# **Quality Assurance Project Plan (QAPP)**

for

# Water Column Monitoring Tasks 4-9 and 13

**Massachusetts Water Resources Authority** 

**Environmental Quality Department Report ENQUAD 2010-02** 



# QUALITY ASSURANCE PROJECT PLAN (QAPP)

for

WATER COLUMN MONITORING 2010 Tasks 4, 5, 6, 7, 8, 9, 13

**MWRA Harbor and Outfall Monitoring Project** 

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# A. PROJECT MANAGEMENT VERSION 0

#### A.1. TITLE AND APPROVALS

# QUALITY ASSURANCE PROJECT PLAN (QAPP)

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#### **MWRA Harbor and Outfall Monitoring Project**

#### Prepared by:

Battelle
Massachusetts Water Resources Authority
University of Rhode Island Graduate School of Oceanography
University of Massachusetts at Dartmouth
Pausacaco Plankton

March 9, 2010

#### **REVIEW AND APPROVALS**

Ms. Ellen Baptiste-Carpenter	Date
Battelle Project Manager	
Mr. Scott Libby	Date
Battelle Technical Manager	Date
Ms. Rosanna Buhl	Date
Battelle Project QA Officer	
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MWRA Water Column Project Area Manager	
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MWRA EM & MS Manager	

### Quality Assurance Project Plan REVISION HISTORY

Revision Number	Affected Section(s)	Effective Date	Summary of Changes	Approval (Initials/ Dates)

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## A.3. DISTRIBUTION LIST

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

NAME	DATE SENT
Michael Mickelson (MWRA)	
Ken Keay (MWRA)	
Maury Hall (MWRA)	
Wendy Leo (MWRA)	
Yong Lao (MWRA)	
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Scott Libby (Battelle)	
Jeff Turner (University of Massachusetts Dartmouth Campus; UMD)	
Candace Oviatt (University of Rhode Island; URI)	
David Borkman (Pausacaco Plankton)	

#### 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. Mike Mickelson is the Massachusetts Water Resources Authority (MWRA) Harbor and Outfall Monitoring (HOM) Project Manager and the MWRA Water Column Monitoring Technical Manager. He will be informed of all matters pertaining to work described in this Quality Assurance Project Plan (QAPP).

Mr. Ken Keay is the MWRA HOM Deputy Project Manager and will serve as a backup to Dr. Mickelson. Mr. Keay has primary administrative and budgetary oversight of the program.

Ms. Wendy Leo is the MWRA EM&MS Database Manager.

Dr. Andrea Rex is the Director of the MWRA Environmental Quality Department.

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.

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 is 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 activities conducted by Battelle for the project.

Ms. Deirdre Dahlen is Battelle's Laboratory Coordinator and is responsible for overseeing laboratory activities in the contract.

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.

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

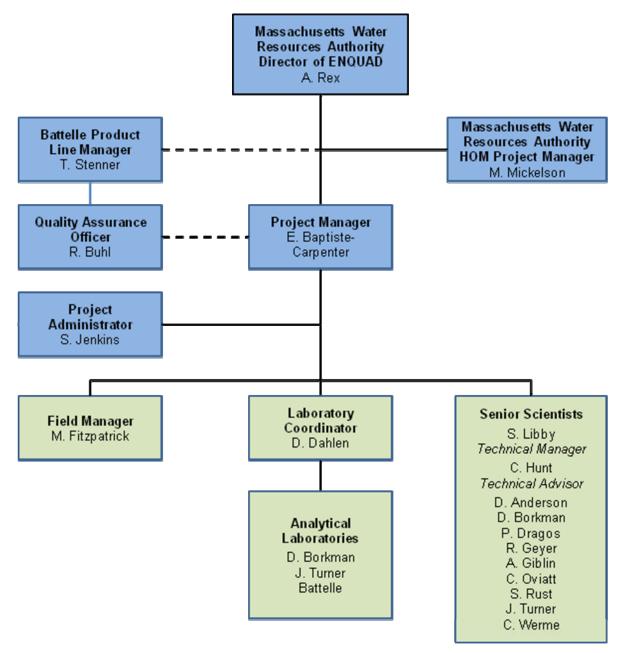


Figure A-1. Project Management Structure and Water Column Study Organization

#### A.5. PROBLEM DEFINITION/BACKGROUND

The Massachusetts Water Resources Authority (MWRA) has implemented a long-term marine environmental monitoring plan (MWRA 1991, 1997, 2004) 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/MDEP 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). On September 6, 2000 the program entered the outfall discharge monitoring phase designed to assess potential environmental impact of the effluent discharge into Massachusetts Bay, and evaluate compliance with the discharge permit.

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). Changes in physical water properties, nutrient concentrations, dissolved oxygen, phytoplankton biomass, and phytoplankton and zooplankton community composition in Massachusetts Bay and Cape Cod Bay will be monitored. To date no substantial change has been observed in the bays related to the outfall diversion (Libby et al. 2009a).

A comprehensive review of the data to date in June 2003 led to revisions, with concurrence from the Outfall Monitoring Science Advisory Panel and the EPA, to the Ambient Monitoring Plan that were first implemented in February 2004 (MWRA 2004). The most substantial changes to the water column monitoring program 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 Quality Assurance Project Plan (CWQAPP) for Water Column Monitoring: 2004 – 2005 and 2006 – 2007 (Libby *et al.* 2005, 2006). Currently, MWRA is operating the bay outfall under an expired permit (expired August 2005) and is required to follow the monitoring plan included in the August 2000 permit. Due to the delay in the new permit, MWRA has proposed another substantial change to the monitoring plan (MWRA 2009) and is awaiting concurrence from EPA. Battelle participated in the development of the proposed plan under HOM6 and anticipates modifying this QAPP as necessary once the changes are approved.

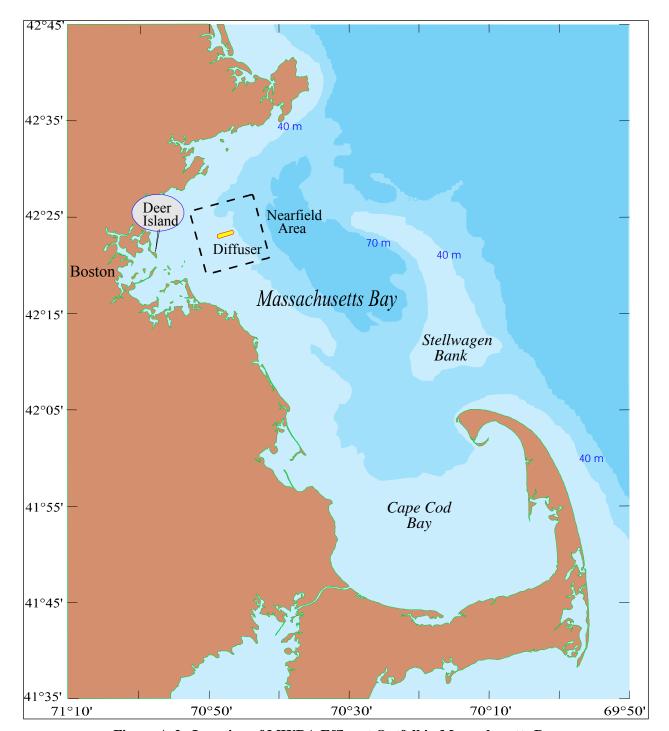


Figure A-2. Location of MWRA Effluent Outfall in Massachusetts Bay

#### A.6. PROJECT/TASK DESCRIPTION

The HOM Project water column surveys have been conducted since 1992 and are scheduled to continue through 2010. This QAPP describes activities specific to the six nearfield and six combined nearfield/farfield water column surveys of Massachusetts Bay and Cape Cod Bay scheduled to be conducted in 2010. 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, hydrographic and water quality parameters, nutrient concentrations, and metabolism will be measured. Phytoplankton and zooplankton communities will also be described. The study objectives are described below.

- Task 4 Data Management and Data Quality Control: 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 Nearfield Surveys:** Develop a three-dimensional picture of seasonal variability of water column properties in the Nearfield.
- Task 6 Farfield Surveys: Determine conditions in the water column throughout Massachusetts and Cape Cod Bays; 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; and compare water quality of Massachusetts and Cape Cod Bays.
- Task 7 Water Chemistry and Metabolism: Characterize the water quality by measuring concentrations of dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate), total dissolved organic nitrogen and phosphorous, dissolved organic carbon, particulate carbon and nitrogen, particulate phosphorous, biogenic silica, chlorophyll a and phaeopigments, total suspended solids (TSS), dissolved oxygen (DO), respiration, and primary productivity.
- Task 8 Plankton Taxonomy: Characterize the phytoplankton and zooplankton communities and describe changes in community structure.
- **Task 9 Buoy Servicing:** Provide a vessel as a stable platform for 2-5 people who will service Buoy 44103. Collect data and samples to collaborate buoy sensor data.
- **Task 13 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 HOM7 are defined by the outfall discharge permit (NPDES MA0103284. 1999) and the Contingency Plan thresholds which are based on permit limits. Threshold limits are described in a set of MWRA SOPs (Appendix III). The method detection limit (MDL) requirements are driven by these thresholds because it is imperative that analytical testing be sensitive enough to distinguish the parameters of concern both at and above background levels. In addition, the general contract conditions further define the accuracy and sensitivity of geospatial (GPS) instrumentation to ensure that sampling locations are within 300± 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	SeaBird SBE-29	decibars	0 to 1000	0.1%	0.1
Temperature	SeaBird SBE-3	°C	-5 to +35	0.001	0.01
Conductivity	SeaBird SBE-4	mS/cm	0 to 70	0.03	0.01
Dissolved Oxygen	SeaBird SBE-43	mg/L	0 to 15	0.50	0.05
Fluorometer (Chl a)	Wetlabs WetStar	μg/L	0.03 to 75	0.03	0.01
Transmissometer (20-	Wetlabs 25 cm C-star	m-1	0 to 40	0.20	0.01
cm) In situ irradiance	Biospherical QSP-2200PD	μE m-2 s-1	0.14 to 5000	10	1
On-Deck irradiance	Biospherical QSR-2240	μE m-2 s-1	0.14 to 5000	10	1
	<u> </u>		0-99.9		
Altimeter	Benthos PSA-916	M	0-99.9	0.1	0.025
Echosounder (depth)	Furuno 943	М	0 to 200	2	0.1
Navigation	North Star 952XDW (WAAS Capable)	degree	World	2 m	2 m
Depth	Yellow Springs Instruments (YSI) (Medium)	feet or meters	0 to 200 ft, 61 m	±0.4 ft, ±0.12 m	0.001 ft, 0.001 m (Resolution)
Optical Dissolved Oxygen	YSI ROX	%	0 to 500	0 to 200%: ±1% of reading or 1% air saturation, whichever is greater; 200 to 500%: ±15% of reading	10.00% (Resolution)
Optical Dissolved Oxygen	YSI ROX	mg/L	0 to 50	0 to 20 mg/L: ± 0.1 mg/L or 1% of reading, whichever is greater; 20 to 50 mg/L: ±15% of reading	0.01 (Resolution)
Conductivity	YSI 6560 Sensor	mS/cm	0 to 100	±0.5% of reading + 0.001 mS/cm	0.001 to 0.1 mS/cm (Resolution)
Temperature	YSI 6560 Sensor	°C	-5 to +50	±0.15°C	0.01°C (Resolution)
Salinity	YSI 6560 Sensor	PPT	0 to 70	±1% of reading or 0.1 ppt, whichever is greater	1 Ppt (Resolution)

#### 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 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, 2008, and 2009b). 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 to wet chemistry data collected during each survey, the electronic data is post-calibrated by MWRA using the wet chemistry data.

#### 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 is 100%: all nearfield and farfield stations must be sampled to be considered complete. At each station (except zooplankton-only stations F32 and F33), discrete samples will be collected at 5 depths (only 3 depths collected at stations F30 and F31) 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 studies, and measurements of bottom-water DO are successfully collected. The goal for water sample analysis is 100% completeness for respiration, zooplankton, phytoplankton, and productivity analysis. However, a 10% loss 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, TSS, respiration, productivity, 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 (2009). Specific requirements from this QMP which relate to HOM7 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 HOM7 will have documented certification of the appropriate SOPs. The Quality Assurance unit maintains the training records for each staff member. The Battelle Project QA Officer is responsible for ensuring that the technical and management staff members are familiar with both the site and HOM7 specific 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.

On buoy servicing surveys requiring divers, the buddy system will always be used. Additionally, all divers on the project are certified by the American Academy of Underwater Sciences (AAUS). The subcontracted divers are responsible for keeping their diving certifications up to date, and will provide all of their own safety gear.

#### 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 submitting training records and certificates to his/her supervisor and for updating his 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, URI, Pausacaco Plankton and UMD 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 Environmental Monitoring and Management System (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. All data submissions to MWRA are sent via email in the absence of the HOML application and copied to the project archive mailbox (^BCO Dux HOM7; HOM7@battelle.org). The ASCII data files are also stored on the projects file server under the HOM7 project Task 4 deliverables. This server is backed up to tape nightly. Once the HOML application goes online, electronic data submissions will be made through the system. A copy of the submission will still be sent by email to the project archive mailbox.

#### A.9.2 Documents

For each nearfield survey, one survey plan, one survey summary email, and one survey report will be prepared. For combined nearfield and farfield surveys, these documents will also be combined. A total of 12 nearfield and combined nearfield/farfield surveys and two (or more if needed) buoy service surveys will be reported as described below.

Collection data from water column surveys (Tasks 5 and 6), *in situ* data processing (Task 4), data loading and quality assurance (Task 4) and sample analysis (Tasks 7 and 8) are reported to MWRA in various forms as defined in the HOM7 contract. Tasks 5 and 6 will be reported in survey reports while Tasks 7

(Water Chemistry and Metabolism) and 8 (Plankton Taxonomy) will be reported in data sets used to generate data reports. Task 7 data will be used in Nutrient and Respiration/Productivity data reports (as described in Sections A.9.3.1 and A.9.3.2) and Task 8 data will be used in Plankton Data Reports (Section A.9.3.3). Supporting data collected during Task 9 Buoy servicing will be recorded on prepared forms and reported to MWRA (Section A.9.2.4). Data synthesis reports (Task 13) are described in Section A.9.4. Survey-related deliverables that will be generated under this QAPP include:

- 12 Survey Plans (one for each of the Nearfield water column surveys; farfield surveys plans will be combined with the Nearfield Plans)
- 1 Survey Plan that covers all 2010 Task 9 buoy service support
- 12 Survey Reports (one for each of the Nearfield water column surveys; farfield surveys reports will be combined with the Nearfield Reports)
- 2 Survey Reports (one for each buoy service survey, if additional surveys are requested (subtask 9.3) a survey report will be submitted for each additional survey)
- 12 Email Survey Summaries (including the rapid phytoplankton results)
- 4 Hydrographic and Nutrient Data Report Review letters
- 4 Metabolism Data Report Review letters
- 4 Phytoplankton Data and Zooplankton Data report Review letters

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 OP118Ain 2010 with analysis continuing through 2011. This document is designed following EPA/QA R-5 and is based largely on water quality CWQAPPs of the MWRA monitoring program described in Libby *et al.* (2002, 2005, 2006, 2008, and 2009b). 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. In the case of combined surveys, a single plan covering all aspects of the combined surveys will be submitted to MWRA. Each survey plan will follow Battelle SOP 6-043 *Preparation, Distribution, and Implementations of Field Survey Plan*<sup>1</sup>s that is based on the guidelines established by U.S. Environmental Protection Agency 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

<sup>1</sup> Battelle SOPs are provided to MWRA as Appendix D in hard copy format.

-

- 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

#### 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 analysis, observations from marine mammal sightings, and identify technical problems encountered and resolutions. These summaries will also include photo documentation of the two marine debris tows, and if available, 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, 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 and a station data table generated by MWRA data management staff. The sample collection table will be a tabular summary of stations occupied, station locations, and samples collected versus planned. A station data table will also be included in the report. This table includes data from each station and depth including arrival time, coordinates, depth, sample ID, and others. MWRA will generate this table and provide it to Battelle for inclusion in the survey report. 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.

The survey reports for the Task 9 buoy service support will include the information described above and in addition will include the *in situ* calibration measurements and titrated DO results obtained from the one meter depth sample. The *in situ* measurements will include temperature, salinity, depth, chlorophyll, and dissolved oxygen obtained from an over-the-side type instruments such as a YSI 6600 sonde or equivalent. These data will be reported in a spreadsheet format that mirrors the HOML database structure.

#### A.9.3 Data Report Review and Comment

Four Hydrography and Nutrient, four Metabolism, and four Plankton data reports will be generated by MWRA for monitoring year 2010. The data reports are created directly from the EM&MS database. Battelle will perform a technical review and comment on the initial data report.

#### A.9.4 Synthesis Reports (Task 13)

The data delivered above will be used in the Water Column Summary Report prepared under Task 13. MWRA comment 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 13.1)

All data for the annual water quality summary report will come from the EM&MS database. Authors will request data extracts. The annual water quality summary report will provide a rapid synthesis of results from water column monitoring activities conducted under Tasks 5-8 during 2010. 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 NH<sub>4</sub> 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 12) and include both the presentations and the submitted abstracts as appendices.

#### A.9.4.2 Outfall Monitoring Overview (Task 13.3)

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 HOM7 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	<b>Due Date</b>		
T	ask 2 Progress Tracking			
QA/QC Corrective Action Log	NA	Quarterly from March 15, 2010 to September 15, 2011.		
Progress Report and Cost Estimate; triplicate copies	NA	Monthly; February 2010 to December 2011		
Invoice and Accrued Services Estimates	NA	Monthly; January 2010 to November 2011		
	Task 3 QAPP			
QAPP for Water Column Monitoring (Draft)	NA	January 15, 2010		
QAPP for Water Column Monitoring (Final)	NA	February 2010		
	Task 4 Data Sets			
Water Column Data Sets	Each survey	1 week after survey		
Hydrographic Data Sets	Each survey	2 weeks after end of each survey		
Oxygen/Respiration Data Sets	Each survey	3 weeks after end of each survey		
	Early February Nearfield/Farfield	March 15, 2010		
	Late February Nearfield/Farfield	March 31, 2010		
	March Nearfield	April 30, 2010		
	Early April Nearfield/Farfield	May 15, 2010		
	May Nearfield	June 30, 2010		
	June Nearfield/Farfield	July 30, 2010		
Productivity Data Sets	July Nearfield	August 31, 2010		
	August Nearfield/Farfield	September 30, 2010		
	Early September Nearfield	October 15, 2010		
	Late September Nearfield	November 15, 2010		
	October Nearfield/farfield	November 30, 2010		
	November Nearfield	December 31, 2010		
	February – April	June 30, 2010		
Plankton Data Sets	May – June	August 31, 2010		
rianktun Data Sets	July – August	October 31, 2010		
	September – November	January 31, 2011		
Daview Comments for D / D	February – April	August 15, 2010		
Review Comments for Data Reports:	May – June	October 15, 2010		
Hydrographic and Nutrient, Metabolism, and Plankton	July – August	December 15, 2010		
iviciauunsin, and rianktun	September – November	March 15, 2011		

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

Deliverable	Survey Period	<b>Due Date</b>	
Year's electronic word processing files for the survey plans and final survey reports, including all graphics and tables	January – December	One month after field year	
Tasks 5 a	and 6 Survey-Related Rej	ports	
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 9 Buoy Servicing		
Survey Plan	One	February 15, 2010	
Survey Report Tasks 9.2 and 9.3	Each survey	3 weeks after survey	
Task 13 S	ynthesis or Interpretive R	eports	
Water Column Summary – Draft	February – December	April 2011	
Water Column Summary – Final	reditially - December	May 2011	
Outfall Monitoring Overview–Drafts	February – December	May and August 2011	
Outfall Monitoring Overview– Final	February – December	September 2011	

#### B. DATA GENERATION AND ACQUISITION

#### **B.1. SAMPLING PROCESS DESIGN**

#### **B.1.1** Nearfield and Farfield Water Column Surveys (Tasks 5 and 6)

Water column sampling will be conducted 12 times in 2010 (Figure B-1). Figure B-2 shows the location of the 7 nearfield stations and Figure B-3 shows the 28 farfield stations that will be sampled. Table B-1 and Table B-2 identify the location, depth and station type for each of the nearfield and farfield stations, respectively.

#### **B.1.2** Sampling Locations and Frequency

Nearfield stations are located within five kilometers of the outfall. Two station types (B and MRP) are sampled in the nearfield. Table B-3 shows sub-sampling by station type and sample depth. Stations N04 and N18 will be sampled early in the day to allow time for measurements of primary production (photosynthesis). Net tows for quantifying anthropogenic debris on the ocean surface will be conducted twice during each nearfield survey at stations N01 and N21. Additionally, the rapid phytoplankton sample will be collected at N18. Each nearfield survey should be completed within one day to allow comparisons between stations.

Farfield stations are located beyond the nearfield to (1) cover regional-scale oceanographic processes in Massachusetts Bay and Cape Cod Bay; (2) broadly characterize reference areas; and (3) to verify that impacts by the outfall plume are not found beyond the nearfield. Each farfield sampling will be completed in two to three sequential days when possible. The farfield areal productivity station (F23) will be sampled early in the day on the nearfield survey day to confine all productivity processing to one day. If requested separately by MWRA, Cape Cod Bay stations F01, F02, and F03 will be sampled during the farfield surveys. Additionally during the first three farfield surveys of the year, two additional

stations (F32 and F33) will be profiled for hydrographic data and sampled for zooplankton if MWRA requests that Battelle conduct the Cape Cod Bay sampling. The QAPP includes all five of these Cape Cod Bay stations in sample counts and schedules; individual survey plans will define whether or not these stations are to be visited. The farfield surveys will capture the ecological conditions six times during the year: winter (early February), late winter (late February to early March), spring (early April), early summer (mid-June), late summer (mid-August), and fall (mid-October).

Week	Sun	Mon	Tue	Wed	Thu	Fri	Sat	Week	Sun	Mon	Tue	Wed	Thu	Fri	Sat
1						1-Jan	2-Jan	27	27-Jun	28-Jun	29-Jun	30-Jun	1-Jul	2-Jul	3-Jul
2	3-Jan	4-Jan	5-Jan	6-Jan	7-Jan	8-Jan	9-Jan	28	4-Jul	5-Jul	6-Jul	7-Jul	8-Jul	9-Jul	10-Jul
3	10-Jan	11-Jan	12-Jan	13-Jan	14-Jan	15-Jan	16-Jan	29	11-Jul	12-Jul	13-Jul	14-Jul	15-Jul	16-Jul	17-Jul
	17-Jan	18-Jan	19-Jan	20-Jan	21-Jan	22-Jan	23-Jan	30	18-Jul	19-Jul	20-Jul	21-Jul	22-Jul	23-Jul	24-Jul
4	24-Jan	25-Jan	26-Jan	27-Jan	28-Jan	29-Jan	30-Jan	31	25-Jul	26-Jul	27-Jul	28-Jul	29-Jul	30-Jul	31-Jul
5	31-Jan	1-Feb	2-Feb	3-Feb	4-Feb	5-Feb	6-Feb		1-Aug	2-Aug	3-Aug	4-Aug	5-Aug	6-Aug	7-Aug
6	7-Feb	8-Feb	9-Feb	10-Feb	11-Feb	12-Feb	13-Feb	32	8-Aug	9-Aug	10-Aug	11-Aug	12-Aug	13-Aug	14-Aug
7	14-Feb	15-Feb	16-Feb	17-Feb	18-Feb	19-Feb	20-Feb	33	15-Aug	16-Aug	17-Aug	18-Aug	19-Aug	20-Aug	21-Aug
8	21-Feb	22-Feb	23-Feb	24-Feb	25-Feb	26-Feb	27-Feb	34	22-Aug	23-Aug	24-Aug	25-Aug	26-Aug	27-Aug	28-Aug
9	28-Feb	1-Mar	2-Mar	3-Mar	4-Mar	5-Mar	6-Mar	35	29-Aug	30-Aug	31-Aug	1-Sep	2-Sep	3-Sep	4-Sep
10	7-Mar	8-Mar	9-Mar	10-Mar	11-Mar	12-Mar	13-Mar	36	5-Sep	6-Sep	7-Sep	8-Sep	9-Sep	10-Sep	11-Sep
11	14-Mar	15-Mar	16-Mar	17-Mar	18-Mar	19-Mar	20-Mar	37	12-Sep	13-Sep	14-Sep	15-Sep	16-Sep	17-Sep	18-Sep
12	21-Mar	22-Mar	23-Mar	24-Mar	25-Mar	26-Mar	27-Mar	38	19-Sep	20-Sep	21-Sep	22-Sep	23-Sep	24-Sep	25-Sep
13	28-Mar	29-Mar	30-Mar	31-Mar	1-Apr	2-Apr	3-Apr	39	26-Sep	27-Sep	28-Sep	29-Sep	30-Sep	1-Oct	2-Oct
14	4-Apr	5-Apr	6-Apr	7-Apr	8-Apr	9-Apr	10-Apr	40	3-Oct	4-Oct	5-Oct	6-Oct	7-Oct	8-Oct	9-Oct
15	11-Apr	12-Apr	13-Apr	14-Apr	15-Apr	16-Apr	17-Apr	41	10-Oct	11-Oct	12-Oct	13-Oct	14-Oct	15-Oct	16-Oct
16	18-Apr	19-Apr	20-Apr	21-Apr	22-Apr	23-Apr	24-Apr	42	17-Oct	18-Oct	19-Oct	20-Oct	21-Oct	22-Oct	23-Oct
17	25-Apr	26-Apr	27-Apr	28-Apr	29-Apr	30-Apr	1-Mav	43	24-Oct	25-Oct	26-Oct	27-Oct	28-Oct	29-Oct	30-Oct
18	2-Mav	3-Mav	4-Mav	5-Mav	6-Mav	7-Mav	8-May	44	31-Oct	1-Nov	2-Nov	3-Nov	4-Nov	5-Nov	6-Nov
19	9-May	10-May	11-May	12-May	13-May	14-May	15-May	45	7-Nov	8-Nov	9-Nov	10-Nov	11-Nov	12-Nov	13-Nov
20	16-May	17-May	18-May	19-May	20-May	21-May	22-May	46	14-Nov	15-Nov	16-Nov	17-Nov	18-Nov	19-Nov	20-Nov
21	23-May	24-Mav	25-May	26-May	27-May	28-May	29-Mav	47	21-Nov	22-Nov	23-Nov	24-Nov	25-Nov	26-Nov	27-Nov
22	,	,	,		.,	,	,	48	28-Nov	29-Nov	30-Nov	1-Dec	2-Dec	3-Dec	4-Dec
23	30-May	31-May	1-Jun	2-Jun	3-Jun	4-Jun	5-Jun	49	5-Dec	6-Dec	7-Dec	8-Dec	9-Dec	10-Dec	11-Dec
24	6-Jun	7-Jun	8-Jun	9-Jun	10-Jun	11-Jun	12-Jun	50							
25	13-Jun	14-Jun	15-Jun	16-Jun	17-Jun	18-Jun	19-Jun	51	12-Dec	13-Dec	14-Dec	15-Dec	16-Dec	17-Dec	18-Dec
26	20-Jun	21-Jun	22-Jun	23-Jun	24-Jun	25-Jun	26-Jun	52	19-Dec	20-Dec	21-Dec	22-Dec	23-Dec	24-Dec	25-Dec
								53	26-Dec	27-Dec	28-Dec	29-Dec			

	Key	Tasks	Survey Description
Į		5	Nearfield Water Column
I		6	Farfield Water Column

Figure B-1. HOM7 Water Column Sampling Schedule, 2010

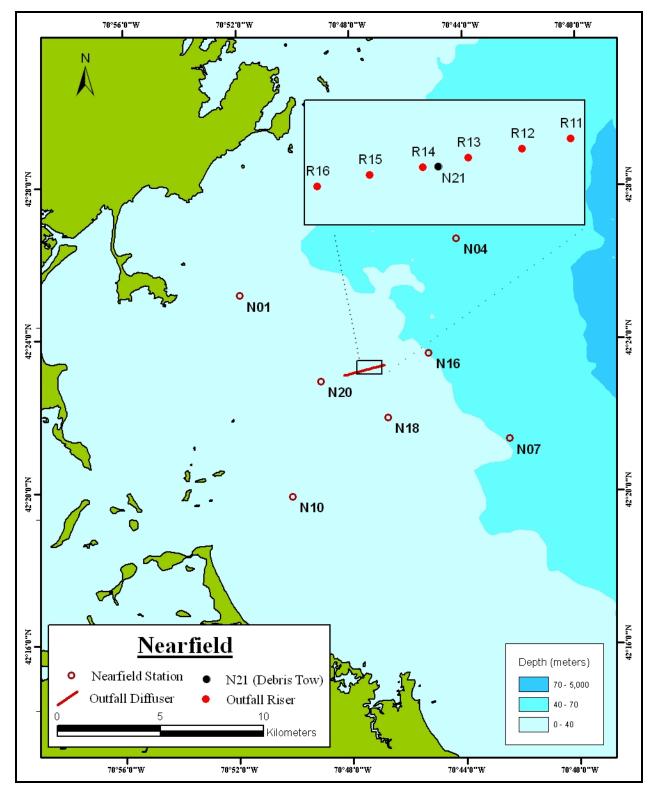


Figure B-2. Nearfield Water Column Sampling Stations. Inset of Station N21 Located along the Outfall Diffuser near Riser 14 – Risers are 38 m apart.

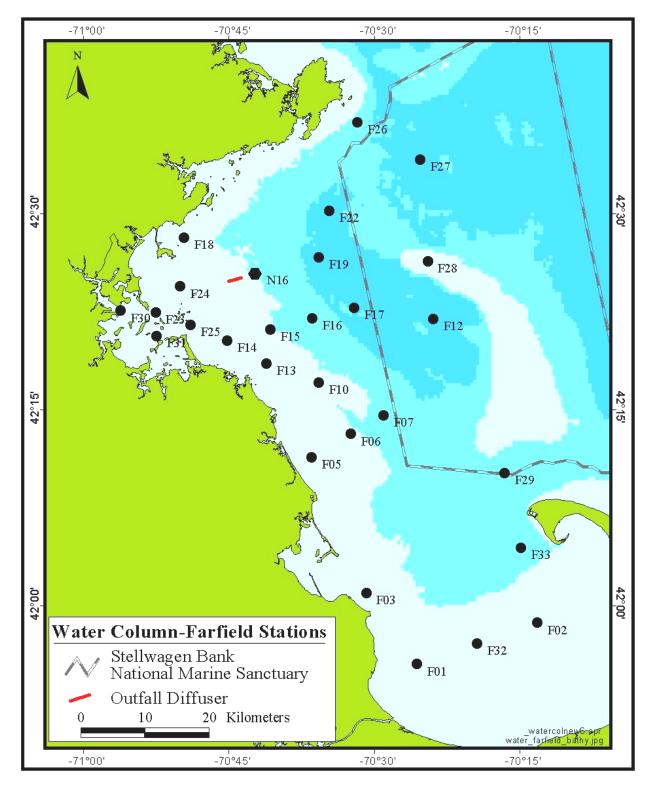


Figure B-3. Farfield Water Column Sampling Stations

Table B-1. Nearfield Water Column Sampling Stations

Station	Latitude	Longitude	Depth	Station
	(N)	<b>(W)</b>	(m)	Type
N01	42.419	-70.865	31.2	В
N04 <sup>1</sup>	42.444	-70.737	49.8	MRP
N07	42.356	-70.706	50.2	В
N10	42.332	-70.834	24.8	В
N16	42.394	-70.753	42.2	В
N18 <sup>1</sup>	42.366	-70.778	26.6	MRP
N20	42.382	-70.817	31.3	В
$N21^2$	42.388	-70.785	34.8	Debris tow

<sup>&</sup>lt;sup>1</sup> Stations N04 and N18 will be sampled early enough in the day to initiate photosynthesis incubations.

Table B-2. Farfield Water Column Stations

Station	Latitude(N)	Longitude(W)	Depth (m)	Station Type					
F01 <sup>1</sup>	41.851	-70.453	26.2	M					
F02 <sup>1</sup>	41.908	-70.228	32.1	M					
F03 <sup>1</sup>	41.950	-70.548	16.2	Е					
F05	42.139	-70.650	19.1	Е					
F06	42.171	-70.577	33.0	M					
F07	42.197	-70.516	54.1	Е					
F10	42.242	-70.637	32.9	Е					
F12	42.330	-70.423	90.3	Е					
F13	42.268	-70.735	25.0	M					
F14	42.300	-70.808	18.7	Е					
F15	42.316	-70.728	38.3	Е					
F16	42.331	-70.650	59.0	Е					
F17	42.346	-70.571	76.4	Е					
F18	42.442	-70.888	24.9	Е					
F19	42.415	-70.637	80.0	BR					
F22	42.480	-70.618	79.5	M					
F23 <sup>2</sup>	42.339	-70.942	24.7	MRP					
F24	42.375	-70.896	21.2	M					
F25	42.322	-70.876	15.0	M					
F26	42.602	-70.565	52.8	M					
F27	42.550	-70.447	105.1	M					
F28	42.410	-70.433	30.5	Е					
F29	42.117	-70.290	64.7	Е					
F30	42.341	-71.008	12.1	Н					
F31	42.306	-70.940	15.0	Н					
F32 <sup>3</sup>	41.880	-70.341	30.2	Z					
F33 <sup>3</sup>	42.013	-70.259	44.1	Z					
N16 <sup>4</sup>	42.394	-70.753	42.2	M					

<sup>&</sup>lt;sup>1</sup>Stations F01, F02, and F03 will be sampled during weeks 6, 9, 115, 25, 34, and 43 if separately requested by MWRA.

<sup>&</sup>lt;sup>2</sup> Station N21 is no longer sampled, but is the location for one of the debris tows.

<sup>&</sup>lt;sup>2</sup>Station F23 will be sampled early enough in the day to initiate photosynthesis incubations.

<sup>&</sup>lt;sup>3</sup> Stations F32 and F33 will be sampled during weeks 6, 9, and 15, if CCB sampling is requested by MWRA.

<sup>&</sup>lt;sup>4</sup> Station N16 will be visited on two separate days during combined nearfield and farfield surveys.

	Station Type Code								
	Nearfield Farfield					Analyses Per Year			
	В	MRP	BR	E	Н	M	MRP	Z	,
Number stations each type per survey	5	2	1	12	2	10	1	2	
Number of surveys per year	12	12	6	6	6	6	6	3	
Subsample Analysis	Number of Analyses per Station								
Dissolved Inorganic Nutrients	5	5	5	5	3	5	5	0	1176
Other Nutrients*									
Dissolved Organic Carbon		3	3		3	3	3	0	504
Total Dissolved Nitrogen	3								
Total Dissolved Phosphorous				0					
Particulate Organic Carbon									
Particulate Organic Nitrogen									
Particulate Phosphorous									
Biogenic Silica									
Chlorophyll a/phaeophytin a	5	5	5	0	3	5	5	0	816
Total suspended solids <sup>1</sup>	3	3	3	0	3	3	3	0	504
Phytoplankton – whole water <sup>2</sup>	0	2	0	0	2	2	2	0	204
Phytoplankton – screened water <sup>2</sup>	0	2	0	0	2	2	2	0	204
Zooplankton	0	1	0	0	1	1	1	1	108
Respiration <sup>1</sup>	0	3	3	0	0	0	3	0	108
Primary Productivity	0	5	0	0	0	0	5	0	150

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

#### **B.1.3** Hydrocasts and Sensor Measurements

Hydrographic data will be collected at all nearfield and farfield stations. During the combined surveys, nearfield station N16 will be visited on both the nearfield and the farfield survey days. 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 (SPAR), navigational position, and time will be recorded concurrently with the hydrocast measurements.

#### **B.1.4** Water Collection and Zooplankton Net Tows

During the upcast at each station (except stations F32 and F33), 9–L Rosette sampling bottles will be used to collect water from five depths: bottom, mid-bottom, middle (chlorophyll a maximum), mid-surface, and surface. Due to relatively shallow depths at Boston Harbor stations F30 and F31, only bottom, middle, and surface depths are sampled. 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). Vertical net tows to collect zooplankton will be conducted according to the scheme shown in Table B-3.

<sup>&</sup>lt;sup>1</sup>Samples collected at three depths (bottom, mid-depth, and surface)

<sup>&</sup>lt;sup>2</sup>Samples collected at two depths (mid-depth and surface)

Cape Cod stations will only be sampled if requested by MWRA – stations F01, F02, and F03 will be sampled during each Farfield survey and stations F32 and F33 will be sampled during the first three farfield surveys of the year (weeks 6, 9, and 15). A detailed listing of samples collected at each station during nearfield and farfield surveys is provided in Appendix I.

#### **B.1.5** Whale Observations

During each nearfield survey and the first three farfield surveys of the year (January 1 through May 31), 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 and when the vessel is in Massachusetts Bay or Cape Cod Bay. All sightings will be recorded on standardized marine mammal field sighting logs (see Section B.2.8). The sampling vessels will operate according to protocols mandated by the Commonwealth of Massachusetts regarding right whales (Appendix II).

#### **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** Floating Debris

To address National Marine Fisheries Service (NMFS) concerns about potential anthropogenic debris entering the marine environment, MWRA instituted surface net tows to sample for plastics and other such floatable objects in 1999. On all nearfield surveys, a Neuston net (1 x 2 meter with 500-µm mesh) will be towed twice to capture any floating man-made debris. Tows will be conducted near the inshore (western) side of the nearfield and in the vicinity of the outfall (between N16 and N20) for 10 minutes at 2 knots. The outfall tow will be conducted through the visible plume. In the event that the plume is not visible (under choppy or highly stratified conditions) the tow will start near station N21, and go along the outfall tunnel following the risers, which will be visible either on the NavSam or GPS chart or on the echosounder. If survey track and operations permit, the western tow should be well inshore of the nearfield proper. The beginning and end coordinates of each tow will be recorded on the survey log. Shipboard processing is described in Section B.2.7.

#### **B.1.8** Buoy Service Support (Task 9)

Under this task Battelle will provide vessel support to MWRA and National Data Buoy Center (NDBC) to service instruments on the Massachusetts Bay weather buoy 44013. The Battelle crew will include a Chief Scientist, Captain and deck hand. Two planned surveys, in March and October of 2010 are planned under Task 9.2. Task 9.3 may include up to two unanticipated buoy maintenance surveys. These 'asneeded' surveys, tentatively scheduled for February and August, will be mobilized within 2 weeks of notification by MWRA. Prior to the first survey, Battelle will prepare a survey plan for the year's activities, describing generic survey dates, vessel, personnel, and field methods. Prior to each survey, Battelle will provide guidance and participate in decisions about weather and coordination of participants, schedule the boat and crew (including subcontracted divers when necessary), mobilize the boat, verify sufficient safety gear for the field crew, and perform all logistical coordination.

During each survey, Battelle staff will

- Transport and deliver the buoy maintenance team to the buoy as directed by the team
- Assist with line-handling and gear transfers from the vessel
- Collect 2 chlorophyll samples and 3 dissolved oxygen samples at 1-meter depth
- Process chlorophyll and dissolved oxygen samples as described in Section B.2.5 for Tasks 5 7.
   The dissolved oxygen samples will be titrated either on board or back at Battelle within the 24 hour holding time as stated in Section B.4.1.
- Collect near surface *in situ* readings with a calibrated YSI according to SOP 5-324 *Operation of Yellow Springs Instrument (YSI) 6 Series Multi-Parameter Sondes*. The readings will include temperature, salinity, depth, dissolved oxygen (mg/L and % saturation), and chlorophyll fluorescence. All readings will be recorded on the weather buoy servicing log form (Figure B-4). The buoy servicing log form includes information on the titrated dissolved oxygen results, a chronology of the day's events, a listing of the survey crew and the *in situ* readings. Following completion of the survey, the buoy servicing log form will be scanned and e-mailed to the MWRA Project Manager. This form along with associated sample processing forms and chains of custody will be included in the survey logbook for each survey. Chlorophyll samples will be delivered to MWRA within one week of collection.
- Hold station for 90 minutes after buoy service is complete so field technicians can remotely monitor the data being reported from the buoy.
- Deliver survey data to MWRA in a spreadsheet format that mirrors the HOML database structure. Data will include: *in situ* measurements (temperature, salinity, depth, chlorophyll, and dissolved oxygen) and titrated DO results obtained from the one meter depth sample.

#### **B.1.9** 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); biogenic silica; TSS; chlorophyll a and phaeophytin. URI analyzes samples for primary productivity. Battelle will analyze samples for initial DO concentrations and final DO concentrations after incubation at in situ temperatures (±2°C). MWRA will calculate net respiration rates. Scientists from Pausacaco Plankton and UMD will analyze phytoplankton and zooplankton community structure, respectively. The sample analyses are summarized in Table B-4. Sampling and analytical methods are described in Sections B.2 and B.4, respectively.

#### **B.1.10 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 both nearfield and farfield surveys are presented in Appendix I.

Weather Buoy Servicing LogForm	Date: Page: _	_of				
WB101 Daily Log	Recorded by:					
Weather Observations	<u>YSI Data</u>					
Time:	Time:	-				
Wind Speed & Direction:	Lat./Long.:/					
Wave Height (ft):	Temp (°C):	-				
Instrument Information	Salinity (ppt):	-				
GPS unit:	Chla (µg/L):	-				
YSI make/model number:	DO (mg/L):					
Sample Ids	DO % Sat:	_				
DO:,,	Depth (m):	-				
Chla:,						
<u>Chronology/Notes</u>						

Figure B-4. Weather Buoy Servicing Log Form

## **B.1.11**

Table B-4. Water Column Sample Analyses

Parameter Lab		Units	Instrument	Reference		
Dissolved oxygen	Battelle	mg/L	Radiometer TitraLab	Battelle SOP 5-317 and Oudot et al. (1988)		
Respiration	Battelle	μM/hr	Radiometer TitraLab	Battelle SOP 5-317 and Strickland and Parsons (1972)		
Primary production by <sup>14</sup> C	URI	mgC/m³/h	Packard TriCarb scintillation counter Model 2900	Strickland and Parsons (1972); Lewis and Smith (1983); Libby et al. (2002)		
Whole-water phytoplankton	Whole-water phytoplankton PP <sup>1</sup> E6Cell		Olympus BH-2 compound microscope with phase-contrast optics	Borkman (1994), Borkman et al. (1993), Turner et al. (1995)		
Screened phytoplankton	PP	Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Turner et al. (1995)		
Rapid phytoplankton	PP	Cells/L (approx.)	Olympus BH-2 compound microscope with phase-contrast optics	Turner et al. (1995)		
Zooplankton	UMD	Indiv./m <sup>3</sup>	Wild M-5 dissecting microscope	Libby et al. (2002)		
In situ Measurements						
Conductivity	Battelle	mS/cm	Seabird SBE-4	SBE-25 CTD Manual/ Battelle SOP 3-183		
Temperature	Battelle	С	Seabird SBE-3	SBE-25 CTD Manual/ Battelle SOP 3-183		
Pressure	Battelle	db	Seabird SBE-29	SBE-25 CTD Manual/ Battelle SOP 3-183		
Dissolved oxygen	Battelle	mg/L	Seabird SBE 43	Weiss (1970)/Battelle SOP 3-180		
Chlorophyll fluorescence	Battelle	μg/L	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		
In situ irradiance	Battelle	μEm-2sec-1	Biospherical QSP-200L	Biospherical Manual/ Battelle SOP 3-127		
Surface irradiance	Battelle	μEm-2sec-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-52	Furuno Manual/Battelle SOP 3-129		
Navigational position	Battelle	degree	Northstar 941X	Northstar 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		

<sup>1</sup>PP = Pausacaco Plankton

#### **B.1.12** Schedule of Activities and Deliverables

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Table B-5 lists the delivery schedule for the various water-column monitoring reports and provides the planned schedule for all farfield and nearfield surveys and associated deliverables.

	Additional		Planned Due Date <sup>2</sup>				
Survey Surveys Combined		Plan	Date Start	Date End	Summary	Draft Report	
WF101	WN101	1/25/2010	2/1/2010	2/4/2010	2/11/2010	2/25/2010	
WF102	WN102	2/15/2010	2/22/2010	2/25/2010	3/4/2010	3/18/2010	
WN103	None	3/9/2010	3/16/2010	3/16/2010	3/23/2010	4/6/2010	
WF104	WN104	3/29/2010	4/5/2010	4/8/2010	4/15/2010	4/29/2010	
WN106	None	5/4/2010	5/11/2010	5/11/2010	5/18/2010	6/1/2010	
WF107	WN107	6/7/2010	6/14/2010	6/16/2010	6/23/2010	7/7/2010	
WN109	None	7/13/2010	7/20/2010	7/20/2010	7/27/2010	8/10/2010	
WF10B	WN10B	8/9/2010	8/16/2010	8/18/2010	8/25/2010	9/8/2010	
WN10C	None	8/24/2010	8/31/2010	8/31/2010	9/7/2010	9/21/2010	
WN10D	None	9/21/2010	9/28/2010	9/28/2010	10/5/2010	10/19/2010	
WF10E	WN10E	10/11/2010	10/18/2010	10/21/2010	10/28/2010	11/11/2010	
WN10F	None	11/2/2010	11/9/2010	11/9/2010	11/16/2010	11/30/2010	

Table B-5. Schedule of Water Column Surveys and Related Survey Reports

#### **B.2.** SAMPLING METHODS

Methods for collection and analysis of samples are described in the following sections. Analyses will be performed by Battelle, DLS, URI, Pausacaco Plankton, and UMD 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 a Northstar dGPS interfaced to the BOSS computer. The GPS receiver has six dedicated channels and is capable of locking onto six different satellites at one time. To correct the GPS calculations, the Northstar dGPS will receive correction data from one of three USCG dGPS broadcast sites: Montauk Point, NY, Chatham, MA, or Portsmouth Harbor, NH (Figure B–5). This capability ensures strong signal reception, and accurate and reliable positioning with 2-second updates.

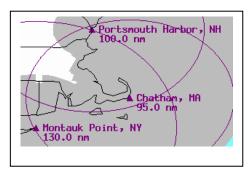


Figure B-5. dGPS Master Stations Coverage

#### **B.2.2** Vessel Handling

Boston Harbor, Massachusetts Bay, and Cape Cod Bays are heavily trafficked by commercial, fishing, and recreational vessels. Endangered whales, as well as numerous other marine mammals seasonally frequent the Bays. The licensed boat captain will operate the vessel in a professional manner at all times

<sup>&</sup>lt;sup>1</sup> WN: water column nearfield; WF: water column farfield

<sup>&</sup>lt;sup>2</sup> Tentative dates. Actual dates will be determined based on the previous survey completion date.

during surveys to ensure the safety of passengers and crew and to minimize the possibility of collisions with other traffic (46 CFR 185<sup>2</sup>) or with marine mammals (50CFR parts 217 and 222). Also required by National Marine Fisheries Service's rules, 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).

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 eliminated from the light measurement data 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 is collected according to Battelle SOP No. 5-275 At Sea Collection of hydrographic Data using CTD/Rosette System.

- Battelle-designed and fabricated winch with 150 m of 9-conductor double-armored galvanized-steel cable and sheave (The HOM6 CWQAPP in correctly identified the cable as stainless steel).
- 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).
  - o 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 at the point of measurement) mounted level with the pressure sensor
  - WET Labs WETStar chlorophyll fluorometer (intake at same depth as the pressure sensor)
  - o Biospherical QSP-200L spherical quantum scalar irradiance sensor that measures underwater photosynthetically active radiation (PAR) mounted 1 m above the pressure

<sup>&</sup>lt;sup>1</sup> 46 CFR 185, Subpart C – Miscellaneous Operating Requirements Sec. 185.304 Navigation underway:

<sup>(</sup>a) The movement of vessel shall be under the direction and control of the master or a licensed mate at all times. The master shall operate the vessel keeping the safety of the passengers and crew foremost in mind by directing the vessel in order to prevent a casualty. Special attention should be paid to:

<sup>(1)</sup> The current(s) velocity and direction of the transiting area;

<sup>(2)</sup> Tidal state;

<sup>(3)</sup> Prevailing visibility and weather conditions;

<sup>(4)</sup> Density of marine traffic;

<sup>(5)</sup> Potential damage caused by own wake;

<sup>(6)</sup> The danger of each closing visual or radar contact;

<sup>(7)</sup> Vessel's handling characteristics; and

<sup>(8)</sup> Magnetic variation and deviation errors of the compass

sensor<sup>3</sup>. (The HOM6 CWQAPP 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-52 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<sup>©</sup>)
- Color printer
- Navigation:
  - o Northstar 952-XDW dGPS system aboard the R/V *Aquamonitor*
  - o Northstar 941-XD dGPS system as backup

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-6). Once the data are acquired, they are automatically written to a data file and logged 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. Hard-copy printouts of position fixes will be made during discrete sampling events such as triggering of Rosette sampling bottles. 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.

<sup>&</sup>lt;sup>3</sup> 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).

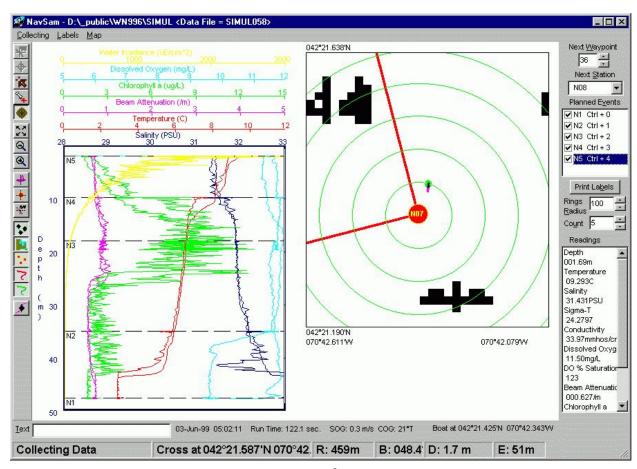


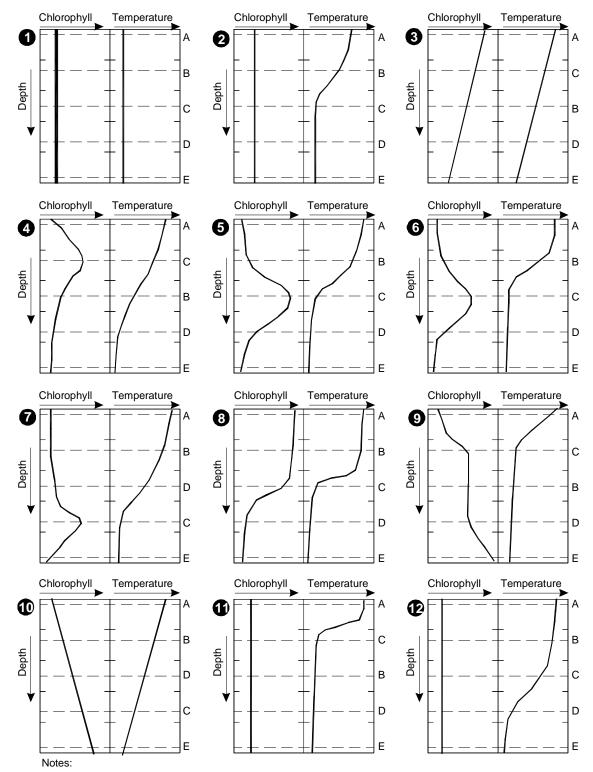
Figure B-6. Sample NavSam<sup>©</sup> Data Acquisition Screen

#### **B.2.4** Water Sampling

Water samples for dissolved inorganic nutrients, dissolved organic nutrients, particulate nutrients, chlorophyll *a*, TSS, DO, primary production 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<sup>©</sup> will be set to the hydrographic profiling mode and a data cast file will be opened. NavSam<sup>©</sup> 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 until completely submerged 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), the unit 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<sup>©</sup> 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 I Table I-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-7 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-7 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. Onboard processing is described in Section B.2.5.
- 7. After collecting the surface water sample, the operator will close the data cast file.
- 8. NavSam<sup>©</sup> will be put into navigation mode with a file created for transit to the next station.



- Mid-depth 'C' must be less than 30 meters and cannot be the bottom
- At station type 'P', try to position mid-bottom 'D' at 10% incident mid-depth 'C' at 25% incident light, and mid-surface 'B' at 50% incident

Figure B-7. 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 I tables lay out the required subsampling required for nearfield and farfield water column surveys, respectively.

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-8 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-6.

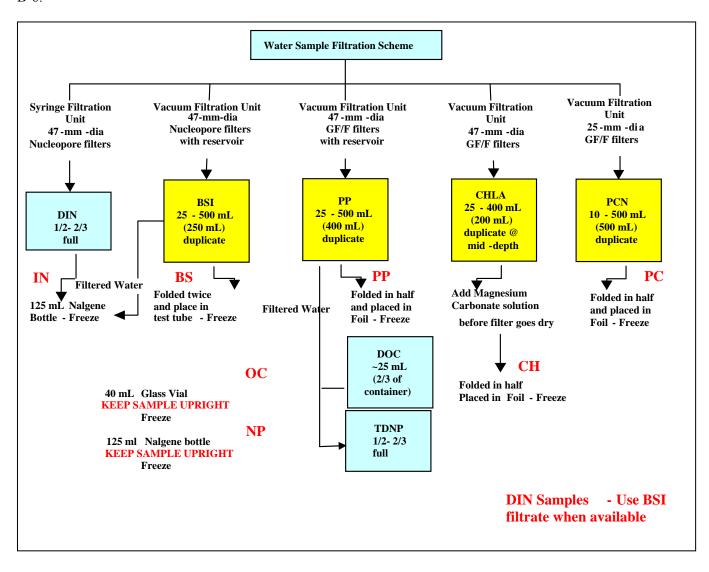


Figure B-8. Onboard Processing Flow Chart

Table B-6. Sample Volumes, Containers, and Processing for Field Samples

Parameter	Laboratory	Station Type	Nearfield Qty	Farfield Qty	Sample Volume (Target) <sup>1</sup>	Sample Containers <sup>2</sup>	Shipboard Processing/ Preservation	Maximum Holding Time to Analysis
Following sample	es are subsam	pled from w	ater collected	l with Niski				
Dissolved Inorganic Nutrients	DLS	All	35	126	60 mL	125-mL polyethylene bottle	Pass through a Nucleopore membrane filter. Freeze until analysis.	28 days
Dissolved Organic Carbon	DLS	B, BR, H, M, MRP	21	42	25 mL	40-mL borosilicate glass vial	Pass through a borosilicate GF/F filter. Freeze filtrate until analysis.	28 days
Total Dissolved Phosphorus and Nitrogen	DLS	B, BR, H, M, MRP	21	42	60 mL	125-mL polyethylene bottle	Pass through a borosilicate GF/F filter. Freeze filtrate until analysis.	28 days
Particulate Organic Carbon and Nitrogen	DLS	B, BR, H, M, MRP	21	42	500 mL	Whatman GF/F glass fiber filter	Pass sample through a GF/F filter, wrap filter in foil and freeze until analysis.	28 days
Particulate Phosphorus	DLS	B, BR, H, M, MRP	21	42	400 mL	Whatman GF/F glass fiber filter	Pass sample through a GF/F filter, wrap filter in foil and freeze until analysis.	28 days
Biogenic Silica	DLS	B, BR, H, M, MRP	21	42	250 mL	Nucleopore polycarbonate filter	Pass sample through a Nucleopore filter, wrap filter in foil and freeze until analysis.	90 days
Chlorophyll a/ Phaeopigments	DLS	B, BR, H, M, MRP	35	66	200 mL	Whatman GF/F glass fiber filter	Pass through glass fiber filter. Fix with saturated MgCO3 solution, wrap in foil. Freeze until analysis.	4 weeks
Total Suspended Solids	DLS	B, BR, H, M, MRP	21	42	1 L	1 Liter dark Bottle	Store water at 4°C up to and during transport to DLS for filtration.	7 days
Respiration/ Dissolved Oxygen	Battelle	BR, MRP	6	6	300 mL	300 mL glass BOD bottle	Initial measurements (triplicate) - fix per Oudot et al. (1988). Titrate within 24 hours. Final measurements (triplicate) - incubate in dark at <i>in situ</i> temperature for 7±2 days. Fix and titrate as per initial samples.	24 hours
<sup>14</sup> C Production and DIC	URI	MRP	10	5	1L	1 Liter dark polyethylene bottle	Store at 4° C up to and during transport to URI for incubation.	< 8 hours (DIC <8h to preserve; <30 days from preservation to analysis)
Phytoplankton (Whole Water)	Pausacaco Plankton	H, M, MRP	4	26	800 mL	1000 mL HDPE bottle	Preserve with Utermöhl's solution.	6 months
Phytoplankton (Screened Water)	Pausacaco Plankton	H, M, MRP	4	26	4 L	1000 mL HDPE bottle	Strain through a 20 µm mesh; wash retained organisms into a jar. Fix with formalin to 5 percent solution.	6 months
Net tows								
Zooplankton	UMD	H, M, MRP, Z	2	13 (15) <sup>3</sup>	800 mL	1000 mL glass bottle	Wash into jar. Fix with formalin to 10% solution.	6 months
Man Made Debris	Battelle	na	2	0	10 min	Plastic container	Photograph and transfer to containers and archive.	NA

<sup>&</sup>lt;sup>1</sup> Volume processed for analysis. Total volumes removed from Rosette sampling bottles are listed in Appendix I Tables I-1 and I-2.

<sup>2</sup> Name brand items (e.g., Nuclepore, Whatman) may be substituted with comparable items from a different manufacturer.

<sup>4</sup> Quantities for the first three farfield surveys.

#### **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 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 is filtered into the bottle for analysis. Alternatively, according to Battelle SOP No. 5-266, *Nutrient Sample Processing*, the filtrate from the biogenic silica preparation may be used for these samples as pressure and vacuum filtration processes give similar results. The sample bottle will be labeled and the sample will be frozen. The samples will remain frozen until analyzed.

#### **B.2.5.2** Dissolved Organic Carbon

Samples for dissolved organic carbon (DOC) will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. A 25-mL aliquot will be obtained from the particulate phosphorous filtrate. The sample will be passed through a Whatman 47-mm-diameter GF/F and collected in a polysulfon filtration flask. A clean 40-mL borosilicate glass (or Teflon) vial will be rinsed three times with filtrate then filled with approximately 25 mL of filtrate. Samples will be frozen onboard and stored frozen until analysis.

# **B.2.5.3** 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 clean 125-mL white polyethylene (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.

# **B.2.5.4** 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 10 and 500 mL of sample will be filtered<sup>4</sup>, depending on particulate density. The samples will be collected on 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. Samples will be processed in duplicate, but only one filter will be analyzed. The second filter is for duplicate analysis (1 per 20 samples) or as backup.

#### **B.2.5.5** 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 sample<sup>3</sup> 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. Samples will be processed in duplicate, but only one filter will be analyzed. The second filter is for duplicate analysis (1 per 20 samples) or as backup.

<sup>&</sup>lt;sup>4</sup>Exact volume filtered will be recorded on sample label and any deviations from standard volume (500 ml for PCN, 200 for Chla, 400 ml for PP, and 250 for BSi) will be noted in station log.

#### **B.2.5.6** Biogenic Silica

Samples for biogenic silica will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample<sup>5</sup> will be collected on 47-mm-diameter Nuclepore membrane filters (0.4-µm pore size) using a vacuum-filter system. Each filter will be folded in quarters and placed in a labeled foil pouch and stored frozen until analysis. Samples will be processed in duplicate, but only one filter will be analyzed. The second filter is for duplicate analysis (1 per 20 samples) or as backup.

# **B.2.5.7** 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 sample<sup>4</sup> 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 MgCO<sub>3</sub> 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.

#### **B.2.5.8** Total Suspended Solids

Whole water samples for TSS are collected in 1-L dark bottles and stored on ice ( $\sim$ 4°C) and in the dark until they can be delivered to DLS for processing and analysis. A 7-day holding time from collection to analysis was established in a study conducted by the University of Rhode Island (Albro *et al.* 1998).

# **B.2.5.9** Respiration

Water will be collected in six 300—mL BOD bottles at each of three depths (surface, mid-depth, and bottom). 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 (1988) and Battelle SOP 5-317. Three bottles will be fixed immediately according to Battelle SOP 5-317, *Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860 & TIM840* and used to determine initial DO concentration (described above). These 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. The other three bottles will be incubated in the dark, in temperature-controlled incubators that are maintained to within 2°C of *in situ* temperature. The incubation will last from five to nine days depending upon ambient water temperatures (longer in winter/shorter in summer). After the incubation period, the dark BOD bottles will be fixed for the determination of DO concentrations. These samples will be analyzed within 24 h of being fixed.

# **B.2.5.10** Primary Productivity Analysis by <sup>14</sup>C and Dissolved Inorganic Carbon

At each productivity station, samples from each of 5 depths from the Rosette sampling bottle are screened through a 300- $\mu$ m-mesh screen (to remove large zooplankton) into opaque 1-L polyethylene bottles. The bottles will be rinsed three times with sample prior to filling. The samples will be placed in a cooler and transferred to the URI laboratory within a maximum of 8 hours of water sampling. The collected volume is used for both productivity analysis by  $^{14}$ C and dissolved inorganic carbon.

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<sup>&</sup>lt;sup>5</sup> Exact volume filtered will be recorded on sample label and any deviations from standard volume (500 ml for PCN, 200 for Chla, 400 ml for PP, and 250 for BSi) will be noted in station log.

# **B.2.5.11** 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.

# **B.2.5.12** Screened and Rapid-Analysis Phytoplankton

For the screened and 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-µm-mesh screen. Using a squeeze bottle containing seawater that has passed through the 20-µm-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. The plankton samples 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 "M", "H", and "Z" type stations, a vertical-oblique zooplankton tow will be conducted with a 0.5-m diameter 102 um-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 provided 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 in Section B.2.6. The flow meter reading before and after the tow, the tow time, and the depth of the tow will be recorded on the zooplankton custody form.

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 a couple of times 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 a 10% formalin to seawater solution. All zooplankton samples will be stored at ambient temperature in the dark until they are analyzed.

# **B.2.7 Floating Debris**

Collection of floating debris is described in Section B.1.7. After the net tow is completed, the sample will be emptied into a white dissection basin for a visual, qualitative inspection. The basin will have a black stripe along the bottom, either paint or electrical tape, to provide contrast. Types and relative amounts of anthropogenic and natural debris will be documented in the survey log. Each sample will be digitally photographed with the date, time, and survey ID, along with a ruler for visual scale. The basin filled with sample should take up the entire frame of the photograph. Photographs will be taken both with and without the flash to ensure a quality photo has been taken. Identifiable anthropogenic materials (*e.g.*, plastics) will be retained and archived. Digital images will be included in the survey email summary and described in the survey report.

#### **B.2.8** Whale Observation

During each nearfield survey and the first three farfield 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 and when the vessel is in Massachusetts Bay or Cape Cod Bay. The observer will scan the ocean surface by eye for a minimum of 40 minutes every hour. The horizon will be swept  $180^{\circ}$  during transit between stations ( $\pm$  90° of heading) and 360° while on station. All sightings will be recorded on standardized marine mammal field sighting logs (Figure B-9). 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.

Right whale sightings will be immediately reported to the National Marine Fisheries Service Northeast Right Whale Sighting Advisory System, Woods Hole MA (see Appendix II for contact information).

#### **B.3.** SAMPLE HANDLING AND CUSTODY

# **B.3.1** Sample Custody

Nearfield and farfield 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-10). For samples that are not analyzed

						Mari	ne M	amn	nal S	ight	ings	Log						
Task:	7	Гуре:		[	Date:		Page _	of _	_			(	Observ	er:				
Date	Time	Positi Sigh		Vessel Heading		Mammal Sighting				Weath	ner Cor	nditions			Gla	are		
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
							С	ode Li	st									
	Specie	76								Sea	State							
	Mn Bp Eg	Hump Finba Right	back v ck wha whale	ıle			-			0 1 2	Glas: Catp		3 4 5	1.5 - 3 - 6 > 6 ft	ft	_		
	Ba Lag		whale		dolphir	1				Wind	d Speed	d (knots	)					
	Pp Gn Bn	Pilot v Blue v	whale	oise						0 1 2	0 – 5 5 – 1 10 –	0	3 4 5	15 – 20 - 2 > 25		_		
	Bp Lal	Sei w White	hale beaked	daloh h	in					Swe	ll (feet)							
	Pv G	Harbo Gray	r seal seal	·						0	None 1 – 3		2 3	3 – 6 > 6		=		
H Hooded seal Ha Harp seal Glare										Glar	е							
		Unido	ntified	baleen	whale					0 1	None Mild	<u> </u>	2 3	Mode Seve		=		
	UB UO	Unide	ntified							UP Unidentified Phocid Visibility (miles)								
	_	Unide	ntified							Visib	oility (mi None		4	3-5		_		

Figure B-9. Example of Marine Mammal Sightings Log and Relevant Codes

by DLS (e.g. plankton, respiration, productivity) 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 WF061, with "WF" indicating that it is a farfield water column survey, "06" indicating the survey year, and "1" signifying the first survey of the year (for surveys higher than 9, letters are used where A and B are equal to 10 and 11, respectively). 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.

Samples collected during Task 9 will be identified in the same manner as the water column samples except the *sample\_marker* will always be 001. The *event\_id* will be WB10x where x is an incrementing number from 1 to 4. The *protocol\_id* followed by rep number will be concatenated to the end of the sample id to create a unique bottle id (ex: WB104001DO2 will be the second of the triplicate dissolved oxygen samples collected on the fourth weather buoy servicing of 2010).

Sample custody for DO and chlorophyll samples collected during Task 9 buoy service surveys will be documented by hand using a standard Battelle custody form (SOP 6-040 Sample Custody, Receipt, and Handling for Field Activities). Sample custody will be maintained as described in this section.

The scientific crew member operating the data collection system will fill out the station log (Figure B-11) at each station. These logs will be put into a survey logbook prior to the survey. 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 hydrocast CTD data will be logged and stored electronically on the computer's hard disk. When Rosette sampling bottles are closed, the operator will enter the Group ID and 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 during field collection as the sample is packed into laboratory specific coolers, and chain-of-custody forms are generated by NavSam<sup>©</sup> 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-12, Figure B-13, and Figure B-14).
- The NavSam<sup>©</sup> 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. Log sheets will include custody information in any instances where separate custody forms are not used (e.g., respiration samples). 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 6 years after project completion, and then provide them to MWRA upon request.

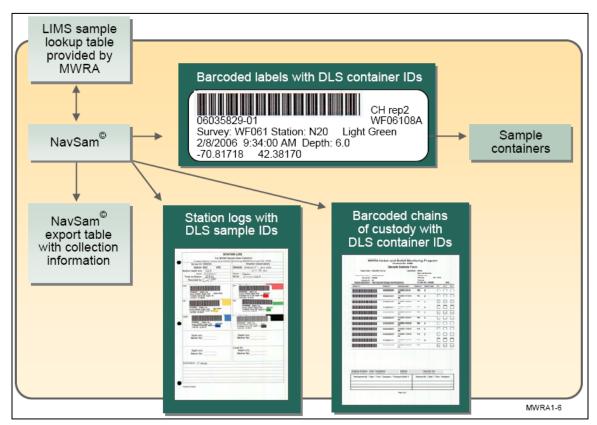


Figure B-10 Depiction of Linkage from DLS LIMS to NavSam<sup>©</sup>

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

Analysis Codes	Description	Laboratory
AP	Primary productivity	URI
BS	Biogenic silica	DLS
СН	Chlorophyll	DLS
DO	Dissolved Oxygen	Battelle
IC	Dissolved inorganic carbon	URI
IN	Dissolved inorganic nutrients	DLS
NP	Total dissolved nitrogen and phosphorous	DLS
OC	Dissolved organic carbon	DLS
PC	Particulate carbon and nitrogen	DLS
PP	Particulate phosphate	DLS
RE	Respiration	Battelle
RP	Rapid analysis phytoplankton	Pausacaco Plankton
SW	Screened water phytoplankton	Pausacaco Plankton
TS	Total suspended solids	DLS
WW	Whole water phytoplankton	Pausacaco Plankton
ZO	Zooplankton	UMD

ST	ATION LOG
For BOSS	Sample Data Collection
The second secon	and Outfall Monitoring Project No. N007559
Survey ID: WF101	Weather Observations
Station: N18 WN	General:
Bottom Depth (m):	
Date:	Seas:
Time on Station:	Wind:
Recorded by:	
LevelID: 0 (Station Arrival)	LevelID: 1 (Bottom)
D - (I- ()	Depth (m):
Marker No:	Marker No:
IVIAINEL INO.	IVIAIREI IVO.
LevelID: 2 (Mid-Bottom)	LevelID: 3 (Mid-Depth (C-Max))
Depth (m):	Depth (m):
Marker No:	Marker No:
LevelID: 4 (Mid-Surface)	LevelID: 5 (Surface)
Depth (m):	Depth (m):
Marker No:	Marker No:
LevelID: 6 (Zooplankton Tow)	
Depth (m):	Depth (m):  Marker No:
Marker No:	Marker No:
	Level ID:
Depth (m):	Depth (m):
Marker No:	Marker No:
Comments:	

Printed by NavSam

Figure B-11. Example Sample Station Log

MEASUREM		
	SS Sample Data	
Project Name: MWRA Harbor and Ou		
Survey ID: WF101	Protoco	ol ID: ZO
Station: F01		Starting Flowmeter Reading
		Ending Flowmeter Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		Formalin added (ml)
	Date:	Recorded by:
Station: F02		Starting Flowmeter Reading
		Ending Flowmeter Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F06		1. Starting Flowmeter Reading
		2. Ending Flowmeter Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F13		Starting Flowmeter Reading
		2. Ending Flowmeter Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F22		Starting Flowmeter Reading
		2. Ending Flowmeter Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:

Printed by NavSam

Figure B-12. Example of a Zooplankton Custody Form

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

Today's Date:	2/16/2010 10:06:41	Laborato	ory: MWRA				
			Dept. La	b Services			
Chain-of-Custody #:	WF101-NP-0066		190 Tafts	s Ave			
Survey ID:	WF101		Winthrop	o MA	02152		
Analysis ID :	NP		Yong La	0			
Analysis Description :	Total Dissolved Nitrogen and Pho	sphorous	617-660-	7841 (Phone)		(Fax	t)
Bottle ID:	Bottle ID:	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	2060600	2/2/2010 8:21:14 AM	BB11				
	2060627	2/2/2010 8:23:22 AM	BK11				
	2060628	2/2/2010 6:37:08 PM	BK31				
	2060633	2/2/2010 12:31:48 PM	BK21				
	2062037	2/2/2010 9:56:29 AM	F01	Α			
	2062055	2/2/2010 9:55:14 AM	F01	С			
	2062066	2/2/2010 9:53:48 AM	F01	E			
	2062076	2/2/2010 10:58:02 AM	F02	Α			
	2062089	2/2/2010 10:56:43 AM	F02	С			
	2062101	2/2/2010 10:54:57 AM	F02	E			
	2062179	2/2/2010 5:37:07 PM	F19	Α			
	2062191	2/2/2010 5:36:07 PM	F19	С			
	2062203	2/2/2010 5:33:10 PM	F19	E			
	2062213	2/2/2010 5:08:41 PM	F22	A			
	2062226	2/2/2010 5:07:38 PM	F22	С			
	2062237	2/2/2010 5:05:05 PM	F22	E			
Shipping Condition - Ro	oom Temperature:	Cold(ice):	F	rozen(ice):			
Received Condition - Ro	om Temperature:	Cold(ice):		ozen(ice):			
Relinquished By / D	ate / Time / Company / Tran	nsport-Airbill #	Received	By / Date /	Γime / C	Compan	У
							-
			- market - under		200		

Page 1 of 2

Figure B-13. Example of Water Chemistry Custody Form with LIMS generated IDs

# **MWRA Harbor and Outfall Monitoring Program**

# Project No. N007559 Sample Custody Form

Today's Date: 2/16/2010 10:06:51

Laboratory: University of Massachusetts, Dartmouth

**Biology Department** 

Chain-of-Custody #: WF101-ZO-0074

285 OldWestport Road

Survey ID: WF101 Analysis ID: ZO

North Dartmouth MA 02747-2300

Dr. Jefferson Turner

Analysis Description : Zooplankton			508-999-	8229 (Phone)	508-999-8	3197 (Fax	()
Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	WF10105AZO1	2/2/2010 9:56:31 AM	F01	z			
	WF101063ZO1	2/2/2010 10:25:56 AM	F32	Z			
	WF101074ZO1	2/2/2010 10:58:03 AM	F02	Z			
	WF101080ZO1	2/2/2010 11:33:00 AM	F33	Z			
	WF1010C9ZO1	2/2/2010 2:37:42 PM	F27	Z			
	WF1010E1ZO1	2/2/2010 4:28:08 PM	F26	z			
	WF1010EFZO1	2/2/2010 5:08:43 PM	F22	z			
	WF101113ZO1	2/2/2010 6:12:18 PM	N16	Z			

Cold(ice):	Frozen(ice):
ransport-Airbill #	Received By / Date / Time / Company

Page 1 of 1

Figure B-14. Example of Custody Form with NavSam<sup>©</sup> 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 Battelle's 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.

Battelle, DLS, URI, Pausacaco Plankton, and UMD will produce electronic data under this task. At Battelle, the electronic files for respiration data will remain in the custody of the Task Leader (Ms. Annie Murphy) 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 HOM7 data management team for submission to MWRA.

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. Candace Oviatt (URI)] until an independent QA audit has been completed. With the exception of DLS data, once the data have passed the independent laboratory QA audit, 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. DLS data will be processed in its entirety by MWRA staff.

## **B.3.3** Custody of Water Samples

During field collection, NavSam<sup>©</sup> will create chain forms from the sample table used to generate sample labels, thereby creating a link between the sample and data recorded on the chain form. The chain forms will have the same Bottle ID (LIMS or NavSam<sup>©</sup>) 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<sup>©</sup> prior to delivering the samples to the laboratory.

- Nutrient and TSS 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. During farfield surveys samples may be hand-delivered to MWRA once the survey is complete. 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.
- Productivity samples are stored on ice during the survey and delivered to URI staff at the dock within two hours of collection.
- Zooplankton and farfield phytoplankton samples are returned to Battelle and hand-delivered after the survey; nearfield phytoplankton samples are shipped via Federal Express.
- 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 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 and the Battelle Laboratory Coordinator will be notified. The 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 to the Battelle Laboratory Coordinator with the data submission and maintained in the MWRA project files. 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.* 2008) for Nutrient and Chlorophyll Analyses for Outfall Monitoring (January 2008, revision in preparation):

- Dissolved Inorganic Nutrients
- Dissolved Organic Carbon
- Total Dissolved Nitrogen and Phosphorus
- Particulate Carbon and Nitrogen
- Particulate Phosphorus
- Biogenic Silica
- Chlorophyll a and Phaeophytin
- Total Suspended Solids

#### **B.4.1 Respiration**

The rate of oxygen consumption will be calculated by MWRA using 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*. Two sets of triplicate DO samples will be collected for each respiration analysis. The first set will be fixed and analyzed immediately providing a measurement of DO concentration for that sampling depth as well as the initial DO concentration for the respiration calculation. The second set will be fixed and analyzed after the incubation period and provide a measure of the final or dark bottle DO concentration.

# **B.4.2** Primary Production by <sup>14</sup>C

Primary production is measured using a small volume/short incubation time method (Lewis and Smith, 1983) using procedures from Strickland and Parsons (1972). Additional details may be found in Libby *et al.* 2005 Appendix C. Prior to receipt of the productivity samples, 20 mL borosilicate vials (18 per depth sample) are spiked with 100  $\mu$ L of 10  $\mu$ Ci/mL (1 $\mu$ Ci for 5 mL of water) Carbon-14 ( $^{14}$ C) stock solution. The vials are chilled if they are not to be filled with sample water immediately. Under subdued yellow light, individual samples are gently mixed thoroughly and approximately 500 mL are poured into a repipette. (The repipette is rinsed twice with ~50 mL of sample prior to use.) The delivery tip of the repipette is flushed three times and 5 mL of sample is pipetted into the spiked 20 mL borosilicate vials. A total of 18 vials (16 light and 2 dark) are filled for each depth, capped, and the two dark vials are immediately placed into opaque covers. Each vial is placed into a specified location in an incubation tray. Neutral-density screening is applied to selected vials to achieve the desired range of light intensity (0-

2000  $\mu E \ m^{-2} \ s^{-1}$ ). The trays are placed into a light (250 W Tungsten-halogen lamps) and temperature controlled incubator and are incubated within 2°C of the *in situ* temperature. The exact length of the incubation is used in calculating productivity; it is nearly always one hour. When productivity is low the incubation period may be increased to two hours. It is not always possible, especially during summer-stratified conditions (large temperature gradient surface to bottom), to maintain the incubators at a temperature within 2°C of the *in situ* temperature throughout the incubation period. Therefore, a correction factor [C.F. = exp (0.0693 (*in situ* temperature – average incubation temperature))] is applied to hourly productivity values before fitting P-I curves. This correction is performed by MWRA.

Time and temperature are recorded at the start and end of the incubation period. The light intensity at each vial location within the incubator is measured before the incubation period. Light is measured with a LiCor 192SA cosine irradiance sensor, which is calibrated every two years (calibration factors are stored in the LiCor data logger). Upon removal from the incubator,  $200~\mu L$  of 0.10N HCl is added to each vial. Vials remain uncapped while gently agitated in the dark for a minimum of 36 hours (not to exceed 40 hours). After this time period, 17 mL of MP Biomedicals Universol Scintillation Cocktail is added and the tightly capped vials are shaken vigorously. All samples are dark adapted for at least 12 hours prior to being counted.

To calculate the specific activity added on each incubation date, 100 μL of 10 μCi/mL  $^{14}$ C stock is added to each of three vials containing 3 mL of β-phenylethylamine. After the stock is added, 17 mL of scintillation cocktail is added. The three specific activity vials, along with one blank containing 17 mL of Universol, are counted with each set of samples. Measurements are counted on a Packard TriCarb Liquid Scintillation Counter (Model 2900). The scintillation counter is configured to measure single labeled  $^{14}$ C samples as disintegrations per minute (DPM) for five minutes. All samples are measured once completing the entire set, then the process is repeated twice more, resulting in three measurements for each sample. The Model 2900 was calibrated on January 2009, using Packard's  $^{14}$ C and  $^{3}$ H standards and background. The  $^{14}$ C and  $^{3}$ H efficiencies were 95.27% and 62.33%, respectively.

Light profile data are reviewed during phase 1 post-survey processing, again prior to delivery to MWRA and finally by MWRA after delivery and loading into EM&MS, during which data are qualified for:

- Ship shadow, manifested as reduced light values usually near the surface;
- Significant occurrences of a positive slope (light increasing with depth), not caused by corresponding increasing ambient light;
- Significant blips, beyond typical background noise, (approximately > 1/5th of a decade).

Profiles of light with and without correction for surface irradiance will be used by MWRA to develop the best available profile curve. Any other anomalies in light profiles noted during this analysis that lead to the exclusion of data from the fit will be communicated to the Battelle Data Management Team. MWRA will fit the light profiles and use the results in the calculation of daily production.

**Daily Incident Light Field.** Incident light data are collected and recorded at 15-minute intervals by MWRA at Deer Island using a Biospherical Instruments QSR-240 reference scalar irradiance sensor. The same model instrument is used to routinely measure incident light on deck during surveys. The MWRA sensor is calibrated and maintained by MWRA similarly to the Battelle sensor as described in Section B.6 (calibration coefficients recorded in the MWRA database). The incident light data collected at Deer Island are used as the photoperiod incident light ( $I_0$ ) time series described below. The Deer Island data are collected using a scalar sensor and the light intensity measured in the incubator is collected with a cosine sensor.

The cosine values are converted by MWRA to scalar readings using an empirically determined equation:

scalar = 
$$19.2 + 1.098 (\cos) - 0.00011 (\cos)^2$$

with both scalar and cosine light intensity in units of  $\mu E m^{-2} sec^{-1}$ . The  $r^2$  for the empirical equation is 0.997. The light data are converted prior to fitting the P-I curves.

## **B.4.3** Dissolved Inorganic Carbon

Subsamples for DIC analysis are siphoned out of the productivity sample at URI with a small-bore tube into a 40ml vial so as not to introduce any air bubbles. After replacing the volume 2 times, the tube is removed and two drops (0.1 mL) of Sodium Azide are added for preservation. The vial is capped with a Teflon/silica septa, making sure no bubbles are present, and stored at 4° C until analysis. Duplicate samples are collected, from which three replicates are measured. Samples are not filtered, but interference from particulate inorganic carbon is negligible.

Analysis is performed on an OI Total Organic Carbon Analyzer Model 1010, which can analyze aqueous samples for DIC in the range from 1 ppb to 10,000 ppm C with no sample pre-treatment, prepurging, or dilution. Inorganic carbon is determined by the measurement of carbon dioxide released by acidification of a sample. As the pH of the sample is lowered, carbonate and bicarbonate ions are converted to dissolved carbon dioxide. This carbon dioxide is purged from solution, concentrated by trapping, then desorbed and carried into a non-dispersive infrared analyzer (NDIR) that has been calibrated to directly display the mass of carbon dioxide detected. This mass is equivalent to the mass of DIC in the sample. Concentration of DIC is calculated by dividing this mass by the sample volume.

# **B.4.4** Whole-Water Phytoplankton

The methods discussed below have been used for the identification and enumeration of phytoplankton species during HOM3 through HOM6. 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  $500 \times = 1/48$  of one ml of concentrate, and at  $250 \times = 1/24$  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  $500 \times$  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  $10^6$  cells per liter.

The two-step counting protocol allows for improved precision in estimating abundances of small ( $<10\mu m$  greatest axial linear dimension) and larger phytoplankton forms. Counting large numbers of small forms at  $500\times$  increases the precision of the estimated abundances of these forms. The counts at  $250\times$  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  $250\times$  analysis, the  $500\times$  objective can be used as needed to resolve key taxonomic characters.

# **B.4.5** Screened Phytoplankton (Dinoflagellates)

As with whole water plankton, the methods discussed below have been used for the identification and enumeration of phytoplankton species during HOM3 through HOM6. A taxonomist will identify and count the following target dinoflagellates. Additional taxa may be noted at the discretion of the taxonomist

Alexandrium tamarense Alexandrium fundyense Ceratium spp. Dinophysis spp. Gymnodinium spp. Gyrodinium spp. Prorocentrum spp. Protoperidinium spp.

The 4 liter seawater sample will be sieved through a 20µm Nytex mesh in the field to yield a 50-100 ml intermediate sample that is further concentrated via gravitational settling in the laboratory. Settling will be done in glass cylinders having a height to diameter ratio of greater than 5 to 1. Typically the sample concentration ratio will be 1,000 to 1, derived from the 4 L (seawater volume) to 4 ml (concentrate volume). However, final concentrate volumes >4 ml may be used if >20µm particles (which will obscure cells in the counting chamber) are abundant in a sample. One ml of the concentrated seawater sample will be placed in a 1ml Sedgewick-Rafter chamber and horizontal paths of the chamber will be scanned at 250X magnification. Counting will continue until the end of the path in which 400 or greater taxa are observed, or after scanning one complete (1ml) Sedgwick-Rafter chamber. Using typical sample volumes, observation of one (1) cell in a scan of the entire Sedgwick-Rafter chamber will yield an abundance estimate of 1 cell per liter in the sea; as follows:

[1 cell / 1ml concentrate scanned \* 4 ml SW concentrate] / 4 liters seawater = 1 cell L<sup>-1</sup> seawater

#### **B.4.6** 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.

#### **B.4.7** Zooplankton

The methods discussed below have been used for the identification and enumeration of zooplankton species during HOM3 through HOM6. 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 water 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 and Table B-9. 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 and Table B-9. If the *in situ* fluorometer readings for chlorophyll a exceed 20 µg/L, an additional chlorophyll a sample will be collected at that depth.

#### **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 followed by a triple rinse of Milli-Q water. Between stations and at the end of the day, the equipment is triple rinsed with Milli-Q.

#### **B.5.3** Field blanks

Field blank processing for dissolved parameters follows the exact procedures for sample processing, but with Milli-Q water in place of seawater. Milli-Q water is supplied by DLS. For DIN, there are two types of sample processing: 1) collection of DIN samples from the filtrate of the BSi station, and 2) collection of DIN from the dedicated DIN station (using syringes and filter cartridges). Field blanks for DIN are collected by each of these methods. Filter blanks are collected for PC/PN, PP, biogenic silica, and chlorophyll by placing a new, unused filter directly into the appropriate sample container (test tube for BSI; foil packet for other parameters). Table B-8 and Table B-9 detail the collection of field blank samples. All samples will be labeled with a bar-coded label produced by NavSam<sup>©</sup> 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 being filled the Milli-Q water supplied by DLS without a triple rinse. These samples will also be labeled with a bar-coded label produced by NavSam<sup>©</sup> prior to being stored in the freezer. A duplicate label for each field blank is pasted into the survey log book.

# **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 and Table B-9 detail the collection of field replicate samples.

Table B-8. QA/QC Samples for Nearfield.

Analysis Type	Qty	Depths	Stations
Field Replicates			
Dissolved inorganic nutrients	1	Mid-depth	All stations except N18
(DIN)			
Other nutrients (DOC, TDNP)	1	Mid-depth	N16
Chlorophyll	1	Mid-depth	All stations
TSS	1	Mid-depth	N01 and N10
Blanks			
Filter Blanks for PC/PN, PP,	2/day/parameter	NA	Collected at the beginning and end of the
Biogenic Si, Chlorophyll			sampling day.
Field Blanks:	3/day/parameter	NA	One blank for each analysis will be
DIN – BSi filtrate			collected at the beginning of the day,
DIN –DIN syringes			mid-day, and at the end of the day. If
TDNP			only half-day of sampling is needed then
			only 2 sets of field blanks are required.
Bottle Blank for DIN, TDNP	3	NA	One blank per container type per day with
			morning field blanks.

Table B-9. QA/QC Samples for Farfield.

Analysis Type	Qty	Depths	Stations
Field Replicates			
Dissolved inorganic nutrients (DIN)	1	mid-depth	F02, F06, F13, F22, F25, F27, and N16
(DIN)			
Nutrients (DOC, TDNP)	1	mid-depth	N16
Chlorophyll	1	mid-depth	B, M, H, R, and P stations.
TSS	1	Mid-depth	F02 and F19
Blanks			
Filter blanks for PC/PN, PP,	2/day/parameter	NA	Collected at the beginning and end of the
Biogenic Si, Chlorophyll			sampling day.
Field Blanks:	3/day/parameter	NA	One blank for each analysis will be
DIN – BSi filtrate			collected at the beginning of the day, mid-
DIN –DIN syringes			day, and at the end of the day. If only
TDNP			half-day of sampling is needed then only
			2 sets of field blanks are required.
Bottle Blank for DIN, TDNP	3	NA	One blank per container type per day with
			morning field blanks.

# **B.5.5** Laboratory Program

Table B-10 summarizes the laboratory measurement quality objectives for water column monitoring under this contract. Section B.4 provides additional details on the analytical procedures (*e.g.*, prepared standards) that will ensure data quality, and Section B.6 describes instrument calibration methods.

# **B.5.6** Precision and Accuracy

Precision and accuracy of laboratory procedures are ensured by the analysis of QC samples including procedural/filter blanks, prepared standards, SRMs, laboratory replicates and field replicates, as applicable. Table B-10 summarizes the laboratory QC samples analyzed by Battelle and URI for HOM7 water column parameters. Measures of precision and accuracy for analysis performed by DLS are described in MWRA DLS QAPP Nutrient and Chlorophyll Monitoring (Leo *et al.* 2008, revision in preparation). The QC procedures used to access accuracy and precision of phytoplankton and zooplankton methods are described below.

Table B-10. Measurement Quality Objectives for analyses by Battelle and URI

O	uality Control Sample Type	Frequency	Data Quality Indicator	Corrective Action
	anks	1 3		
	Primary Productivity by <sup>14</sup> C (Dark bottle)	One with every station	<100 DPM	Results examined by laboratory manager, task leader, or project manager. Corrective action (e.g., reanalysis, data qualifier) is documented.
	DIC (Procedural Blank)	One with every station	≤ 0.4 mg C/L	As above
St	andards			
	Primary Productivity by <sup>14</sup> C (Spiking solution)	3 per survey	≤5% PD¹	As above
La	aboratory Replicates			
	Primary Productivity by <sup>14</sup> C (Triplicate exposures)	All samples	$\leq 10\% \text{ RSD}^2$	As above
	DIC (duplicate samples analyzed three times each by the instrument)	One each station depth	≤5% RSD <sup>2</sup>	As above
	Dissolved Oxygen	Respiration stations at Bottom, Mid, &Surface Depths	≤5% RSD <sup>2</sup>	As above

<sup>&</sup>lt;sup>1</sup> Percent Difference (PD) = [(nominal concentration – measured concentration)/nominal concentration] x 100%.

#### **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.4.4, for this program, a minimum of 400 entities (solitary single cells, chains, or colonies) will be tallied for each

<sup>&</sup>lt;sup>2</sup> Relative Standard Deviation (RSD) = (Standard deviation x 100) / average

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 then 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 ensure the accuracy and comparability of the results. Two whole water samples from each of the farfield/nearfield combined surveys in February (one survey), April, June, August and October will be analyzed in duplicate. This range of samples should cover the major taxonomic groupings and various levels of abundance. 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 RPD for total and the most dominant species should be  $\leq 20\%$ . 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** Screened Water Phytoplankton

As with whole water phytoplankton, counts of 400 phytoplankton cells will provide a precision of  $\pm 10\%$  of the mean. A minimum of 400 entities of the target dinoflagellate taxa will be counted, or an entire Sedgwick-Rafter cell, whichever comes first. Similar to whole water plankton, 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 ensure the accuracy and comparability of the results. Two screened water samples from each of the farfield/nearfield combined surveys in February (one survey), April, June, August and October will be analyzed in duplicate. The results, as RPD, will be included in the data submission to Battelle. The RPD for total and the most dominant species should be  $\leq 20\%$ . If the RPD is greater than 20 a second aliquot will be counted and the three results used to calculate the 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. Two samples from each of the farfield/nearfield combined surveys in February (one survey), April, June, August and October will be analyzed in duplicate. This range of samples should cover the major taxonomic groupings and various levels of abundance. The results, as RPD, will be included in the data submission to Battelle. The RPD for total and the most dominant species should be  $\leq 20\%$ . 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.5.7** Completeness

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

#### **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, 2008, and 2009b), 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 for Nutrient and Chlorophyll Monitoring (Leo *et al.* 2008, revision in preparation).

# 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<sup>©</sup> 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 Seabird 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  $\pm$  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  $\pm$  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

The Data Sonic PSA-916 altimeter is calibrated at Battelle annually according to the manufacturer's instructions. Records of calibration and factory maintenance are documented on the instrument history sheet in the field management files.

#### B.6.1.4 In Situ Dissolved Oxygen

The software gain and offset of the dissolved oxygen sensors (SeaBird Model 43) will be calibrated annually at SeaBird. 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 Lab 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  $50 \,\mu\text{g/L}$  chlorophyll in a *Thalassiosira weissflogii* phytoplankton culture). The fluorometer data, displayed with the NavSam® program, will approach 0.0  $\mu\text{g/L}$  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-200L 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  $\mu$ E 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.

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-200L** (Underwater Irradiance Sensor)

The Biospherical Instruments Logarithmic Output Oceanographic Light Transducer (QSP-200L) 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-200L 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-200L 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).

If it is clear that the instrument calibration has drifted over time and the factory calibration is no longer appropriate, deep profile readings could 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-200 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 Northstar 952-XDW 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 as follows:

- 1. An absolute position is obtained from published charts with a position accuracy approaching 2 sec (approx. 40 m). Alternatively, if a second GPS is available, the coordinates from the second GPS can be used for the absolute position.
- 2. The NavSam<sup>©</sup> 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, the data are manually entered into the first or last station log for that day.

#### **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<sup>©</sup> operator at appropriate depths during the upcast.

#### **B.6.1.10** Nets and Flowmeter

All nets used for zooplankton and marine debris 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, then it will be replaced using a back-up unit stored on the survey vessel.

## B.7. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Calibration procedures for laboratory instruments are summarized in Table B-11. All laboratory calibration records will be reviewed by analysis task leaders and maintained in laboratory notebooks. 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 for Nutrient and Chlorophyll Monitoring (Leo *et al.* 2008, revision in preparation).

Parameter	Instrument Type	Initial Calibration			Continuing	Corrective Action	
		No. Stds	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	
Dissolved oxygen for respiration	Radiometer Titralab TM	1	NA	Prior to analysis for each survey	NA	NA	Investigate, recalibrate
Primary Production by <sup>14</sup> C	Packard TriCarb Liquid Scintillation Counter Model 2900	1	Sealed standard (1.333 x 10 <sup>5</sup> dpm)	Prior to sample analysis	PD from true value ≤2%	NA	Investigate, recalibrate
DIC	TOC Analyzer	5	$R^2 \ge 0.990$	Each analysis day	24 mg C/L RSD ≤5%	Beginning and end of sample run	Investigate, recalibrate

**Table B-11. Calibration Procedures for Laboratory Instruments** 

# 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.
- Deionized 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 standards must be certified as at least 96% pure or the lot-specific analysis purity be incorporated into calculation of the standard concentration. Standards 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 HOM7 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-15 illustrates the water-column-monitoring data processing strategy for data entry into the MWRA Environmental Monitoring and Management System (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 and conductivity using the equations of Fofonoff and Millard (1983), and dissolved oxygen percent saturation is calculated from dissolved oxygen 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.

NavSam<sup>©</sup> records both the raw and calibrated data. During data reduction, NavSam<sup>©</sup>'s post-processing module or another method will be used to (1) correct the raw irradiance for the fact that light sensor is at the top of the rosette while the depth sensor is at the bottom of the rosette and (2) 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<sup>©</sup> export). After the editing is complete, the profile upcast data recorded during discrete water sample collection will be processed. NavSam<sup>©</sup> 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  $\pm$  2.5 seconds of the moment of bottle closing). These files will serve as the export file to the EM&MS database.

Step 1 in the previous paragraph corrects for the depth offset of the irradiance sensor. 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 will simply let the corrected depth equal the raw depth minus the vertical offset. The new method gives smoother light profiles and more data near the surface.

Project-specific SOP MWRA 001 *Processing and Calibrating CTD Data and Creating Profile Data Files* 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. Laboratory replicates generated by BOS, Pausacaco Plankton, URI, and UMD will be reported as mean sample values; DLS will report only the first laboratory replicate. All field replicates will be reported as individual sample values.

### Calculation of Dissolved Oxygen and Respiration

The concentration of DO in units of (mg O<sub>2</sub> L<sup>-1</sup>) will be determined using the following equation:

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

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.

The calculation of net respiration will be performed by MWRA.

#### **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 to MWRA electronically in the absence of the

HOML Web application. Once the HOML application goes online, Battelle will submit data through this application.

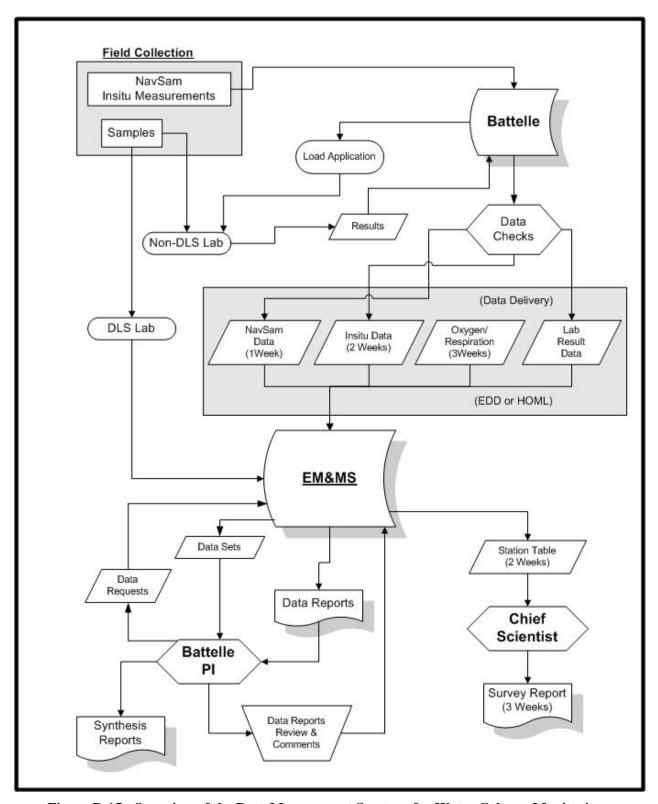


Figure B-15. Overview of the Data Management Strategy for Water Column Monitoring

# **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<sup>©</sup> 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 SOP MWRA 001 *Processing and Calibrating CTD Data and Creating Profile Data Files*.

# **B.10.2.2** Hydrographic Data

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

- Date, time, location, and final calibrated sensor data associated with each water sample (upcast data)
- Date, time, location, and final calibrated vertical profile sensor data that has been bin-averaged into 0.5-m bins (downcast data)

A database application will be used to load the hydrographic data from the processing database directly into Battelle's database. Table B-12 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.

# **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 database 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-16). 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

Table B-12. Database Codes for Hydrographic Parameters

Parameter	Param_Code	Unit_Code	Instr_Code <sup>1</sup>	Meth_Code
Conductivity	CONDTVY	mS/cm	SB4_(Serial Number)	BOSS
Dissolved Oxygen	DISS_OXYGEN	mg/L	DO3_(Serial Number)	BOSS
Fluorescence	FLUORESCENCE	ug/L	WS_(Serial Number)	BOSS
in situ 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	С	SB3_(Serial Number)	BOSS
Transmissivity	TRANS	m-1	T1R25_(Serial Number)	BOSS
Percent Saturation, Dissolved Oxygen	PCT_SAT	PCT	DO3_(Serial Number)	BOSS

<sup>&</sup>lt;sup>1</sup> Instrument codes: (Serial Number) indicates unique probe serial number

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-17), 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.

Within the loading application, the data entered by the laboratory is translated into the correct codes and inserted into database tables with the same structure as the matching EM&MS table. Table B-13 shows the qualifiers to be used by the laboratory. Database codes for plankton taxonomy and species qualifiers are presented in Table B-14 and Table B-15, respectively.

Table B-16 shows the analytical parameters, codes, and units of measure for the analytes collected under this task. Database code descriptions are provided in Table B-17. 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*.

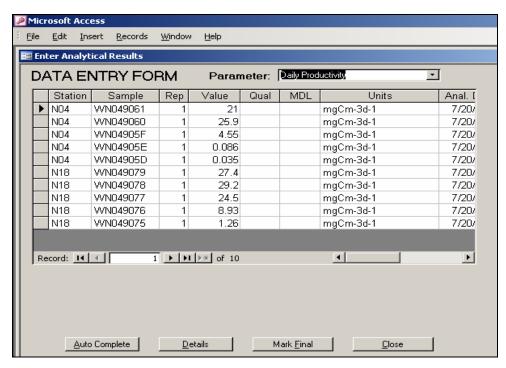


Figure B-16. Example of Loading Application Data Entry Form

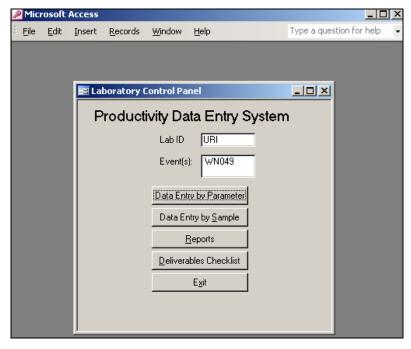


Figure B-17. Loading Application Main Menu

**Table B-13. 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 ≥5x MDL	Yes
c	Ambient	Yes
d	Accuracy does not meet data quality objectives	Yes
Е	Calibration level exceeded	Yes
e	Results not reported, value given is NULL, see comments field	No
f	Value reported <mdl< td=""><td>Yes</td></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
0	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

Table B-14. Database Codes for Plankton Taxonomy

Plankton Analysis	Unit_Code	Meth_Code	Anal_Lab_ID
Whole-Water Phytoplankton	E6CELLS/L	COU_WW	PP
Screened Phytoplankton	CELLS/L	SCR20U	PP
Zooplankton	ind/m3	COU_ZO	UMD

Table B-15. Database Codes for Species Qualifiers

Qualifier	Description
A	Adult (not sexed)
В	Cyst
С	Copepodites
F	Female
K	Colonial species, not counted individually
L	Larvae
M	Male
N	Nauplii
0	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-16. 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
Incubation Temperature for Respiration	INCUB_TEMP_RESP	С	BOS		
Incubation Time for	INCUB_TIME_RESP	hours	BOS		
Respiration					
Incubation Time	INCUB_TIME_PROD	hours	URI		
Incubation Temperature	INCUB_TEMP_PROD	C	URI		
Irradiance measured with	COS_IRRAD	uEm-2sec-1	URI		
cosine sensor					
Dissolved inorganic carbon	DIC	mg C/L	URI	TOC_1010	LIBBY09

Table B-16 Database Codes for Chemistry Analytical and Experimental Parameters, continued

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Radioactivity count in	DPM	DPM	URI	PTLSC2900	LIBBY09
disintegrations per minute					
dpm in a vial containing only	DPM_BLANK	DPM	URI	PTLSC2900	LIBBY09
scintillation cocktail					
dpm of dark incubated	DPM_DARK	DPM	URI	PTLSC2900	LIBBY09
bottles					
dpm of the specific activity	DPM_SP_ACT	DPM	URI	PTLSC2900	LIBBY09
vial					

Table B-17. Description of Database Codes

Field_Name	Code	Description
ANAL LAB ID	BOS	Battelle Ocean Sciences, Duxbury, MA
ANAL_LAB_ID ANAL_LAB_ID	DLS	MWRA Department of Laboratory Services, Winthrop, MA
ANAL LAB ID	UMD	University of Massachusetts, Dartmouth, MA
ANAL LAB ID	URI	University of Rhode Island, Narragansett, RI
ANAL LAB ID	PP	Pausacaco Plankton, Saunderstown, RI
INSTR CODE	DO3 (Serial Number)	SeaBird D.O. probe, model SBE-43
INSTR_CODE	LIG2	Biospherical model QSR-240 hemispherical scalar irradiance sensor
INSTR CODE	LIG4	Biospherical Instruments QSP-200L: quantum scalar irradiance profiling sensor
INSTR CODE	PTLSC2900	Packard Tri Carb Liquid Scintillation Counter Model 2900
INSTR CODE	RTL	Radiometer TitraLab Titrator
INSTR CODE	SB3 (Serial Number)	SeaBird temperature sensor, model SBE-3
INSTR CODE	SB4 (Serial Number)	SeaBird 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	CHLASWFLU	Chlorophyll a-sea water-fluorometric
METH CODE	COU WW	Enumeration method for whole-water phytoplankton (Libby et al. 2002)
METH CODE	COU ZO	Enumeration method for zooplankton (Libby et al. 2002)
METH_CODE	LIBBY02	Productivity calculated as in Libby et al. 2002 CWQAPP for water quality monitoring: 2002-2005
METH CODE	LIBBY09	Libby PS et al. CWQAPP for water quality monitoring: 2008-09 revised productivity
METH CODE	OUD88	Oudot et al. (1988)
METH_CODE	PHAESWFLU	Phaeophytin-sea water-fluorometric
METH CODE	SCR20U	Large dinoflag. screening technique 20 microns
UNIT_CODE	С	Degrees Celsius
UNIT_CODE	CELLS/L	Cells per liter
UNIT_CODE	db	Decibars
UNIT_CODE	DPM	Disintegrations per minute
UNIT_CODE	E6CELLS/L	Millions of cells per liter
UNIT_CODE	hours	Hours
UNIT_CODE	ind/m3	Individuals per cubic meter
UNIT_CODE	m-1	Inverse meters
UNIT_CODE	mg/L	Milligrams per liter
UNIT_CODE	mg C/L	Milligrams carbon 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

Table B-17. Description of Database Codes, continued

Field_Name	Code	Description
UNIT_CODE	uM	Micromoles per liter
UNIT_CODE	uM/hr	Micromoles per liter per hour
UNIT_CODE	m	Meters
UNIT_CODE	mS/cm	Millisiemens per centimeter
UNIT_CODE	PCT	Percent

#### **B.10.3** Loading Analytical and Experimental Data into the Harbor Studies 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 a button on 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. The supporting documentation files are included with the data submission. Data deliverables will be combined only with permission from MWRA.

# C. ASSESSMENT AND OVERSIGHT

# C.1. ASSESSMENTS AND RESPONSE ACTIONS

#### **C.1.1** Performance and System Audits

The Battelle QA Officer for the Harbor and Outfall Monitoring Project is Ms. Rosanna Buhl. She will direct the conduct of at least one systems audit to ensure that Tasks 5, 7, and8 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. For electronically acquired data (*e.g.*, navigational data), Ms. Buhl will verify that computer software used to process the data has been validated. 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 V) that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality and a QC narrative of activities.

The Battelle QA Officer will conduct an initiation audit and, as needed, laboratory and field inspections to access compliance with the Quality Management Plan and this QAPP.

Performance audits (e.g., the analysis of SRMs or participation in intercomparison studies) are used to determine quantitatively the accuracy of the total measurement system or its components. Each laboratory is responsible to participate in such studies as available and appropriate.

#### **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 Harbor and Outfall Monitoring Project, including the schedule, costs, and technical performance. She is responsible for identifying and resolving problems that (1) have not been addressed timely or successfully at a lower level, (2) influence multiple components of the project, (3) necessitate changes in this QAPP, or (4) require consultation with Battelle management or with MWRA. 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 Laboratory Coordinator or 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 Section 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<sup>©</sup> 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, achieved method detection limits, 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-13) 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 (Mr. Scott Libby) and Laboratory (Ms. Deirdre Dahlen) Managers and a data report review letter will be sent to MWRA.

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# **Appendix I**

Nearfield and Farfield Sample Collection Requirements

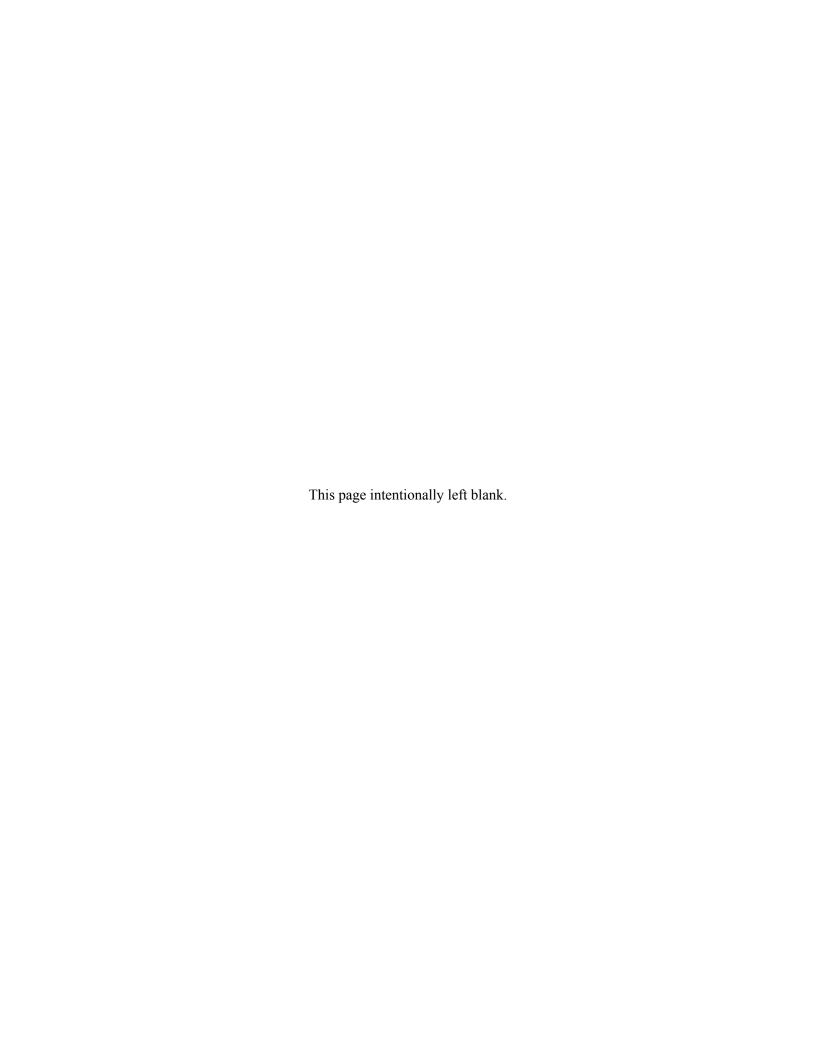


Table I-1. Nearfield Water Column Sampling Plan.

Tab	10 1		Mearment wa	ici C	orum	III Du	ութւ	mg I i	a11.											
StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L collection bottles	Dissolved Inorganic Nutrients	Dissolved Organic Carbon	Total Dissolved Nitrogen and Phosphorous	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Rapid Analysis Phytoplankton	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Diss
			Protocol C	Code		IN	OC	NP	PC	PP	BS	СН	TS	RP	WW	SW	ZO	RE	AP	IC
			Volume	(L)		1	0.1	0.1	1	0.6	0.3	0.5	1	4	1	4	1	1	1	1
			1_Bottom	8.5	2	1	1	1	2	2	2	1	1							
			2_Mid-Bottom	2.5	1	1						1								
N01	30	В	3_Mid-Depth	10	2	2	1	1	2	2	2	2	2							
			4_Mid-Surface	2.5	1	1						1								
			5_Surface	8.5	2	1	1	1	2	2	2	1	1							
			1_Bottom	15.5	2	1	1	1	2	2	2	1	1					6	1	1
			2_Mid-Bottom	4.5	1	1						1							1	1
N04	50	М	3_Mid-Depth	22.1	2	2	1	1	2	2	2	2	1		1	1		6	1	1
		R	4_Mid-Surface	4.5	1	1						1							1	1
		Р	5_Surface	20.6	2	1	1	1	2	2	2	1	1		1	1		6	1	1
			6_Net Tow														1			
			1_Bottom	10.5	2	1	1	1	2	2	2	1	1							
			2_Mid-Bottom	2.5	1	1						1								
N07	52	В	3_Mid-Depth	10	2	2	1	1	2	2	2	2	1							
			4_Mid-Surface	2.5	1	1						1								
			5_Surface	10.5	2	1	1	1	2	2	2	1	1							
			1_Bottom	8.5	2	1	1	1	2	2	2	1	1							
			2_Mid-Bottom	2.5	1	1						1								
N10	25	В	3_Mid-Depth	10	2	2	1	1	2	2	2	2	2							
			4_Mid-Surface	2.5	1	1						1								
			5_Surface	8.5	2	1	1	1	2	2	2	1	1							
			1_Bottom	8.5	2	1	1	1	2	2	2	1	1							
			2_Mid-Bottom	2.5	1	1						1								
N16	40	В	3_Mid-Depth	10.2	2	2	2	2	2	2	2	2	1							
			4_Mid-Surface	2.5	1	1						1								
			5_Surface	8.5	2	1	1	1	2	2	2	1	1							
			1_Bottom	15.5	2	1	1	1	2	2	2	1	1					6	1	1
		М	2_Mid-Bottom	4.5	1	1						1							1	1
N18	30	R	3_Mid-Depth	26.1	3	1	1	1	2	2	2	2	1	1	1	1		6	1	1
		Р	4_Mid-Surface	4.5	1	1						1							1	1
			5_Surface	20.6	2	1	1	1	2	2	2	1	1		1	1		6	1	1
			6_Net Tow														1			
			1_Bottom	8.5	2	1	1	1	2	2	2	1	1							
l			2_Mid-Bottom	2.5	1	1						1								
N20	31	В	3_Mid-Depth	10	2	2	1	1	2	2	2	2	1							
			4_Mid-Surface	2.5	1	1						1								
			5_Surface	8.5	2	1	1	1	2	2	2	1								
	<u> </u>			Tot	als	41	22	22	42	42	42	42	23	1	4	4	2	36	10	10
	d Bl					6	3	3											<u> </u>	ш
_	er Bl								2	2	2	2								ш
Bott	le B	lank				1	1	1												

Table I-2. Farfield Water Column Sampling Plan (4 Pages).

			Tubic 1 2		HICK	1 11 a		Olui			7	<u> </u>	т (т	- 450	5)•				
StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L collection bottles	Dissolved Inorganic Nutrients	Dissolved Organic Carbon	Total Dissolved Nitrogen and	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
			Protocol (	Code		IN	OC	NP	PC	PP	BS	СН	TS	WW	SW	ZO	RE	AP	IC
			Volume			1	0.1	0.1	1	0.3	0.3	0.5	1	1	4	1	1	1	1
<u> </u>			1_Bottom		•						2			'	7	'	'	'	
				7.9	2	1	1	1	2	2		1	1						
			2_Mid-Bottom	2.5	1	1						1							
F01	26	М	3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1	1				
			4_Mid-Surface	2.5	1	1_						1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow													1			
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1						1							
F02	32	М	3_Mid-Depth	15	2	2	1	1	2	2	2	2	2	1	1				
		e e	4_Mid-Surface	2.5	1	1						1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
		ł	6_Net Tow	13								ï				1			
-																			
			1_Bottom	1	1	_1_													
		ļ	2_Mid-Bottom	1	1	1													
F03	16	Е	3_Mid-Depth	1	1	1													
			4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
			1_Bottom	1	1	1													
			2_Mid-Bottom	1	1	1									i				
F05	19	Е	3_Mid-Depth	1	1	1									i				
. 00		_	4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
-				•					_	_	_	1							
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1						1							
F06	33	М	3_Mid-Depth	15	2	2	1	1	2	2	2	2	1	1	1				
			4_Mid-Surface	2.5	1	1						1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
<u></u>			6_Net Tow													1			
			1_Bottom	1	1	1													
		ĺ	2_Mid-Bottom	1	1	1													
F07	54	Е	3_Mid-Depth	1	1	1													
			4 Mid-Surface	1	1	1													
			5_Surface	1	1	1													
-			1_Bottom	1	1	1													
				$\overline{}$															
		_	2_Mid-Bottom	1	1	1													
F10	33	ŀ	3_Mid-Depth	1	1	1													
			4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
1			1_Bottom	4	1	1													
			2_Mid-Bottom	2	1	1													
F12	90	Е	3_Mid-Depth	2	1	1													
1		ĺ	4_Mid-Surface	2	1	1													
1		L																	

StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L collection bottles	Dissolved Inorganic Nutrients	Dissolved Organic Carbon	Total Dissolved Nitrogen and	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
			Protocol 0	Code		IN	ОС	NP	PC	PP	BS	СН	TS	WW	SW	ZO	RE	AP	IC
			5_Surface	4	1	1													
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1						1							
F13	25	М	3_Mid-Depth	15	2	2	1	1	2	2	2	2	1	1	1				
			4_Mid-Surface	2.5	1	1						1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow													1			
			1_Bottom	1	1	1													
			2_Mid-Bottom	1	1	1													
F14	19	Е	3_Mid-Depth	1	1	1													
			4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
			1_Bottom	1	1	1													
			2_Mid-Bottom	1	1	1													
F15	38	Е	3_Mid-Depth	1	1	1													
			4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
			1_Bottom	1	1	1													
			2_Mid-Bottom	1	1	1		İ											
F16	59	Е	3_Mid-Depth	1	1	1		i							i				
			4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
			1_Bottom	1	1	1													
			2_Mid-Bottom	1	1	1													
F17	76	Е	3_Mid-Depth	1	1	1		İ											
			4_Mid-Surface	1	1	1		i							İ				
			5_Surface	1	1	1		i											
Ħ			1_Bottom	1	1	1		i											
			2_Mid-Bottom	1	1	1													
F18	25	Е	3_Mid-Depth	1	1	1													
			4_Mid-Surface	1	1	1		i											
			5_Surface	1	1	1		i							i				
			1_Bottom	7	2	1	1	1	2	2	2	1	1				6		
			2_Mid-Bottom	2	1	1						1							
F19	80	BR	3_Mid-Depth	7	2	1	1	1	2	2	2	2	2				6		
			4_Mid-Surface	2	1	1						1							
			5_Surface	7	2	1	1	1	2	2	2	1	1				6		
			1_Bottom	8.5	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1						1							
F22	80	М	3_Mid-Depth	10	2	2	1	1	2	2	2	2	1	1	1				
			4_Mid-Surface	2.5	1	1						1							
			5_Surface	8.5	2	1	1	1	2	2	2	1	1	1	1				
			6_NET TOW													1			
			1_Bottom	18	3	1	1	1	2	2	2	1	1				6	1	1

StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L collection bottles	Dissolved Inorganic Nutrients	Dissolved Organic Carbon	Total Dissolved	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
			Protocol (	Code		IN	ОС	NP	РС	PP	BS	СН	TS	WW	SW	ZO	RE	AP	IC
			2_Mid-Bottom	8.5	1	1						1						1	2
F23	25	MRP	3_Mid-Depth	24	3	1	1	1	2	2	2	2	1	1	1		6	1	1
			4 Mid-Surface	7.5	1	1						1						1	1
			5_Surface	23	3	1	1	1	2	2	2	1	1	1	1		6	1	1
			6_Net Tow					i							i	1			
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1						1							
F24	21	М	3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1	1				
			4 Mid-Surface	2.5	1	1			_			1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow											Ė		1			
			1_Bottom	9.9	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1		•				1	_ •						
F25	15	М	3_Mid-Depth	15	2	2	1	1	2	2	2	2	1	1	1				
123	13		4_Mid-Surface	2.5	1	1				_	_	1							
$\vdash$			5_Surface		2	1	1	1	2	2	2	1	1	1	1				
				15			-					-	_	_		4			
$\vdash$			6_Net Tow	0.5	•											1			
			1_Bottom	8.5	2	1	1	1	2	2	2	1	1						
<b>500</b>			2_Mid-Bottom	2.5	1	1						1							
F26	53		3_Mid-Depth	10	2	1	1	1	2	2	2	2	1	1	1				
$\vdash$			4_Mid-Surface	2.5	1	1						1							
$\vdash$			5_Surface	8.5	2	1	1	1	2	2	2	1	1	1	1				
$\vdash$			6_NET TOW													1			
			1_Bottom	7.9	2	1_	_1_	1	2	2	2	1_	1						
			2_Mid-Bottom	2.5	1	1						1							
F27	105		3_Mid-Depth	15	2	2	1	1	2	2	2	2	1	1	1				
			4_Mid-Surface	2.5	1	1						1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow													1			
			1_Bottom	1	1	1													
			2_Mid-Bottom	1	1	1													
F28	30		3_Mid-Depth	1	1	1													
			4_Mid-Surface	1	1	1													
			5_Surface	1	1	1													
			1_Bottom	2	1	1													
			2_Mid-Bottom	2	1	1													
F29	65	Е	3_Mid-Depth	2	1	1													
			4_Mid-Surface	2	1	1													
			5_Surface	2	1	1													
			1_Bottom	9.9	2	1	1	1	2	2	2	1	1						
			3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1	1				
F30	12	Н	5_Surface	15	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow													1			
<del></del>			1_Bottom	9.9	2	1	1	1	2	2	2	1	1						

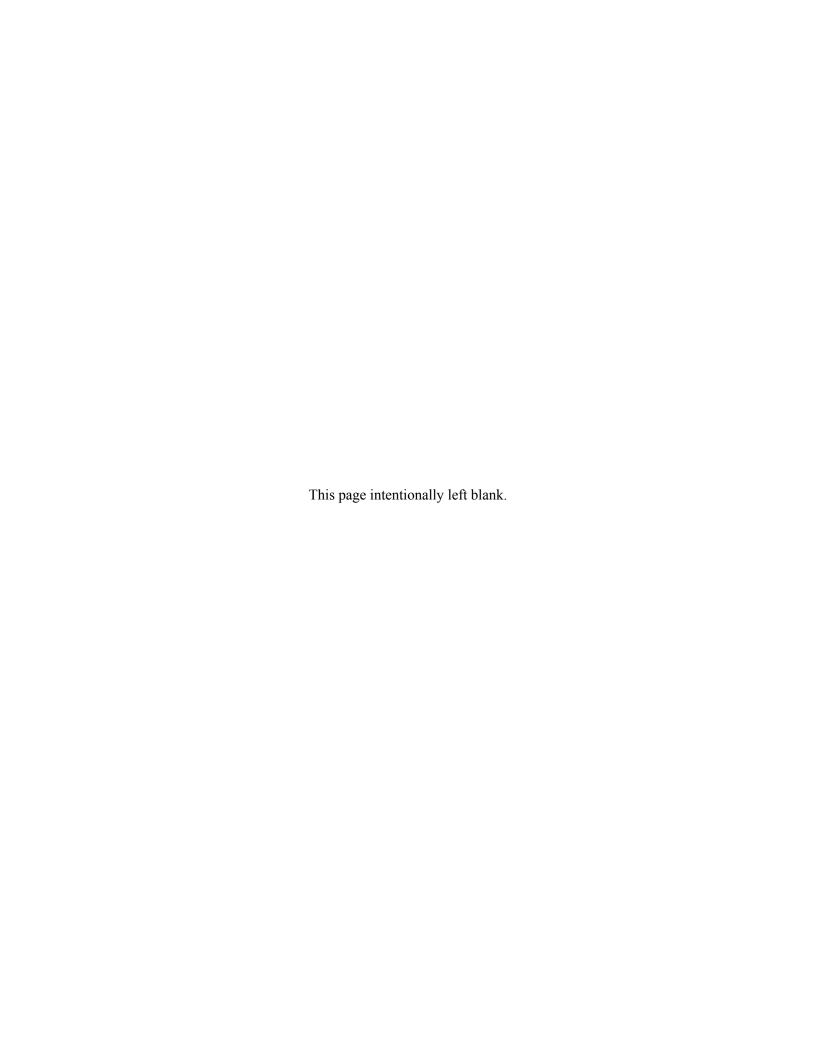
StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L collection bottles	Dissolved Inorganic Nutrients	Dissolved Organic Carbon	Total Dissolved Nitrogen and	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
			Protocol (	Code		IN	OC	NP	PC	PP	BS	СН	TS	WW	SW	ZO	RE	AP	IC
			3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1	1				
F31	15	Н	5_Surface	15	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow													1			
F32	30	Z	6_Net Tow													1			
F33	44	Z	6_Net Tow													1			
			1_Bottom	8.1	2	1	1	1	2	2	2	1	1						
			2_Mid-Bottom	2.5	1	1						1							
N16	42	М	3_Mid-Depth	15	2	2	2	2	2	2	2	2	1	1	1				
			4_Mid-Surface	2.5	1	1						1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1				
			6_Net Tow													1			
				Tot	tals	133	43	43	84	84	84	80	44	26	26	15	36	5	6
	Field	Blank	(per day)			6	3	3											
	Filte	r Blank	(per day)						2	2	2	2							
	Bottle	e Blank	k (per day)			1	1	1											

<sup>\*</sup> Stations F32 and F33 are sampled only during weeks 6, 9, and 15.

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# **Appendix II**

Right Whale Guidance Protocol for Vessels Operated/Contracted by the Commonwealth of Massachusetts (21 November 1997)



# Guidance Protocol on the Interaction with Whales Specifically Northern Right Whales for Vessels Operated/Contracted by the Commonwealth of Massachusetts

#### Introduction

The northern right whale is the most endangered large whale in the world. In the western north Atlantic the population is estimated to be about 300 animals. Massachusetts coastal waters are part of the range of the northern right whale and Cape Cod Bay has been designated a critical habitat for the whale under the federal Endangered Species Act because of its high use by the species in the late winter and early spring for feeding. The Great South Channel, east of Cape Cod, has also been designated critical habitat because of its importance to the right whale as a feeding area. It has been determined that the most significant human induced causes of mortality are ship strike and entanglements in fishing gear.

#### **Purpose**

The purpose of this protocol is to give guidance to the vessels owned by the Commonwealth and those operating under contract to the Commonwealth as to proper operational procedures if the vessels should encounter whales - *i.e.*, sighting and reporting procedures, and entanglement and carcass reporting protocol.

#### **Applicability**

This protocol will apply to all vessels owned by the Commonwealth of Massachusetts and/or contracted out by the Commonwealth of Massachusetts.

# Geographic Scope/Operational Scope

This protocol applies to all applicable vessels operating in or adjacent to Commonwealth waters. When vessels are operating in the designated critical habitat areas (Cape Cod Bay or the Great South Channel) heightened operation is applicable, especially during the late winter and spring when the right whales are expected to be located in these areas.

#### **Sightings of Right Whales**

The Executive Office of Environmental Affairs and the National Marine Fisheries Service is interested in receiving reports from individuals who observe right whales during vessel operations. Reports should be made to the National Marine Fisheries Service Clearinghouse. Patricia Gerrior, NMFS Right Whale Early Warning System Coordinator, who manages the Clearinghouse and her numbers are 508-495-2264 (work), 508-495-2393 (fax) and pager 508-585-8473. Please report your name, agency and phone numbers at which you can be contacted. The vessel's name, the date, time and location of the sighting, the numbers of whales sighted and any other comments that may be of importance. If a camera or video camera is available please take some photographs. These photographs should be provided to Pat Gerrior or Dan McKiernan, Massachusetts Division of Marine Fisheries. They will in turn send copies to the New England Aquarium for comparison to the Right Whale Photo Identification Catalog. Please remember that Massachusetts has Right Whale Conservation Regulations (322 CMR 12:00) which establishes a 500 yard buffer zone surrounding a right whale. Vessels shall depart immediately from any buffer zone created by the surfacing of a right whale.

#### Physical Contact with a Whale

If a vessel owned by the Commonwealth of Massachusetts or under contract with the Commonwealth of Massachusetts comes into physical contact with any whale it should be noted in the vessel's logbook. The vessel's logbook should include the time and location of the incident; weather and sea conditions; vessel speed; the species of whale struck if known; the nature of any injures to crew, and/or the whale, and/or damage to the vessel. Also record the name of any other vessels in the area that may have witnessed the incident or can provide information about circumstances. A copy of the vessel's log for the entire trip should be submitted to the Director of the Division of Marine Fisheries, the Director of the Division of Law Enforcement, the Secretary of Environmental Affairs and the National Marine Fisheries Service, Northeast Region in Gloucester.

If after hitting the whale, the animal is incapacitated or appears to have life threatening injuries and the vessel is safe and secure, immediately call the Center for Coastal Studies, entanglement hotline at 800-900-3622 or via their pager at 508-803-0204 and the Massachusetts Environmental Police Communications Center at 800-632-8075 or 617-727-6398. Stay with the whale until the Coast Guard or Center for Coastal Studies arrives on scene.

#### **Entanglements**

If the vessel come upon or entangles a right whale immediately notify the Center for Coastal Studies' entanglement hotline at 800-900-3622 or via their pager at 508-803-0204 and the Massachusetts Environmental Police Communications Center at 800-632-8075 or 617-727-6398. Do not attempt to remove any debris from the whale, stay on station with the whale or follow at a safe distance. As relocating an entangled whale can be extremely difficult, staying on station or following the animal is very important. However, if following the whale is not possible contact, the Coast Guard and/or the Center for Coastal Studies and note the last direction the animal was heading and any other pertinent information that would assist in relocating the whale.

### **Stranded Whales**

For a stranded right whale please notify the Stranding Network immediately call Connie Merigo or Howard Krum, New England Aquarium, Central Wharf, Boston, MA 02110. The standing Network's hotline is 617-973-5247 (pager) or as a second resort call 617-973-5246/6551.

# **QUICK REFERENCE**

# **Sightings & Photographs**

Patricia Gerrior, NMFS Right Whale Early Warning System Coordinator, manages the Clearinghouse and her numbers are 508-495-2264 (work), 508-495-2393 (fax) and pager 508-585-8473

#### **Photographs**

Dan McKiernan, Massachusetts Division of Marine Fisheries, 19th Floor, 100 Cambridge Street, Boston, MA 02202. 617-727-3193 ext. 369.

#### **Entanglements or Injured whales**

Center for Coastal Studies, entanglement hotline at 800-900-3622 or pager at 508-803-0204

Massachusetts Environmental Police Communications Center at 800-632-8075 or 617-727-6398.

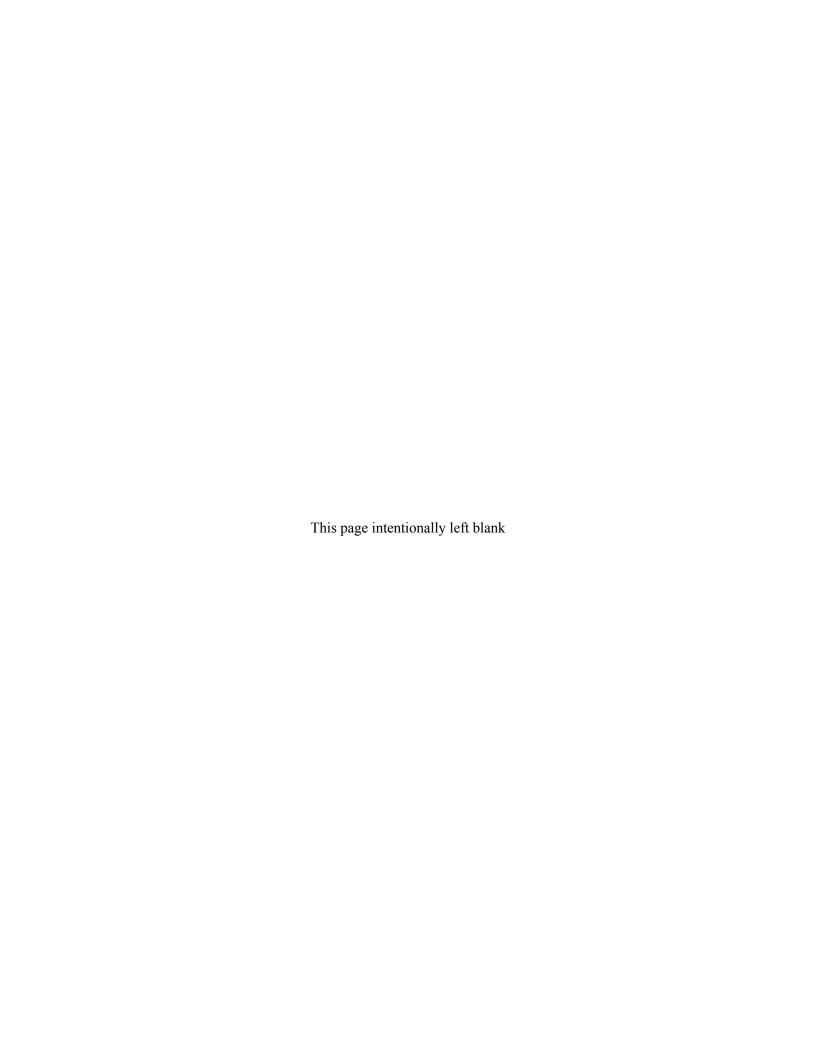
#### **Stranded Animals**

The standing Network's hotline is 617-973-5247 (pager) or as a second resort call 617-973-5246/6551.

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**Appendix III** 

**MWRA SOPs** 



#### **Appendix III**

# MWRA Standard Operating Procedures

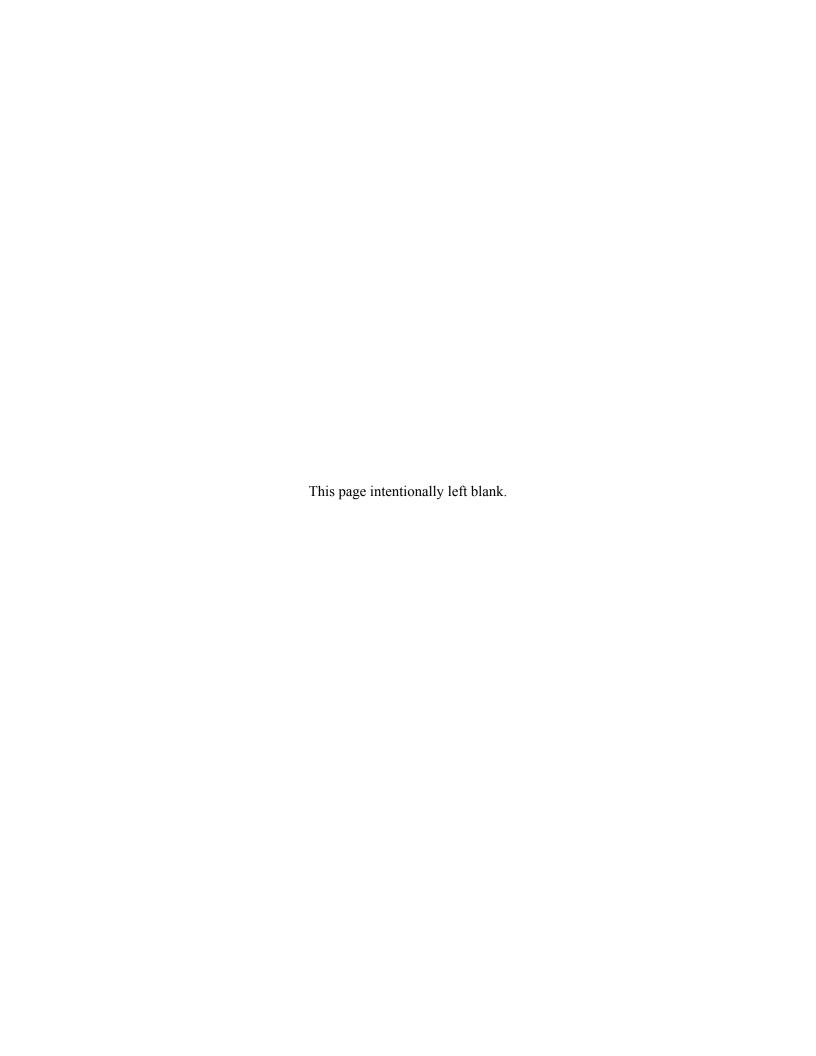
MWRA has provided hard copies of the following MWRA SOPs referenced in this document.

- 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

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Appendix IV

**Battelle SOPs** 



#### Appendix IV

#### **Battelle Standard Operating Procedures**

MWRA	SOP	001:	Post-Sur	vev CTD	Water (	Column	Data	Processing

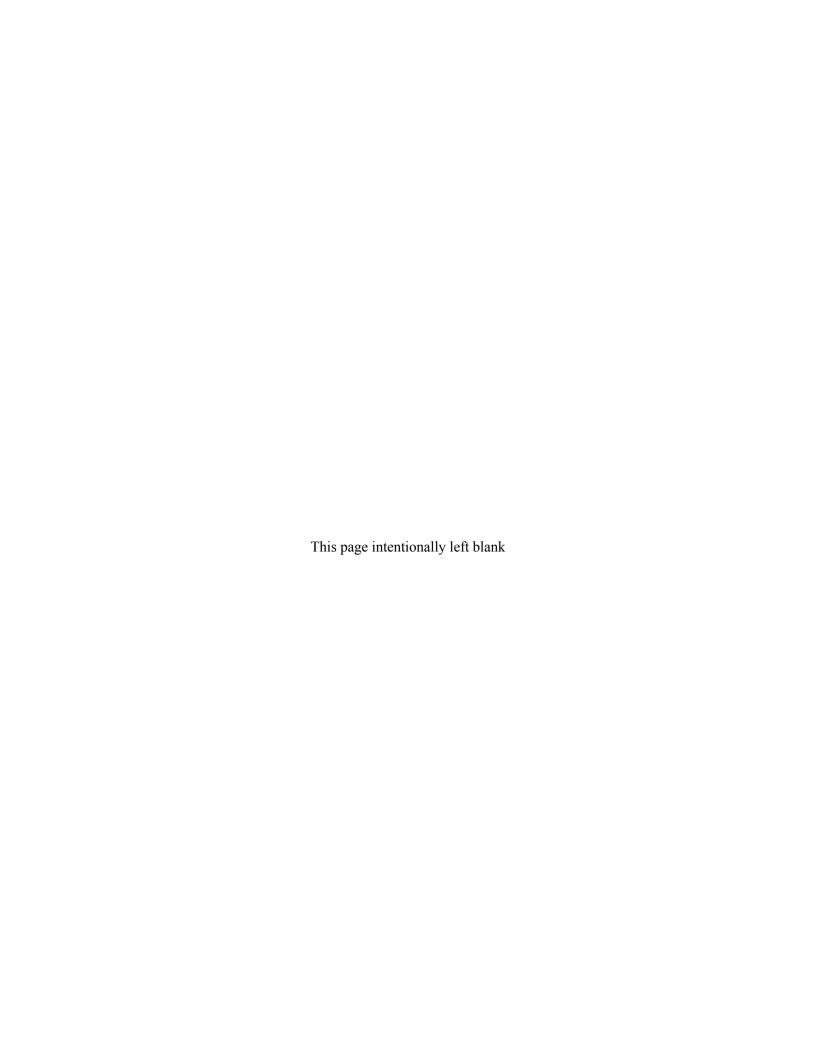
- MWRA SOP 004: Loading and Reporting Water Column Data
- MWRA SOP 008: Integrating MWRA Client ID Numbers into the NavSam© Survey Database
- SOP 3-118: Northstar 941XD and 952XDW Differential GPS Navigation System
- SOP 3-127: Biospherical Irradiance Sensors
- SOP 3-129: Operation of the Furuno FCV-582 Color Video Sounder
- SOP 3-163: Wetstar Fluorometer
- SOP 3-174: Operation and Maintenance of the Wetlabs C-Star Transmissometer
- SOP 3-180: Seabird Electronics Model 43 Dissolved Oxygen Sensor
- SOP 3-183: Seabird 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 5-324: Operation of Yellow Springs Instrument (YSI) 6 Series Multi-Parameter Sondes
- SOP 6-029: Survey Set-up and Sample Tracking Using NavSam<sup>©</sup> Software
- SOP 6-040 Sample Custody, Receipt, and Handling for Field Activities
- SOP 6-043: Preparation, Distribution, and Implementation of Field Survey Plans

Hard copies of the Battelle SOPs referenced in this document have been provided to MWRA in the hard copy version of the Draft QAPP.

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**Appendix V** 

**QA Statement** 



# Appendix V MWRA Harbor and Outfall Monitoring Project

# **Quality Assurance Statement**

MWRA Task Number/Title:	
Description of Data Set or Deliverable:	

# Part I. Description of Audit and Review Activities

$\checkmark$	Part II. Accuracy				
	1. QC samples and calibration standards were analyzed according to the QAPP and the				
	acceptance criteria were met. Corrective action for exceedances was taken.				
	2. Samples were analyzed according to the procedures specified in the QAPP.				
	3. 100% hand-entered and/or manually calculated data were checked for accuracy.				
	4. Calculations performed by software are verified at a frequency sufficient to ensure that the				
	formulas are correct, appropriate, and consistent.				
	5. For each cut and paste function, the first and last data value was verified vs. the source data.				
	6. Data are reported in the units specified in the QAPP.				
	7. 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.				
	8. Results of QC data and activities defined in QAPP Section 5.6 are attached and percent				
	differences or recoveries calculated				

✓	Part III. Completeness
	9. All samples received are reported.
	10. All parameters specified in the QAPP for this task are reported.

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

Signature of Reviewer/Date	Signature of Task Leader/Date



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