTION AND ZOOPLANKTON NET TOWS

Discrete water samples will be collected during the upcast of the Rosette system at each station at five depths: bottom, 3 intermediate depths, and at the surface. The intermediate depths are not fixed or evenly spaced but instead will be adjusted to capture important features revealed by the downcast profiles, such as the subsurface chlorophyll maximum (SCM) if it is present. The depth of the SCM receives special attention and will be sampled for phytoplankton, *Alexandrium*, dissolved oxygen, and chlorophyll. The other two intermediate depths will straddle the SCM when it is near mid-depth in the water column; they will both be deeper than a shallow SCM, and they will both be shallower than a deep SCM. The flexible sampling for the SCM is achieved by simply changing the sequence of triggering of the pre-labeled color-coded Niskin bottles in the rosette. From 2004-2010, the SCM was located at the middle intermediate depth 63% of the time, the shallowest intermediate depth 32% of the time, and at the deepest intermediate depth only 6% of the time. To simplify planning (Table B-3), labeling of sample bottles, and discussion of approach, we have assigned the SCM to mid-depth. Therefore, the other intermediate-depths are called mid-surface and mid-bottom in this QAPP for convenience.

On deck, water from the Rosette bottles will be subsampled for analysis of dissolved inorganic nutrients and other analytes as determined by the station type (Table B-3). Phytoplankton and *Alexandrium* samples will be collected and vertical net tows to collect zooplankton will be conducted at all stations except station N21 (Table B-3). A detailed listing of samples collected at each station during the water column surveys is provided in Appendix III.

B.1.5 WHALE AND FLOATABLES OBSERVATIONS

During each water column survey, a dedicated trained whale observer will conduct sighting watches while on station and during transit between stations. The sighting operations will occur during daylight hours. All sightings will be recorded on standardized marine mammal field sighting logs (see Section B.2.7).

The whale observer and Battelle team field personnel will also observe the sea surface in the vicinity of the boat and note the presence of anthropogenic debris/floatables at each station and while underway. Particular attention will be paid while in the vicinity of stations N01, N18, and N21. Any notable observations will be documented in the survey summary and report. The whale and floatables observations will also be compiled in an electronic spreadsheet for submittal to MWRA along with water column survey dataset under Task 4. The spreadsheet is a simple table listing survey, date, time, location, and information on what was observed (with respect to vicinity of stations N01, N18, and N21).

B.1.6 SHIPBOARD PROCESSING OF DISCRETE WATER SAMPLES

Sample aliquots are removed from the Rosette sampling bottles and are processed aboard ship according to Battelle SOP No. 5-266, *Nutrient Sample Processing* in preparation for shipment to the analytical laboratories. The water sample filtration scheme is detailed and graphically shown in Section B.2.5.

B.1.7 LABORATORY PROGRAM

Water samples collected during the surveys will be analyzed by MWRA DLS to determine concentrations of dissolved inorganic nutrients (DIN; nitrate, nitrite, ammonium, phosphate, and silicate); dissolved and particulate organic nutrients (carbon, nitrogen, and phosphorus); chlorophyll a and phaeophytin. Battelle will analyze samples for DO concentrations. Scientists from Pausacaco Plankton and UMD will analyze phytoplankton and zooplankton community structure, respectively. *Alexandrium* counts will be conducted by scientists at WHOI. The sample analyses are summarized in Table B-4. Sampling and analytical methods are described in Sections B.2 and B.4, respectively.

Table B-4. Water Column Sample Analyses

Parameter	Lab	Units	Instrument	Reference
Laboratory Measurements				
Dissolved oxygen	Battelle	mg/L	Radiometer TitraLab	Battelle SOP 5-317 and Oudot <i>et al.</i> (1988)
Whole-water phytoplankton	PP ¹	E6Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Borkman (1994), Borkman <i>et al.</i> (1993), Turner <i>et al.</i> (1995)
<i>Alexandrium fundyense</i>	WHOI	Cells/L	Zeiss epifluorescence microscope with filter sets complementary to the probe/fluorochrome combination used.	Anderson <i>et al.</i> (2005)
Rapid phytoplankton	PP	Cells/L (approx.)	Olympus BH-2 compound microscope with phase-contrast optics	Turner <i>et al.</i> (1995)
Zooplankton	UMD	Indiv./m ³	Wild M-5 dissecting microscope	Libby <i>et al.</i> (2002)
In situ Measurements				
Conductivity	Battelle	mS/cm	Sea-Bird SBE-4	SBE-25 CTD Manual/ Battelle SOP 3-183
Temperature	Battelle	C	Sea-Bird SBE-3	SBE-25 CTD Manual/ Battelle SOP 3-183
Pressure	Battelle	db	Sea-Bird SBE-29	SBE-25 CTD Manual/ Battelle SOP 3-183
Dissolved oxygen	Battelle	mg/L	Sea-Bird SBE 43	Weiss (1970)/Battelle SOP 3-180
Chlorophyll fluorescence	Battelle	µg/L	WET Labs WETStar	WET Labs WETStar Manual/Battelle SOP 3-163
Transmissometry	Battelle	m ⁻¹	WET Labs C-Star	WET Labs C-Star Manual/Battelle SOP 3-174
<i>In situ</i> irradiance	Battelle	µEm ² sec ⁻¹	Biospherical QSP-2200PD	Biospherical Manual/ Battelle SOP 3-127
Surface irradiance	Battelle	µEm ² sec ⁻¹	Biospherical QSR-240	Biospherical Manual/ Battelle SOP 3-127
Altimeter	Battelle	m	Data Sonic PSA-916	Data Sonic Manual
Bottom depth	Battelle	m	Furuno FCV-582	Furuno Manual/Battelle SOP 3-129
Navigational position	Battelle	Degree	Furuno GP33 Northstar 941XD	Northstar or Furuno Manual/Battelle SOP 3-118
Sigma-t (calculated)	Battelle	unitless	Calculated based upon conductivity, temperature and pressure	SBE-25 CTD Manual/ Battelle SOP 3-183
Salinity (calculated)	Battelle	PSU	Calculated based upon conductivity, temperature and pressure	SBE-25 CTD Manual/ Battelle SOP 3-183

¹PP = Pausacaco Plankton

B.1.8 MONITORING PARAMETERS AND COLLECTION FREQUENCY

Table B-4 lists analytical parameters and *in situ* hydrographic measurements generated by Battelle and Table B-3 presents the collection frequency of each. Sample collection plans for the water column surveys are presented in Appendix III.

B.1.9 SCHEDULE OF ACTIVITIES AND DELIVERABLES

Table A-2 lists the schedule for delivery of all data reports, data exports, and synthesis reports. Table B-1 provides the planned schedule for all routine water column surveys and associated survey deliverables

B.2 SAMPLING METHODS

Methods for collection and analysis of samples are described in the following sections. Analyses will be performed by Battelle, DLS, Pausacaco Plankton, UMD, and WHOI as defined below.

B.2.1 NAVIGATION

Vessel positioning during sampling operations will be accomplished with Battelle's BOSS navigation system. This system consists of either a Northstar (portable) or Furuno (mounted) dGPS interfaced to the BOSS computer. The Northstar dGPS receiver has six dedicated channels and is capable of locking onto six different satellites at one time, while the Furuno dGPS is capable of locking onto up to 12 satellites. To correct the GPS calculations, the Northstar and Furuno dGPS will receive correction data from one of three United States Coast Guard dGPS broadcast sites: Montauk Point, NY, Chatham, MA, or Portsmouth Harbor, NH (Figure B-1). This capability ensures strong signal reception, and accurate and reliable positioning with 2-second updates.

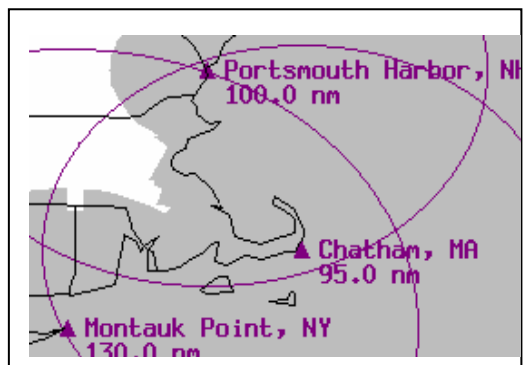


Figure B-1. dGPS Master Stations Coverage

B.2.2 VESSEL HANDLING

Boston Harbor and Massachusetts Bay are heavily trafficked by commercial, fishing, and recreational vessels. Endangered whales, as well as numerous other marine mammals seasonally frequent the Bay. The licensed boat captain will operate the vessel in a professional manner at all times during surveys to ensure the safety of passengers and crew and to minimize the possibility of collisions with other traffic or with marine mammals. Before departure the chief scientist will obtain a Right Whale Update (either by signing up at <http://www.nero.noaa.gov/shipstrike/> or by sending a blank email to ne.rw.sightings@noaa.gov). NOAA will reply automatically with an email that says whether and where speed zones are in effect. For vessels shorter than 65 ft, such as the 60-ft RV Tioga, the speed restrictions are voluntary, but the email alert serves to heighten crew awareness. As required of all vessels by NMFS's rules (50 CFR 224.103 (c), and <http://www.nero.noaa.gov/Protected/mmp/viewing/regs/>), the vessel will maintain a minimum distance of 500 yards from right whales. If a right whale is within 500 yards of a sampling station, the vessel will wait at least 30 minutes for the right whale to move out of range or the station will be sampled as close to nominal as possible while maintaining the minimum required distance from the right whale(s). Sightings are reported to NOAA in Section B.2.7 below.

At each sampling station, the vessel will be positioned upwind/upcurrent of the target station position with distance dependent upon wind/current strength and expected drift. The objective is to sample as close to the nominal station coordinates as possible, but at no more than 300m off the station. The vessel

heading will be selected such that the underwater unit will be deployed on the side of the boat facing the sun and relative to the prevailing seas. The vessel will maintain this position during the cast. If a vessel positioning or safety issue causes shading of the CTD, the shading incident will be noted in the station log and shading will be qualified during post-processing.

B.2.3 HYDROGRAPHIC PROFILES

The hydrographic profile sampling equipment and data acquisition equipment consists of the following apparatus and instruments. Hydrographic Profile data are collected according to Battelle SOP No. 5-275 *At Sea Collection of Hydrographic Data using CTD and Rosette System*.

- 5- and 9-L Rosette sampling bottles (*e.g.*, Go-Flo or Niskin)
- Sea-Bird 32 Carousel Water Sampling System or General Oceanics model 1015 Rosette system
- Sea-Bird SBE-25 CTD system (one additional SBE-25 serves as backup) mounted on the Rosette and equipped with the following:
 - Sea-Bird SBE-43 DO sensor (intake at same depth as the pressure sensor) produces an oxygen-dependent electrical current and incorporates a thermistor for determining membrane temperature (three additional SBE-43 serve as backups).
 - WET Labs C-Star 25 cm-pathlength transmissometer that provides *in situ* measurements of optical beam transmission (related to the concentration of suspended matter in the water over the sensor's 25-cm pathlength; the sensor is located mid-Niskin bottle about 20 cm above the pressure sensor).
 - WET Labs WETStar chlorophyll fluorometer (intake at same depth as the pressure sensor)
 - Biospherical QSP-2200PD spherical quantum scalar irradiance sensor that measures underwater photosynthetically active radiation (PAR) – mounted 1 m above the pressure sensor². (The HOM6 QAPP incorrectly identified the mount height as 90 cm above the pressure sensor).
- Data Sonic PSA 916 altimeter provides a measurement of underwater unit height from the bottom – mounted level with the pressure sensor
- Biospherical QSR-240 reference hemispherical quantum scalar irradiance sensor that measures on-deck radiation conditions (*e.g.*, due to atmospheric conditions)
- Furuno FCV-582 video echosounder with color display and NMEA-0183 output to provide bathymetric measurements during vertical and horizontal profiling operations
- Computer with custom data-acquisition software (NavSam[®])
- Color printer
- Navigation:
 - Furuno GP33 dGPS system aboard the R/V *Tioga*
 - Northstar 941-XD dGPS system portable system

Battelle's software, NavSam[®] acquires data from all profile electronic-sampling-systems and navigation systems at the rate of four times per second. Once per second the software displays all of the information on a color monitor. The screen is split to show sensor data on the left and navigation data on the right (Figure B-2). Once the data are acquired, they are automatically written to a data file and logged

² Location of light sensor relative to the pressure sensor (located at the bottom of the CTD) for depth offset of *in situ* irradiance (see Section B.10.1.1).

concurrently with position data and date and time from the navigation system. The navigation portion of the display will show the position of the vessel compared to the coastlines digitized from standard NOAA charts, navigation aids, preset sampling locations, and vessel track. Set up of NavSam[®] for survey operations is described in SOP 6-029 *Survey Set-up and Sample Tracking Using NavSam[®] Software*. During hydrocast operations, position fixes will be electronically recorded at 1-second intervals. During transit between stations, position fixes and deck irradiance (upon request) will be electronically recorded at 4 Hz. Additionally, between stations, position fixes will be stored at five minute intervals. Continuous irradiance measurements will be conducted from one-half hour before sunrise to one-half hour after sunset. Weather and waves permitting, the vessel will be oriented to avoid shading of the light sensors.

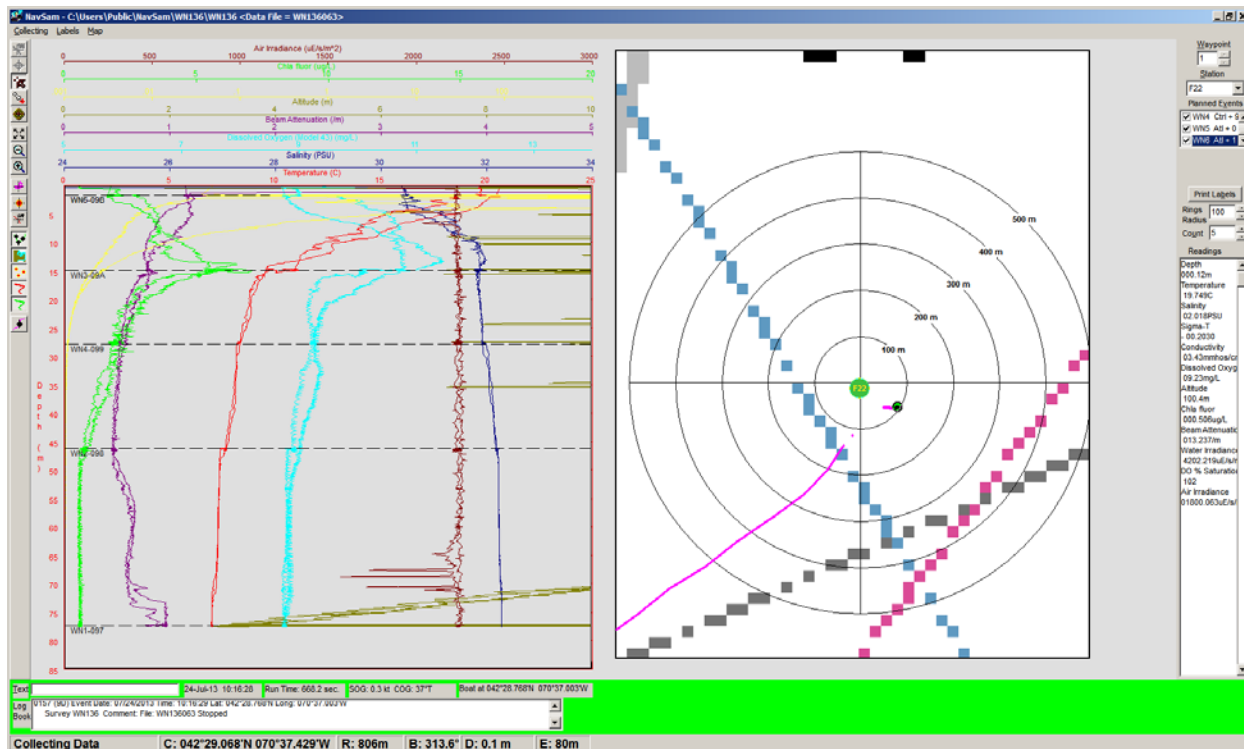


Figure B-2. Sample NavSam[®] Data Acquisition Screen

B.2.4 WATER SAMPLING

B.2.4.1 ROUTINE WATER COLUMN SURVEYS (TASK 5)

Water samples for dissolved inorganic nutrients, dissolved organic nutrients, particulate nutrients, chlorophyll *a*, DO and phytoplankton will be obtained with an underwater Rosette unit equipped with sampling bottles (GO-FLO, Niskin or comparable brand – referred to as Rosette sampling bottles in this document). The Rosette system is combined with the hydrographic profiling system. The following water sampling/hydrographic profiling procedures will be followed:

1. Before the start of each cast, each of the Rosette sampling bottles will be opened and attached to the Rosette triggering system.
2. After the vessel is positioned, NavSam[®] will be set to the hydrographic profiling mode and a data cast file will be opened. NavSam[®] will acquire data from the equipment while the underwater unit is on-deck prior to deployment. The operator will review the sensor data to verify that all sensors have reasonable in-air readings (*i.e.*, comparison of *in situ* vs. surface irradiance, beam attenuation less than 0.5/m). During the first deployment of the day, the pressure sensor will be used to adjust the depth offset based on atmospheric pressure.
3. After a successful on-deck check out, the underwater unit will be lowered into the water to a depth of approximately 5 meters and held in this position.
4. The Rosette will be held at this depth for at least one minute while sensors equilibrate (*e.g.*, stable salinity, dissolved oxygen, and temperature readings) and the pump evacuates air from the plumbing, the rosette will be returned to the surface (remaining submerged), and it will then be lowered (downcast) at a descent rate of about 0.5 m/s to within 3-5 m of the sea floor.
5. During the downcast, NavSam[®] will record the hydrographic data and display these data on a computer screen. The Chief Scientist will monitor the downcast data to ensure data are within expected ranges and profiles are typical of the conditions expected during a survey. Once the profile is taken, the Chief Scientist will review the real-time display of data to determine the five water-sampling depths for the upcast. These are based on defined locations relative to a subsurface chlorophyll maximum detected by *in situ* fluorometer. The 5 sampling depths are designated surface (A), mid-surface (B), mid-depth (C), mid-bottom (D), bottom (E) as listed in Appendix III Table III-1, although actual sampling depths would not necessarily be evenly spaced. At all stations, the C-depth sample will represent the chlorophyll maximum. Depending on the depth of chlorophyll maximum, the mid-surface and mid-depth or mid-bottom and mid-depth levels can be exchanged. In these cases the C-depth can be switched to a shallower (B-depth) or deeper (D-depth) to represent the subsurface chlorophyll maximum, as deemed appropriate by the Chief Scientist. For example, scenario 4 of Figure B-3 shows an intense and shallow chlorophyll maximum. In this case, the sampling protocol for the mid-depth and mid-surface would be exchanged so that the chlorophyll maximum would receive the full suite of analyses usually allocated to the water column mid-depth. If the chlorophyll maximum is at the surface, the C depth code is assigned to a subsurface maximum. Scenario 7 of Figure B-3 shows an intense and deep chlorophyll maximum, thus the protocols for mid-depth and mid-bottom would be exchanged. In scenarios 9 and 11, the switch of C and B depths is driven by the importance of sampling at the pycnocline as fluorescence was consistent over these depths.
6. During the upcast, the unit will be maintained at each of the selected five depths until the sensor readings stabilize (*i.e.*, little fluctuation in the instrument readings), typically this is 20-30 seconds (may be longer in summer under strongly stratified conditions). Water will be collected by closing one or more Rosette sampling bottles, depending on the water volume needed for analysis. When the Rosette deck unit indicates that the bottles are closed, this event will be flagged electronically in the NavSam[®] data file. This marks the vessel position and the concurrent *in situ* water column parameters (salinity, temperature, turbidity, DO, chlorophyll *a*,

irradiance, and depth) and links them to water collected in a particular set of Rosette sampling bottles. The NavSam[®] software will also generate unique color-coded, bar-coded sample-bottle labels for attachment to sample bottles and survey logs. Those bottles to be analyzed by DLS will be labeled with the DLS Bottle IDs provided by DLS as Sample Numbers that are entered into NavSam[®] prior to the survey according to Battelle MWRA SOP 008, *Integrating MWRA Client ID Numbers into the NavSam[®] Survey Database*. Onboard processing is described in Section B.2.5.

7. After collecting the surface water sample, the operator will close the data cast file, the rosette will be brought on board, and the Niskin bottles will be subsampled for processing.
8. NavSam[®] will be put into navigation mode with a file created for transit to the next station.

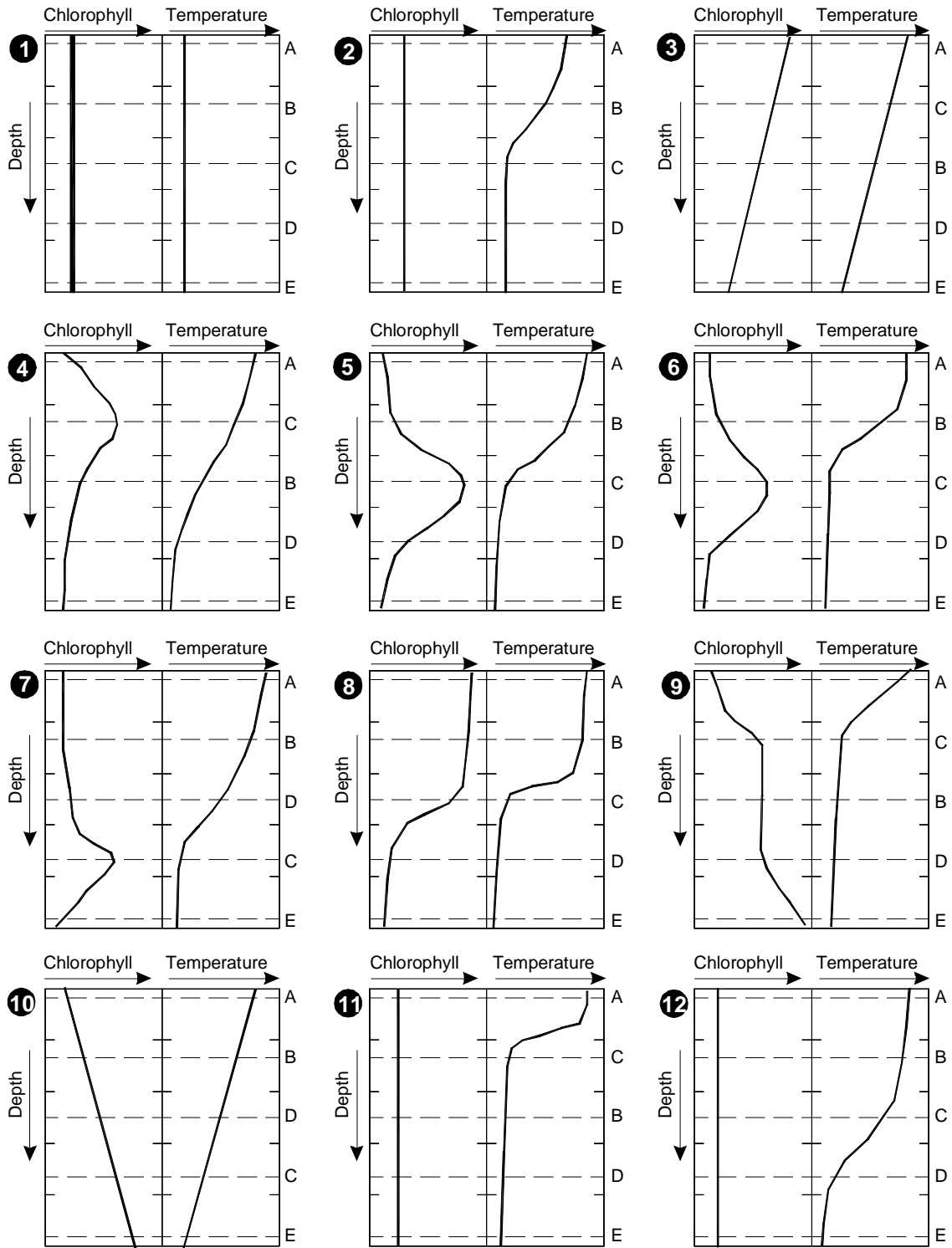


Figure B-3. Twelve Scenarios for Selecting Sample Depths

B.2.5 ONBOARD SAMPLE PROCESSING

Depending on the subsampling requirements at each station, some or the entire following onboard sample processing procedures will be conducted. Appendix III tables lay out the required subsampling required for the Task 5 water column surveys.

Water from the Rosette sampling bottles is transferred to 1-L opaque polyethylene jars for onboard processing (filtration) of nutrients and chlorophyll. These transfer jars will be rinsed three times with Rosette sampling bottle water before filling with water up to the neck of the jar. All filtration units (syringe and vacuum apparatus) will be rinsed with 10% HCl at the beginning of the survey day and with deionized water between sampling stations. The filtrate sample bottles will be rinsed three times with filtrate prior to filling. Figure B-4 summarizes the onboard processing of the dissolved and particulate nutrient subsamples from the 1-L opaque polyethylene jars. The figure summarizes Battelle SOP No. 5-266, *Nutrient Sample Processing*. Sample volumes, containers, and storage conditions are listed in Table B-5.

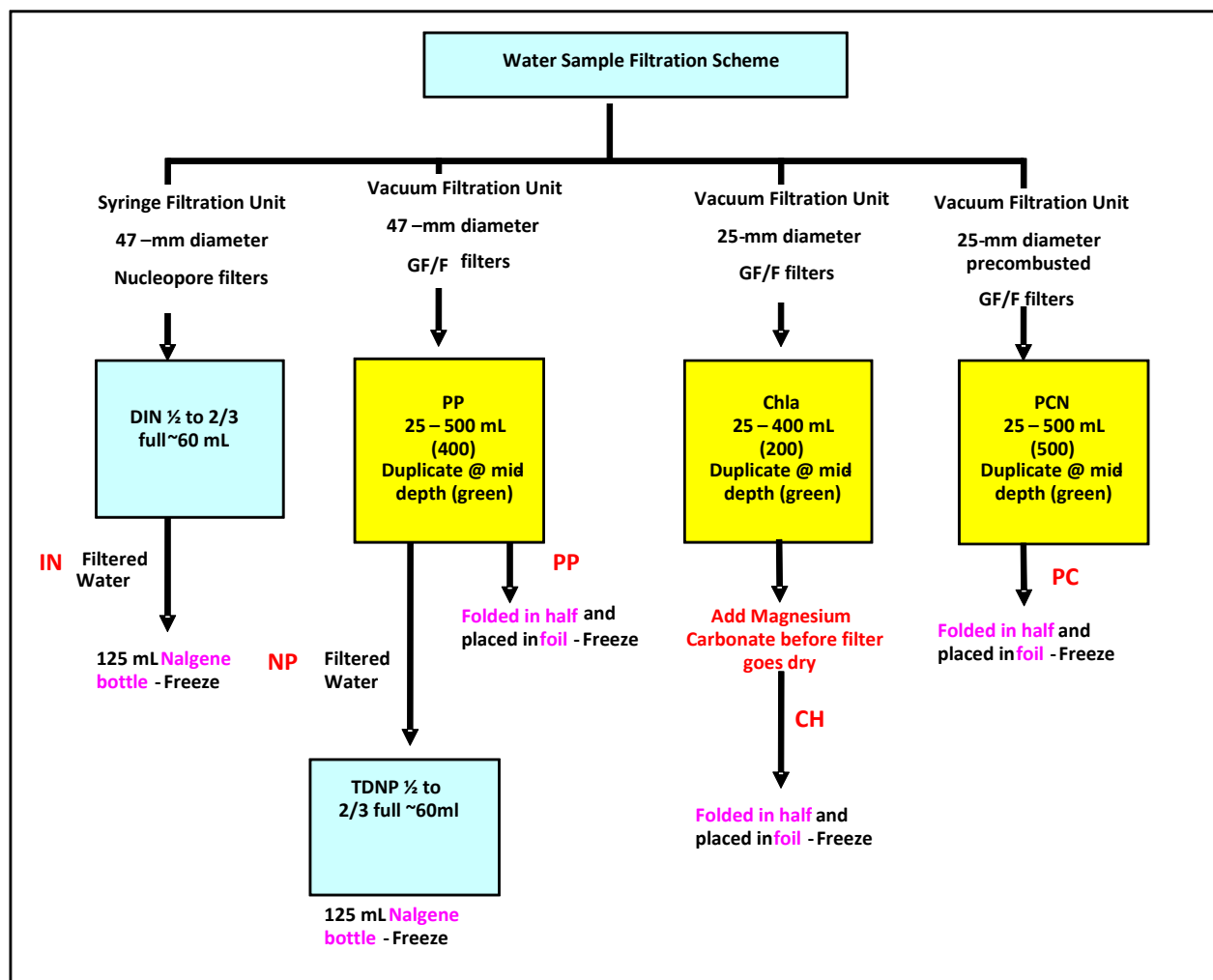


Figure B-4. Onboard Processing Flow Chart

Table B-5. Sample Volumes, Containers, and Processing for Field Samples

Parameter	Station Types	Sample Volume (Target) (mL)	Sample Containers ^b	Shipboard Processing/ Preservation ^b	Maximum Holding Time to Analysis
Hydrographic Profiles ^a	All	NA	NA	Record data to CD.	NA
Subsamples from PVC Rosette Bottles					
Dissolved inorganic nutrients	All	60	125-mL polyethylene bottle	Pass through a Nucleopore membrane filter. Freeze until analysis.	28 days
Total dissolved phosphorus and nitrogen	All	60	125-mL polyethylene bottle	Pass sample through a GF/F. Freeze filtrate until analysis.	28 days
Particulate organic carbon and nitrogen	All	25-500 (500)	Whatman GF/F in foil	Pass through a GF/F. Freeze filter until analysis.	28 days
Particulate phosphorus	All	25 – 500 (400)	Whatman GF/F in foil	Pass sample through a GF/F. Freeze filter until analysis.	28 days
Chlorophyll <i>a</i> and phaeopigments	All, Task 9	25 – 200 (200)	Whatman GF/F in foil	Pass through GF/F filter. Fix with a saturated MgCO ₃ solution. Freeze filter until analysis.	4 weeks
Dissolved Oxygen	O, Task 9	300	300 mL glass BOD	Fix samples on board and titrate within 24 h.	24 hours
Phytoplankton (whole water)	M, O	800	1000 mL HDPE bottle	Preserve with Utermöhl's solution.	6 months
<i>Alexandrium</i>	M, O	4000	15 mL centrifuge tube	Strain through a 20-µm mesh netting; wash retained organisms into centrifuge tube. Preserve with formalin. Store upright in the dark on ice.	24 hours until transfer to methanol; 2 weeks
Rapid phytoplankton	Station N18 mid-depth	4000	1000-mL HDPE bottle	Strain through a 20-µm mesh netting; wash organisms into bottle; preserve with formalin and store in the dark.	6 days
Sample from vertical net tow					
Zooplankton	M, O	800	1000-mL HDPE bottle	Wash with screened seawater into jar. Preserve with formalin.	6 months

HDPE: High-density polyethylene

GF/F: pre-ashed glass fiber filter

^a Conductivity, temperature, pressure, dissolved oxygen, chlorophyll *a* fluorescence, transmissometry, *in situ* irradiance, surface irradiance, bottom depth, navigational position, date/time

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

B.2.5.1 DISSOLVED INORGANIC NUTRIENTS

A 60-mL syringe will be used to inject sample water from a transfer jar, through an in-line filter (Nuclepore 47-mm-diameter, 0.4-µm-membrane-fiber filter) and into a 125-mL white polyethylene (Nalgene) bottle. At the start and end of each survey day the 60-mL syringe is rinsed with 10% HCl solution then with Milli-Q. Additionally, the syringe is rinsed with Milli-Q between each station. The sample processing begins with the syringe receiving a triple rinse with site water. The bottle is then rinsed three times with filtered site water and 60 mL of site water is filtered into the bottle for analysis (Battelle SOP No. 5-266, *Nutrient Sample Processing*). The sample bottle will be labeled and the sample will be frozen. The samples will remain frozen until analyzed. A duplicate sample will be collected from the mid-depth (chl_a maximum) at stations F22, F23, N04, and N18 (1 duplicate analysis per 20 samples is required by DLS (Leo *et al.* 2011)).

B.2.5.2 TOTAL DISSOLVED NITROGEN AND PHOSPHORUS

Samples for total dissolved nitrogen and phosphorus will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. A 60-mL aliquot will be obtained from the particulate phosphorus filtrate. The sample will be passed through a Whatman 47-mm-diameter GF/F and collected in a polysulfon filtration flask. A 125-mL HDPE (Nalgene) bottle will be rinsed three times with filtrate, shaken to remove excess sample and then filled with approximately 60 mL of filtrate. Samples will be stored upright and frozen until analysis. A duplicate sample will be collected from the mid-depth (chla maximum) at stations F22, F23, N04, and N18 (1 duplicate analysis per 20 samples is required by DLS (Leo *et al.* 2011)).

B.2.5.3 PARTICULATE CARBON AND NITROGEN

Samples for particulate carbon and particulate nitrogen will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample will be filtered³, depending on particulate density. The samples will be collected on a precombusted 25-mm GF/F filters (nominal pore size 0.7 µm) using a vacuum-filter system. Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. A duplicate sample will be collected from the mid-depth (chla maximum) at each station. The second filter is for duplicate analysis (1 duplicate analysis per 20 samples is required by DLS (Leo *et al.* 2011)).

B.2.5.4 PARTICULATE PHOSPHORUS

Samples for particulate phosphorus will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample⁴ will be collected on 47-mm GF/F using a vacuum-filter system. Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. A duplicate sample will be collected from the mid-depth (chla maximum) at each station. The second filter is for duplicate analysis (1 duplicate analysis per 20 samples is required by DLS (Leo *et al.* 2011)).

B.2.5.5 CHLOROPHYLL A AND PHAEOPHYTIN

Samples for chlorophyll *a*/phaeophytin determination will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 25 and 400 mL sample⁴ for chlorophyll *a* analysis will be collected on Whatman 25-mm-diameter GF/F using a vacuum-filter system. The final volume should result in a light green/brown residue on the filter and will be noted on the sample label. A saturated solution of MgCO₃ will be added to the sample during filtration to aid retention and buffer the sample against low pH (which converts chlorophyll to phaeophytin). Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. A duplicate sample will be collected from the mid-depth (chla maximum) at each station. The second filter is for duplicate analysis (1 duplicate analysis per 20 samples is required by DLS (Leo *et al.* 2011)).

B.2.5.6 DISSOLVED OXYGEN

Water will be collected in three 300-mL BOD bottles at each of three depths (surface, mid-depth, and bottom) at stations F22, F23, N04 and N18. Using a hose (about 50-cm long) attached to the outlet on the Rosette sampling bottle, fill the BOD bottle from the bottom up with a minimum of bubbles and turbulence. After filling the BOD bottles, the DO samples will be fixed with manganese sulfate and alkali-iodide-azide powder pillows as described in Oudot *et al.* (1988) and Battelle SOP 5-317,

³Exact volume filtered will be recorded on sample label and any deviations from standard volume (500 mL for PCN, 200 mL for Chla, and 400 mL for PP) will be noted in station log.

Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860 & TIM840. The DO samples will be titrated either on board the vessel or onshore within 24 hours of being fixed. Bottles will be kept dark until the samples are analyzed.

B.2.5.7 WHOLE-WATER PHYTOPLANKTON

Water from the Rosette sampling bottle will be poured into a graduated cylinder that has been cut at the 850 mL mark. Before filling the cylinder to 800 mL, it is rinsed twice with water from the Rosette sampling bottle. The filled cylinder is then poured into a 1-L bottle containing 8 mL of Utermöhl's solution preservative. The preserved samples are stored at ambient temperature and in the dark until analysis. The Utermöhl's solution is prepared as described in Guillard (1973): 100 g potassium iodide, 50 g iodine, and 50 g sodium acetate each are dissolved incrementally in distilled water to a final volume of 1 L. The whole-water sample will be transferred to Pausacaco Plankton for analysis.

B.2.5.8 ALEXANDRIUM FUNDYENSE

The *Alexandrium* samples will be collected as 4-liter 20- μ m screened samples from the surface and mid-depth waters. Each sample will be rinsed into a 15-mL centrifuge tube with filtered seawater (a funnel may be used), then the appropriate volume of formalin added. For example, if there are 14 mL of sample add 1 mL concentrated formalin (37% formaldehyde). *Alexandrium* samples are stored upright on ice and in the dark. The *Alexandrium* samples will be transferred to WHOI within 24 hours of the survey for processing and analysis.

B.2.5.9 RAPID-ANALYSIS PHYTOPLANKTON

For the rapid analysis samples, a 4-L graduated cylinder is rinsed twice and filled (to 4-L) with sample water from the Rosette sampling bottle. The water from the filled cylinder is passed through a 20- μ m-mesh screen. Using a squeeze bottle containing seawater that has passed through the 20- μ m-mesh screen, the seawater is squirted back through the screen to wash the retained plankton into a 1-L sample bottle and the sample will be preserved with enough formalin to produce a 5% formalin to seawater solution (e.g., 5 mL:100 mL). The plankton sample will be stored at ambient temperatures in the dark until analyzed. The rapid analysis sample will be transferred to Pausacaco Plankton for immediate analysis.

B.2.6 ZOOPLANKTON SAMPLING

At all M and O type stations, a vertical-oblique zooplankton tow will be conducted with a 0.5-m diameter 102 μ m-mesh net equipped with a flow meter. Sampling procedures are detailed in SOP 5-280 *Phytoplankton and Zooplankton Sample Collection*. Tows will be in a vertical-oblique fashion, with just enough headway to keep the net stretched out. Tows will be made through approximately the upper 25 m (or less, at shallow stations) of the water column. Because nets are equipped with flow meters, net clogging is apparent when the flow meter is visibly not turning as the retrieved net nears the surface. In the event of net clogging due to large numbers of phytoplankton, the net will be emptied and rinsed with filtered seawater, and a second tow conducted over a shorter period of time (less depth). In addition, because it is not always easy to see the flow meter turning upon net retrieval, survey technicians will immediately review the flow meter readings for reasonableness. A reasonable reading for an average net tow is 500-1500 turns. The initial reading will be subtracted from the final reading and recorded on the log sheet to confirm that this range has been met. If the reading does not fall within this range, the tow will be repeated, as above. The flow meter will not be 'rezeroed' between stations. This will provide a cross-check of the flow meter readings (i.e. the final reading from the previous station should be the initial reading of the current station). When the net does not clog and a sample is collected successfully, the material retained by the net will be transferred to a jar as described below. The flow meter reading

before and after the tow, the tow time, and the depth of the tow will be recorded on the zooplankton measurement log (Figure B-5).

After conducting the net tow, the net is suspended with the net opening 7-9 feet above the deck. The suspended net is washed down from the outside of the net with running seawater. Excess water is drained through the netting. The lower part of the net is again washed down from the outside of the net. This is repeated until the net bottle is about ½ full and the netting is clear of material. The net bottle is removed from the end of the net and the retained water with material is transferred to a 1-L plastic jar. If ctenophores (e.g. *Mnemiopsis leidyi*) are encountered, the sample will be passed through a coarse mesh screen to remove the ctenophores prior to preserving the sample. The ctenophores will be transferred to a graduated cylinder and the volume of material will be recorded on the zooplankton log sheet. Using water from a squeeze bottle that was pre-screened with a 20-µm-mesh screen, any remaining material in the net bottle is washed into the plastic jar. Immediately, the sample will be preserved with enough formalin to produce at least a 10% formalin to seawater solution (e.g. 100 mL:800 mL). All zooplankton samples will be stored at ambient temperature in the dark until they are analyzed at UMD.

B.2.7 WHALE AND FLOATABLES OBSERVATIONS

During water column surveys, a trained whale observer will conduct sighting watches while on station and during transit between stations. The sighting operations will occur during daylight hours. The observer will scan the ocean surface by eye for a minimum of 40 minutes every hour. The horizon will be swept 180° during transit between stations (±90° of heading) and 360° while on station. All sightings will be recorded on standardized marine mammal field sighting logs (Figure B-6). Header fields for sighting logs will include observer name and position on vessel; date; survey number; Chief Scientist, Captain, and vessel name. Data fields on sighting logs will include: time, vessel position and heading (every 10 minutes), sighting event code (on or off watch, transiting or on station), relative bearing to sighting and distance from vessel, species name, group size, sea state, wind speed, swell, visibility, cloud cover, precipitation, and angle and severity of glare. A sighting while on station will be noted. Comments will be included, as needed. Although reporting of sightings of healthy right whales is voluntary for all vessels, reasonable effort will be made to report sightings within 12 hours by calling 866-755-6622, which reaches the North Atlantic Right Whale Sighting Advisory System (<http://www.nefsc.noaa.gov/psb/surveys/SAS.html>).

The whale observer and Battelle team field personnel will also observe the sea surface in the vicinity of the boat at each station and while underway and note the presence of anthropogenic debris/floatables (e.g. paper, plastics, and floating bits of fat), especially those potentially associated with wastewater (e.g. tampon applicators) in the station log. Particular attention will be paid while in the vicinity of stations N01, N18, and N21 (note that station N21 is above the outfall) and any notable observations at these three stations will be documented in the floatables table (Table B-6). These observations include – visible plume, seagulls feeding along the diffuser line, fat particles visible (with a description), and other wastewater related or anthropogenic debris. No entry will be made if nothing is observed. The data table will be submitted to MWRA along with the hydrographic data. The observations will also be reported in the survey summary and survey report as described in Section B.1.5.

Table B-6. Example of floatables table to be submitted to MWRA and included in survey report.

Survey ID	Survey Date/Time	Station	Observations: Visible plume, seagulls feeding along the diffuser line, Fat particles visible (describe), wastewater related and other anthropogenic debris
WN141	02/04/14 08:01	N01	Mylar balloon
WN141	02/04/14 11:01	N21	Visible plume, many small fat particles, several (5-10) plastic wrappers
WN141	02/04/14 11:25	N18	

<h2>Zooplankton Measurement Log</h2>	
For BOSS Zooplankton Tow data for MWRA Water Column Surveys	
Project Name: Harbor and Outfall Monitoring MWRA Project No. 100001957	
Survey ID: WN111	Protocol ID: ZO
Station: F23 <div style="text-align: center; border: 1px solid black; padding: 5px;">Label Here</div>	Ending Flowmeter Reading _____ Starting Flowmeter Reading: _____ Total Revolutions: _____ Tow Time (mm:ss.ss) _____ Depth of Tow (M) _____ Formalin added (ml) _____ Date: _____ Recorded by _____
Station: N01 <div style="text-align: center; border: 1px solid black; padding: 5px;">Label Here</div>	Ending Flowmeter Reading _____ Starting Flowmeter Reading: _____ Total Revolutions: _____ Tow Time (mm:ss.ss) _____ Depth of Tow (M) _____ Formalin added (ml) _____ Date: _____ Recorded by _____
Station: N04 <div style="text-align: center; border: 1px solid black; padding: 5px;">Label Here</div>	Ending Flowmeter Reading _____ Starting Flowmeter Reading: _____ Total Revolutions: _____ Tow Time (mm:ss.ss) _____ Depth of Tow (M) _____ Formalin added (ml) _____ Date: _____ Recorded by _____
Station: F22 <div style="text-align: center; border: 1px solid black; padding: 5px;">Label Here</div>	Ending Flowmeter Reading _____ Starting Flowmeter Reading: _____ Total Revolutions: _____ Tow Time (mm:ss.ss) _____ Depth of Tow (M) _____ Formalin added (ml) _____ Date: _____ Recorded by _____
Station: N18 <div style="text-align: center; border: 1px solid black; padding: 5px;">Label Here</div>	Ending Flowmeter Reading _____ Starting Flowmeter Reading: _____ Total Revolutions: _____ Tow Time (mm:ss.ss) _____ Depth of Tow (M) _____ Formalin added (ml) _____ Date: _____ Recorded by _____
Comments: <div style="border: 1px solid black; height: 40px; margin-top: 5px;"></div>	

Figure B-5. Example of a Zooplankton Measurement Log

Marine Mammal Sightings Log																		
Task:		Type:		Date:		Page ___ of ___				Observer:								
Date	Time	Position at Sighting		Vessel Heading		Mammal Sighting				Weather Conditions						Glare		
mmddyy	24-h clock	Latitude (°N)	Longitude (°W)	Direction	Speed	Species	Angle Rel. to Boat	Distance (m)	No. in Group	Sea State	Wind Speed	Swell	Visibility	Cloud Cover	Rain	Fog	Angle from Boat Head.	Glare Code

Code List			
<u>Species</u>		<u>Sea State</u>	
Mn	Humpback whale	0	Glass 3 1.5 - 3 ft
Bp	Finback whale	1	Catpaw 4 3 - 6 ft
Eg	Right whale	2	3 in - 1.5 ft 5 > 6 ft.
Ba	Minke whale		
Lag	Atlantic whitesided dolphin		
<u>Wind Speed (knots)</u>			
Pp	Harbor porpoise	0	0 - 5 3 15 - 20
Gn	Pilot whale	1	5 - 10 4 20 - 25
Bn	Blue whale	2	10 - 15 5 > 25
Bp	Sei whale		
Lal	Whitebeaked dolphin		
<u>Swell (feet)</u>			
Pv	Harbor seal	0	None 2 3 - 6
G	Gray seal	1	1 - 3 3 > 6
H	Hooded seal		
Ha	Harp seal		
<u>Glare</u>			
UB	Unidentified baleen whale	0	None 2 Moderate
UO	Unidentified Odontoceti	1	Mild 3 Severe
UP	Unidentified Phocid		
<u>Visibility (miles)</u>			
		0	None 4 3 - 5
		1	< ¼ 5 5 - 10
		2	¼ - 1 6 10
		3	1 - 3 7 Unlimited

Figure B-6. Example of Marine Mammal Sightings Log and Relevant Codes

B.3 SAMPLE HANDLING AND CUSTODY

B.3.1 SAMPLE CUSTODY

Water column samples collected in the field will be identified by either a DLS LIMS ID supplied by MWRA or by an ID generated by NavSam[®] software. At least one week prior to a survey, MWRA will provide a text file of DLS LIMS Sample Numbers for all analyses conducted by DLS. The DLS LIMS Sample Numbers will be imported into the NavSam[®] Planned Subsample Table using a look-up table that contains the DLS LIMS Bottle ID for each station, depth, analyte, and replicate (in NavSam[®] the LIMS Sample Numbers become Bottle IDs). Battelle SOP MWRA 008 *Integrating MWRA Client ID Numbers into the NavSam[®] Survey Database* describes this process. The DLS LIMS Bottle ID will be printed on the sample labels, and the corresponding Sample ID will go on the station log forms. These IDs will be

linked to the NavSam[®] data capture system (Figure B-7). For samples that are not analyzed by DLS (e.g. plankton and dissolved oxygen) Bottle IDs will be generated by concatenating the NavSam[®] *Sample ID* with the analysis code (Table B-7) and replicate number. The *Sample ID* will identify the water collected in the Rosette sampling bottles from a certain depth during a particular station on the specified survey. The five character *Event ID* will be unique to each survey, such as WN114, with “WN” indicating that it is a water column survey, “11” indicating the survey year, and “4” signifying the fourth survey of the year. The *sample_marker* is a non-repeating (within a survey) number generated by the NavSam[®] software during the closing of a set of Rosette sampling bottles at one depth or at completion of the vertical net tow.

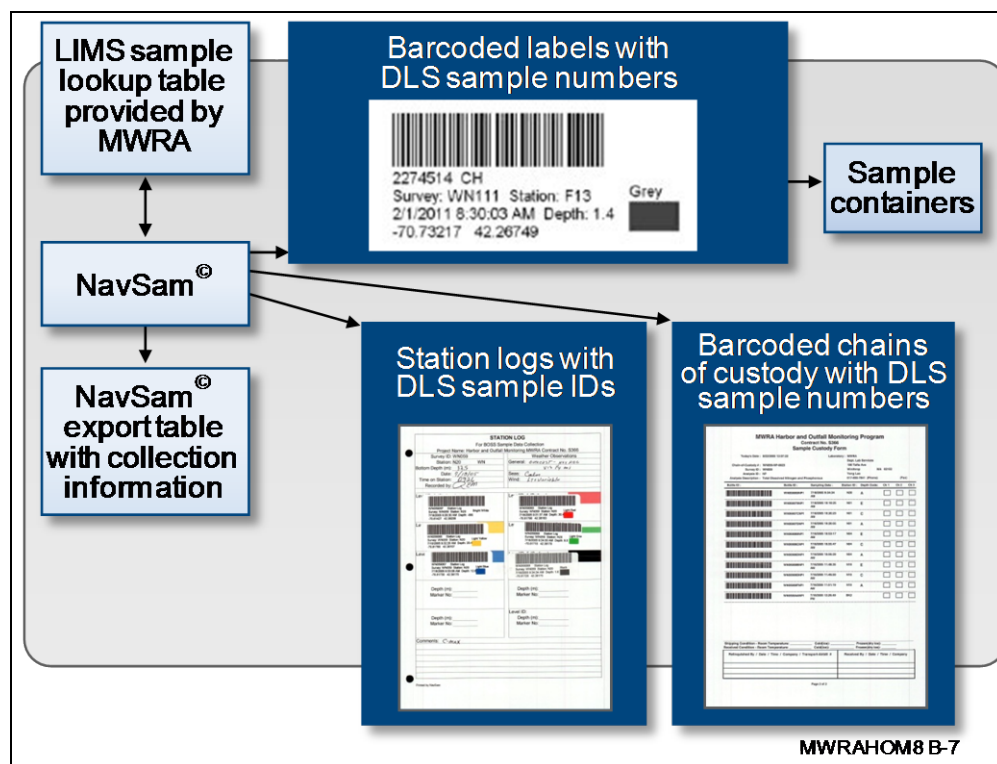


Figure B-7. Depiction of Linkage from DLS LIMS to NavSam[®]

Table B-7. Analysis Codes used in Bottle ID or used as Label Abbreviations

Analysis Codes	Description	Laboratory
AL	Alexandrium	WHOI
CH	Chlorophyll	DLS
DO	Dissolved Oxygen	Battelle
IN	Dissolved inorganic nutrients	DLS
NP	Total dissolved nitrogen and phosphorous	DLS
PC	Particulate carbon and nitrogen	DLS
PP	Particulate phosphate	DLS
RP	Rapid analysis phytoplankton	PP
WW	Whole water phytoplankton	PP
ZO	Zooplankton	UMD

A survey logbook containing station logs, instrument calibration data, and other forms will be assembled prior to each survey. The scientific crew member operating the data collection system will fill out the station log (Figure B-8) at each station. The log includes fields for entering pertinent information about each station, such as time on station, bottom depth, weather observations, and general comments. During the hydrocasts, CTD data will be logged and stored electronically on the computer's hard disk. When Rosette sampling bottles are closed, the operator will mark an event into the CTD data file and the survey electronic log.

Sample chain-of-custody (custody) begins immediately upon sample collection:

- The Chief Scientist assumes custody of the samples and confirms that samples are stored at the QAPP-defined temperature while held on the survey vessel.
- Each sample bar code label is scanned following field collection as the sample is packed into laboratory specific coolers, and chain-of-custody forms are generated by NavSam[®] and printed. Custody forms document the project name, station ID, sample-type designation, DLS LIMS Bottle ID or NavSam[®] Bottle ID, sample date and time, and other pertinent sample information (Figure B-5, Figure B-9, and Figure B-10).
- The NavSam[®] Custody File is compared to the sample bottles and any discrepancies are resolved.
- When the custody of samples is transferred, the custody form will be signed by both the staff member that relinquishes custody and the staff member assuming custody for the samples.
- The relinquishing staff member will retain a photocopy of the signed chain.
- Upon receipt at the laboratory, the laboratory custodian compares bottle IDs to the chain-of-custody forms, verifies sample integrity and temperature, signs and dates the "Received By" section of the custody form, and logs the samples into the laboratory sample tracking system.

Battelle will retain the original custody forms and log forms in a Sample Log Book that will provide full sample tracking procedures. Any problems related to the receipt or condition of samples will also be documented in the Sample Log Book. This log will be available to MWRA staff for review at any time. As with all raw project files, Battelle will maintain these records for 10 years after project completion. At the end of this period Battelle will contact MWRA to identify records that should be transferred to MWRA. The remainder will be destroyed.

STATION LOG	
For BOSS Sample Data Collection	
MWRA Harbor Outfall Monitoring Project No. 100001957	
Survey ID: WN111 Station: N04 Bottom Depth (m): _____ Date: _____ Time on Station: _____ Recorded by: _____	Weather Observations General: _____ Seas: _____ Wind: _____
LevelID: 0 (Station Arrival) Depth (m): _____ Marker No: _____	LevelID: 1 (Bottom) Depth (m): _____ Marker No: _____
LevelID: 2 (Mid-Bottom) Depth (m): _____ Marker No: _____	LevelID: 3 (Mid-Depth (C-Max)) Depth (m): _____ Marker No: _____
LevelID: 4 (Mid-Surface) Depth (m): _____ Marker No: _____	LevelID: 5 (Surface) Depth (m): _____ Marker No: _____
LevelID: 6 (Zooplankton Tow) Depth (m): _____ Marker No: _____	Depth (m): _____ Marker No: _____
Depth (m): _____ Marker No: _____	Level ID: Depth (m): _____ Marker No: _____
Comments: _____ _____ _____ _____ _____	

Printed by NavSam

Figure B-8. Example Station Log

MWRA Harbor and Outfall Monitoring Program

Project No. 100001957

Sample Custody Form

Today's Date : 2/15/2011 12:59:39 PM
















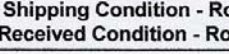
Laboratory : MWRA
 Dept. Lab Services
 190 Tafts Ave
 Winthrop MA 02152
 Yong Lao
 617-660-7841 (Phone) (Fax)

Chain-of-Custody # : WN111-PC-0006

Survey ID : WN111

Analysis ID : PC

Analysis Description : Particulate Carbon and Nitrogen

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	2274497	2/1/2011 2:45:58 PM	BF2		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274498	2/1/2011 7:08:51 AM	BF1		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274561	2/1/2011 10:11:04 AM	F15	C	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274562	2/1/2011 10:11:04 AM	F15	C	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274568	2/1/2011 9:09:07 AM	F06	A	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274571	2/1/2011 9:08:31 AM	F06	B	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274577	2/1/2011 9:07:58 AM	F06	C	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274578	2/1/2011 9:07:58 AM	F06	C	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274583	2/1/2011 9:07:16 AM	F06	D	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274587	2/1/2011 9:06:36 AM	F06	E	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274591	2/1/2011 9:42:29 AM	F10	A	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274594	2/1/2011 9:41:51 AM	F10	B	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274600	2/1/2011 9:41:07 AM	F10	C	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274601	2/1/2011 9:41:07 AM	F10	C	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274604	2/1/2011 9:40:07 AM	F10	D	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	2274608	2/1/2011 9:39:09 AM	F10	E	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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

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

Figure B-9. Example of Water Chemistry Custody Form with LIMS generated IDs

MWRA Harbor and Outfall Monitoring Program

Project No. 100001957

Sample Custody Form

Today's Date : 2/15/2011 12:56:29 PM

Laboratory : University of Massachusetts, Dartmouth
 Biology Department
 285 OldWestport Road
 North Dartmouth MA 02747-2300
 Dr. Jefferson Turner
 508-999-8229 (Phone) 508-999-8197 (Fax)

Chain-of-Custody # : WN111-ZO-0011

Survey ID : WN111

Analysis ID : ZO

Analysis Description : Zooplankton

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	WN111056ZO1	2/1/2011 8:30:07 AM	F13	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN111069ZO1	2/1/2011 9:09:10 AM	F06	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN111079ZO1	2/1/2011 9:42:31 AM	F10	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN111087ZO1	2/1/2011 10:12:19 AM	F15	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN111097ZO1	2/1/2011 10:44:01 AM	N07	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN1110A5ZO1	2/1/2011 11:13:50 AM	N18	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN1110D3ZO1	2/1/2011 12:44:16 PM	F22	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN1110ECZO1	2/1/2011 1:31:18 PM	N04	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN111102ZO1	2/1/2011 2:09:57 PM	N01	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN111116ZO1	2/1/2011 2:43:53 PM	F23	Z	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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

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

Figure B-10. Example of Custody Form with NavSam[®] generated IDs

B.3.2 CUSTODY OF ELECTRONIC DATA

Field custody of electronic data will be the responsibility of the survey Chief Scientist. The field custody of the electronic data consists of backing up the survey data to a thumb drive or CD each day. The data will be transferred to the Battelle data management team upon completion of the survey. The field data are then loaded to Battelle's server system where they are backed up daily. All field data are submitted electronically via MWRA's HOML application web site.

Battelle, DLS, Pausacaco Plankton, UMD, and WHOI will produce electronic data under this task. At Battelle, the electronic files for DO data will remain in the custody of the Task Leader (Mr. Matt Fitzpatrick) until all analyses are completed and data have been audited. Two copies of each type of electronic file will be made. Set 1 will remain in custody of the Task Leader in the Task notebook. Set 2 will be transferred to the Battelle data management team for submission to MWRA's HOML web site.

Electronic data will remain in the custody of laboratory managers or custodians [Dr. Yong Lao (DLS), Dr. Jefferson Turner (UMD), Dr. David Borkman (Pausacaco Plankton), and Dr. Don Anderson (WHOI)] until an independent review has been completed. With the exception of DLS data, once the data have passed the independent review, three copies of each type of electronic file will be made. Set 1 will remain in the custody of each laboratory custodian and Sets 2 and 3 will be sent to the Battelle. Set 2 is a hardcopy of the data table and QA/QC statements from the laboratory. The hardcopy will be used by Battelle QAU to audit the electronic data submission to MWRA and will be archived with the project files. Set 3 is the data in an electronic format that is given to the Battelle data management team for submission to MWRA's HOML web site. DLS data will be processed in its entirety by MWRA staff.

B.3.3 CUSTODY OF WATER SAMPLES

During field collection, NavSam[®] will create chain of custody forms from the sample table used to generate sample labels, thereby creating a link between the sample and data recorded on the chain of custody form. The chain of custody forms will have the same Bottle ID (LIMS or NavSam[®]) as the corresponding label on the sample container, ensuring the tracking of sample location and the status.

The Chief Scientist will retain custody of samples during the survey. He is responsible for verifying each Bottle ID vs. the custody forms generated by NavSam[®] prior to delivering the samples to the laboratory.

- Nutrient samples are returned to Battelle by the Chief Scientist or designee for secure storage at the appropriate temperature requirements after completion of the survey day. Once the sample check off process is complete, the Chief Scientist will e-mail the DLS lab staff an Excel file that contains the collected Bottle IDs, along with date/time, station, analysis code, and depth code of sample collection. The samples may be shipped via Federal Express or hand-delivered to MWRA once the survey is complete.
- *Alexandrium* samples are returned to Battelle and hand-delivered to WHOI within 24-hrs.
- Zooplankton and phytoplankton samples are returned to Battelle and hand-delivered or shipped via Federal Express after the survey to UMD and Pausacaco Plankton.
- All frozen samples will be shipped on ice with protective layers of foam or bubble wrap to ensure samples remain intact and frozen during shipment. Plankton samples are shipped with appropriate packaging (vermiculite and bubble wrap), but do not require temperature preservation.

Upon receipt of the samples at Battelle or another laboratory, the designated Sample Custodian will examine the samples, verify that sample-specific information recorded on the chain is accurate and that the sample integrity is uncompromised, log the samples into the laboratory tracking system, complete the

custody forms, and sign the chain form so that transfer of custody of the samples is complete. Any discrepancies between sample labels and transmittal forms, and unusual events or deviations from the project QAPP will be documented in detail on the chain and the Battelle Field Manager will be notified. The designated Sample Custodian at each laboratory will then sign and keep the original chain forms. Copies of the signed chain will be faxed to the Battelle Field Manager within 24 hours of receipt. The original chain forms will be submitted with the data submission and maintained in the Sample Log Book. Sample numbers that include the complete field ID number will be used to track the samples through the laboratory. Alternately, unique laboratory IDs may be assigned by each laboratory for use during their sample analyses, but the data will be reported to the database by using the field-generated sample number.

Samples that have been analyzed and have passed their holding times will be discarded. No samples will be archived.

B.4 ANALYTICAL METHODS

A full description of the following analyses is provided in MWRA DLS QAPP (Leo *et al.* 2011) for Nutrient, Chlorophyll, and Fat-Particle Analyses for Outfall Monitoring:

- Dissolved Inorganic Nutrients
- Total Dissolved Nitrogen and Phosphorus
- Particulate Carbon and Nitrogen
- Particulate Phosphorus
- Chlorophyll a and Phaeophytin
- Fat Particle composition

B.4.1 DISSOLVED OXYGEN

Dissolved oxygen concentrations will be determined following the method described by Strickland and Parsons (1972) and Battelle 5-317, *Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860 & TIM840*. A set of triplicate DO samples will be collected for each analysis. The triplicate samples will be fixed immediately, and analyzed with 24 hrs of fixation providing a measurement of DO concentration for that sampling depth.

B.4.2 WHOLE-WATER PHYTOPLANKTON

The methods discussed below have been used for the identification and enumeration of phytoplankton species during HOM3 through HOM8. At the laboratory, Utermöhl's-preserved whole seawater samples will be prepared for analysis by concentrating the sample by gravitational settling as described by Borkman (1994), Borkman *et al.* (1993), and Turner *et al.* (1995). The method is similar to the methods of Hasle (1959), Iriarte and Fryxell (1995), and Sukhanova (1978). Samples will be settled in graduated cylinders with no more than a 5-to-1 height-to-width ratio.

Phytoplankton abundance is calculated by dividing the number of cells counted by the volume examined in Sedgwick-Rafter chamber. The theoretical maximum possible volume that would be examined would be an entire Sedgwick-Rafter cell (1 mL). Typical volumes are one path of the cell which at 500× = 1/48 of one mL of concentrate, and at 250× = 1/24 of one mL of concentrate. The volume of sample examined is dependent on number of cells encountered and how long it takes to reach cut-offs of 75 entities of the top 3 taxa and 400 cells total. Calculation of abundance also accounts for the concentration factor used in the settling process. Normally, the volume processed is 800 mL of whole-water sample, settled to 50 mL of concentrate, for a 16:1 ratio. For example, using typical sample and settling volumes, a count of a single cell in four paths scanned at 500× would yield an estimate of 750 cells per liter as follows:

[1 cell/4 paths * 48 paths / 1ml S-R * 50ml settling volume] / 0.8 L seawater = 750 cells L⁻¹.

Final abundance estimates will be reported as units of 10⁶ cells per liter.

The two-step counting protocol allows for improved precision in estimating abundances of small (<10µm greatest axial linear dimension) and larger phytoplankton forms. Counting large numbers of small forms at 500× increases the precision of the estimated abundances of these forms. The counts at 250× allow for the examination of a larger volume of the sample, thereby increasing the likelihood of encountering larger, less abundant (or rare) forms. During the 250× analysis, the 500× objective can be used as needed to resolve key taxonomic characters.

B.4.3 ALEXANDRIUM SAMPLES

The *Alexandrium* samples will be identified, counted, and quantified using a fluorescent probe technique. These methods have been used during the *Alexandrium* Rapid Response surveys during HOM4 through HOM8 (Libby 2006). The samples will be delivered to WHOI within 24 hrs of the survey where the sample will be centrifuged and the formalin removed by aspiration leaving the pellet intact. The pellet will then be resuspended with 100% cold methanol for analysis and storage. For optimal results, this process should occur within 24 hours after fixation in formalin. The sample cannot tolerate long time periods in formalin because the rRNA signal in the cell is lost due to excessive cross-linking of the nucleic acids by the formalin. Although 24 hours is the optimal time frame, it is expected that the fluorescent probes will provide acceptable results on samples stored up to one week in formalin (Anderson pers. comm.).

Fluorescent probes will be used to confirm and enumerate the *Alexandrium fundyense* that are present. This requires the use of a molecular probe that has been developed for this species (Anderson *et al.* 2005). The NA-1 probe conjugated to Texas Red will be used to identify and enumerate *A. fundyense* (North American ribotype). The samples will be examined for the presence of *A. fundyense* cells using a Zeiss epifluorescence microscope at 100X magnification. The microscope will be fitted with filter sets complementary to the probe/fluorochrome combination used. Control samples containing cells of *A. fundyense* will be processed simultaneously to confirm the reliability of the staining procedure.

B.4.4 RAPID-ANALYSIS SAMPLES

The screened, rapid-analysis samples will be examined for qualitative impression of the dominant taxa and specific harmful or toxic alga (*i.e.*, *Alexandrium fundyense*, *Phaeocystis pouchetii*, *Pseudo-nitzschia* spp.). Within six days of sample receipt at the counting laboratory, an aliquot of this sample will be qualitatively analyzed using the Sedgwick-Rafter counting cell and viewed through an Olympus BH-2 compound microscope (phase-contrast optics) to quickly verify the presence or absence of nuisance species. The analysis will also produce a qualitative impression of the types and abundance of dominant taxa. These results will be reported in the survey summary and survey report.

B.4.5 ZOOPLANKTON

The methods discussed below have been used for the identification and enumeration of zooplankton species during HOM3 through HOM8. At the lab, each sample for zooplankton is transferred to 70% ethanol solution to prevent inhalation of formalin fumes during counting. Samples are reduced to aliquots of at least 250 animals with a Folsom plankton splitter, and animals are counted under a dissecting microscope and identified to the lowest possible taxon. In most cases, this will be to species; adult copepods will be additionally characterized by sex. Counts of all copepodite stages of a given copepod genus will be combined. Copepod nauplii will not be identified to genus or species because nauplii

species cannot be reliably identified to those levels by using a dissecting microscope. Meroplankters cannot be identified to genus or species in most cases, and such organisms will be identified to the lowest reliable taxon, such as barnacle nauplii, fish eggs, or gastropod veligers.

Concentrations of total zooplankton and all identified taxa are calculated based on the number of animals counted, multiplied by the aliquot concentration factor, and divided by the volume of filtered by the net.

For instance, if 400 animals were counted in a 1/256 split, and the volume filtered was 4.2 cubic meters, then the calculation would be $400 \times 256 = 102,400$, and $102,400$ divided by $4.2 = 24,381$ animals per cubic meter.

B.5 QUALITY CONTROL

B.5.1 FIELD PROGRAM

Field QC samples are defined in Table B-8. In addition, it is critical that sensors and measurement equipment are operating correctly and are equilibrated prior to use. Specifically, the Chief Scientist must verify that the DO sensor is equilibrated, light sensor is operational (deck check) and the zooplankton flowmeters are working properly at each station. QA/QC samples will be collected at various stations as per Table B-8.

B.5.2 DECONTAMINATION

Sample processing equipment is cleaned during each survey day. All filtering equipment (the filtering apparatus, syringes, graduated cylinders, etc.) is rinsed with 10% HCl in the morning and at the end of the day followed by a triple rinse of Milli-Q water. Between stations the equipment is triple rinsed with Milli-Q.

B.5.3 FIELD BLANKS

Field blank processing for dissolved parameters follows the same procedures used for sample processing, but with Milli-Q water in place of seawater. Milli-Q water is supplied by DLS. For DIN, field blanks are collected from the DIN station using syringes and filter cartridges. TDNP field blanks are collected from the PP filtration flasks after processing Milli-Q through a glass fiber filter like a regular sample. Filter blanks are collected for PC/PN, PP, and chlorophyll by placing a new, unused filter directly into the appropriate sample container (foil packet). Table B-8 details the collection of field blank samples. All samples will be labeled with a bar-coded label produced by NavSam[®] then stored in the freezer. In addition to the processed field blanks, bottle blanks will be collected at the same time as the morning field blank for DIN and TDNP. The bottle blank is used to evaluate non-processing elements of contamination (e.g. Milli-Q, sample containers, etc). The bottle blank will consist of a clean, unused sample bottle filled the Milli-Q water supplied by DLS without a triple rinse. These samples will be labeled with a bar-coded label produced by NavSam[®] and stored in the freezer. A duplicate label for each field blank is pasted into the survey log book. MWRA will use the results of the field blanks to assess the impact of field and laboratory-related contamination on water samples.

B.5.4 FIELD REPLICATES

Field replicates are taken at a number of stations each day. Replicates consist of the processing of a second sample from the upcast in the exact manner as the primary sample. Replicates provide information regarding the variability of samples processed in the field. Table B-8 details the collection of field replicate samples.

Table B-8. QA/QC Samples for Water Column Surveys.

Analysis Type	Qty	Depths	Stations
Field Replicates			
Dissolved inorganic nutrients (DIN)	1	Mid-depth	F22, F23, N04, and N18
TDN/TDP	1	Mid-depth	F22, F23, N04, and N18
Chlorophyll, PP, PC/PN	1	Mid-depth	All stations
Dissolved oxygen	Collected in triplicate	Surface, mid-depth, and bottom	F22, F23, N04, and N18
Blanks			
Filter Blanks for PC/PN, PP, Chlorophyll	2/day/parameter	NA	Collected at the beginning and end of the sampling day.
Field Blanks: DIN TDN/TDP	3/day/parameter	NA	One blank for each analysis will be collected at the beginning of the day, mid-day, and at the end of the day. Mid-day blanks will typically be collected between N21 and F22.
Bottle Blank for DIN, TDN/TDP	1/day	NA	One blank per container type at the beginning of each day

B.5.5 LABORATORY PROGRAM

Table B-9 summarizes the laboratory measurement quality objectives for water column monitoring under this contract. Section B.4 details the analytical procedures that will ensure data quality; Section B.6 describes instrument calibration methods.

Table B-9. Measurement Quality Objectives for Analyses by Battelle

Quality Control Sample Type	Frequency	Data Quality Indicator	Corrective Action
Field Replicates			
Dissolved oxygen	Triplicate bottles for all DO samples collected	≤5% RSD ¹	Results examined by task leader, technical manager or project manager. The data are qualified and associated comments are documented

¹ Relative Standard Deviation (RSD) = (Standard deviation x 100) / average

B.5.6 PRECISION AND ACCURACY

Table B-9 summarizes the laboratory QC samples analyzed by Battelle for HOM9 water column parameters. Precision and accuracy of DLS laboratory procedures are assessed through the analysis of QC samples including procedural/filter blanks, prepared standards, SRMs, laboratory replicates and field replicates, as applicable. Measures of precision and accuracy for analysis performed by DLS are described in Leo *et al.* (2011). The QC procedures used to assess accuracy and precision of phytoplankton and zooplankton methods are described below.

B.5.6.1 WHOLE-WATER PHYTOPLANKTON

Based on a study conducted by Guillard (1973), counts of 400 phytoplankton cells will provide a precision of $\pm 10\%$ of the mean. Following the analytical protocols described in Section B.4.2, for this program, a minimum of 400 entities (solitary single cells, chains, or colonies) will be tallied for each sample. Unicellular forms (*e.g.*, *Cryptomonas* spp., microflagellates), aggregate forms (*e.g.*, *Phaeocystis pouchetii*), and chained forms (*e.g.*, *Skeletonema* spp.) will each count as one entity towards the 400-entities-counted-per-sample minimum tally. To increase precision of the abundance estimates for the most abundant taxa, when practical at least 75 entities of each of the three most abundant taxa will be counted in each sample. The overall goal is to enumerate a minimum of 400 entities total and the 3 most abundant taxa to at least 75 entities each. An additional data quality procedure will be performed on the whole water phytoplankton samples. A subset of samples will be counted in duplicate by a different taxonomist or as a blind recount by the same taxonomist to provide an estimate of the variability in the analysis and quantify the accuracy and comparability of the results. One whole water sample from each of the water column surveys will be analyzed in duplicate. The results, as relative percent difference (RPD), will be included in the data submission to Battelle as an estimate of the variability in the analysis. The precision method quality objective (MQO) for the total and the single most dominant species is $\leq 20\%$. If the RPD is greater than 20 a second aliquot will be counted and the three results used to calculate the relative standard deviation (RSD), which should be $\leq 20\%$.

B.5.6.2 ALEXANDRIUM

The *Alexandrium* samples will be identified, counted, and quantified using a fluorescent probe technique. As with the whole water phytoplankton, counts of 400 cells will provide a precision of $\pm 10\%$. Based on the sample collection (4 liters) and processing protocols, an RPD of $< 20\%$ would be expected for any cell abundances of 50 cells/L or greater. When *Alexandrium* abundances reach levels > 50 cells/L during a survey, a duplicate sample will be analyzed (1 per 20 samples collected). The results and RPD will be included in the data submission to Battelle as an estimate of the variability in the analysis. The precision MQO for *Alexandrium* counts > 50 cells/L is $\leq 20\%$. If the RPD is greater than 20% a third replicate will be counted and the three results used to calculate the relative standard deviation (RSD), which should be $\leq 20\%$.

B.5.6.3 ZOOPLANKTON

Zooplankton samples will be split with a Folsom plankton splitter, and an aliquot of at least 250 animals will be counted. If the total count in a split is less than 250 animals, the other half of the split is counted to make a combined split. If that still does not yield enough animals, then the penultimate split is counted. One sample from each of the water column surveys will be analyzed in duplicate. The results, as RPD, will be included in the data submission to Battelle. The precision MQO for total and the single most dominant species/group is $\leq 20\%$.

B.5.7 COMPLETENESS

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

B.5.8 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 (Albro *et al.* 1993; Bowen *et al.* 1998; Libby *et al.* 2002, 2005, 2006, 2009, 2010, and 2011; Libby 2006), 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. Specific, potential comparability issues are addressed in Albro *et al.* (1998).

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

B.5.9 REPRESENTATIVENESS

Representativeness is addressed primarily in sampling design. The laboratory measurements that will be made during the water quality monitoring task 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 provided to MWRA with the data. Significant deviations will be discussed in the quarterly QA/QC Corrective Action reports.

B.5.10 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 (MDL) and instrument detection limits (IDL) provide the sensitivity goals for the proposed procedures. IDLs for field instruments are provided in Table A-1. MDLs for DLS analysis are in the MWRA DLS QAPP (Leo *et al.* 2011).

B.6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Logs of maintenance and repairs of instruments will be stored in the instrument files maintained by Battelle and by each laboratory. Maintenance of and repairs to instruments will be in accordance with manufacturers' manuals. Any deviations to this policy will be noted.

Most equipment used for hydrographic profiles is factory calibrated initially, and returned to the manufacturer for annual recalibration. Calibration records are maintained in the field equipment maintenance and calibration files. Prior to each survey, the NavSam[®] operator is responsible for ensuring that the most recent calibration records with factory offset forms are inserted into the survey log for all primary and back-up equipment. The Chief Scientist is responsible for verifying that the offsets and calibration factors for each piece of equipment have been entered into the data set-up files. The set-up and verification will be documented in the survey logbooks.

The Battelle Instrument History sheet and the factory calibration sheets along with records of periodic checks are maintained in the field equipment files.

B.6.1 HYDROGRAPHIC PROFILING EQUIPMENT

B.6.1.1 PRESSURE (DEPTH) SENSOR

At the beginning of each day of each survey, the software offset of the Sea-Bird SBE-29 pressure sensor is set to read zero meters when the sensor is on deck. The offset is entered into the equipment setup file. The offset of the pressure reading is affected by the atmospheric pressure. After the correction is made, the readings are checked again and should be with ± 0.1 m. The readings are recorded on the instrument calibration forms entered into NavSam[®] and are archived with all the sensor data. The day-to-day drift is ± 0.2 m for the normal range of atmospheric pressure.

B.6.1.2 TEMPERATURE AND CONDUCTIVITY

The software gain and offset of the temperature and conductivity sensors (SBE-3 and SBE-4, respectively) are calibrated annually at the factory. The factory calibration settings are not changed by Battelle.

The SBE conductivity sensor incorporates a fixed precision resistor in parallel with the cell. When the cell is dry and in air, the sensor's electrical circuitry outputs a frequency representative of the fixed resistor. This frequency is recorded on the Calibration Certificate and should remain stable (within 1 Hz) over time. The primary mechanism for calibration drift in conductivity sensors is the fouling of the cell by chemical or biological deposits. Fouling changes the cell geometry, resulting in a shift in cell constant. Accordingly, the most important determinant of long-term sensor accuracy is the cleanliness of the cell. The conductivity readings (observed as salinity values) will be continually evaluated based on historical values and professional judgment. In the event that large drifts in the conductivity measurements are observed, the SBE conductivity sensor will be replaced and the faulty sensor sent to the manufacturer to be refurbished and recalibrated.

All sensors on the SBE-25 are rinsed with deionized water at the end of each survey day. Following completion of surveys, the equipment is returned to the Battelle shop for a full cleaning with tap water, followed by deionized water rinses.

B.6.1.3 ALTIMETER AND ECHOSOUNDER

The Data Sonic PSA-916 altimeter and Furuno FCV-582 video echosounder are sent to the manufacture as necessary for maintenance. Records of factory maintenance are documented on the instrument history sheet in the field management files. The NavSam[®] operator checks the height above bottom (altimeter) and bottom depth (echosounder) against the sensor depth (pressure) readings to confirm that all three are consistent (bottom depth minus sensor depth equals altimeter reading).

B.6.1.4 *IN SITU* DISSOLVED OXYGEN

The software gain and offset of the DO sensors (Sea-Bird Model 43) will be calibrated annually at Sea-Bird. The calibration settings may be changed thereafter using manufacturer software in conjunction with results from Winkler titrations. The DO sensor is rinsed with deionized water at the end of each survey day. Following completion of surveys, the sensor is returned to the Battelle shop for a full cleaning with tap water, followed by deionized water rinses.

B.6.1.5 TRANSMISSOMETER

The WET Labs C-Star transmissometer is calibrated annually by the manufacturer. A review of the calibration coefficients for the transmissometer shows that it is quite stable from year to year. The drift of the transmissometer is dependent on the amount of time it is operated.

Before each survey the windows of the transmissometer will be rinsed with deionized water. To check that the transmissometer is working properly, each survey day the blocked and unobstructed readings in air will be observed. Typical blocked readings in air are greater than 40/m and typical unblocked readings in air are less than 0.5/m. Periodically throughout the survey day, the optics of the transmissometer will be rinsed with deionized water and checked for salt residues and cleaned as necessary.

B.6.1.6 *IN SITU* CHLOROPHYLL A FLUOROMETER

The WETStar fluorometer is sent to the manufacturer for maintenance and recalibration annually. A review of the calibration coefficients for this instrument indicates it is stable from year to year. The factory calibration is based on instrument response in distilled water and a 0.5 mg/L coproporphyrin standard solution (fluorescence signal equivalent to 50 µg/L chlorophyll in a *Thalassiosira weissflogii* phytoplankton culture). The fluorometer data, displayed with the NavSam[®] program, will approach 0.0 µg/L when the instrument is on deck. The on-deck reading will be checked prior to each survey day. Then, when the CTD is in the water, the reading will again be checked for a reasonable value. Errant readings will instigate corrective action. All errant readings and resultant corrective actions will be noted in the survey logbook. As daily maintenance, the fluorometer will be rinsed with deionized water. The *in situ* fluorescence readings will be calibrated by MWRA using the chlorophyll *a* data measured in the laboratory from discrete bottle samples.

B.6.1.7 IRRADIANCE PROFILING AND ON-DECK SENSORS

The proper conversion factors for the sensor voltages to engineering units are contained on the calibration certificate issued with the instrument, and are updated during factory recalibrations. These records are stored and maintained in the field equipment files.

QSR-240 (On-deck Irradiance Sensor)

The Biospherical Instruments Solar Reference Scalar Irradiance Sensor (QSR-240) is designed for monitoring total incident radiation in air. It is deployed at the surface as a surface irradiance reference sensor in conjunction with a profiling sensor in water column. When operated together, the QSR-240 sensor measures the sunlight in air to provide the reference ambient irradiance and the QSP-2200PD underwater sensor measures the sunlight penetrating the water column at depth.

The QSR-240 Sensor is calibrated annually by Biospherical Instruments Inc. In addition, this instrument should be checked every two to three months, depending on the amount of use, by verifying operation on a clear day. Solar irradiance at local noon, measured on a clear day, is typically between 2000 and 3000 µE m⁻²sec⁻¹ depending upon the time of year. Any deviation of >40% is strong evidence of a problem. Whenever the instrument's calibration is in question for any reason, the instrument will be returned to Biospherical Instruments for recalibration and examination. Additionally, prior to each survey the sensor will be capped (dark), and an average of at least 20 readings will be recorded in the survey electronic files. The average reading should be 0 ±10 µE m⁻²sec⁻¹.

The Teflon collector sphere of the QSR-240 may become dirty during normal use. If any attempt is made to rotate, remove, tighten, push, or pull on the small white sensor ball, the calibration will be ruined and the unit must be sent the manufacturer for repair and recalibration. The sphere may be gently cleaned with soap and warm water, or a solvent such as alcohol, by using a soft tissue or towel. Acids, abrasive

cleaners or brushes cannot be used as this will mar the surface of the sphere and void the instrument's calibration. If the sphere becomes damaged or heavily soiled, the instrument will be returned to the manufacturer for service and re-calibration. Maintenance records are maintained in the field equipment files.

The irradiance shield will be kept as clean as possible by periodically wiping with a damp cloth with care to avoid touching the Teflon sphere. A qualified technician will conduct maintenance. Battelle SOP for Biospherical Irradiance Sensors (No. 3-127) provides a complete description of the setup, use, calibration and maintenance of the QSR-240 On-deck Irradiance Sensor.

QSP-2200PD (Underwater Irradiance Sensor)

The Biospherical Instruments Logarithmic Output Oceanographic Light Transducer (QSP-2200PD) is calibrated annually using a National Institute of Standards and Technology traceable 1000-watt type FEL Standard of Spectral Irradiance. Biospherical Instruments Inc. 5340 Riley Street San Diego, CA. 92110-2621, performs instrument calibration. The Battelle Calibration Results Check Sheet for Biospherical Irradiance Sensor QSP-2200PD is used to convert factory calibration coefficients to calibration coefficients in units used by the onboard computers. The factory calibration offset is applied to the data to achieve "zero" readings. The operation of the sensor is checked at the beginning of each survey day on deck capped (dark) and against the Biospherical QSR-240 surface irradiance sensor. The values from the QSP-2200PD sensor should be close to zero for the dark reading and approximately 40-50% higher than the surface irradiance sensor for the uncovered reading on deck. The difference in the readings between the two sensors is caused by field-of-view differences and a correction factor is applied to the underwater sensor to account for its lower collection efficiency when immersed. Calibration data are stored in the field equipment files (initial) or the survey log (daily survey check). The capped readings will be entered into the NavSam[®] calibration coefficient entry form as an offset, which will bring the on deck dark readings close to zero.

If it is clear that the instrument calibration has drifted over time and the factory calibration is no longer appropriate, deep profile readings may be used to determine a new calibration offset. These values could also be subtracted during data processing to remove any small zero offset remaining after applying the factory calibration coefficients for previous surveys. Following identification of this problem, the sensor will be returned to the manufacturer for maintenance and recalibration.

The Battelle Instrument History sheet and the factory calibration sheets along with records of periodic checks are maintained in the field equipment files.

The QSP-2200PD will be rinsed with deionized water after use. A qualified technician will conduct maintenance. The protective cap will be installed after the irradiance collector has dried. In addition, the o-rings should be replaced yearly when the instrument is returned to the manufacturer for calibration. Although its casing is robust, the sensor sphere of the underwater sensor is as delicate as that of the surface light sensor.

B.6.1.8 NAVIGATION EQUIPMENT

Once the Furuno GP33 or Northstar 941-XD dGPS Navigation System has been switched on, there is typically no other setup interaction necessary between the NavSam[®] operator and the navigation system. The dGPS will also conduct an automatic self-test. The dGPS will display a latitude-longitude (L/L) position once the system has acquired an acceptable fix. The dGPS system guarantees position accuracy on the order of 2-5 meters 50% of the time, and to 10 meters 95% of the time.

Position checks will be performed twice per day (start and end of survey operations) as follows:

1. An absolute position is obtained for a land-based calibration point (published positions or repeat visits with multiple dGPS readings). Alternatively, if a land-based calibration point is not available and a second dGPS is available, the coordinates from the second dGPS can be used for the absolute position.
2. The NavSam[®] program is set to calibration-navigation mode.
3. Thirty fixes are obtained by the program, averaged, and then compared to the absolute position entered by the operator.
4. If a printer is connected to the system, a printout of the calibration is obtained. Otherwise, NavSam[®] will save a screen capture to the program files directory.

B.6.1.9 ROSETTE SAMPLING BOTTLES

The Rosette sampling bottles are maintained by conducting annual functional checkouts including replacing worn, damaged components. During the surveys, the bottles are closed between stations. Just before arriving at a station, the bottles are opened and their release cords attached to the Rosette mechanism. The bottles are "cleaned" during the downcast by the flushing of sample water through the bottles. The bottles are closed by the NavSam[®] operator at appropriate depths during the upcast.

B.6.1.10 NETS AND FLOWMETER

All nets used for zooplankton tows and the flowmeter will be rinsed with fresh water and inspected for damage following each survey. If a flowmeter fails to produce expected results in the field, *i.e.*, readings appear lower than expected after a cast, it will be replaced using a back-up unit stored on the survey vessel.

B.7 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

The only laboratory instrument used for this program is the Radiometer Titralab models TIM860 and TIM840. These instruments are calibrated by the manufacture and serviced every two years. A certified titer solution (nominal 0.05N sodium thiosulfate) is used for the DO analysis. Calibration of field instrumentation is incorporated into the maintenance discussion of Section B.6. Calibration of DLS instruments is described in the MWRA DLS QAPP (Leo *et al.* 2011).

B.8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Prior to use, supplies and consumables will be inspected and tested to ensure that they conform to the required level of quality. Any defective material will be replaced before the sampling event or before analysis begins. Supplies and consumables consist of: sample containers, filters, filtration apparatus, preservation solutions (e.g., formalin, Lugol's solution), deionized water, laboratory reagents, and standards.

- Sample containers are either cleaned by the laboratory or purchased new. Containers must be cleaned according to SOPs prior to use and must be rinsed three times with station water prior to being filled with sample. Field blanks assess potential contamination of containers and sampling equipment.
- All filtering equipment (the filtering apparatus and graduated cylinders) are cleaned daily prior to use. The equipment gets a 10% HCl rinse in the morning followed by a triple rinse of Milli-Q water. Between stations the equipment gets a triple rinse with Milli-Q.

- Filters for chlorophyll and dissolved nutrients are used directly from the manufacturer and are not cleaned or treated. Filters for particulate carbon and nitrogen are precombusted and supplied by MWRA.
- Preservation solutions must be prepared using at least reagent grade chemicals and HPLC grade solvents. Solutions must be assigned an expiration date of 1 year.
- Milli-Q water must be collected into cleaned containers and refreshed prior to each survey.
- Laboratory reagents must be at least reagent grade. Dry reagents must be assigned an expiration date of no more than 5 years; be stored in a clean, desiccated environment, away from light, and be traceable to receipt and certificate of analysis. Reagent solutions must be assigned an expiration date of no more than 1 year and be stored appropriately. Each laboratory must maintain a chemical tracking inventory.
- Laboratory certified solutions (e.g. DO titer – 0.05N solution of sodium thiosulfate) must be certified as at least 96% pure or the lot-specific analysis purity (e.g. DO 0.05N titer comes with Certificate of Analysis) be incorporated into all calculations. Certified solutions must be assigned an expiration date “as received” based on the manufacturer’s expiration date, or a date consistent with laboratory SOPs.

B.9 NONDIRECT MEASUREMENTS

The HOM9 monitoring program utilizes data from previous programs, other Massachusetts Bay monitoring programs, satellite imagery and mooring data, in order to continually assess the state of Boston Harbor and Massachusetts Bay. These secondary data are used “as received” and not censored.

B.10 DATA MANAGEMENT (TASK 4)

Figure B-11 illustrates the water-column-monitoring data processing strategy for data entry into the MWRA EM&MS and accessing the data for various reports. The data from the program will be compared by MWRA to the caution and warning threshold parameters included in the MWRA Contingency Plan (MWRA 2001).

B.10.1 DATA REDUCTION

B.10.1.1 HYDROGRAPHIC AND NAVIGATION DATA

The hydrographic data generated during the survey consists of rapidly sampled, high-resolution measurements of conductivity, temperature, depth, DO, fluorescence, transmissometry, underwater light levels, total incident radiation, and bathymetry. The BOSS data-acquisition software assigns a unique data filename to each vertical profile made during the survey. All data will be electronically logged with date, time, and concurrent vessel-position data. In the field, in real time, Battelle’s NavSam[®] software converts the raw sensor analog signals into engineering units using instrument calibration coefficients. Salinity and density are calculated from temperature, conductivity and depth using the equations of Fofonoff and Millard (1983), and DO percent saturation is calculated from DO concentration, temperature, and salinity using the equations of Weiss (1970). The station arrival time is marked as an event in NavSam[®] upon arrival at the station.

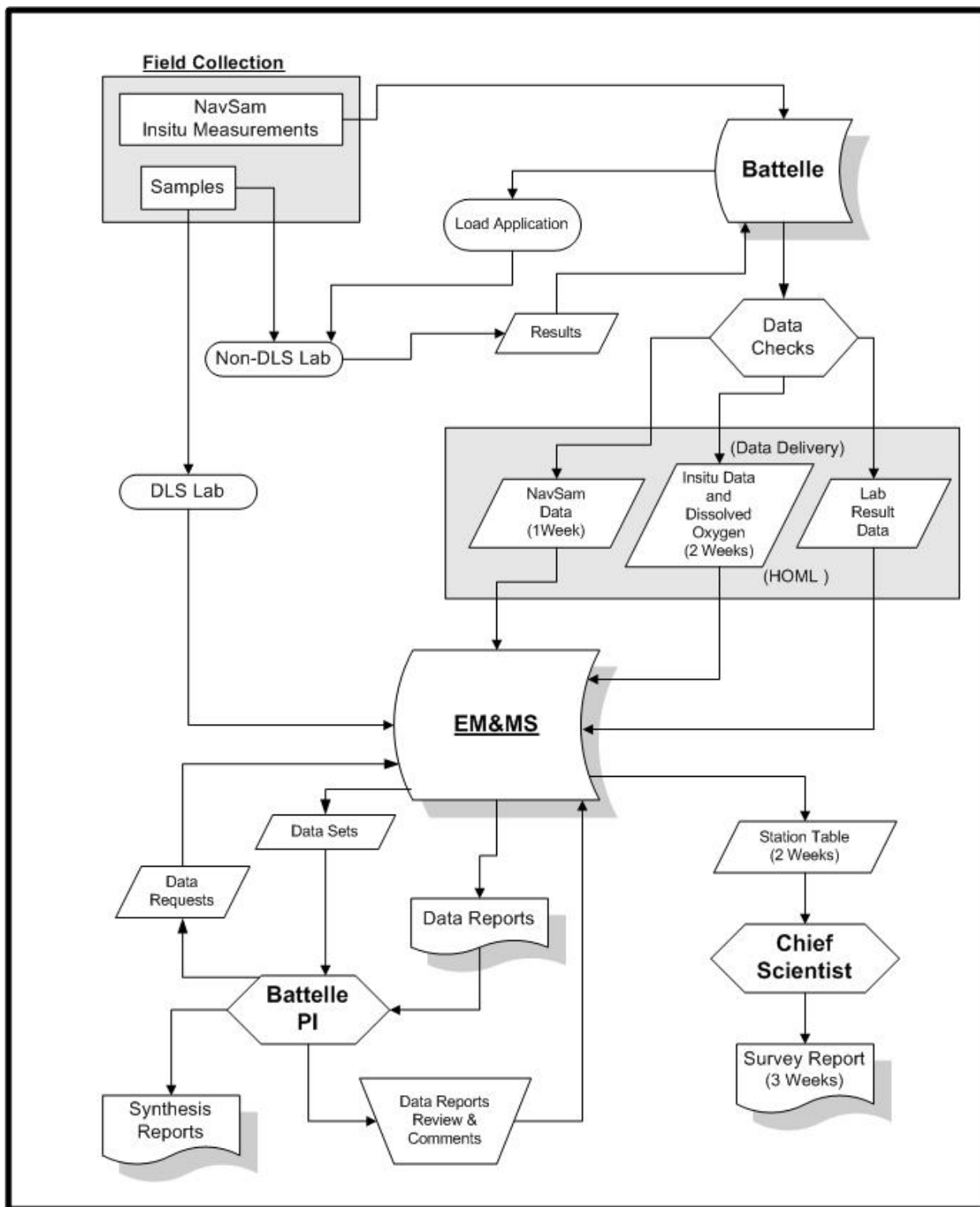


Figure B-11. Overview of the Data Management Strategy for Water Column Monitoring

NavSam[®] records both the raw and calibrated data. During data reduction, NavSam[®]'s post-processing module or another method will be used to visually review the profiles and mark any data as bad or suspect as appropriate. (If an alternative method is used, it will be documented in the deliverable letter submitted with the Oracle[®] export). After the editing is complete, the profile upcast data recorded during discrete water sample collection will be processed. NavSam[®] post-processing will result in two tables. The first will contain the downcast data that excludes the ship's upward motions and is averaged to 0.5-m depth bins. The second table will average the upcast data corresponding to discrete samples (data within ± 2.5 seconds of the moment of bottle closing). These files will serve as the export file to the EM&MS database.

Prior to 2010 Battelle corrected the raw irradiance with a lookup algorithm: let the corrected irradiance at depth i equal the raw irradiance at depth j , where depth j is just greater than depth i plus the vertical offset. Starting in 2010 Battelle applied the offset in Oracle[®] following the averaging steps. The new method gives a smoother light profile and no loss of data near the surface. Project-specific MWRA SOP 001: *Post-Survey CTD Water Column Data Processing* describes these procedures.

B.10.1.2 LABORATORY DATA

Data reduction procedures and formulae are defined in laboratory SOPs. All laboratory data will be either electronically transferred from the instrument or manually read from the instrument display (or optical field of a microscope) and entered into a loading application or appropriate database formats (see DLS exception below) provided by the Battelle Data Management Team. Data in laboratory notebooks will be manually entered into the loading application. All data reduction will be performed electronically either by the instrument software or in a spreadsheet and will be validated according to procedures described in Section D.2. The format for final data submission is described below. DLS will report only the first laboratory replicate. All field replicates will be reported as individual sample values.

Calculation of Dissolved Oxygen

The concentration of DO in units of ($\text{mg O}_2 \text{ L}^{-1}$) will be determined using the following equation:

$$\text{DO} = \frac{A F}{V}$$

where: A = Volume of titrant in (mL)

V = Volume of DO sample (mL; based on measured bottle capacity)

F = Factor based on standardization of thiosulfate titrant against a potassium iodate standard of known molarity.

B.10.2 REPORTING DATA TO BE LOADED INTO THE DATABASE

All field and non-DLS laboratory data to be loaded into the EM&MS will be submitted to Battelle in electronic format. The field data collection will be available for data loading directly off the ship. The laboratories will be supplied a loading application based on collection data that will increase data quality and data flow efficiency. These applications eliminate the need for data reporting formats and deliver many of the QC checks upstream to the laboratories. Formats for delivering electronic data are included in the contract but these formats are subject to change. The current delivery formats are available from the data management lead at Battelle (Greg Lescarbeau) or the data management lead at MWRA (Wendy Leo). Battelle's data management staff will process all data into the appropriate HOML format as defined in the contract. These submissions will be delivered electronically through MWRA's HOML Web application.

B.10.2.1 NAVIGATION AND SAMPLE COLLECTION DATA

Navigation and sample collection data will be processed on-board the survey vessel and be ready for loading upon arrival at Battelle. A database application developed as part of the NavSam[®] system will query the on-board database tables for the fields necessary to populate the *Event*, *Station*, *Sample* and *Bottle* tables. The data will be submitted to EM&MS in the HOML format. All database constraints developed by MWRA will be applied to the tables so that the data are checked during the insert. The loading of sample collection data is detailed in MWRA SOP 001: *Post-Survey CTD Water Column Data Processing*.

B.10.2.2 HYDROGRAPHIC DATA

Battelle will submit to EM&MS the following two types of data collected with the BOSS sensor package:

- Date, time, location, and factory calibrated sensor data associated with each water sample (upcast data). Dissolved oxygen and fluorescence is calibrated by MWRA based upon laboratory results.
- Date, time, location, and factory calibrated vertical profile sensor data that has been bin-averaged into 0.5-m bins (downcast data). Dissolved oxygen and fluorescence is calibrated by MWRA based upon laboratory results.

A database application will be used to load the hydrographic data from the processing database directly into Battelle’s database. Table B-10 shows the database codes for the hydrographic parameters. Database constraints will be in place to provide an initial check of the data integrity and validity.

Table B-10. Database Codes for Hydrographic Parameters

Parameter	Param_Code	Unit_Code	Instr_Code ¹	Meth_Code
Conductivity	CONDTVY	mS/cm	SB4_(Serial Number)	BOSS
Raw dissolved oxygen (not calibrated)	DO_RAW	mg/L	DO3_(Serial Number)	BOSS
Raw fluorescence (not calibrated)	FLU_RAW	ug/L	WS_(Serial Number)	BOSS
<i>in situ</i> Irradiance level	LIGHT	uEm-2sec-1	LIG4_(Serial Number)	BOSS
Salinity	SAL	PSU	SB4_(Serial Number)	BOSS
Density as measured by sigma-t	SIGMA_T		SB4_(Serial Number)	BOSS
Surface irradiance level	SURFACE_IRRAD	uEm-2sec-1	LIG2_(Serial Number)	BOSS
Temperature	TEMP	C	SB3_(Serial Number)	BOSS
Transmissometry	TRANS	m-1	T1R25_(Serial Number)	BOSS
Dissolved oxygen percent saturation (from uncalibrated probe)	PCT_SAT_RAW	PCT	DO3_(Serial Number)	BOSS

¹ Instrument codes: (*Serial Number*) indicates unique probe serial number; in the case of DO_3, the membrane thickness may also be included for instrument serial number 448

B.10.2.3 ANALYTICAL AND EXPERIMENTAL DATA

The data reporting for analytical and experimental data begins with the Battelle Data Management Team who will populate a loading application that is then sent to each non-DLS laboratory for their data entry. As defined above, the collection data from field activities are delivered to the data manager as an Access database. Sample Ids and analysis protocols are extracted from this database and used to populate a table within the laboratory loading application. A separate loading application is prepared for each data deliverable. Data contributors open the database and are presented with a form that already contains the Sample Ids and analyte list for their data submittal (Figure B-12). The laboratory enters the results and other supporting information such as qualifiers. All entries are constrained by the rules of EM&MS.

Errors are caught on entry and fixed by the data contributor. Primary keys are in place so duplication cannot occur. Entry applications are developed on an individual laboratory basis. Laboratory staff receive one day of training on the application prior to their first set of samples. When data entry is complete, the loading application is sent back to Battelle.

The loading application provides the laboratory many available functions (Figure B-13), including hardcopy report, QC checks, exception report, and analysis summary. The hardcopy report function allows the laboratory to create a hardcopy report to check for entry errors and to submit a final report to Battelle with the data deliverable. The QC checks are comprised of the applicable sections of EM&MS check and constraints scripts and also checks for outliers. This report gives the data contributor a chance to confirm the reasonableness of their data prior to submission to Battelle. The exception report checks the data that were expected against the results loaded. The data contributor must account for any entries in the exception report. The analysis report produces a report of the number of analyses by analyte. A copy of this report is included with the data deliverable and with the invoice for the analyses.

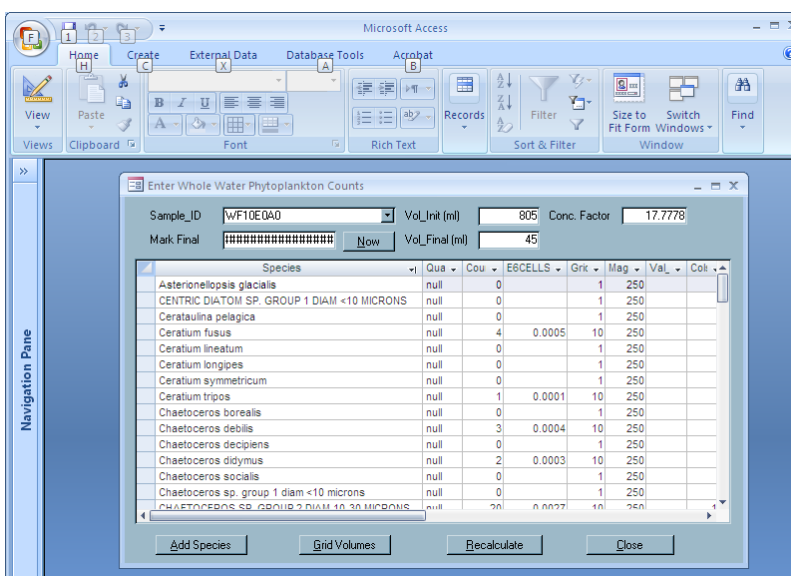


Figure B-12. Example of Loading Application Data Entry Form

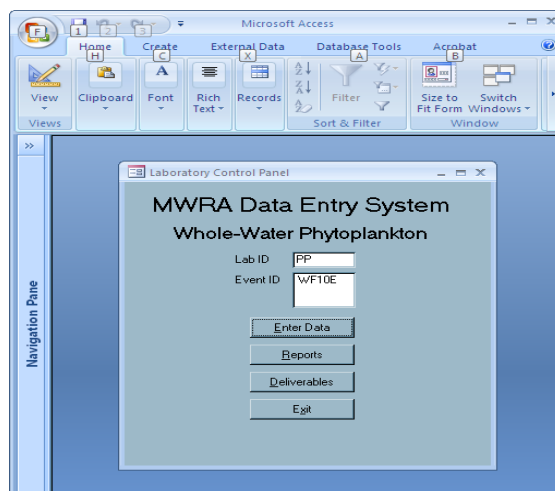


Figure B-13. Loading Application Main Menu

Within the loading application, the data entered by the laboratory are translated into the correct codes and inserted into database tables with the same structure as the matching EM&MS table. Table B-11 shows the qualifiers to be used by the laboratory. Database codes for plankton taxonomy and species qualifiers are presented in Table B-12 and Table B-13, respectively.

Table B-14 shows the analytical parameters, codes, and units of measure for the laboratory analysis (DO) performed under this task. Database code descriptions are provided in Table B-15. The laboratory will have the ability to add additional codes to describe their results but the new qualifiers will be highlighted in the exception report. Battelle will notify MWRA concerning the new qualifier and will adjust the code table in the application to agree with any changes to the EM&MS code list table. MWRA has the responsibility for maintaining the code list for the EM&MS. A laboratory submission is not accepted as complete unless it includes the QA statement, QA/QC corrective action log, electronic data, hardcopy data report, exceptions report, and analysis summary. Processing of laboratory data is further described in MWRA SOP 004, *Loading and Reporting Water Column Data*.

Table B-11. Laboratory Qualifiers

Qualifier	Description	Value Reported?
	Value is not qualified	Yes
A	Value above maximum detection limit, e.g. too numerous to count or beyond range of instrument	Yes
a	Not detected - value reported as negative or null	No, may be a negative
b	Not blank corrected, blank $\geq 5x$ MDL	Yes
c	Ambient	Yes
d	Accuracy does not meet data quality objectives	Yes
E	Calibration level exceeded	Yes
e	Results not reported, value given is NULL, see comments field	No
f	Value reported $<MDL$	Yes
g	Recovery outside DQO	Yes
h	Reported value is extrapolated beyond the standard curve	Yes
j	Estimated value	Yes
L	Analytical concentration reported from dilution	Yes
o	Value out of normal range judged fit for use by principal investigator	Yes
P	Present but uncountable, value given is NULL	Yes
p	Lab sample bottles mislabeled - caution data use	Yes
q	Possibly suspect/invalid and not fit for use. Investigation pending.	Yes
R	Outlier data point not used in calibration regression or curve fit	Yes
r	Precision does not meet data quality objectives	Yes
s	Suspect/Invalid. Not fit for use	Yes
T	Holding time exceeded	Yes
v	Arithmetic mean	Yes
w	This datum should be used with caution, see comment field	Yes

B.10.3 LOADING ANALYTICAL AND EXPERIMENTAL DATA INTO THE EM&MS DATABASE

Data submissions from the laboratories are the final loading applications. The submissions are logged in upon receipt and a copy is maintained on file under the login id. Data are loaded into a temporary table space using queries in the application. A transfer script will copy the data into the proper table(s) in Battelle's database. Data loading from the laboratories receive a QA review prior to electronic submission to MWRA. Any issues are corrected in the database will be well-documented in a script that is available to MWRA upon request. A check script will be run on the database prior to export of a dataset to ensure that all data conform to QC checks and database constraints. Project-specific SOP MWRA 004 *Loading and Reporting Water Column Data* describes these procedures.

B.10.4 REPORTING DATA TO MWRA

The data associated with each water column survey will be submitted to MWRA in the appropriate HOML format via their HOML Web application. Additional QA checks are conducted on these data through steps that are part of the HOML Web loading process. The supporting documentation files are included with the data submission letter. Data deliverables will be combined only with permission from MWRA.

Table B-12. Database Codes for Plankton Taxonomy

Plankton Analysis	Unit_Code	Meth_Code	Anal_Lab_ID
Whole-Water Phytoplankton	E6CELLS/L	COU_WW	PP
<i>Alexandrium fundyense</i>	CELLS/L	NA1	WHO6
Zooplankton	ind/m3	COU_ZO	UMD

Table B-13. Database Codes for Species Qualifiers

Qualifier	Description
A	Adult (not sexed)
B	Cyst
C	Copepodites
F	Female
K	Colonial species, not counted individually
L	Larvae
M	Male
N	Nauplii
O	Ova
S	Spores
T	Trochophore
V	Veliger
Y	Cyprids
Z	Zoea
null	No value, used as a place holder for a key field

Table B-14. Database Codes for Chemistry Analytical and Experimental Parameters

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Dissolved Oxygen	DISS_OXYGEN	mg/L	BOS	RTL	OUD88

Table B-15. Description of Database Codes

Field_Name	Code	Description
ANAL_LAB_ID	BOS	Battelle Ocean Sciences, Duxbury, MA
ANAL_LAB_ID	DIL	MWRA Department of Laboratory Services, Winthrop, MA
ANAL_LAB_ID	UMD	University of Massachusetts, Dartmouth, MA
ANAL_LAB_ID	PP	Pausacaco Plankton, Saunderstown, RI
ANAL_LAB_ID	WHO6	Woods Hole Oceanographic, Woods Hole, MA (D. Anderson)
DEPTH_UNIT_CODE	m	Meters
INSTR_CODE	DO3_(Serial Number)	Sea-Bird D.O. probe, model SBE-43
INSTR_CODE	LIG2	Biospherical model QSR-240 hemispherical scalar irradiance sensor
INSTR_CODE	LIG4	Biospherical Instruments QSP-2200PD: quantum scalar irradiance profiling sensor
INSTR_CODE	RTL	Radiometer TitraLab Titrator
INSTR_CODE	SB3_(Serial Number)	Sea-Bird temperature sensor, model SBE-3
INSTR_CODE	SB4_(Serial Number)	Sea-Bird conductivity sensor, model SBE-4C
INSTR_CODE	T1R25	WET Labs C-Star 25cm transmissometer 660 nm fixed wavelength
INSTR_CODE	TOC_1010	OI model 1010 TOC analyzer
INSTR_CODE	WS_(Serial Number)	WETStar miniature fluorometer, model ws-3-mf-p
METH_CODE	BOSS	Battelle Ocean Sampling System
METH_CODE	COU_WW	Enumeration method for whole-water phytoplankton (Libby <i>et al.</i> 2002)
METH_CODE	COU_ZO	Enumeration method for zooplankton (Libby <i>et al.</i> 2002)
METH_CODE	NA1	Enumeration of <i>Alexandrium</i> (Anderson <i>et al.</i> 2005)
METH_CODE	OUD88	Oudot <i>et al.</i> (1988)
SAMP_VOL_UNIT_CODE	L	Liter
UNIT_CODE	C	Degrees Celsius
UNIT_CODE	CELLS/L	Cells per liter
UNIT_CODE	db	Decibars
UNIT_CODE	E6CELLS/L	Millions of cells per liter
UNIT_CODE	ind/m3	Individuals per cubic meter
UNIT_CODE	m-1	Inverse meters
UNIT_CODE	mg/L	Milligrams per liter
UNIT_CODE	PSU	Practical salinity units
UNIT_CODE	uEm-2sec-1	Micro-Einsteins per square meter per second
UNIT_CODE	ug/L	Micrograms per liter
UNIT_CODE	mS/cm	Millisiemens per centimeter
UNIT_CODE	PCT	Percent

C ASSESSMENT AND OVERSIGHT

C.1 ASSESSMENTS AND RESPONSE ACTIONS

C.1.1 PERFORMANCE AND SYSTEM AUDITS

The Battelle QA Officer for the HOM9 Project is Ms. Rosanna Buhl. She will direct the conduct of at least one technical systems audit (TSA) to ensure that Tasks 4, 5, 6, and 7 are carried out in accordance with this QAPP. A systems audit will verify the implementation of the Quality Management Plan and this QAPP for Water Quality monitoring.

Tabular data reported in deliverables, and associated raw data generated by Battelle will be audited under the direction of the Project QA Officer. Raw data will be reviewed for completeness and proper documentation. Errors noted in data audits will be communicated to analysts and corrected data will be verified.

Audits of the data collection procedures at each of the laboratories will be the responsibility of the laboratories. Each laboratory is fully responsible for the QA of the data it submits. Data must be submitted in QAPP-prescribed formats; no other formats will be acceptable. All data must be independently reviewed prior to submission to the Battelle Database Manager and must be accompanied by a signed QA statement (Appendix IV) that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality and a QC narrative of activities.

In addition to the TSA, the Battelle QA Officer will conduct laboratory and field inspections as needed to access compliance with the Quality Management Plan and this QAPP.

C.1.2 CORRECTIVE ACTION

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 HOM9 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. Mr. Scott Libby is the Battelle Technical Manager and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise.

Identification of problems and corrective action at the laboratory level (such as meeting data quality requirements) will be resolved by laboratory staff or by laboratory managers (see Figure A-1). Issues that affect schedule, cost, or performance of the water-column monitoring tasks will be reported to the Battelle Project Manager. Battelle's Technical Manager will be notified of any issues affecting data quality. The Technical Manager and task leaders will be responsible for addressing these issues and, with the Project Manager, will be responsible for evaluating the overall impact of the problem on the project and for discussing corrective actions with the MWRA Project Management. Systematic problems identified during audits, inspections, or by project staff will be entered into the Corrective Action Logger, assigned to appropriate staff for root cause analysis, and tracked by the QA officer.

C.2 REPORTS TO MANAGEMENT

It is important that data quality issues be reported to the appropriate management level so that appropriate solutions are implemented. Data or performance quality issues are reported to Battelle management team

in real time via email. Action items are discussed, assigned, and results reported to the QA Officer. Persistent project issues that are not addressed satisfactorily by the project manager are reported to Battelle's Energy & Environment Deputy General Manager during QA review meetings. In addition, data quality and performance issues are reported in the corrective action log submitted to MWRA each quarter and are discussed during the monthly management meetings, as necessary.

D DATA VALIDATION AND USABILITY

D.1 DATA REVIEW, VERIFICATION, AND VALIDATION

It is a requirement of this project that all data be reviewed, verified, and validated prior to and after entry into the EM&MS database. The measurement quality objectives, sensitivity requirements, and monitoring thresholds are used to accept, reject, or qualify the environmental monitoring data generated for this project.

D.2 VALIDATION AND VERIFICATION METHODS

Data verification and validation procedures are used throughout the data collection, analysis, and reporting process to assess data quality.

Field sampling data are verified through the chain-of-custody process that compares NavSam[®] Bottle IDs to sample bottle labels. Sampling documentation is verified through the review and approval of each survey log book by the field manager. Entry of field sample data in EM&MS is verified when the QA Officer audits the survey report vs. the survey log book documentation.

Laboratory data are verified through internal audits of calibration, analysis, and sample results. The results of these audits are documented in QA Statements that are submitted with each data set. Each laboratory is responsible for the quality of their data. At a minimum, the following verification requirements must be incorporated into laboratory data reviews.

- Any data that are hand-entered (i.e., typed) are verified by qualified personnel prior to use in calculations or entry into the database.
- All manual calculations are performed by a second staff member to verify that calculations are accurate and appropriate. For data submitted from DLS, only 20% of manual calculations are verified by a second staff member.
- Calculations performed by software are verified at a frequency sufficient to ensure that the formulas are correct, appropriate, and consistent, and that calculations are accurately reported. All modifications to data reduction algorithms are verified prior to submission of data to MWRA.

Data validation is performed by reviewing holding times, instrument calibration results, and QC sample results. The criteria for these data quality requirements are presented in Sections A.7, B.5, B.6, B.7, and B.8. Data qualifiers (Table B-11) and comments are used to define in the database the usability of the data.

D.3 RECONCILIATION WITH USER REQUIREMENTS

Several procedures are used to assess the usability of the data. During generation of the data reports, MWRA will run QC Checks of the EM&MS database to assess data reasonableness and identify outliers. Electronic submissions are loaded to temporary files prior to incorporation into the database, and are analyzed selectively using methods such as scatter plots, univariate and multivariate analyses, and range checks to identify suspect values.

Once data have been generated and compiled in the laboratory, senior project scientists review data to identify and make professional judgments about any suspicious values. All suspect data are reported with a qualifier and appropriate comment. These data may not be used in calculations or data summaries without the review and approval of a knowledgeable Senior Scientist. No data measurements are eliminated from the reported data or database and data gaps are never filled based on other existing data.

If samples are lost during shipment or analysis, it is documented in the data qualifiers and comments submitted to MWRA and maintained in the database.

Final data reports submitted by MWRA will be reviewed by the Technical Manager (Mr. Scott Libby) and a data report review letter will be sent to MWRA.

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- Battelle SOP 5-280: *Phytoplankton and Zooplankton Sample Collection*. 2009.
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Appendix I

MWRA SOPs

Appendix I MWRA Standard Operating Procedures

MWRA has provided electronic copies of the following MWRA SOPs referenced in this document.

SOP-01 Calculation method for threshold values for *Alexandrium*

SOP-08 Calculation methods for annual and seasonal threshold values and baselines for chlorophyll

SOP-16 Calculation method for water column bottom dissolved oxygen depletion rate threshold

SOP-17 Calculation method for water column bottom dissolved oxygen threshold

SOP-27 Calculation methods for seasonal threshold values for *Phaeocystis pouchetii* and *Pseudonitzschia* multiseries

Appendix II

Battelle SOPs

Appendix II

Battelle Standard Operating Procedures

MWRA SOP 001: Post-Survey CTD Water Column Data Processing

MWRA SOP 004: Loading and Reporting Water Column Data

MWRA SOP 008: Integrating MWRA Client ID Numbers into the NavSam[®] Survey Database

SOP 3-118: Northstar 941XD and 952XDW Differential GPS Navigation System

SOP 3-127: Biospherical Irradiance Sensors

SOP 3-129: Operation of the Furuno FCV-582 Color Video Sounder

SOP 3-163: WETStar Fluorometer

SOP 3-174: Operation and Maintenance of the WET Labs C-Star Transmissometer

SOP 3-180: Sea-Bird Electronics Model 43 Dissolved Oxygen Sensor

SOP 3-183: Sea-Bird Electronics SBE-25 Sealogger CTD System

SOP 5-266: Nutrient Sample Processing

SOP 5-275: At Sea Collection of Hydrographic Data using CTD and Rosette System

SOP 5-280: Phytoplankton and Zooplankton Sample Collection

SOP 5-317: Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method
Using the Radiometer Titralab TIM860 and TIM840

SOP 6-029: Survey Set-up and Sample Tracking Using NavSam[®] Software

SOP 6-040 Sample Custody, Receipt, and Handling for Field Activities

SOP 6-043: Preparation, Distribution, and Implementation of Field Survey Plans

Electronic copies of the Battelle SOPs referenced in this document have been provided to MWRA
with the Draft QAPP.

Appendix III

Water Column Survey
Sample Collection Requirements

Appendix IV
QA Statements

MWRA HOM9

Project Task Number/Title: Task 4 Alexandrium

Event of Data Set or Deliverable: #####

Quality Assurance Statement

I. Description of Audit and Review Activities:

II. Accuracy:

	1. Custody of All samples were transferred properly and maintained except as described in part IV.
	2. All of the samples on the COC were received and all required test performed except as described in part IV.
	3. QC samples and calibration standards were analyzed according to the QAPP and the acceptance criteria were met. Corrective action for exceedences was taken.
	4. Samples were analyzed according to the procedures specified in the QAPP.
	5. 100% hand-entered and/or calculated data were checked for accuracy.
	6. Calculations performed by software are verified at a frequency sufficient to ensure that the formulas are correct, appropriate, and consistent.
	7. For each cut and paste function, the first and last data value was verified vs. the source data.
	8. Data are reported in the units specified in the QAPP.
	9. Qualifiers are assigned properly. Distinguish between suspect (s) – reported, but not used in calculations, and error (e) – data unavailable due to instrument failure or sample loss.
	10. Results of QC data and activities defined in QAPP Section B.5.6 are attached and relative percent differences calculated

III. Completeness:

	11. All samples received are reported.
	12. All parameters specified in the QAPP for this task are reported.

IV. Description of outstanding issues or deficiencies noted above that may affect data quality.

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Alexandrium

Event of Data Set or Deliverable: #####

QA/QC Corrective Action Log

Date of Occurrence	Description of Activity or Problem	Description of Corrective Action (Initial and Ultimate)	Status of Corrective Action/Date Complete

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Dissolved Oxygen

Event of Data Set or Deliverable: #####

Quality Assurance Statement

V. Description of Audit and Review Activities:

VI. Accuracy:

	1. Custody of All samples were transferred properly and maintained except as described in part IV.
	2. All of the samples on the COC were received and all required test performed except as described in part IV.
	3. QC samples were analyzed according to the QAPP and the acceptance criteria were met.
	4. QC data with DQO calculated is in data package. Corrective action for exceedences was taken and documented in package.
	5. Samples were analyzed according to the procedures specified in the QAPP.
	6. 100% hand-entered and/or calculated data were checked for accuracy.
	7. For each cut and paste function, the first and last data value was verified vs. the source data.
	8. Data are reported in the units specified in the QAPP.
	9. Qualifiers are assigned properly. (a = number < 0, e= data not available, s= suspect data, T= did not meet 24 hr holding time)
	10. All data recorded on the raw data sheets matches the data saved in the TIM860 or TIM840.

VII. Completeness:

	11. All samples received are reported.
	12. All parameters specified in the QAPP for this task are reported.
	13. All documentation is present: Laboratory Data Report for DO Analysis Lab Deliverables Raw Data Sheets Mean Titer Form Chain of Custody QA/QC Misc. Doc. Signature Page

VIII. Description of outstanding issues or deficiencies noted above that may affect data quality.

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Hydrographic Data

Event of Data Set or Deliverable: #####

Quality Assurance Statement

I. Description of Audit and Review Activities:

The data set was reviewed by the project physical oceanographer after processing as prescribed in SOP MWRA-001.

II. Accuracy:

	1. Instrument calibration coefficient files checked.
	2. Irradiance data depth offset checked.
	3. Profiles plotted and spikes, noise, and shadows marked and removed.
	4. Profiles reviewed for reasonableness.
	5. Summary table generated.
	6. Summary tables reviewed for reasonableness.
	7. Qualifiers are assigned properly where necessary.
	8. Corrective action taken for any data deemed outside reasonable range (source of error investigated).
	9. Samples were analyzed in accordance to the procedures specified in the QAPP and applicable SOPs except as described in part IV.
	10. 100% of hand-entered and/or calculated data were checked for accuracy except as in part IV.
	11. Data are reported in the units specified in the QAPP.

III. Completeness

	12. All samples received are reported.
	13. All parameters specified in the QAPP for this task are reported.

IV. Description of outstanding issues or deficiencies noted above that may affect data quality.

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Whole-Water Phytoplankton

Event of Data Set or Deliverable: #####

Quality Assurance Statement

IX. Description of Audit and Review Activities:

X. Accuracy:

	1. Custody of All samples were transferred properly and maintained except as described in part IV.
	2. All of the samples on the COC were received and all required test performed except as described in part IV.
	3. QC samples and calibration standards were analyzed according to the QAPP and the acceptance criteria were met. Corrective action for exceedences was taken.
	4. Samples were analyzed according to the procedures specified in the QAPP.
	5. 100% hand-entered and/or calculated data were checked for accuracy.
	6. Calculations performed by software are verified at a frequency sufficient to ensure that the formulas are correct, appropriate, and consistent.
	7. For each cut and paste function, the first and last data value was verified vs. the source data.
	8. Data are reported in the units specified in the QAPP.
	9. Qualifiers are assigned properly. Distinguish between suspect (s) – reported, but not used in calculations, and error (e) – data unavailable due to instrument failure or sample loss.
	10. Results of QC data and activities defined in QAPP Section B.5.6 are attached and percent differences or recoveries calculated

XI. Completeness:

	11. All samples received are reported.
	12. All parameters specified in the QAPP for this task are reported.

XII. Description of outstanding issues or deficiencies noted above that may affect data quality.

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Whole-Water Phytoplankton

Event of Data Set or Deliverable: #####

QA/QC Corrective Action Log

Date of Occurrence	Description of Activity or Problem	Description of Corrective Action (Initial and Ultimate)	Status of Corrective Action/Date Complete

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Zooplankton

Event of Data Set or Deliverable: #####

Quality Assurance Statement

XIII. Description of Audit and Review Activities:

XIV. Accuracy:

	13. Custody of All samples were transferred properly and maintained except as described in part IV.
	14. All of the samples on the COC were received and all required test performed except as described in part IV.
	15. QC samples and calibration standards were analyzed according to the QAPP and the acceptance criteria were met. Corrective action for exceedences was taken.
	16. Samples were analyzed according to the procedures specified in the QAPP.
	17. 100% hand-entered and/or calculated data were checked for accuracy.
	18. Calculations performed by software are verified at a frequency sufficient to ensure that the formulas are correct, appropriate, and consistent.
	19. For each cut and paste function, the first and last data value was verified vs. the source data.
	20. Data are reported in the units specified in the QAPP.
	21. Qualifiers are assigned properly. Distinguish between suspect (s) – reported, but not used in calculations, and error (e) – data unavailable due to instrument failure or sample loss.
	22. Results of QC data and activities defined in QAPP Section B.5.6 are attached and percent differences or recoveries calculated

XV. Completeness:

	23. All samples received are reported.
	24. All parameters specified in the QAPP for this task are reported.

XVI. Description of outstanding issues or deficiencies noted above that may affect data quality.

Signature of Reviewer/Date

Signature of Task Leader/Date

MWRA HOM9

Project Task Number/Title: Task 4 Zooplankton

Event of Data Set or Deliverable: #####

QA/QC Corrective Action Log

Date of Occurrence	Description of Activity or Problem	Description of Corrective Action (Initial and Ultimate)	Status of Corrective Action/Date Complete

Signature of Reviewer/Date

Signature of Task Leader/Date

ADDENDUM number 1
to the

**FINAL QUALITY ASSURANCE PROJECT PLAN FOR
WATER COLUMN MONITORING 2014-2016
Tasks 4, 5, 6, 7, 10**

MWRA Harbor and Outfall Monitoring Project

Prepared for:

**MASSACHUSETTS WATER RESOURCES AUTHORITY
Environmental Quality Department
100 First Avenue
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Prepared by:

**Mr. Scott Libby
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Ms. Rosanna Buhl**

**Battelle
Norwell, MA 02061**

**Contract No. OP216A
Task 8 Task Order 7
Project No. 100041494**

July 28, 2016

ADDENDUM NUMBER 1
to the
FINAL QUALITY ASSURANCE PROJECT PLAN FOR
WATER COLUMN MONITORING 2014-2016
Tasks 4, 5, 6, 7, 10

MWRA Harbor and Outfall Monitoring Project
REVIEW AND APPROVALS

Signature on file
Ms. Ellen Baptiste-Carpenter
Battelle Project Manager

07-28-16
Date

Signature on file
Mr. Scott Libby
Battelle Technical Manager

07-28-16
Date

Signature on file
Ms. Rosanna Buhl
Battelle Project QA Officer

07-28-16
Date

Signature on file
Mr. Kenneth Keay
MWRA Project Manager

07-29-16
Date

Signature on file
Mr. Douglas Hersh
MWRA EM & MS Manager

08-01-16
Date

INTRODUCTION

The purpose of Addendum 1 to the Final Quality Assurance Project Plan (QAPP) for the Massachusetts Water Resources Authority (MWRA) is to describe one additional *in situ* measurement (pH) approved by MWRA for surveys remaining in 2016. This addendum is necessary to document the data quality objectives associated with this additional measurement.

All activities conducted for the MWRA Harbor and Outfall Monitoring study (HOM) must be conducted according to the requirements of the February 11, 2014 Final QAPP unless specifically modified by this addendum. This addendum must become an integral part of the Final QAPP by addition to the pdf version.

A.6 PROJECT/TASK DESCRIPTION

A pH sensor will be integrated with the current sensor suite to support the collection of *in situ* pH data during water column surveys WN167, WN168, and WN169.

A.7 QUALITY OBJECTIVES AND CRITERIA

Table A-1 of the final HOM9 QAPP is amended for the addition of pH measurements.

Table A-1 Addendum. Accuracy and Precision of Instrument Sensors

Sensor	Model	Units	Range	Accuracy	Precision
pH	SeaBird SBE-18	pH Engineering Units	0 - 14	± 0.1	± 0.1

A.7.3.3 Comparability

The *in situ* pH data collected using the SeaBird SBD-18 will be comparable to that of other hydrographic studies that use instruments of similar accuracy.

A.9.2.1 Quality Assurance Project Plan

This QAPP Addendum 01 describes the collection of pH data for MWRA's water column monitoring program to be conducted under MWRA Contract OP216A in August, September, and October 2016. The pH data will be included in the synthesis report prepared under Task 10.

B.1.3 HYDROCASTS AND SENSOR MEASUREMENTS

Section B.1.3 paragraph 1 is amended to read:

Hydrographic data will be collected at all water column stations. At each station, a hydrocast will be conducted with an underwater unit consisting of a conductivity–temperature–depth (CTD) system, various sensors (pH, dissolved oxygen, chlorophyll fluorescence, optical beam transmittance, light irradiance (PAR), and altimeter), and a water-sampling system equipped with up to twelve 9-L Rosette sampling bottles.

In situ pH will be collected at each of the 11 stations in Massachusetts Bay for surveys WN167, WN168, and WN169 as part of the hydrographic data collected during hydrocasts described in the final QAPP. Data from the pH sensor (both downcast and upcast) will be processed along with the other *in situ* parameters.

B.1.9 SCHEDULE OF ACTIVITIES AND DELIVERABLES

The following deliverable product(s) are related to the collection of *in situ* pH measurements:

Subtask 1: Task Order proposal and QAPP Addendum. The QAPP addendum will be submitted prior to conducting the August survey.

Subtask 2: Collection of pH data on surveys WN167, WN168, and WN169. Calibrated sensor and updated NavSam software will be deployed on survey WN167, pending return of recalibrated sensors from SeaBird. If the calibrated sensors are not available in time for survey WN167 in August, then measurements will begin in September on survey WN168. Schedule issues will be communicated as they become known.

Subtask 3: Delivery of the pH data along with the hydrographic data deliverable. Data processing changes will be completed within one week of WN167 to meet the deadline for delivery of hydrographic data.

Progress on the Task Order will be documented in the monthly progress report.

B.2.3 HYDROGRAPHIC PROFILES

One bullet is added to this section:

- Sea-Bird SBE-18 pH sensor will be mounted upright on the Rosette sampler (one Sea-Bird SBE-18 pH sensor will serve as back-up). A new cable will enable the SBE-18 to interface with the existing CTD.
- The pH data will be plotted along with the other *in situ* data in the NavSam display and reviewed in real-time during the CTD cast.

B.6.1.11 pH

The SBE-18 pH sensor is factory calibrated and sent to the manufacturer for maintenance and recalibration annually. A backup sensor is also calibrated and available should the primary sensor fail. The factory calibration uses precision buffer solutions (4, 7, and 10 pH \pm 0.02 pH) for calibration. The results are tabulated on a certificate furnished with each sensor. The pH probe is a sealed unit. At the end of each survey day, the sensor array is rinsed with deionized water and stored in the supplied soaker bottle attachment that prevents the reference electrode from drying out during storage.

B.10.1 DATA REDUCTION

Data from the pH sensor (both downcast and upcast) will be processed along with the other *in situ* parameters. Downcast data will be 0.5 meter bin averaged throughout the downcast, and 10 readings before and after closing the niskin bottles will be averaged to obtain an upcast reading. The lead sensor data processor will review the data for readings that are consistent with typically observed readings throughout Massachusetts Bay (pH values of 7.5 – 8.5). Erroneous data such as spikes and obvious data outliers will be removed from the raw data prior to data reduction and loading into the Battelle's copy of the EM&MS Oracle database.

- No changes to MWRA's code list will be necessary as the pH sensors are currently in the code list as S18_180177 and S18_180442.
- The process for loading hydrographic data via HOML will be unchanged by the addition of the pH data.

B.10.2.2 HYDROGRAPHIC DATA

Battelle will modify data loading routines to accept the new data stream. Any changes to the quality control checks that MWRA runs against EM&MS due to the addition of the pH data will be added to Battelle's processing to ensure compliance with the database business rules. The export routine to generate the HOML file will be updated. The hydrographic data including the pH data will be uploaded via HOML following current procedures.

C. ASSESSMENT AND OVERSIGHT

The Battelle QA Officer will review calibration records prior to the first use of the SBE-18 pH sensor.