## **Quality Assurance Project Plan**

# for water column monitoring 2006-2007 Tasks 4, 5, 6, 7, 8, 11 MWRA Harbor and Outfall Monitoring Project

Massachusetts Water Resources Authority Environmental Quality Department Report ENQUAD 2006-03



# QUALITY ASSURANCE PROJECT PLAN (QAPP)

for

WATER COLUMN MONITORING 2006 – 2007 Tasks 4, 5, 6, 7, 8, 11

**MWRA Harbor and Outfall Monitoring Project** 

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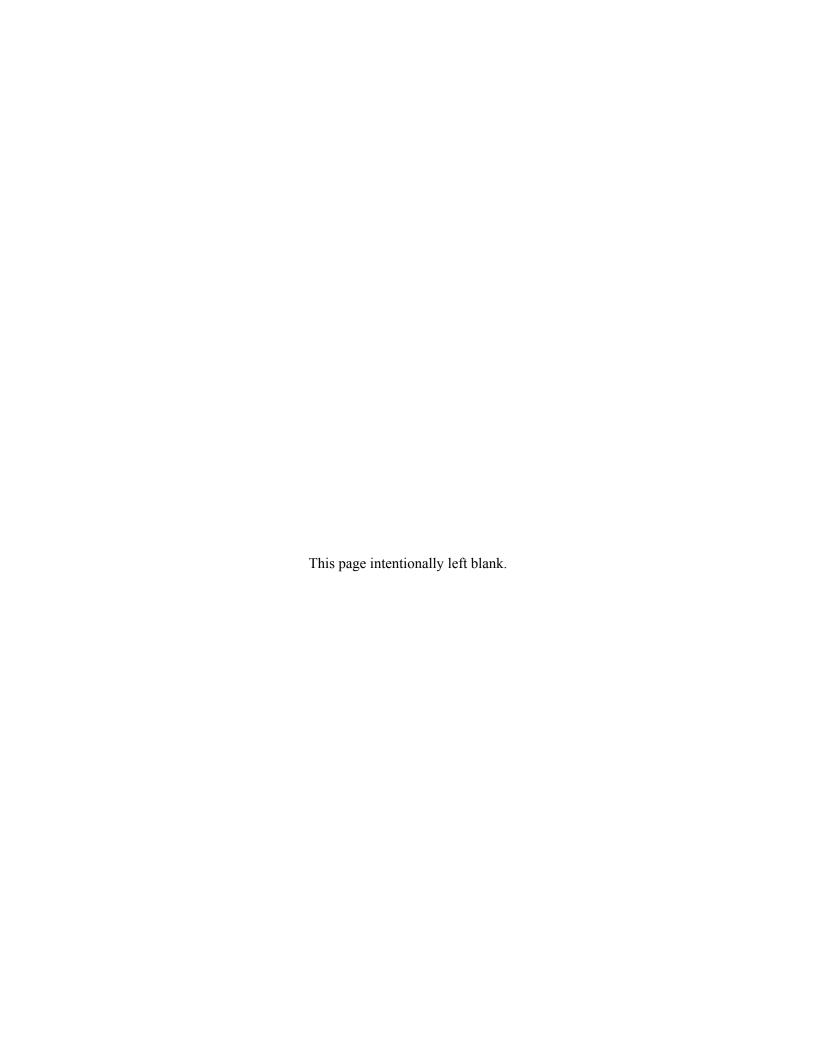
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> > March 22, 2006



## A. PROJECT MANAGEMENT

#### **VERSION 0**

#### A.1. TITLE AND APPROVALS

# QUALITY ASSURANCE PROJECT PLAN (QAPP) for

WATER COLUMN MONITORING 2006 – 2007 Tasks 4, 5, 6, 7, 8, 11

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

## Prepared by:

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March 22, 2006

#### **REVIEW AND APPROVALS**

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

## Quality Assurance Project Plan REVISION HISTORY

Revision Number	Affected Section(s)	Effective Date	Summary of changes	Approval (Initials/ dates)

## A.2. TABLE OF CONTENTS

A. PRO	DJECT MANAGEMENT	1
A.1.	TITLE AND APPROVALS	1
A.2.	TABLE OF CONTENTS	3
A.3.	DISTRIBUTION LIST	6
A.4.	PROJECT AND TASK ORGANIZATION.	7
A.5.	PROBLEM DEFINITION/BACKGROUND	8
A.6.	PROJECT/TASK DESCRIPTION	
A.7.	QUALITY OBJECTIVES AND CRITERIA	11
	A.7.1 Data Quality Objectives	
	A.7.2 Measurement Quality Objectives	
	A.7.3 Navigational and Hydrographic Data	
	A.7.4 Water Sampling	
A.8.	SPECIAL TRAINING AND CERTIFICATION	
	A.8.1 Technical Training	
	A.8.2 Safety Training	
	A.8.3 Responsibilities	
A.9.	DOCUMENTS AND RECORDS	
	A.9.1 Data Recording	
	A.9.2 Documents	
	A.9.3 Data Report Review and Comment	
	A.9.4 Synthesis Reports (Task 11)	
D DAT		
B. DA I	TA GENERATION AND AQUISITION	
B.1.	SAMPLING PROCESS DESIGN	
	B.1.1 Nearfield and Farfield Water Column Surveys (Tasks 5 and 6)	
	B.1.2 Sampling Locations and Frequency	
	B.1.3 Hydrocasts and Sensor Measurements	
	B.1.4 Water Collection and Zooplankton Net Tows	
	B.1.5 Whale Observations	
	B.1.6 Shipboard Processing of Discrete Water Samples	
	B.1.7 Floating Debris	
	B.1.8 Laboratory Program	
	B.1.9 Monitoring Parameters and Collection Frequency	
	B.1.10 Schedule of Activities and Deliverables	
B.2.	Sampling Methods	31
	B.2.1 Navigation	
	B.2.2 Vessel Handling	
	B.2.3 Hydrographic Profiles	32
	B.2.4 Water Sampling	
	B.2.5 Onboard Sample Processing	37
	B.2.6 Zooplankton Sampling	41
	B.2.7 Floating Debris	42
	B.2.8 Whale Observation	
B.3.	SAMPLE HANDLING AND CUSTODY	
	B.3.1 Sample Custody	
	B.3.2 Custody of Electronic Data	
	B.3.3 Custody of Water Samples	50

B.4.	ANALY	FICAL METHODS	51
	B.4.1	Respiration	51
	B.4.2	Primary Production by <sup>14</sup> C	
	B.4.3	Dissolved Inorganic Carbon	
	B.4.4	Whole-Water Phytoplankton	54
	B.4.5	Screened Phytoplankton (Dinoflagellates)	54
	B.4.6	Rapid-Analysis Samples	55
	B.4.7	Zooplankton	55
B.5.	QUALIT	Y CONTROL	56
	B.5.1	Field Program	56
	B.5.2	Decontamination	56
	B.5.3	Field blanks	56
	B.5.4	Field Replicates	56
	B.5.5	Laboratory Program	58
	B.5.6	Precision and Accuracy	
	B.5.7	Completeness	
	B.5.8	Comparability	
	B.5.9	Representativeness	
	B.5.10	Sensitivity	
B.6.		MENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE	
	B.6.1	Hydrographic Profiling Equipment	
B.7.		MENT/EQUIPMENT CALIBRATION AND FREQUENCY	
B.8.		TION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES	
B.9.		ECT MEASUREMENTS	
B.10.		IANAGEMENT (TASK 4)	
	B.10.1	Data Reduction	
	B.10.2	Reporting Data to be Loaded into the Database	
	B.10.3	Loading Analytical and Experimental Data into the Harbor Studies Database	
	B.10.4	Reporting Data to MWRA	
C. ASS	ESSMEN'	T AND OVERSIGHT	75
C.1.	ASSESSI	MENTS AND RESPONSE ACTIONS	75
	C.1.1	Performance and System Audits	75
	C.1.2	Corrective Action	75
C.2.	REPORT	S TO MANAGEMENT	76
D. DAT	A VALII	OATION AND USABILITY	76
D.1.	DATA R	EVIEW, VERIFICATION, AND VALIDATION	76
D.1.		TION AND VERIFICATION METHODS	
D.3.		CILIATION WITH USER REQUIREMENTS	
E. REF	ERENCE	S	77
		LIST OF FIGURES	
Eiger	A 1 Decia	at Managamant Structure and Water Calumn Study Organization	O
		ct Management Structure and Water Column Study Organization	
		tion of MWRA Effluent Outfall in Massachusetts Bay	
		field Water Column Sampling Strations. Inset of Station N21 Located along the O	
		Riser 14 – Risers are 38 m apart.	
		eld Water Column Sampling Stations	
	I WIII	with Column Camping Camono	∠∪

Figure B-4. dGPS	MasterStations Coverage	31
Figure B-5. Samp	le NavSam <sup>©</sup> Data Acquisition Screen	34
	ve Scenarios for Selecting Sample Depths	
	ard Processing Flow Chart	
Figure B-8. Exam	ple of Marine Mammal Sightings Log and Relevant Codes	43
Figure B-9 Depict	tion of Linkage from DLS LIMS to NavSam <sup>©</sup>	45
	ple Station Log	
Figure B-11. Exar	nple of a Zooplankton Custody Form	47
	mple of Water Chemistry Custody Form with LIMS generated IDs	
Figure B-13. Exar	mple of Custody Form with NavSam <sup>©</sup> generated IDs	49
Figure B-14. Over	rview of the Data Management Strategy for Water Column Monitoring	66
Figure B-15. Exar	nple of Loading Application Data Entry Form	71
Figure B-16. Load	ling Application Main Menu	71
	LIST OF TABLES	
Table A-1 Accura	acy and Precision of Instrument Sensors	12
	Report Quality Control Checks – Water Quality Area (These QC checks will be	12
	MWRA)	19
Table A-3. Schedu	ule of Data Reports, Data Exports, and Synthesis Reports	22
Table B-1. Nearfic	eld Water Column Sampling Stations	27
Table B-2. Farfiel	d Water Column Stations	27
Table B-3. Subsar	nples by Station Type Code and Sample Depth Class	28
Table B-4. Water	Column Sample Analyses	30
Table B-5. Schedu	ule of Water Column Surveys and Related Survey Reports	31
	e Volumes, Containers, and Processing for Field Samples	
	sis Codes used in Bottle ID or used as label abbreviations	
	C Samples for Nearfield.	
	C Samples for Farfield.	
Table B-10. Meas	urement Quality Objectives for analyses by Battelle and URI	58
Table B-11. Calib	ration Procedures for Laboratory Instruments	64
	urement Frequency for Variables Involved in Calculation of Primary Production	
	pase Codes for Hydrographic Parameters	
	ratory Qualifiers	
	pase Codes for Plankton Taxonomy	
Table B-16. Datab	pase Codes for Species Qualifiers	73
Table B-1/. Datat	pase Codes for Chemistry Analytical and Experimental Parameters	73
Table B-18. Desci	ription of Database Codes	/4
	APPENDICES	
Appendix A	Nearfield and Farfield Sample Collection Requirements	
Appendix B	Right Whale Guidance Protocol for Vessels Operated/Contracted by the Commonwealth of Massachusetts (21 November 1997)	
Appendix C	MWRA Standard Operating Procedures	
Appendix D	Battelle Standard Operating Procedures	

## A.3. DISTRIBUTION LIST

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

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Wendy Leo (MWRA)	
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Jeff Turner (UMASS)	
Candace Oviatt (URI)	
David Borkman (URI)	

#### 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 Resource 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. Alex Mansfield 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 Manager 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.

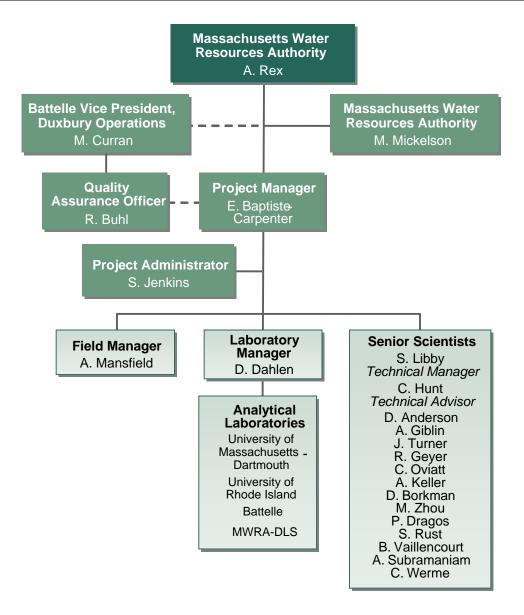


Figure A-1. Project Management Structure and Water Column Study Organization

#### 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 1998). 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 monitoring addresses the public concerns that it be safe to eat fish and shellfish, that natural resources are unharmed, that it be safe to swim, and that the receiving water look clear and be free of floating material. Harbor monitoring is needed to chart the recovery of Boston Harbor resulting from cessation of sludge discharge, ongoing system improvements, and diversion of the effluent previously discharge into the Harbor. The monitoring data will assist with planning of further capital improvements.

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.

A principal concern with the offshore outfall discharge is nutrients and their resultant eutrophication effects on the water column. Three specific effects are of paramount concern: (1) lowered dissolved oxygen concentrations (hypoxia/anoxia), (2) stimulation of nuisance/noxious algae populations, and (3) alteration of the offshore food web. Water quality monitoring centers on measurements keyed to these three principal ecological effects, including measurements of other physical and chemical properties. For example, temperature, salinity, and turbidity are used to distinguish water masses and are fundamental background data for interpreting biological fluctuations. Physical features such as thermal stratification strongly influence the expression of nutrient enrichment effects. Measured nutrient concentrations (particulate and dissolved forms) aid water mass analyses, assess biological variability in light of nutrient variability, and, ultimately, link cause (nutrient loading) and effect. Zooplankton monitoring, in tandem with physical and chemical measurements, may help explain any observed changes in the phytoplankton.

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 changes to the water column monitoring program include reducing the number of nearfield surveys from 17 to 12 and reducing the number of nearfield stations from 21 to 7. These changes were supported by statistical analysis of baseline and post-discharge data collected from 1992-2002, which indicate that there will be little loss of information or in the ability of the monitoring program to detect changes (MWRA 2003). In 2003, the monitoring plan was revised to omit the urea sampling in the water column. 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 (QAPP) for Water Column Monitoring: 2004 – 2005 (Libby *et al.* 2005). This version of the CWQAPP includes those changes and additional changes specified for the water column monitoring program for HOM5 in field operations, analytical laboratories, and data management activities.

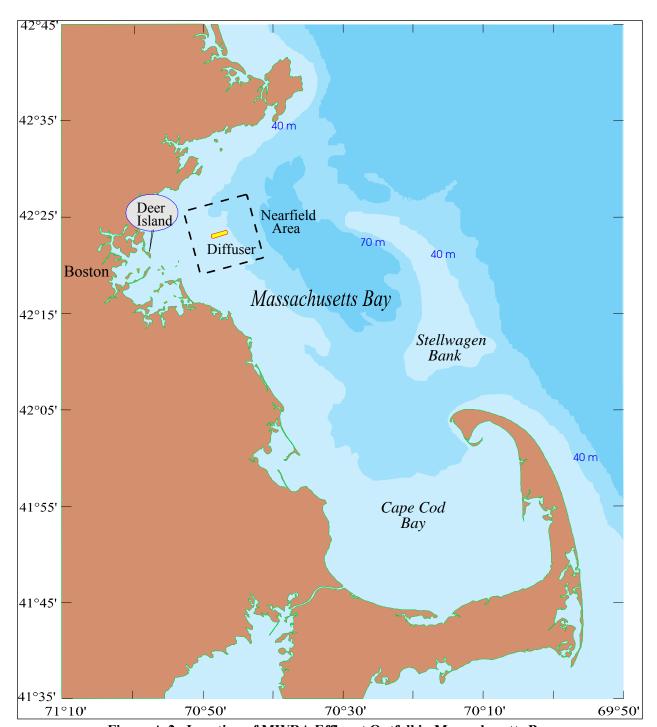


Figure A-2. Location of MWRA Effluent Outfall in Massachusetts Bay

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

The HOM Project water column surveys have been conducted since 1992 and are scheduled to continue through 2007. 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 annually in 2006 and 2007. 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 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 11 Synthesis Reports:** The results of the sampling and analytical tasks will be reported 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 HOM5 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 an MWRA SOP (Appendix C). 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

Precision and accuracy objectives for navigation and hydrographic sampling are presented in Table A-1. Section B5 provides details on sampling procedures established to ensure data quality. Section B6 and B7 contain instrument calibration methods and specifications. Navigational accuracy of 10m is required for this program.

Sensor	Vendor	Units	Range	Accuracy	Precision
Pressure	SeaBird SBE-25	decibars	0 to 1000	0.1%	0.1
Temperature		°C	-5 to +35	0.001	0.01
Conductivity		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-cm)	Wetlabs 25 cm C-star	m-1	0 to 40	0.20	0.01
In situ irradiance	Biospherical QSP-2200PD	μE m-2 s-1	0.14 to	10	1
			5000		
On-Deck irradiance	Biospherical QSR-2240	μE m-2 s-1	0.14 to	10	1
			5000		
Altimeter	Benthos PSA-916	m	0-99.9	0.1	0.025
Echosounder (depth)	Furuno 943	m	0 to 200	2	0.1
Navigation	North Star 952XDW (WAAS	degree	World	2 m	2 m
	Capable)				

Table A-1. Accuracy and Precision of Instrument Sensors

## A.7.3.2 Completeness

Battelle's navigation software system outputs navigation positions at an interval of 2-seconds. The software system will display all position fixes and save these fixes in an electronic file during hydrocasts and sampling operations. The project's time interval requirement for obtaining positions during sampling is 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 Hz) and navigation systems (2-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.

#### 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). Except 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 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

#### A.7.4.1 Precision and Accuracy

Precision and accuracy of water sampling procedures are quantified by the collection of field 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.

## A.7.4.2 Completeness

The nearfield surveys will be considered complete if all seven stations are sampled. All farfield stations must be sampled for the farfield survey 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 notebook. 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.

## 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 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, and transported 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 ACES requirements for personnel qualifications and training are detailed in the Quality Management Plan (QMP), Battelle (2005). Specific requirements from this QMP which relate to HOM5 activities are summarized below.

#### A.8.1 Technical Training

Technical training encompasses technical procedures and the associated quality control 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 HOM5 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 HOM5 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 ESH Officer are responsible for identifying the need for specific safety training. The ESH Officer is responsible for ensuring that safety training is conducted. Safety training is detailed in the Battelle Environmental, Safety, and Health Plan.

## 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. 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 laboratory notebooks 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 will be the responsibility of the laboratory managers to ensure that all data entries and hand calculations are verified in accordance with procedures described in the following sections D.1, D.2, and D.3. In addition to these documentation procedures, station logs associated with field and laboratory custody and tracking will be kept in the survey notebook for each survey. Contents of survey logbooks are defined in Battelle SOP 6-043 "Preparation, Distribution, and Implementation of Field Survey Plans". These notebooks will be stored at Battelle under the supervision of the Project 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 to maintain the data audit trail. These data are processed according to Section B10

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 HOM5). The ASCII data files are also stored on the projects file server under the HOM5 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 24 nearfield and combined nearfield/farfield 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 HOM5 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 A9.3.1 and A9.3.2) and Task 8 data will be used in Plankton Data Reports (section A.9.3.3). Data synthesis reports (Task 11) are described in Section A9.4. Survey-related deliverables that will be generated under this QAPP include:

- 24 Survey Plans (one for each of the Nearfield water column surveys; farfield surveys plans will be combined with the Nearfield Plans)
- 24 Survey Reports (one for each of the Nearfield water column surveys; farfield surveys reports will be combined with the Nearfield Reports)
- 24 Email Survey Summaries (including the rapid phytoplankton results)
- 8 Nutrient Data and Respiration/Productivity Data Report Review letters
- 8 Phytoplankton Data and Zooplankton Data report Review letters

All survey plans and reports will be submitted annually on CD after final acceptance by MWRA. Final synthesis reports will be submitted as electronic word processing documents and PDF files (containing all appendices).

#### 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 OP-44A in 2006-07 with analysis continuing through 2008. 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 and 2005). Water column surveys will be conducted to monitor water properties, nutrient concentrations, and other parameters that measure eutrophication, and to gain a better understanding of the physical processes that will affect the ecological response to the outfall in Massachusetts Bay.

#### 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 the combined surveys will be submitted to MWRA. Each survey plan will follow Battelle SOP 6-043 Preparation, Distribution, and Implementations of Field Survey Plans that is based on the guidelines established by U.S. Environmental Protection Agency for use of their vessels. Each survey

plan will be submitted as a final unbound, double side copy on 3-hole paper at least one week prior to the start of the survey and will include the following information:

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

## A.9.2.3 Survey Email Summary

A survey summary will be delivered to MWRA via Email within 1 week of completion of each 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 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, 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. One unbound, double-sided, 3-hole punched copy of the draft survey report will be submitted to MWRA 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 draft report. The final survey report, 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 draft survey report will be considered final.

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

Four Nutrient, four Respiration/Productivity, and four Plankton data reports will be generated by MWRA per year. The data reports are created directly from the EM&MS database. Battelle will perform a technical review and comment on the initial data report.

Water Column data reports will be submitted to Battelle for review. Included will be all sample collection information summarized from the Survey Reports for each sampling event. Data will be presented in tables containing the results of all individual sample analyses. QC checks of the data will also be included in the data reports in graphical format. The QC checks for the water column analysis data reports are described in Table A-2.

## A.9.3.1 Nutrient Data Reports

Each Nutrient Data Report will contain tabular summaries of concentrations of all nutrient species measured, chlorophyll *a*, DO, and TSS for each bottle sampled and analyzed. The report will also include hydrographic data (salinity, temperature, DO, chlorophyll fluorescence, optical beam transmittance, light irradiance, and sensor altitude above the seafloor), surface irradiance data from Deer Island, and results of QC checks.

#### A.9.3.2 Metabolism Data Reports

Each Metabolism Data Report will include a tabular summaries of water-column respiration rates, primary production calculations including the  $P_{max}$  and P(I) analyses will be provided for each sample depth or profile measured, and results of QC checks.

#### A.9.3.3 Plankton Data Reports

Each Plankton Data Report will contain tabular summaries of phytoplankton and zooplankton counts and identifications and results of QC checks.

# Table A-2. Data Report Quality Control Checks - Water Quality Area (These QC checks will be performed by MWRA).

#### General:

A tabular summary of the following will be included with each data report:

Planned analyses against actual number of analyses

List of missing samples

Individual station depth against expected depth at station MDW depth based on Geo station table

Count of samples with non-detectable results by variable

Number of null values by variable

Parameter	Type of Quality Control Check									
	Plot <sup>1</sup>	Range check <sup>2</sup>								
In situ profile data	1) Comparison of down and upcast (discrete depth) values at depth of upcast sampling events to see if they are within 10%. If not flag for scientists review.	Each variable								
Dissolved Nutrients	<ol> <li>Parameter vs. depth plots (NH<sub>4</sub>, NO<sub>2</sub>+NO<sub>3</sub>, PO<sub>4</sub>, SiO<sub>4</sub>, TDN, TDP and DOC) – plot per parameter per survey including all stations. All plots for one parameter per page.</li> <li>NO<sub>2</sub>+NO<sub>3</sub> vs. SiO<sub>4</sub> including previously accepted data from the data report interval</li> <li>NH<sub>4</sub> vs. PO<sub>4</sub> including previously accepted data from the data report interval</li> <li>TDN vs. TDP including previously accepted data from the data report interval</li> </ol>	Each variable								
Particulate nutrients	<ol> <li>Parameter vs. depth plots (POC, PON, and PartP) – plot per parameter per survey including all stations. All plots for one parameter per page</li> <li>PON vs. POC against Redfield ratio and previously accepted data from the data report interval</li> <li>PartP vs. PON against Redfield ratio and previously accepted data from the data report interval</li> </ol>	Each variable								
Total suspended solids	1) TSS vs. depth plot – one plot per survey including all stations. All plots on one page	TSS								
Chlorophyll Phaeophytin Florescence	<ol> <li>Parameter vs. depth plots (calibrated <i>in situ</i> fluorescence<sup>3</sup>, Chla extracted, and Phaeo) plot per parameter per survey including all stations. All plots for one parameter per page</li> <li><i>In situ</i> fluorescence versus Chla scatter plot against previously accepted data</li> <li>POC versus Chla scatter plot against previously accepted data</li> </ol>	Each variable								
Dissolved Oxygen and %Sat	1) Parameter vs. depth plot (calibrated <i>in situ</i> DO concentration and %saturation) <sup>3</sup> – one plot per survey including all stations. All plots for one parameter per page	Each variable								
Biogenic Si	1) BSI vs. depth plot – one plot per survey including all stations. All plots on one page	BSI								
Respiration	None	Respiration Rate								
Primary Productivity	None	Each calculated variable								
Phytoplankton	None	Total count and total by major group								
Zooplankton	None	Total count and total by major group								

<sup>1</sup> For each data period being reported

<sup>2</sup> Range check against highest and lowest value by sample from baseline period or all previously accepted data. Flag samples outside of this range for more detailed review by senior scientist

<sup>3</sup> In situ data from discrete sampling depths only

## A.9.4 Synthesis Reports (Task 11)

The data delivered above will be used in synthesis reports prepared under Task 11 Annual Water Column Reports, and Nutrient Issues Reviews. A detailed outline of each of the synthesis reports will be prepared for MWRA approval. Following outline approval, a draft report will be prepared and submitted to MWRA. MWRA comments on each report will be provided to Battelle within 4 weeks of report receipt. Final reports, addressing MWRA comments, will be due to MWRA within two weeks of comment receipt. Schedules for all activities, including reports, are provided in Table A-3.

#### A.9.4.1 Annual Water Column Report (Task 11.2)

All data for the annual water quality report will come from the EM&MS database. Authors will request data extracts. The annual water quality report will synthesize results from water column monitoring activities for each calendar year. It will describe the status of the ecosystem, including annual and seasonal patterns. The annual report will provide statistical descriptions of critical parameters and evaluate critical interactions among biological, physical, and chemical factors. The report also will include summaries of annual minimums and maximums (identified according to time and location), frequency distributions, seasonal, and annual averages as appropriate to the monitoring caution and threshold values. The annual report will focus on assessing the status of the ecosystem in comparison to baseline monitoring results and the caution and warning thresholds. Should any exceedances of the relevant monitoring thresholds be observed, Battelle will summarize any assessment of the likely cause conducted by MWRA (supported by Battelle as requested) and whether the cause can be attributed to the outfall.

Each annual water column report will address the following areas:

- Executive Summary (including summary of any thresholds exceeded and possible factors responsible)
- Introduction (program overview, report purpose and organization, summary of baseline results)
- Data Sources and Overview of each Years' Program
- Environmental Setting: Physical Oceanography and Meteorology (Temperature cycle, Salinity, Water Column Stratification, Water Mass Source and Movement, Rainfall, Light cycle)
- Nutrients (Annual cycle in the Nearfield and in Massachusetts Bay and Cape Cod Bay)
- Chlorophyll (Nearfield. Regional and Inter-annual Comparisons)
- Dissolved Oxygen (Annual cycle in the Nearfield and in Massachusetts Bay and Cape Cod Bay, seasonal decline in bottom waters of the Nearfield and Stellwagen Basin)
- Metabolism (Seasonal and Annual Production, chlorophyll specific measures of production, Water column respiration)
- Plankton (Abundance and seasonal succession, regional comparisons, Inter-annual comparisons, and algal nuisance species
- Overview of Annual Results (Integration and Synthesis)
- References

#### A.9.4.2 Nutrient Issues Review (Task 11.4)

This report draws from a variety of reports and data to evaluate the potential for response related to relocation of the MWRA outfall and associated nutrients in Massachusetts and Cape Cod Bays. Topics may vary as information and data gaps are identified.

#### A.9.4.3 Outfall Monitoring Overview (Task 11.5)

This report will summarize key findings of the ambient monitoring program including any special studies and threshold violations. The overview will include data from other facets of the HOM5 program that are monitored under Agreements II and III. The report will be written toward the general public, regulators, and interested scientists.

#### A.9.4.4 Whale Observations Report

An annual Whale Observation Report will be prepared under Task 11.1 in January 2007 and 2008. The annual Whale Observation Report will compile all whale observations for each of the survey years (2006 and 2007). This also includes information on incidental whale observations made during surveys conducted under other portions of the HOM project. MWRA will provide survey reports from Agreements II and III. A tabular summary of the following information will be provided for each sighting: date, start/stop time, survey vessel name, and description of incidental observations by observers other than whale watchers. Summary observations by dedicated observers will include hours of active observation (on the survey), number and species observed, the observer, vessel position at time of observation, time of observation, and comments of the observer regarding the whale's activities. A summary map showing the positions of all sightings and relationship to monitoring stations will be provided.

Table A-3. Schedule of Data Reports, Data Exports, and Synthesis Reports

Deliverable	Survey Period	<b>Due Date</b>			
Survey Plans	urvey-Related Reports  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			
Survey Reports Timur	Data Sets	14 days after receipt of comments			
Water Column Data Sets	Each survey	1 week after survey			
Hydrographic Data Sets	Each survey	2 weeks after end of each survey			
Try drogrup me Butta Sets	February – April	June 30			
	May – June	August 31			
Productivity Data Sets	July – August	October 31			
	September – November	January 31 <sup>st</sup> of the following year			
	February – April	June 30			
	May – June	August 31			
Plankton Data Sets	July – August	October 31			
	September – November	January 31 <sup>st</sup> of the following year			
	February – April	August 15			
Review Comments for Data Sets:	May – June	October 15			
Nutrients, Hydrographic Data,	July – August	December 15			
Productivity, and Plankton	September – November	March 15 of the following year			
Year's electronic word processing files for the survey plans and final survey reports, including all graphics and tables	January – December	One month after each field year			
Synth	esis or Interpretive Reports				
Annual Whale Observation – Draft	Eshmany Dagamhan	Due January of the following year			
Annual Whale Observation – Final	February – December	Due February of the following year			
Annual Water Column – Outline		Due April of the following year			
Annual Water Column – Draft	February – December	Due May of the following year			
Annual Water Column – Final		Due July of following year			
2007 Nutrient Issues Review Outline		Due April 2007			
2007 Nutrient Issues Review Draft		Due May 2007			
2007 Nutrient Issues Review Final		Due July 2007			
Outfall Monitoring Overview– Outline		Due May of the following year			
Outfall Monitoring Overview–Draft	Fohruary Dagamhan	Due June of the following year			
Outfall Monitoring Overview– Final	February – December	Due September of the following year			

## **B. DATA GENERATION AND AQUISITION**

## **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 per year in 2006 and 2007 (Figure B-1). Figure B-2 shows the location of the 7 nearfield stations (Table B-1) and Figure B-3 shows the 28 farfield stations (Table B-2) that will be sampled each year.

				2006							20	007			
Week	Sun	Mon	Tue	Wed	Thu	Fri	Sat	Week	Sun	Mon	Tue	Wed	Thu	Fri	Sat
1	1-Jan	2-Jan	3-Jan	4-Jan	5-Jan	6-Jan	7-Jan	1		1-Jan	2-Jan	3-Jan	4-Jan	5-Jan	6-Jan
2	8-Jan	9-Jan	10-Jan	11-Jan	12-Jan	13-Jan	14-Jan	2	7-Jan	8-Jan	9-Jan	10-Jan	11-Jan	12-Jan	13-Jan
3	15-Jan	16-Jan	17-Jan	18-Jan	19-Jan	20-Jan	21-Jan	3	14-Jan	15-Jan	16-Jan	17-Jan	18-Jan	19-Jan	20-Jan
4	22-Jan	23-Jan	24-Jan	25-Jan	26-Jan	27-Jan	28-Jan	4	21-Jan	22-Jan	23-Jan	24-Jan	25-Jan	26-Jan	27-Jan
5	29-Jan	30-Jan	31-Jan	1-Feb	2-Feb	3-Feb	4-Feb	5	28-Jan	29-Jan	30-Jan	31-Jan	1-Feb	2-Feb	3-Feb
6	5-Feb	6-Feb	7-Feb	8-Feb	9-Feb	10-Feb	11-Feb	6	4-Feb	5-Feb	6-Feb	7-Feb	8-Feb	9-Feb	10-Feb
7	12-Feb	13-Feb	14-Feb	15-Feb	16-Feb	17-Feb	18-Feb	7	11-Feb	12-Feb	13-Feb	14-Feb	15-Feb	16-Feb	17-Feb
8	19-Feb	20-Feb	21-Feb	22-Feb	23-Feb	24-Feb	25-Feb	8	18-Feb	19-Feb	20-Feb	21-Feb	22-Feb	23-Feb	24-Feb
9	26-Feb	27-Feb	28-Feb	1-Mar	2-Mar	3-Mar	4-Mar	9	25-Feb	26-Feb	27-Feb	28-Feb	1-Mar	2-Mar	3-Mar
10	5-Mar	6-Mar	7-Mar	8-Mar	9-Mar	10-Mar	11-Mar	10	4-Mar	5-Mar	6-Mar	7-Mar	8-Mar	9-Mar	10-Mar
11	12-Mar	13-Mar	14-Mar	15-Mar	16-Mar	17-Mar	18-Mar	11	11-Mar	12-Mar	13-Mar	14-Mar	15-Mar	16-Mar	17-Mar
12	19-Mar	20-Mar	21-Mar	22-Mar	23-Mar	24-Mar	25-Mar	12	18-Mar	19-Mar	20-Mar	21-Mar	22-Mar	23-Mar	24-Mar
13	26-Mar	27-Mar	28-Mar	29-Mar	30-Mar	31-Mar	1-Apr	13	25-Mar	26-Mar	27-Mar	28-Mar	29-Mar	30-Mar	31-Mar
14	2-Apr	3-Apr	4-Apr	5-Apr	6-Apr	7-Apr	8-Apr	14	1-Apr	2-Apr	3-Apr	4-Apr	5-Apr	6-Apr	7-Apr
15	9-Apr	10-Apr	11-Apr	12-Apr	13-Apr	14-Apr	15-Apr	15	8-Apr	9-Apr	10-Apr	11-Apr	12-Apr	13-Apr	14-Apr
16	16-Apr	17-Apr	18-Apr	19-Apr	20-Apr	21-Apr	22-Apr	16	15-Apr	16-Apr	17-Apr	18-Apr	19-Apr	20-Apr	21-Apr
17	23-Apr	24-Apr	25-Apr	26-Apr	27-Apr	28-Apr	29-Apr	17	22-Apr	23-Apr	24-Apr	25-Apr	26-Apr	27-Apr	28-Apr
18	30-Apr	1-May	2-May	3-May	4-May	5-May	6-May	18	29-Apr	30-Apr	1-May	2-May	3-May	4-May	5-May
19	7-May	8-May	9-May	10-May	11-May	12-May	13-May	19	6-May	7-May	8-May	9-May	10-May	11-May	12-May
20	14-May	15-May	16-May	17-May	18-May	19-May	20-May	20	13-May	14-May	15-May	16-May	17-May	18-May	19-May
21	21-May	22-May	23-May	24-May	25-May	26-May	27-May	21	20-May	21-May	22-May	23-May	24-May	25-May	26-May
22	28-May	29-May	30-May	31-May	1-Jun	2-Jun	3-Jun	22	27-May	28-May	29-May	30-May	31-May	1-Jun	2-Jun

Figure B-1. HOM5 Water Column Sampling Schedule, 2006-2007

24	18-Jun	19-Jun	20-Jun	21-Jun	22-Jun	23-Jun	24-Jun	24	17-Jun	18-Jun	19-Jun	20-Jun	21-Jun	22-Jun	23-Jun
25	25-Jun	26-Jun	27-Jun	28-Jun	29-Jun	30-Jun	1-Jul	25	24-Jun	25-Jun	26-Jun	27-Jun	28-Jun	29-Jun	30-Jun
26	2-Jul	3-Jul	4-Jul	5-Jul	6-Jul	7-Jul	8-Jul	26	1-Jul	2-Jul	3-Jul	4-Jul	5-Jul	6-Jul	7-Jul
27 28	9-Jul	10-Jul	11-Jul	12-Jul	13-Jul	14-Jul	15-Jul	27 28	8-Jul	9-Jul	10-Jul	11-Jul	12-Jul	13-Jul	14-Jul
29	16-Jul	17-Jul	18-Jul	19-Jul	20-Jul	21-Jul	22-Jul	29	15-Jul	16-Jul	17-Jul	18-Jul	19-Jul	20-Jul	21-Jul
30	23-Jul	24-Jul	25-Jul	26-Jul	27-Jul	28-Jul	29-Jul	30	22-Jul	23-Jul	24-Jul	25-Jul	26-Jul	27-Jul	28-Jul
31	30-Jul	31-Jul	1-Aug	2-Aug	3-Aug	4-Aug	5-Aug	31	29-Jul	30-Jul	31-Jul	1-Aug	2-Aug	3-Aug	4-Aug
32	6-Aug	7-Aug	8-Aug	9-Aug	10-Aug	11-Aug	12-Aug	32	5-Aug	6-Aug	7-Aug	8-Aug	9-Aug	10-Aug	11-Aug
33	13-Aug	14-Aug	•	16-Aug	17-Aug	18-Aug	19-Aug	33	12-Aug	13-Aug	14-Aug	15-Aug	16-Aug	17-Aug	18-Aug
34	20-Aug	21-Aug	22-Aug	23-Aug	24-Aug	25-Aug	26-Aug	34	19-Aug	20-Aug	21-Aug	22-Aug	23-Aug	24-Aug	25-Aug
35	27-Aug	28-Aug	•	30-Aug	31-Aug	1-Sep	2-Sep	35	26-Aug	27-Aug	28-Aug	29-Aug	30-Aug	31-Aug	1-Sep
36	3-Sep	4-Sep	5-Sep	6-Sep	7-Sep	8-Sep	9-Sep	36	2-Sep	3-Sep	4-Sep	5-Sep	6-Sep	7-Sep	8-Sep
37	10-Sep	11-Sep	12-Sep	13-Sep	14-Sep	15-Sep	16-Sep	37	9-Sep	10-Sep	11-Sep	12-Sep	13-Sep	14-Sep	15-Sep
38	17-Sep	18-Sep	19-Sep	20-Sep	21-Sep	22-Sep	23-Sep	38	16-Sep	17-Sep	18-Sep	19-Sep	20-Sep	21-Sep	22-Sep
39	24-Sep	25-Sep	26-Sep	27-Sep	28-Sep	29-Sep	30-Sep	39	23-Sep	24-Sep	25-Sep	26-Sep	27-Sep	28-Sep	29-Sep
40	1-Oct	2-Oct	3-Oct	4-Oct	5-Oct	6-Oct	7-Oct	40	30-Sep 7-Oct	1-Oct	2-Oct	3-Oct	4-Oct	5-Oct	6-Oct
41	8-Oct	9-Oct	10-Oct	11-Oct 18-Oct	12-Oct	13-Oct	14-Oct	41	14-Oct	8-Oct	9-Oct	10-Oct	11-Oct 18-Oct	12-Oct	13-Oct 20-Oct
42	22-Oct	23-Oct	24-Oct	25-Oct	26-Oct	27-Oct	28-Oct	42	21-Oct	22-Oct	23-Oct	24-Oct	25-Oct	26-Oct	27-Oct
43	29-Oct	30-Oct	31-Oct	1-Nov	2-Nov	3-Nov	4-Nov	43	28-Oct	29-Oct	30-Oct	31-Oct	1-Nov	2-Nov	3-Nov
44	5-Nov	6-Nov	7-Nov	8-Nov	9-Nov	10-Nov	11-Nov	44	4-Nov	5-Nov	6-Nov	7-Nov	8-Nov	9-Nov	10-Nov
45	12-Nov	13-Nov	14-Nov	15-Nov	16-Nov	17-Nov	18-Nov	45	11-Nov	12-Nov	13-Nov	14-Nov	15-Nov	16-Nov	17-Nov
46	19-Nov	20-Nov	21-Nov	22-Nov	23-Nov	24-Nov	25-Nov	46		19-Nov	20-Nov	21-Nov	22-Nov	23-Nov	24-Nov
47	26-Nov	27-Nov	28-Nov	29-Nov	30-Nov	1-Dec	2-Dec	47	25-Nov	26-Nov	27-Nov	28-Nov	29-Nov	30-Nov	1-Dec
48	3-Dec	4-Dec	5-Dec	6-Dec	7-Dec	8-Dec	9-Dec	48	2-Dec	3-Dec	4-Dec	5-Dec	6-Dec	7-Dec	8-Dec
49	10-Dec	11-Dec	12-Dec	13-Dec	14-Dec	15-Dec	16-Dec	49	9-Dec	10-Dec	11-Dec	12-Dec	13-Dec	14-Dec	15-Dec
50	17-Dec	18-Dec	19-Dec	20-Dec	21-Dec	22-Dec	23-Dec	50	16-Dec	17-Dec	18-Dec	19-Dec	20-Dec	21-Dec	22-Dec
51	24-Dec	25-Dec	26-Dec	27-Dec	28-Dec	29-Dec	30-Dec	51	23-Dec	24-Dec	25-Dec	26-Dec	27-Dec	28-Dec	29-Dec
52	31-Dec	1-Jan	2-Jan					52	30-Dec	31-Dec	1-Jan	2-Jan			
Key	Io		cription			1		53							

Figure B-1. HOM5 Water Column Sampling Schedule, 2006-2007, continued

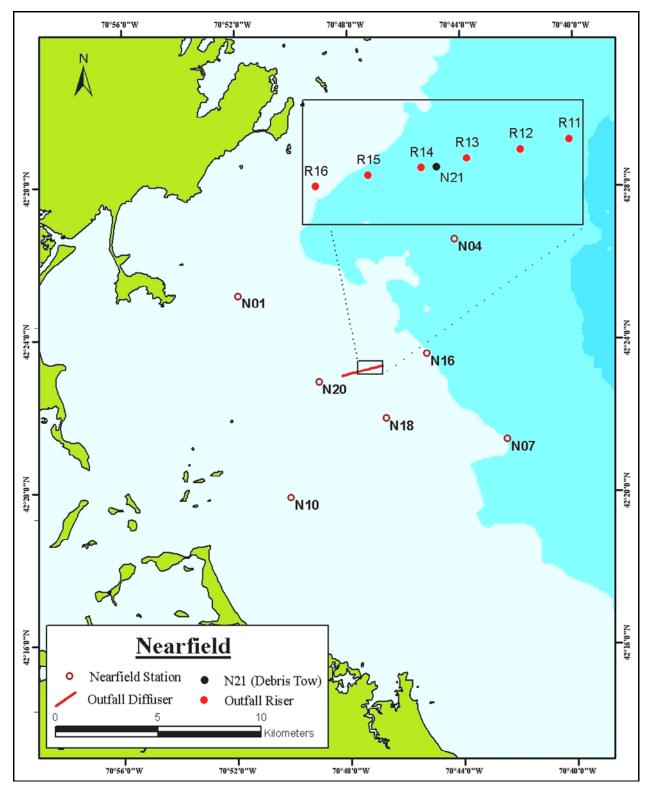


Figure B-2. Nearfield Water Column Sampling Stations. Inset of Station N21 Located along the Outfall Diffuser near Riser 14 – Risers are 38 m apart.

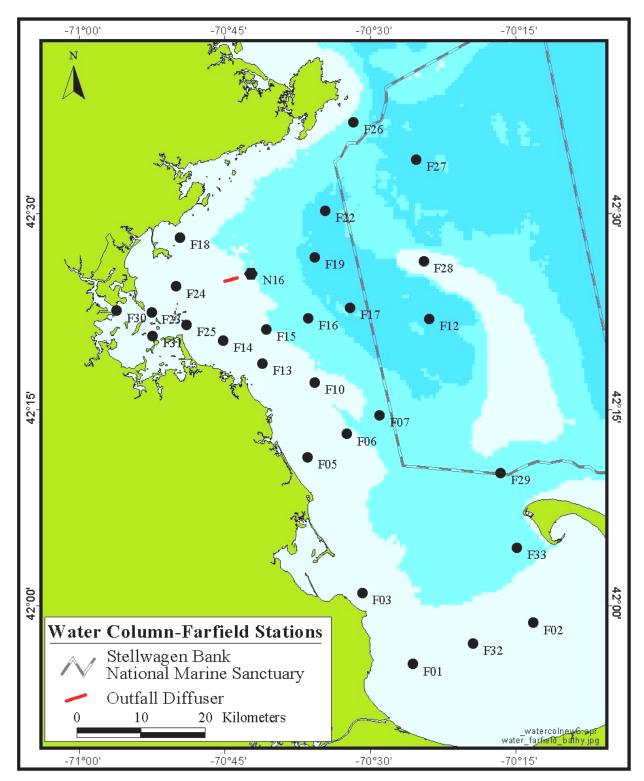


Figure B-3. Farfield Water Column Sampling Stations

Table B-1. Nearfield Water Column Sampling Stations

Station	Latitude	Longitude	Depth	Station
	(N)	(W)	(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 <sup>2</sup>	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	41.851	-70.453	26.2	M		
F02	41.908	-70.228	32.1	M		
F03	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	E		
F17	42.346	-70.571	76.4	E		
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>1</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>2</sup>	41.880	-70.341	30.2	Z		
F33 <sup>2</sup>	42.013	-70.259	44.1	Z		
N16 <sup>3</sup>	42.394	-70.753	42.2	M		

<sup>&</sup>lt;sup>1</sup>Station F23 will be sampled early enough in the day to initiate photosynthesis incubations.

<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> Stations F32 and F33 are sampled only during weeks 6, 9, and 15 each year.

<sup>&</sup>lt;sup>3</sup> Station N16 will be visited on two separate days during combined nearfield and farfield surveys.

#### **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. Nearfield surveys are conducted 12 times per year (Figure B-1). 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 three to four sequential days. The farfield areal productivity station (F23) will be sampled early in the day on the nearfield survey to confine all productivity processing to one day. During the first three-farfield surveys each year, two additional stations (F32 and F33) will be profiled for hydrographic data and sampled for zooplankton. 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).

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

	Station Type Code								
	Ne	arfield	Farfield				Analyses Per Year		
	В	MRP	BR	E	Н	M	MRP	$\mathbf{Z}$	
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	0	3	3	3	0	504
Total Dissolved Nitrogen	3								
Total Dissolved Phosphorous									
Particulate Organic Carbon									
Particulate Organic Nitrogen									
Particulate Phosphorous									
Biogenic Silica									
Chlorophyll <i>a</i> /phaeophytin <i>a</i>	5	5	5	0	3	5	5	0	816
Total suspended solids*	3	3	3	0	3	3	3	0	504
Phytoplankton – whole water**	0	2	0	0	2	2	2	0	204
Phytoplankton – screened water**	0	2	0	0	2	2	2	0	204
Zooplankton	0	1	0	0	1	1	1	1	108
Respiration*	0	3	3	0	0	0	3	0	108
Primary Productivity	0	5	0	0	0	0	5	0	150

<sup>\*</sup>Samples collected at three depths (bottom, mid-depth, and surface)

<sup>\*\*</sup>Samples collected at two depths (mid-depth and surface)

#### **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. Stations F32 and F33 are sampled only during the first three farfield surveys (weeks 6, 9, and 15). A detailed listing of samples collected at each station during nearfield and farfield surveys is provided in Appendix A.

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

During each nearfield survey and the first three farfield surveys of each 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 B2.8). The sampling vessels will operate according to protocols mandated by the Commonwealth of Massachusetts regarding right whales (Appendix B).

## **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. The first tow will start 0.5 miles along heading 300° from station N01. The tow will be conducted at a heading of 060° for 10 minutes at 2 knots. The second tow will be conducted in the vicinity of the outfall, also for 10 minutes at 2 knots. The tow will start to the south of the outfall and will be conducted at a heading of 45° for 10 minutes at 2 knots, crossing the diffuser line on the transect. The beginning and end coordinates of each tow will be recorded

Altimeter

Bottom depth

Navigational position

Sigma-t (calculated)

Salinity (calculated)

Battelle m

Battelle m

Battelle PSU

degree

unitless

Battelle

Battelle

on the survey log. After the net tow is completed, the sample will be emptied into a white dissection basin for a visual, qualitative inspection. 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. If macro algae obscure contents, they will be removed and a second photo taken. Identifiable anthropogenic materials (e.g., plastics) will be retained and archived. Digital images will be included in the survey e-mail summary and described in the survey report.

#### **B.1.8** 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 concentration rate after incubation. MWRA will calculate Net respiration rates. UMD will analyze phytoplankton and zooplankton community structure. The sample analyses are summarized in Table B-4. Sampling and analytical methods are described in Sections B2 and B4, respectively.

## **B.1.9** 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 A.

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	UMD	E6Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Borkman (1994), Borkman et al. (1993), Turner et al. (1995)			
Screened phytoplankton	UMD	Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Turner et al. (1995)			
Rapid phytoplankton	UMD	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-25	SBE-25 CTD Manual/ Battelle SOP 3-183			
Temperature	Battelle	С	Seabird SBE-25	SBE-25 CTD Manual/ Battelle SOP 3-183			
Pressure	Battelle	db	Seabird SBE-25	SBE-25 CTD Manual/ Battelle SOP 3-183			
Dissolved oxygen	Battelle	mg/L	Seabird SBE 43 and 13	Weiss (1970)/Battelle SOPs 3-156 and 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			

Data Sonic PSA-916

Furuno FCV-52

Northstar 941X

Seabird SBE-25

Seabird SBE-25

Data Sonic Manual

Furuno Manual/Battelle SOP 3-129

Northstar Manual/Battelle SOP 3-118

SBE-25 CTD Manual/ Battelle SOP 3-183

SBE-25 CTD Manual/Battelle SOP 3-183

Table B-4. Water Column Sample Analyses

#### **B.1.10** Schedule of Activities and Deliverables

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.

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

			DI ID D / 3					
Survey ID	Additional Surveys Combined	Plan	Planned Due Date <sup>a</sup>					
			Date Start	Date End	Summary	Draft Report		
WF061	WN061	01/30/06	02/06/06	02/09/06	02/16/06	02/30/06		
WF062	WN062	02/20/06	02/27/06	03/02/06	03/09/06	03/23/06		
WN063	None	03/14/06	03/21/06	03/21/06	03/28/06	04/11/06		
WF064	WN064	04/03/06	04/10/06	04/13/06	04/20/06	05/04/06		
WN066	None	05/09/06	05/16/06	05/16/06	05/23/06	06/06/06		
WF067	WN067	06/12/06	06/19/06	06/22/06	06/29/06	07/13/06		
WN069	None	07/18/06	07/25/06	07/25/06	08/01/06	08/15/06		
WF06B	WN06B	08/14/06	08/21/06	08/24/06	08/31/06	09/14/06		
WN06C	None	08/29/06	09/05/06	09/05/06	09/12/06	09/26/06		
WN06D	None	09/26/06	10/03/06	10/03/06	10/10/06	10/24/06		
WF06E	WN06E	10/16/06	10/23/06	10/16/06	10/23/06	11/06/06		
WN06F	None	11/07/06	11/14/06	11/14/06	11/21/06	12/05/06		
WF071	WN071	01/29/07	02/05/07	02/08/07	02/15/07	02/29/07		
WF072	WN072	02/19/07	02/26/07	03/01/07	03/08/07	03/22/07		
WN073	None	03/13/07	03/20/07	03/20/07	03/27/07	04/10/07		
WF074	WN074	04/02/07	04/09/07	04/12/07	04/19/07	05/03/07		
WN076	None	05/08/07	05/15/07	05/15/07	05/22/07	06/06/07		
WF077	WN077	06/11/07	06/18/07	06/21/07	06/28/07	07/12/07		
WN079	None	07/17/07	07/24/07	07/24/07	07/31/07	08/14/07		
WF07B	WN07B	08/13/07	08/20/07	08/23/07	08/30/07	09/13/07		
WN07C	None	08/28/07	09/04/07	09/04/07	09/11/07	09/25/07		
WN07D	None	09/25/07	10/02/07	10/02/07	10/09/07	10/23/07		
WF07E	WN07E	10/15/07	10/22/07	10/15/07	10/22/07	11/05/07		
WN07F	None	11/02/07	11/09/07	11/13/07	11/20/07	12/04/07		

WN: water column nearfield; WF: water column farfield

#### **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 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–4). This capability ensures strong signal reception, and accurate and reliable positioning with 2-second updates.

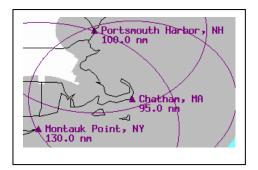


Figure B-4. dGPS MasterStations Coverage

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

#### **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 during surveys to ensure the safety of passengers and crew and to minimize the possibility of collisions with other traffic (46 CFR 185¹) 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 8-conductor double-armored stainless-steel cable and sheave
- 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 (a second SBE-25 and 3 Ocean Sensors OS200-CTDs serve 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 (one additional SBE-43 as backup). A Sea-Bird SBE-13Y, with a YSI type DO sensor, will serve as an additional backup if needed.

<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

- 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
- o 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 90 cm above the pressure sensor<sup>2</sup>
- 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:
  - 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-5). 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. During hydrocast operations, position fixes will be electronically recorded at 2-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 will be electronically recorded at 5-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.

<sup>&</sup>lt;sup>2</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).

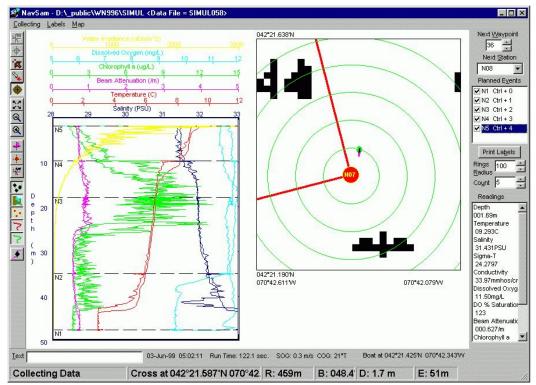


Figure B-5. Sample NavSam<sup>©</sup> Data Acquisition Screen

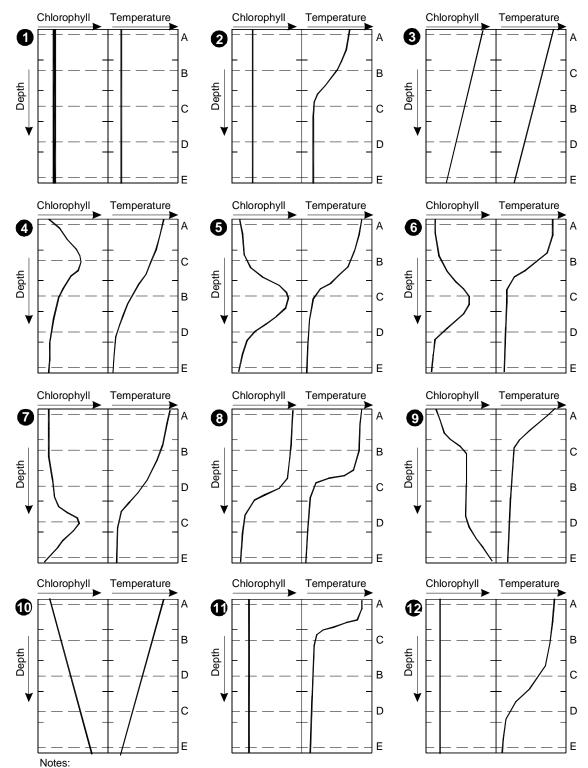
## **B.2.4** Water Sampling

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 Table A-1 in Appendix A, 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 middepth levels can be exchanged. In these cases the C-depth can be switched to a shallower (Bdepth) or deeper (D-depth) to represent the subsurface chlorophyll maximum, as deemed appropriate by the Chief Scientist. For example, scenario 4 of Figure B-6 shows an intense and shallow chlorophyll maximum. In this case, the sampling protocol for the mid-depth and midsurface 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-6 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 30–60 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<sup>©</sup> 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<sup>©</sup> 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 container\_id provided by DLS and previously entered into NavSam<sup>©</sup>. 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-6. 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 A 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-7 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.

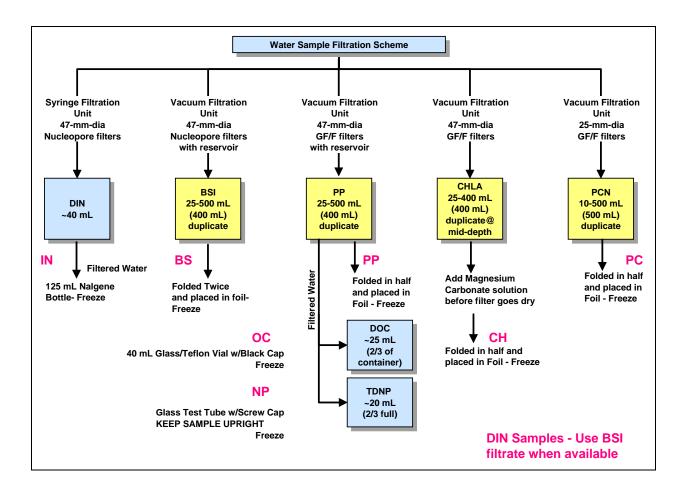


Figure B-7. Onboard Processing Flow Chart

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

Parameter	Laboratory	Station Type	Nearfield Qty	Farfield Qty	Sample Volume (Target) <sup>a</sup>	Sample Containers <sup>b</sup>	Shipboard Processing/ Preservation	Maximum Holding time to analysis
Hydrographic Profile <sup>c</sup>	Battelle	All	7	28	NA	CDs	NA	NA
Following samp	les are subsa	mpled fron	n water coll	ected with	Niskin Bo	ttles		
Dissolved Inorganic Nutrients	DLS	All	35	126	40 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		B, BR, H, M, MRP	21	42	20 mL	40-mL borosilicate glass vial	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	400 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	400 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.	
14C Production	URI	MRP	10	5	1 L	1 Liter dark polyethylene bottle	Store at 4° C up to and during transport to URI for incubation.	< 8 hours
Phytoplankton (Whole Water)	UMD	H, M, MRP	4	26	850 mL	1000 mL HDPE bottle	Preserve with Utermöhl's solution.	6 months
Phytoplankton (Screened Water)		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	TD (D)	TT 3.6		12 (15)d	000 7	1000 7 1	W. 1	7 4
Zooplankton	UMD	H, M, MRP, Z	2	13 (15) <sup>d</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>a</sup> Volume processed for analysis. Total volumes removed from Rosette sampling bottles are listed in Appendix A Tables A1-A2.

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

<sup>&</sup>lt;sup>c</sup> Conductivity, temperature, pressure, dissolved oxygen, chlorophyll a fluorescence, transmissometry, *in situ* irradiance, surface irradiance, bottom depth, navigational position

<sup>&</sup>lt;sup>d</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, 40 mL of the remaining sample 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 20-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 30-mL borosilicate glass vial will be rinsed three times with filtrate, shaken to remove excess sample and then filled with approximately 20 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>3</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>1</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

<sup>&</sup>lt;sup>3</sup> Exact volume filtered will be recorded on sample label and any deviations from standard volume (500 ml for PCN and 400 ml for PP and BSi) will be noted in station log.

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.2.5.6** 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>1</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. 5-265, *Extraction and Analysis of Chlorophyll* a *and Phaeophytin* a *in Seawater using a Turner Designs Model 10AU Fluorometer*. Between 25 and 400 ml samples for chlorophyll *a* analysis will be collected on Whatman 47-mm-diameter GF/F using a vacuum-filter system. The final volume (if <400 ml) 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 (~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* 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-µm-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 <sup>14</sup>C and dissolved inorganic carbon.

## **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, 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 by UMD. The rapid analysis sample will be transferred to UMD 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 µm-mesh net equipped with a flow meter. 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 (*Beroe* sp.) 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

On all nearfield surveys, a Neuston net (1 x 2 meter with 500 micron mesh) will be towed twice to capture any floating man-made debris. The first tow (the control) will start 0.5 miles and 300° from station N01. The tow will be conducted at a heading of 060° for 10 minutes at 2 knots. The second tow will be conducted through the visible outfall plume in the vicinity of station N21, also for 10 minutes at 2 knots. If no visible plume exists, the tow will start at Station N21 and will be conducted at a heading of 45° for 10 minutes at 2 knots, crossing the diffuser line on the transect. The beginning and end coordinates of each tow will be recorded on the survey log. After the net tow is completed, the sample will be emptied into a white dissection basin for a visual, qualitative inspection. 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. There should be no shadows over the basin and a flash will be used unless the day is cloud-free. 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 of each year, 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° during transit between stations (± 90° of heading) and 360° while on station. All sightings will be recorded on standardized marine mammal field sighting logs (Figure B-8). 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 B for contact information).

						Mari	ne M	amn	nal S	ight	ings	Log						
Task:	٦	уре:		[	Date:		Page _	of _	_			(	Observ	er:				
Date	Time	Positi Sigh			ssel iding	N	Mammal Sighting					Weath	er 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	s								Sea	State							
	Mn Bp Eg Ba	Hump Finba Right	back w ck wha whale whale	le			_			0 1 2	Glass Catpa		3 4 5	1.5 - 3 - 6 > 6 ft	ft	-		
	Lag	Atlant	ic white	esided	dolphir	า					Speed					_		
	Pp Gn Bn	Pilot v Blue v	vhale	oise						0 1 2	0 – 5 5 – 1 10 –	0	3 4 5	15 – 20 - 2 > 25				
	Bp Lal	Sei wl White	nale beaked	dalob b	iin					Swel	l (feet)							
	Pv G H	Harbo Gray	r seal seal	·						0	None 1 – 3		2	3 – 6 > 6	į	-		
	На	Harp :								Glare	Э					_		
	UB UO UP	Unide	ntified ntified ntified	Odonto						0	None Mild	•	2	Mode Seve				
	OI .	Jilide	illieu	THOUL	4						ility (mi					_		
										0 1 2	None < ¼ ¼ - 1		4 5 6	3 – 5 5 – 1 10	0			
										3	1 - 3		7	Unlin				

Figure B-8. Example of Marine Mammal Sightings Log and Relevant Codes

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

#### **B.3.1** Sample Custody

Samples collected in the field will be identified by either a LIMS ID supplied by MWRA or by an ID generated by NavSam<sup>©</sup> software. LIMS IDs will be provided for all analyses conducted by DLS. The LIMS IDs will be provided to Battelle as a text file at least one week prior to the survey. LIMS IDs will be imported into the NavSam<sup>©</sup> Collected Subsample Table using a look-up table that contains the DLS LIMS Container ID for each station, depth, analyte, and replicate. The DLS LIMS Container ID will be printed on the sample labels, and station log forms, and a separate label will define the DLS LIMS Sample ID. These IDs will be linked to the NavSam<sup>©</sup> data capture system (Figure B-9).

For samples that are not analyzed by DLS (e.g. plankton, respiration, productivity) Bottle Ids will be generated by concatenating the NavSam<sup>©</sup> 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<sup>©</sup> software during the closing of a set of Rosette sampling bottles at one depth or at completion of the vertical net tow.

The scientific crew member operating the data collection system will fill out the station log (Figure B-10) at each station. These logs will be put into a survey notebook 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 Container ID or NavSam Bottle ID, sample date and time, and other pertinent sample information (Figure B-11, Figure B-12, and Figure B-13)
- The NavSam<sup>©</sup> Custody File is compared to the Planned Sample file 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-ofcustody 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.

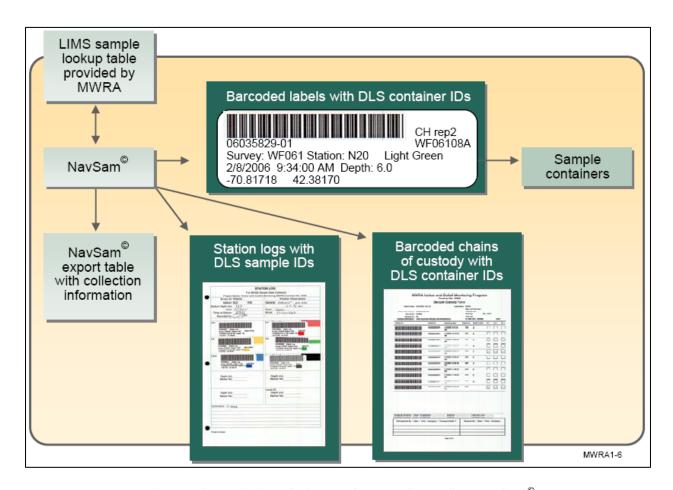


Figure B-9 Depiction of Linkage from DLS LIMS to NavSam<sup>©</sup>

Table B-7. Analysis Codes used in Bottle ID or used as label abbreviations

<b>Analysis Codes</b>	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	UMD
SW	Screened water phytoplankton	UMD
TS	Total suspended solids	DLS
WW	Whole water phytoplankton	UMD
ZO	Zooplankton	UMD

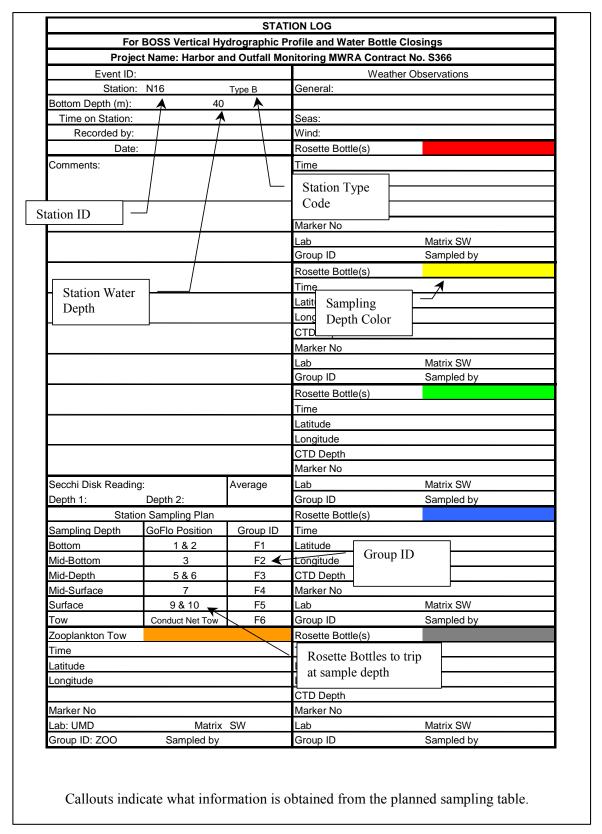


Figure B-10. Sample Station Log

MEASURE	MENT LOG						
For BOS	SS Sample Data Collection						
Project Name: Harbor and Outfall Monitoring MWRA Contract No. S274							
Survey ID: WF052	Protocol ID: SE						
Station: F01	1. First Secchi F	Reading					
	2. Second Secchi F	Reading					
LABEL HERE	3. Tow Time (mm	n:ss.ss)					
	4. Depth of	tow (M)					
	5. Formalin add	led (ml)					
	Date: Recorde	d by:					
Station: F02	1. First Secchi F	Reading					
	2. Second Secchi F	Reading					
LABEL HERE	3. Tow Time (mm	1:ss.ss)					
	4. Depth of	tow (M)					
	5. Formalin add	fed (ml)					
	Date: Recorde	d by:					
Station: F03	1. First Secchi F						
	2. Second Secchi F	Reading					
LABEL HERE	3. Tow Time (mm	1:ss.ss)					
	4. Depth of	tow (M)					
	5. Formalin add	led (ml)					
	Date: Recorde	d by:					
Station: F05	1. First Secchi F	Reading					
	2. Second Secchi F	Reading					
LABEL HERE	3. Tow Time (mm	1:ss.ss)					
	4. Depth of	tow (M)					
	5. Formalin add	led (ml)					
	Date: Recorde	d by:					
Station: F06	1. First Secchi F						
	2. Second Secchi F	Reading					
LABEL HERE	3. Tow Time (mm	n:ss.ss)					
	4. Depth of	tow (M)					
	5. Formalin add	led (ml)					
	Date: Recorde	d by:					

Printed by NavSam

Figure B-11. Example of a Zooplankton Custody Form

# MWRA Harbor and Outfall Monitoring Program Contract No. \$366 Sample Custody Form

Today's Date :	2/22/2006 1:31:	:49 P	Laborat	atory: MWRA				
Chain-of-Custody#:	WF061-BS-00'	51		Dept. La 190 Tafts	ab Services ts Ave			
Survey ID :		71		Winthro		IA 02152		
Analysis ID :	BS			Yong La			-	
Analysis Description :	Biogenic silica				1-7841 (Phone)		(Fax	_
Bottle ID :		Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
		06002302-02	2/10/2006 7:06:04 AM	BF11				
		06002303-02	2/11/2006 6:45:34 AM	BF12				
		06002309-01	2/13/2006 8:00:11 AM	BF13				
		06002311-01	2/10/2006 5:49:56 PM	BF21				
		06002321-01	2/11/2006 4:44:16 PM	BF22				
		06002322-01	2/13/2006 11:41:31 AM	BF23				
		06002330-04	2/13/2006 8:37:14 AM		A			
		06002331-01	2/13/2006 8:37:14 AM	F01	A			
		06002335-04	2/13/2006 8:35:46 AM	F01	С			
		06002337-01	2/13/2006 8:35:46 AM	F01	С			
		06002341-04	2/13/2006 8:34:16 AM	F01	E			
		06002342-01	2/13/2006 8:34:16 AM		E			
		06002345-04	2/13/2006 9:46:11 AM		Α			
		06002346-01	2/13/2006 9:46:11 AM	F02	Α			
Shipping Condition - Re Received Condition - Re			Cold(ice): Cold(ice):		Frozen(dry ice) Frozen(dry ice):			
Relinquished By / D	)ate / Time /	Company / Tr	ansport-Airbill #	Received	d By / Date /	Time /	Compar	ny
				<u> </u>				
			$\overline{}$					

Page 1 of 10

Figure B-12. Example of Water Chemistry Custody Form with LIMS generated IDs

# MWRA Harbor and Outfall Monitoring Program Contract No. \$366

# Sample Custody Form

Today's Date: 2/22/2006 1:32:38 P Laboratory: University of Massachusetts, Dartmouth

**Biology Department** 285 OldWestport Road

Chain-of-Custody #: WF061-ZO-0062 Survey ID: WF061 North Dartmouth MA 02747-2300

Dr. Jefferson Turner Analysis ID: ZO

508-999-8229 (Phone) 508-999-8197 (Fax) Analysis Description: Zooplankton

Bottle ID :	Bottle ID :	Sampling Date :	Station ID:	Depth Code:	Ck 1	Ck 2	Ck 3
	WF0610C1ZO1	2/10/2006 12:03:31 PM	N04	Z			
	WF0610D8ZO1	2/10/2006 1:05:43 PM	N18	Z			
	WF0610EDZO1	2/10/2006 2:03:21 PM	F23	Z			
	WF06112EZO1	2/10/2006 3:48:33 PM	F13	Z			
	WF061160ZO1	2/10/2006 5:12:36 PM	F06	Z			
	WF0611AAZO1	2/11/2006 7:37:22 AM	N16	Z			
	WF0611C3ZO1	2/11/2006 8:27:54 AM	F22	Z			
	WF0611D1ZO1	2/11/2006 9:10:05 AM	F26	Z			
	WF0611EBZO1	2/11/2006 10:27:23 AM	F27	Z			
	WF061267ZO1	2/11/2006 3:08:09 PM	F25	Z			
	WF061275ZO1	2/11/2006 3:28:15 PM	F24	Z			
	WF061283ZO1	2/11/2006 3:55:03 PM	F30	Z			
	WF061292ZO1	2/11/2006 4:16:54 PM	F31	Z			
	WF0612C6ZO1	2/13/2006 8:37:15 AM		Z			
Shipping Condition - Room Tempera Received Condition - Room Tempera	ature:	Cold(ice): Cold(ice):		rozen(dry ice) rozen(dry ice)		_	
Relinquished By / Date / Time	/ Company / Tra	nsport-Airbill #	Receive	d By / Date /	Time /	Compan	y
							$\dashv$

Page 1 of 2

Figure B-13. 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 creating floppy disk or compact disc backups of all electronic data generated each day. The label on the backup media will include a survey ID, date, name of person creating the backup files, and a disk number. The data will be transferred to Battelle's data management team upon completion of the survey. The Field Manager or his designee maintains the disks until the annual archive cycle. HOM5 disks are saved for six years from the time of collection.

Battelle, DLS, URI, 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. Jessica Fahey) 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 HOM5 data management team for submission to MWRA.

Electronic data will remain in the custody of laboratory managers and custodians [Dr. Yong Lao (DLS), Dr. Jefferson Turner (UMD), 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 will be stored in the Task notebook and Set 3 will be 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 sample 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 sample ID vs. the custody forms generated by NavSam<sup>©</sup> prior to delivering the samples to the laboratory. All samples will be delivered to the Battelle Field Sample Custodian who will distribute them to the appropriate laboratory personnel by hand or by Federal Express. All frozen samples will be shipped on dry ice with protective layers of foam or bubble wrap to ensure samples remain intact and frozen during shipment.

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 Manager 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 Sample Custodian within 24 hours of receipt. The original chain forms will be submitted to the Battelle Laboratory Manager 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.* 2006) for Nutrient and Chlorophyll Analyses for Outfall Monitoring (January 2006):

- 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*. 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 Appendix C of Libby et al. 2005. Prior to receipt of the productivity samples, 20 mL borosilicate vials (18 per depth sample) are spiked with 100 μL of 10 μCi/mL (1μCi for 5 mL of water) Carbon-14 (<sup>14</sup>C) stock solution and chilled. Under subdued green 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, 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 µE m<sup>-2</sup> s<sup>-1</sup>). The trays are placed into a light (250 W Tungsten-halogen lamps) and temperature controlled incubator for 1 hour and are incubated within 2°C of the in situ temperature. 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.

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 corrected irradiance sensor, which is calibrated every two years (calibration factors are stored in the LiCor data logger). Upon removal from the incubator,  $200~\mu\text{L}$  of 0.05N HCl is added to each vial. Vials remain uncapped while gently agitated in the dark for a minimum of 20 hours. After this time period, 17 mL of 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,  $100 \,\mu\text{L}$  of  $10 \,\mu\text{Ci/mL}$  <sup>14</sup>C stock is added to each of three vials containing 17 mL of Universol and 3 mL of β-phenylethylamine. 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). Each model is configured to measure single labeled <sup>14</sup>C samples as disintegrations per minute (DPM) for five minutes, and is set to repeat three times. The Model 2900 was calibrated on July 29, 2002, using Packard's <sup>14</sup>C and <sup>3</sup>H standards and background. The <sup>14</sup>C and <sup>3</sup>H efficiencies were 96.3% and 68.7% respectively.

Light profile data are reviewed during phase 1 post-survey processing (and again by Paul Dragos or Carl Albro prior to delivery to MWRA and again by Doug Hersh at 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 provided, so that the best available profile can be fit. MWRA will provide the data directly to URI after each survey's hydrographic data are reviewed and loaded into EM&MS.

Any other anomalies in light profiles noted during this analysis that lead the investigator to exclude data from the fit will be communicated to the Battelle data management team.

**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. MWRA will provide the data directly to URI following each field survey. The cosine values are converted by URI to scalar readings using an empirically determined equation<sup>4</sup>:

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.

<sup>&</sup>lt;sup>4</sup> Equation was updated at URI on March 13, 2002 in comparison with Battelle's *in situ* irradiance sensor (Biospherical model Q-200L).

Calculation of Daily Primary Production. Given the best fit parameters (P<sub>sb</sub> or P<sub>max</sub>, a, b) of the P–I curves obtained for each of the five sampling depths, the *in situ* light intensity (*i.e.* I<sub>z</sub>) at each depth determined from the sum of exponential fits on the *in situ* light field and the photoperiod incident light (I<sub>o</sub>) time series, it is possible to compute daily volumetric production for each depth. To do this at a given depth, instantaneous production, more commonly referred to as hourly production (P(I<sub>z</sub>); mgC m<sup>-3</sup> hr<sup>-1</sup>), is determined for the *in situ* light intensity (I<sub>z</sub>) computed for each 15 minute interval of the photoperiod (6 AM to 6 PM) using the appropriate equations and modeled P–I parameters (Platt *et al.*, 1980 or Webb *et al.*, 1974 see P–I Curves subsection). Daily production at each depth (P(z); mgC m<sup>-3</sup> d<sup>-1</sup>) is calculated as the sum of hourly production values from 6 AM to 6 PM divided by four 15-min intervals per hour.

*Calculation of Daily Areal Production.* Areal production (mgC m<sup>-2</sup> d<sup>-1</sup>) is obtained by trapezoidal integration of daily volumetric production vs. depth down to the depth of the bottom sample. The specific procedure is calculated from five depths  $z_1, z_2, ...z_5$  with values of daily productivity from the previous section  $P(z_1), P(z_2), ... P(z_5)$ . Daily areal production then equals:

$$\sum_{z=1}^{z=5} \frac{(P(z_i) + P(z_{i-1}))}{2} \times (z_i - z_{i-1})$$

where:  $z_0 = 0$  and  $P(z_0) = P(z_1)$ .

Calculation of Chlorophyll-Specific Parameters. MWRA (ENQUAD) will provide chlorophyll data and calibrated fluorescence after DLS completes analysis of chlorophyll samples and ENQUAD calibrates the fluorescence profiles for each survey. Chlorophyll-specific measures of hourly production and related parameters of the fitted P(I) curve are calculated by dividing by chlorophyll concentration. Depth-averaged chlorophyll-specific production (denoted as P') is also of interest and is calculated as:

$$\frac{1}{z_5} \sum_{\tau=1}^{z=5} \frac{\left(P'(z_i) + P'(z_{i-1})\right)}{2} \times (z_i - z_{i-1})$$

where:  $z_0 = 0$  and  $P'(z_0) = P'(z_1)$ .

## **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 a Total Organic Carbon Analyzer Model 700, 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 and HOM4. 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). The Sedgewick Rafter chamber was measured with an ocular micrometer, and was found to have 48 field of view paths at 500X magnification. Typical volumes are one path of the cell which at 500X = 1/48 of one ml of concentrate, and at 250X = 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 500X would yield an estimate of 750 cells per liter, as follows:

[1 cell / 4 paths \* 48 paths / 1ml S-R \* 50 ml settle vol.] / 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.

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, a count of one cell in 4 paths at 500x would typically translate to 1 cell/4 paths \* 48 paths / 1ml \* 800ml / 50ml \* 50ml 1ml = 240,000 cells / L. Final abundance estimates will be reported as units of  $10^6$  cells per liter.

#### **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 and HOM4. 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 sp. Dinophysis sp. Gymnodinium sp. Gyrodinium sp. Prorocentrum sp. Protoperidinium sp.

The 4 liter seawater sample will be sieved through a 20um 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 >20um 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 tamarense and Alexandrium fundyense*, *Phaeocystis* sp., *Pseudo-nitzschia*). 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 and HOM4. Upon return to shore, 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, divided by the volume of water filtered by the net, multiplied by the aliquot concentration factor.

#### **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. If the DO sensor records readings below 6 mg/L, an extra DO sample will be collected at that depth. 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. Milli-Q water supplied by DLS will be dispensed from the carboy to a graduated cylinder for a triple rinsing of the cylinder. This method includes a change from previous decontamination steps. Previously, syringe filtration for DIN samples received no acid or Milli-Q rinses. As a result, this equipment has been a suspected contributor to ongoing NH<sub>4</sub> contamination issues. The rinses have been implemented in HOM5 in an attempt to reduce contamination.

#### **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 by placing the unused filters directly into the appropriate sample containers. 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® then stored in the freezer. In addition to the processed field blanks, a bottle blank will be collected at the same time as the morning field blank. 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® 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 in the exact manner as the primary sample. Replicates provide information regarding the variability of samples collected in the field. Table B-8 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
Biogenic Si, Chlorophyll			the 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
DOC			only half-day of sampling is needed
TDNP			then only 2 sets of field blanks are
			required.
Bottle Blank for DIN, DOC,	3	NA	One blank per container type per day
TDNP			

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
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, Biogenic Si, Chlorophyll	1/20 samples	NA	NA
Field Blanks: DIN – BSi filtrate DIN –DIN syringes DOC TDNP	3/day/parameter	NA	One blank for each analysis will be collected at the beginning of the day, mid-day, and at the end of the day. If only half-day of sampling is needed then only 2 sets of field blanks are required.
Bottle Blank for DIN, DOC, TDNP	3	NA	One blank per container type per day

#### **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 quality control (QC) samples including procedural/filter blanks, prepared standards, SRMs, laboratory replicates and field replicates, as applicable. Appropriate QC samples analyzed in the laboratory for all water column parameters are presented in Table B-10. In many cases, one or more QC samples of a selected type may not be applicable to all water column parameters. For example, procedural blanks are not applicable to dissolved oxygen, plankton or chlorophyll *a* analyses. Measures of precision and accuracy for analysis performed by DLS are described in MWRA DLS QAPP Nutrient and Chlorophyll Monitoring (Leo *et al.* 2006). Supplemental measures of precision and accuracy, not defined in Table B-10 are discussed below.

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

Q	uality Control Sample Type	Frequency	Data Quality Indicator	Corrective Action						
Pı	Procedural Blanks									
	Primary Productivity by <sup>14</sup> C	One with every station	<mdl< td=""><td>Results examined by laboratory manager, task leader, or project manager. Corrective action (e.g., re-extraction, reanalysis, data qualifier) is documented.</td></mdl<>	Results examined by laboratory manager, task leader, or project manager. Corrective action (e.g., re-extraction, reanalysis, data qualifier) is documented.						
Pı	repared Standards and SRM									
	Primary Productivity by <sup>14</sup> C	One with every station	≤2% PD¹	As above						
L	aboratory Triplicates									
	Primary Productivity by <sup>14</sup> C	All samples	$\leq 10\% \text{ RSD}^2$	As above						
	Dissolved Oxygen	Respiration stations at Bottom, Mid, &Surface Depths	≤5% RSD <sup>2</sup>	As above						

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

### **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 sample. Unicellular forms (*e.g.*, *Cryptomonas*, microflagellates), aggregate forms (*e.g.*, *Phaeocystis*), and chained forms (*e.g.*, *Skeletonema*) will each count as one entity towards the 400-entities-counted-persample 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 samples from each of the farfield/nearfield combined

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

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.

## **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.

### **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. An additional data quality procedure to be performed is a blind recount of a subset of samples by the taxonomist to provide an estimate of the variability in the analysis and ensure the accuracy and comparability of the results. 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.

## **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; Libby *et al.* 2005), because field program design and analytical procedures are similar or identical. In addition, the use of written standardized procedures ensures that sample preparation and analyses will be comparable throughout the project and with other projects. 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 and 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.* 2006).

#### 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-25 CTD depth 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. Although the readings are not recorded, 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-25) 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 following additional calibration procedures will be employed. On each water column survey, 6-8 water samples will be collected for salinity measurements. An attempt will be made to collect a range of salinities from different stations and depths (stations and depths with sharp salinity gradients

will be avoided). The samples will be transported to the NOAA Narragansett lab where they will be analyzed using a Guildline Autosal Salinometer. If the CTD is found to be more than 0.1 PSU out of calibration, a post-calibration correction will be applied. 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 will be sent to the factory annually for a systems check. Records of factory maintenance are kept in an 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 Models 43 and 13) 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  $50 \,\mu g/L$  chlorophyll in a *Thalassiosira weissflogii* phytoplankton culture). The fluorometer data, displayed with the NavSam program, will approach 0.0  $\,\mu g/L$  when the instrument is on deck. The ondeck 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. During farfield surveys, the instrument will be turned off between stations to prevent flash-lamp degradation. 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 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<sup>©</sup> 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 calibration 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).
- 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® 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 before the next survey.

## 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.* 2006).

Parameter	Instrument Type	Initial Calibration			Continuing (	Calibration	Corrective Action
		No. Stds	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency	
Dissolved oxygen and respiration	Radiometer Titralab ™	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	3	r > 0.999	Prior to analytical run	PD from Initial ≤2%	Every 20 samples	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 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 HOM5 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-14 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<sup>©</sup> software converts the raw sensor analog signals into engineering units using instrument calibration coefficients. The station arrival time is marked as an event in NavSam<sup>©</sup> 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 will be used to 1) offset the *in situ* irradiance data by 0.9 m to account for distance sensor is located above pressure sensor and 2) visually review the profiles and mark any data as bad or suspect as appropriate. 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 2 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 +/- 5 seconds of the moment of bottle closing). These files will serve as the export file to the EM&MS database. Project-specific SOP MWRA 001 *Processing and Calibrating CTD Data and Creating Profile Data Files* describes these procedures. Salinity and density are calculated from temperature and conductivity using the equations of Fofonoff and Millard (1980), and dissolved oxygen percent saturation is calculated from dissolved oxygen concentration, temperature, and salinity using the equations of Weiss (1970).

#### **B.10.1.2** Laboratory Data

Data reduction procedures and formulae are defined in laboratory SOPs. All data generated by Battelle or another laboratory 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. All laboratory replicates will be reported as mean sample values and all field replicates will be reported as individual sample values.

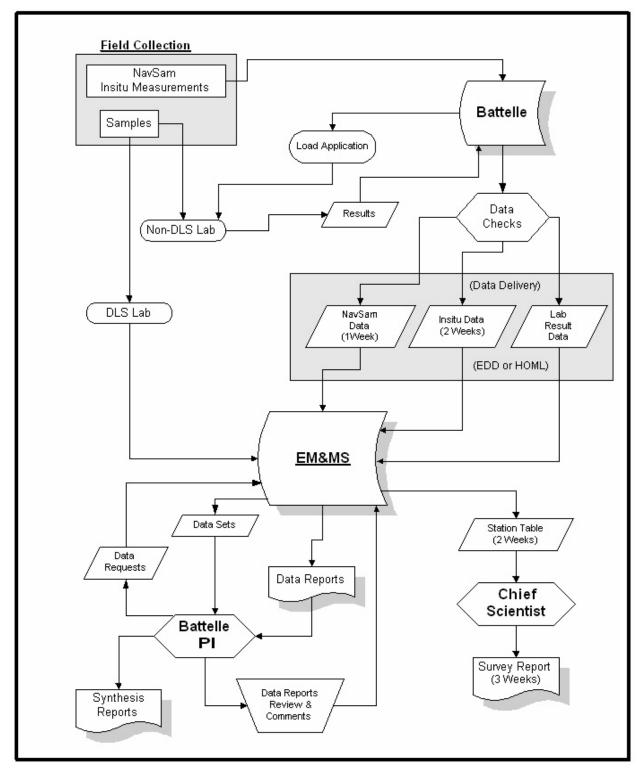


Figure B-14. Overview of the Data Management Strategy for Water Column Monitoring

## Calculation of Dissolved Oxygen and Respiration

The concentration of DO in units of (mg  $O_2$  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.

*Calculation of Primary Production.* Volume specific primary production is calculated using equations similar to that of Strickland and Parsons (1972) as follows:

$$P(i) = \underbrace{(1.05DPM(i))DIC}_{A_{SD}T}$$

$$P(d) = \underbrace{(1.05DPM(d))DIC}_{A_{SD}T}$$

$$A_{sp} = DPM(sa)-DPM(back)$$

where:  $P(i) = primary production rate at light intensity i (<math>\mu gC L^{-1} h^{-1} or mgC m^{-3} h^{-1}$ )

 $P(d) = dark production, (\mu gC L^{-1} h^{-1} or mgC m^{-3} h^{-1})$ 

DPM(i) = dpm of sample incubated at light intensity i

DPM(d) = dpm of dark incubated sample

DPM(back) = background dpm in vial containing only scintillation cocktail

DPM(sa) = specific activity added to incubation samples (DPM)

T = incubation time (h)

DIC=concentration of dissolved inorganic carbon (µg mL<sup>-1</sup>)

Table B-12 shows the frequency that primary productivity measurements and calculations are performed per vial, depth, station, and survey.

Table B-12. Measurement Frequency for Variables Involved in Calculation of Primary Production

Measurement/ Calculation	Vial (16/depth)	Depth (5/stn)	Station	Survey
DPM(i)	√			
P(i)	√			
DIC		<b>V</b>		
P(d)		7		
DPM(d)		1		
Asp			√	
T			√	
DPM(sa)			√	
DPM(back)				√

*P–I curves.* For each of the 5 depths at each photosynthesis station, a P–I curve is calculated from the data P(I) = P(i) - P(d) vs. the irradiance I, I which the incubating sample is exposed. The P–I curves are fit via one of two possible models, depending on whether significant photoinhibition occurs. In cases where photoinhibition is evident, the model of Platt *et al.* (1980) is fit (SAS, 2004) to obtain the theoretical maximum production and terms for light-dependent rise in production and degree of photoinhibition.

$$P(I) = P_{sb}(1-e^{-a})e^{-b}$$

where: P(I) = primary production at irradiance I, corrected for dark fixation (P(i)-P(d))  $P_{sb}$  = theoretical maximum production without photoinhibition  $a = \alpha I/P_{sb}$  where  $\alpha$  is the initial slope the light dependent rise in production  $b = \beta I/P_{sb}$ , where  $\beta$  is a term relaying the degree of photoinhibition.

If it is not possible to converge upon a solution, an alternative model of Webb *et al.* (1974) is similarly fit to obtain the maximum production and the term for light-dependent rise in production.

$$P(I) = P_{max}(1-e^{-a'})$$

where: P(I) = primary production at irradiance I corrected for dark fixation (P(i)-P(d))  $P_{max}$  = light saturated maximum production  $a' = \alpha I / P_{max}$ , where  $\alpha$  is the initial slope the light-dependent rise in production

P<sub>max</sub> and P<sub>sb</sub> are not equivalent but they are mathematically related using the equation:

$$P_{\text{max}} = P_{sb} \left[ \alpha/(\alpha+\beta) \right] \left[ \beta/(\alpha+\beta) \right]^{\beta/\alpha}$$

*Light vs. Depth Profiles.* To obtain a numerical representation of the light field throughout the water column, downcast CTD light profiles are fit (SAS, 2004) to an empirical sum of the exponential equation:

$$I_z = A_1 e^{-a1Z} + A_2 e^{-a2Z} + \dots$$

which is an expansion of the standard irradiance vs. depth equation:

$$I_z = I_o e^{-kZ}$$

where:  $I_z$ =light irradiance at depth Z  $I_o$ =incident irradiance (Z=0) k=extinction coefficient  $A_1, A_2,...$ =factors relating to incident ( $I_o$ = $A_1$ + $A_2$ +...)  $a_1, a_2,...$ =coefficients relating to the extinction coefficient (k= $a_1$ + $a_2$ +...)

The expanded equation is used in most instances as spectral shifts, pigment layering and other factors result in deviation from the idealized standard irradiance vs. depth equation. The simplest form of the expanded equation will be implemented to adequately model the light field, which in the majority of cases will be the sum of two exponentials.

#### **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 quality control checks upstream to the laboratories. Formats for delivering electronic data are included in the contract but these formats are subject to change and have already changed once since the contract was generated. 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 via email in the absence of the HOML application. Once the HOML application goes online, Battelle will submit data electronically through the application.

#### **B.10.2.1** Navigation and Sample Collection Data

Navigation and sample collection data will be processed on-board the survey vessel and be ready for loading upon arrival at Battelle. A database application developed as part of the NavSam<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-13 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.

Param Code Meth Code Parameter Unit Code Instr Code **BOSS** Conductivity CONDTVY mS/cm CTD5 (Serial Number) Conductivity CONDTVY mS/cm SB4 (Serial Number) BOSS Dissolved Oxygen DISS OXYGEN DO3 (Serial Number) BOSS mg/L Fluorescence FLUORESCENCE BOSS μg/L WS (Serial Number) LIG4 (Serial Number) in situ Irradiance level LIGHT uEm-2sec-1 **BOSS** Salinity SAL **PSU** CTD5 (Serial Number) **BOSS** Salinity SAL PSU SB4 (Serial Number) **BOSS** CTD5 (Serial Number) Density as measured by sigma-t SIGMA T **BOSS** SIGMA T SB4 (Serial Number) BOSS Density as measured by sigma-t SURFACE IRRAD Surface irradiance level uEm-2sec-1 LIG2 (Serial Number) **BOSS** Temperature TEMP C CTD5 (Serial Number) **BOSS** Temperature TEMP C SB3-(Serial Number) **BOSS** TRANS T1R25 (Serial Number) BOSS Transmissivity m-1 PCT SAT Percent Saturation, Dissolved Oxygen **PCT** DO3 (Serial Number) BOSS

Table B-13. Database Codes for Hydrographic Parameters

Instrument codes: (Serial Number) indicates unique probe serial number

# **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-15). The laboratory enters the results and other supporting information such as qualifiers. All entries are constrained by the rules of EM&MS. Errors are caught on entry and fixed by the data contributor. Primary keys are in place so duplication cannot occur. Entry applications are developed on an individual laboratory basis. Laboratory staff receive one day of training on the application prior to their first set of samples. When data entry is complete, the database is sent back to Battelle.

The loading application provides the laboratory many available functions (Figure B-16), including hardcopy report, quality control 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 quality control 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-14 shows the qualifiers to be used by the laboratory. Database codes for plankton taxonomy and species qualifiers are presented in Table B-15 and Table B-16, respectively. Table B-17 shows the analytical parameters,

codes, and units of measure for the analytes collected under this task. Additional database codes are described in Table B-18. 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*.

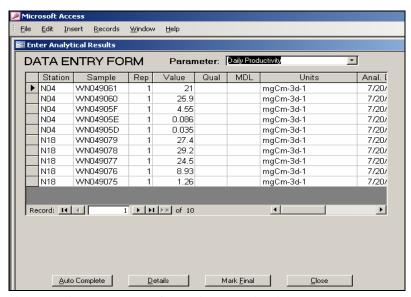


Figure B-15. Example of Loading Application Data Entry Form



Figure B-16. Loading Application Main Menu

Table B-14. 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
С	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	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-15. Database Codes for Plankton Taxonomy

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

Table B-16. Database Codes for Species Qualifiers

Qualifier	Description
A	Adult (not sexed)
В	Cyst
C	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-17. 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	INCUB_TEMP_RESP	С	BOS		
Respiration					
Incubation Time for	INCUB_TIME_RESP	hours	BOS		
Respiration					
Areal Production	AREAL_PROD	mgCm-2d-1	URI	PTLSC2900	LIBBY02
Daily Production	DAILY_PROD	mgCm-3d-1	URI	PTLSC2900	LIBBY02
Maximum for P/I Curve	Pmax	mgCm-3h-1	URI	PTLSC2900	LIBBY02
Alpha parameter for	Alpha	ALPHA	URI	PTLSC2900	LIBBY02
productivity curve	ripiu	7 112 1 1 1 7 1	Old	1 12502700	EIBB I 02
Beta parameter for	Beta	ALPHA	URI	PTLSC2900	LIBBY02
productivity curve					
Hourly Production	HOURLY_PROD	mgCm-3h-1	URI	PTLSC2900	LIBBY02
Incubation Time	INCUB_TIME_PROD	hours	URI		
Incubation Temperature	INCUB_TEMP_PROD	C	URI		
Light Exposure	INCUB_IRRAD_PROD	uEm-2sec-1	URI		
Depth-average chlorophyll- specific primary production	PROD_CHLA_Z	mgC(mg Chla)- 1d-1	URI	PTLSC2900	LIBBY02
Potential Areal Productivity	AREAL_PROD_POT	mgCm-2d-1	URI	PTLSC2900	LIBBY02
Depth-averaged chlorophyll-specific potential primary production	PROD_POT_CHLA_Z	mgC(mg Chla)- 1d-1	URI	PTLSC2900	LIBBY02
Potential Daily Productivity	DAILY_PROD_POT	mgCm-3d-1	URI	PTLSC2900	LIBBY02
R-Squared parameter for					
non-linear curve fit of	PROD_R2		URI	PTLSC2900	LIBBY02
productivity vs. irradiance					
Incubation point for a two-					
point incubation (initial or	INCUB_POINT		URI		
final)					

Table B-18. Description of Database Codes

Field_Name	Code	Description
ANAL LAB ID	BOS	Battelle Ocean Sciences, Duxbury, MA
ANAL_LAB_ID	UMD	University of Massachusetts, Dartmouth, MA
ANAL_LAB_ID	URI	University of Rhode Island, Narragansett, RI
INSTR_CODE	CTD5_(Serial Number)	Ocean Sensors CTD, model OS200
INSTR_CODE	DO3_(Serial Number)	SeaBird D.O. probe, model SBE-43
INSTR_CODE	FLU7	Turner Designs Model 450-003 Fluorometer
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 Santillation Counter Model 2900
INSTR_CODE	RTL	Radiometer TitraLab Titrator
INSTR_CODE	SB4_(Serial Number)	SeaBird conductivity sensor, model SBE-4C
INSTR_CODE	TD9-SHMZ-V	Tekmar-Dorhmann Apollo 9000 Carbon Analyzer
INSTR_CODE	T1R25	WET Labs C-Star 25cm transmissometer 660 nm fixed wavelength
INSTR_CODE	WS_(Serial Number)	WETStar miniature fluorometer, model ws-3-mf-p
METH CODE	1168	Organic carbon by combustion with infrared detection
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	OUD88	Oudot et al. (1988)
METH_CODE	PHAESWFLU	Phaeophytin-sea water-fluorometric
METH CODE	SCR20U	Large dinoflag. screening technique 20 microns
UNIT CODE	ALPHA	mgCm-3h-1uE-1m2s
UNIT CODE	С	Degrees Celsius
UNIT CODE	CELLS/L	Cells per liter
UNIT CODE	db	Decibars
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	mgCm-2d-1	Milligrams of carbon per square meter per day
UNIT_CODE	mgCm-3d-1	Milligrams of carbon per cubic meter per day
UNIT_CODE	mgCm-3h-1	Milligrams of carbon per cubic meter per hour
UNIT_CODE	PSU	Practical salinity units
UNIT_CODE	uEm-2sec-1	Micro-Einsteins per square meter per second
UNIT_CODE	ug/L	Micrograms per liter
UNIT_CODE	uM	Micromoles per liter
UNIT_CODE	uM/hr	Micromoles per liter per hour
UNIT_CODE	m	Meters
UNIT_CODE	mgC(mg Chla)-1d-1	Milligrams of carbon per milligram of chlorophyll a per day
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 data. 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 by a button on the application. A transfer script will copy the data into the proper table in Battelle's database. Data from the laboratories receive a quality assurance review prior to electronic submission to MWRA. Any issues are corrected in the database will be well-documented script that is available to MWRA upon request. The MWRA check script will be run on the database prior to export of a dataset to ensure that all data conform to quality control 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 7-8 are carried out in accordance with this QAPP. A systems audit will verify the implementation of the Quality Management Plan and this QAPP for the work conducted in the 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 will be acceptable. During the time that work is in progress, an inspection will be conducted by each laboratory QA Officer or their designee to evaluate the laboratory data-production process. All data must be reviewed by each laboratory QA Officer prior to submission to the Battelle Database Manager and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality and a QC narrative of activities.

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 Task Leader 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 at the monthly management meetings. Action items are discussed, assigned, and results reported at subsequent meetings. Persistent project issues that are not addressed satisfactorily during weekly meetings are reported to Battelle's Product Line Manager during monthly 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 Quarterly meeting, 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> sample 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 quality control 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-14) 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 A**

Nearfield and Farfield Sample Collection Requirements

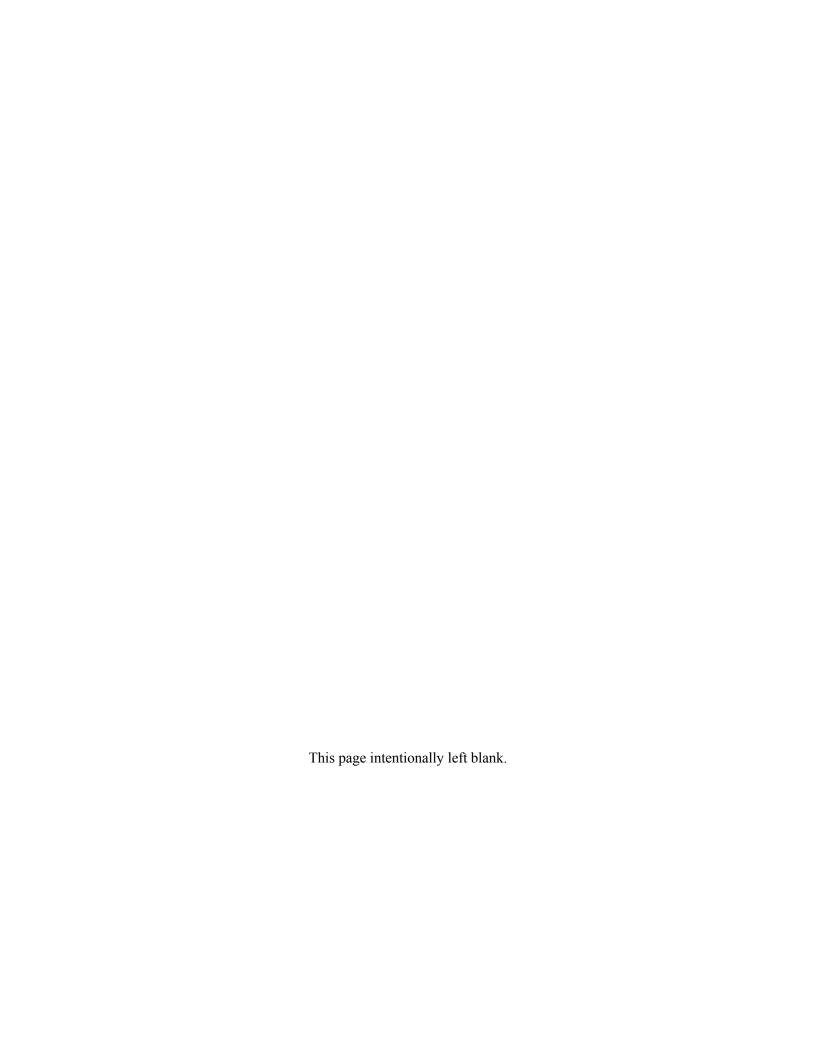


Table A-1. Nearfield Water Column Sampling Plan.

ran	110 1	7-1.	Nearmend wa	atti C		шы	ашр	ning i	iaii.											
StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L GoFlos	Dissolved Inorganic Nutrients	Dissolved Organic Carbon	Tota Nit	Pa Car	Particulate Phosphorous	1	Chlorophyll a	Total Suspended Solids	Rapid Analysis Phytoplankton		0)	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
			Protocol (			IN	OC	NP	PC	PP	BS	С	TS	RP	WW	SW	ZO	RE	AP	IC
			Volume		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							
			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								
			Tot	als	41	22	22	42	42	42	42	23	1	4	4	2	36	10	10	
Fie	ld Bl	ank				6	3	3												
Filte	er Bl	ank							2	2	2	2								
		lank				1	1	1												
							•	•	l				l							

Table A-2. Farfield Water Column Sampling Plan (3 Pages).

Section   Process   Pro				1461	C 11 2		-					~ ****	P	8	111 (5	- "5	05).	,		
Note	StationID	Depth (m)	Station Type			Number of 9-L GoFlos														
				Protocol C	Code		IN	OC	NP	PC	PP	BS	CH	TS	WW	SW	ZO	RE	AP	IC
FOI   26				Volume	(1.)		1	0.1	0.1	1	0.3	0.3	0.5		1	4	1	1	1	1
FO1   26   M   3 Mid-Depth   14   14   1   1   2   2   2   1   1   1   1   1	<del>                                     </del>				` '	- 2									·		÷		·	·
FOIL   26   M   S. Mick-Depth   14   2   1   1   1   2   2   2   2   1   1				_				1	1					-						
A Mid-Surface																				
Surface	F01	26	M		14	2	1	1	1	2	2	2	2	1	1	1				
Surface				4 Mid-Surface	2.5	1	1						1							
Formal   F						2	1	1	1	2	2	2	1	1	1	1				
FO2   32   M   3   Mid-Depth   15   2   2   2   1   1   1   2   2   2   2								_									1			
FO2 32 M 3 Mid-Depth 15 2 2 1 1 1 2 2 2 2 1 1 1 1 1																				
FO2   32   M   3   Mid-Depth   15   2   2   2   1   1   2   2   2   2   2			ļ					1	1	2	2	2		1						
Mile													1							
S. Surface	F02	32	M	3_Mid-Depth	15	2	2	1	1	2	2	2	2	2	1	1				
S. Surface				4 Mid-Surface	2.5	1	1						1							
Formal   F			i					1	1	2	2	2		1	1	1				
FOS   16   E   3.   Mid-Depth   1   1   1   1   1   1   1   1   1					13												4			
FO3 16 E 3 Mid-Depth 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1																				
FO3 16 E 3 Mid-Depth 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1					1	1														
FO3 16 E 3 Mid-Depth 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				2_Mid-Bottom	1	1	1													
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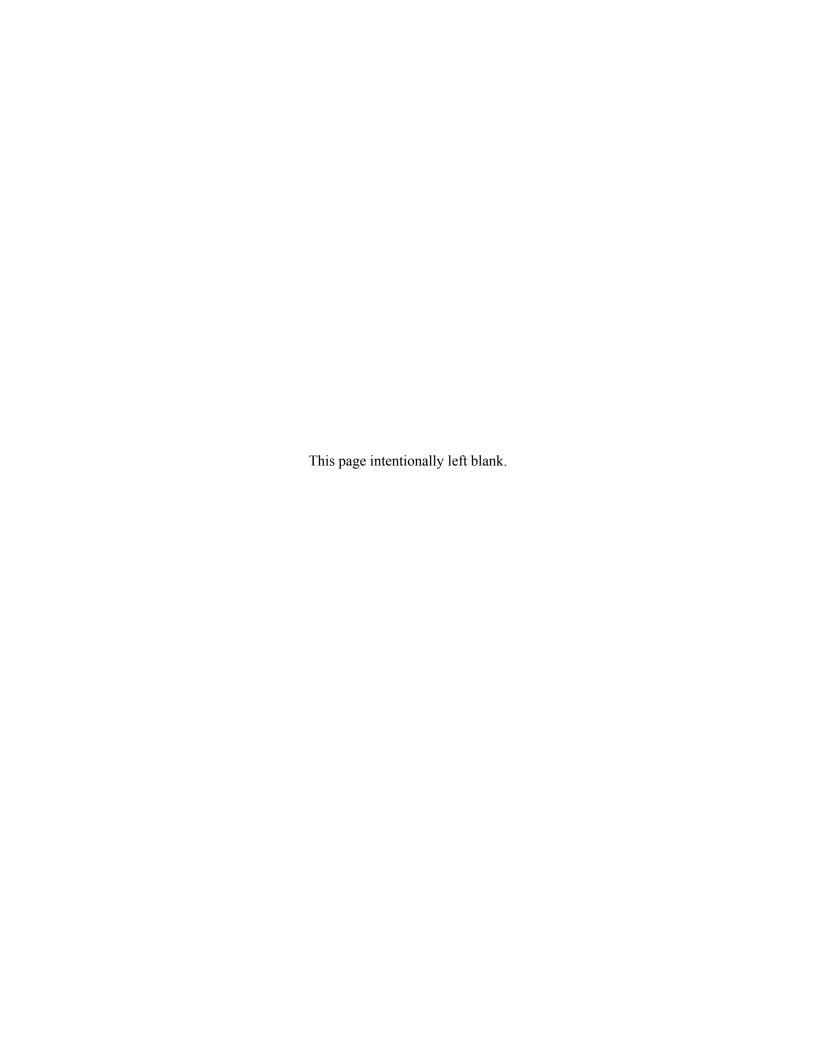
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<sup>\*</sup> Stations F32 and F33 are sampled only during weeks 6, 9, and 15 each year.

# Appendix B

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.

Version 0 March 2006 Appendix B Page 4 of 4

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Appendix C

MWRA SOPs

# Appendix C MWRA Standard Operating Procedures

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

MWRA EM&MS SOP TH.2.2: Calculation methods for annual and seasonal threshold values and baselines for chlorophyll.

MWRA EM&MS SOP TH.3.0: Calculation method for baseline and test values for water column bottom dissolved oxygen depletion rate at the nearfield.

MWRA EM&MS SOP TH.5.1: Calculation methods for seasonal threshold values for *Phaeocystis pouchetii* and *Pseudonitzschia multiseries*.

MWRA EM&MS SOP TH.6.1: Calculation methods for threshold values for *Alexandrium*.

MWRA EM&MS SOP Oxygen: Calculation method for baseline and test values for water column bottom dissolved oxygen and percent saturation at the nearfield and Stellwagen Basin.



MWRA ENQUAD EM&MS SOP TH.2.2

To: Wendy Leo, Mike Mickelson, Ken Keay, Andrea Rex

From: Joe LoBuglio, Suh Yuen Liang

Date: July 18, 2001

Subject: Calculation methods for annual and seasonal threshold values and baselines for

chlorophyll.

# **Revision History:**

Revision 1: October 24, 2001 - Threshold values corrected due to (1) recalibration of 1998-2000 fluorescence data to corrected bottle chlorophyll values and (2) correction of error in baseline data from survey WF984 due to misapplied calibration.

Revision 2: September 21, 2004 - Reduced survey sets used in revised monitoring program (MWRA, 2004), are now used to calculate baseline and post-discharge results.

There are three seasonal and one annual threshold tests for average nearfield areal chlorophyll levels (expressed in mg/m<sup>2</sup>). All four tests are compared to baseline values derived from baseline monitoring data. This memo summarizes the methods used to calculate the baseline and post-discharge test values.

The surveys included in the calculation include those falling in the following time periods (not every year has surveys during each of these times):

early February late July late February late August mid-March (surveys in1992-94 only) early to mid-Sept late September late March mid-October

late May late October/early November

mid-June

early April

Surveys **excluded** include late April, early/mid-July, mid-August, late November/early December, and mid-December.

# Periods Tested:

Period	Baseline years	Threshold level	Baseline Value (mg/m²)
Winter/Spring (Jan 1 - Apr 30)	1992-2000	Caution	238
Summer (May 1 - Aug 31)	1992-2000	Caution	93
Autumn (Sep 1 - Dec 31)	1992-1999	Caution	212
Annual (Sep 6 - Sep 5 for baseline calculation	9/6/1992 -	Caution	118
Jan 1 - Dec 31 for post discharge tests)	9/5/2000	Warning	158

MWRA ENQUAD EM&MS SOP TH.2.2

Data Source (Data from the EM&MS database):

• Downcast fluorescence data (from the PROFILE\_DOWNCAST table, PARAM\_CODE = 'FLUORESCENCE', UNIT\_CODE = 'ug/L') will be used. These data are reported at 0.5-meter depth intervals.

- Where entire surveys have invalid or missing downcast fluorescence data (surveys WF981 and WN99H), the upcast laboratory bottle chlorophyll (from the ANALYTICAL\_RESULTS table, PARAM\_CODE = 'CHLA', UNIT\_CODE = 'ug/L') will be used. These data are taken at five depths per station.
- Nominal station depths are the average station depths during HOM3 station visits. These are stored in the GEO\_STATION table.

# Data to be used in the analysis:

- Only data taken on nearfield survey days will be included. (Nearfield days are specified in the BWQM\_DAY table.)
- All nearfield stations are included. (Nearfield stations have a leading 'N' in their identifier.)
- No surveys will be excluded based on the number of stations sampled per survey. This currently ranges from 3 to 21 stations per survey.
- In order to make the results from the reduced survey set starting in 2004 comparable to the pre-discharge baseline so as not to change the likelihood of exceeding a threshold surveys dropped from the monitoring program are not included in the threshold calculation. The surveys excluded are late April, early/mid-July, mid-August, late November/early December, and mid-December.
- Data qualified as invalid/suspect (those having qualifiers including 's') are excluded. No other exclusions are made. Data qualified as "uncalibrated but deemed fit for use by the principal investigator" or "use with caution" will be used if they exist. All chlorophyll data taken between 1998 and 2000 are qualified as "use with caution". The existence of data that are qualified as "possibly suspect/invalid, investigation pending" (those having qualifiers including 'q') will prevent a calculation from occurring.
- Data qualified as below detection limit ('a' qualifier) are treated as zero values even if the values in the database are negative.
- No exclusions are made based on the fraction of the water column covered by the cast although casts covering less than 50% of the water column depth exist.

# Data Aggregation:

- Data for each individual station and depth for a given nearfield day are averaged to account for multiple casts.
- The average chlorophyll concentration for each station is calculated for each survey.
- Each average station value is multiplied by the nominal station depth to come up with a measure of station areal chlorophyll.
- Each station is assumed to influence an equal area of the nearfield during a particular nearfield day. Therefore, the survey average nearfield chlorophyll areal concentration is calculated simply as the average of the station areal chlorophyll concentrations.

MWRA ENQUAD EM&MS SOP TH.2.2

• A period average is obtained by averaging all the survey averages during the period of interest. No accounting is made for differences in the number of surveys per period for the different years or for unequal spacing of surveys during a particular period.

#### Baseline Calculation:

- The baseline values for each seasonal period are determined by calculating the period average for each year and using the resulting eight or nine values to estimate the upper 95% limit for the period average chlorophyll values. All data for nearfield areal chlorophyll seasonal means are lognormally distributed for each season as shown by a Kolmogorov-Smirnov test. Thus the baseline, that is the 95th percentile of each fitted distribution, is calculated using: Threshold = 10<sup>[baseline log mean + 1.64\*(baseline log std. dev.)]</sup>. The annual means are normally distributed.
- The baseline values for the annual threshold are calculated as 1.5 times (caution) or 2 times (warning) the average of the eight annual averages. The baseline years begin on September 6th.
- Values are rounded to the nearest whole number.

# Threshold Testing:

• For threshold testing, the period average for the current period is compared against the baseline values. An exceedance is recorded if the current period exceeds the baseline value. Although the annual baseline is calculated based on years that begin in September, the annual post-discharge threshold testing value will be based on a calendar year.

#### Approvals:

rr - · · · ·		
Written by:		
	Suh Yuen Liang	Date
Data Group Manager:		
	Wendy Leo	Date
MWRA Manager		
Responsible for Water		
Column Data:	Mike Mickelson	Date



MWRA ENQUAD EM&MS SOP TH.3.0

To: Wendy Leo, Ken Keay, Mike Mickelson

From: Suh Yuen Liang
Date: December 20, 2001

Subject: Calculation method for baseline and test values for water column bottom

dissolved oxygen depletion rate at the nearfield.

The contingency plan threshold comparison for the nearfield bottom-water dissolved oxygen (DO) depletion rate (mg/L/day) is performed each year during the stratification period from June through October. The yearly bottom-water DO depletion rate is compared to the threshold to determine if there is an exceedance (rapid DO decline threshold value can trigger an exceedance). The table below shows the caution and warning values for bottom-water DO depletion rate.

Threshold ID	Testing area	Caution Level (mg/L/day)	Warning Level (mg/L/day)	Baseline Years	Baseline Method
WORATE	Nearfield	0.037	0.049		Arithmetic mean

Table 1: Bottom-water DO Depletion Rate Thresholds.

# Data Source (Data from EM&MS database):

- Dissolved oxygen data (PARAM\_CODE = 'DISS\_OXYGEN', UNIT\_CODE = 'mg/L') are obtained from the water column upcast data (calibrated sensor reading from the PROFILE table).
- Bottom depth classification is obtained from ordered\_depth\_code in the DEPTH\_CLASS table.
- Nearfield stations are specified as station IDs beginning with 'N' on "Nearfield" days.
- "Nearfield" days are specified in the BWQM DAY table.

# Data To Be Used In The Analysis:

- Baseline calculations and threshold testing are performed on all nearfield stations on nearfield days.
- Only data from June 1st to October 31st are included in calculations and there were six to nine surveys per year in the baseline period.
- Data qualified as suspect/invalid (VAL\_QUAL contains 's'), investigation pending (VAL\_QUAL contains 'q'), and missing data (VAL\_QUAL contains 'e') are not used.
   There is one 's' qualified sample at N01 on 13-July-1998 and one missing sample at N10 on 08-Oct-1999 in the baseline years.
- Non-detects ('a' qualified values) are treated as zeros if they occur. (There are currently no non-detects in the data set.)
- Only bottom depths (ORDERED\_DEPTH\_CODE='E') are included. Obtaining the bottom depths necessitates joining the PROFILE table with a view of the SAMPLE and

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ORDERED\_DEPTH\_CLASS tables; this is done in such a way as to ensure no duplication of profile data when multiple samples are taken. For example, there are two samples at station N04 on 04-December-1997 that have the same profile primary keys. Ten duplications of profile data would have created in the data set if profile data with multiple samples were not first fixed. In addition, profile data without a corresponding sample are not included. There were no profile data without a corresponding sample in the baseline calculation.

# Data Aggregation:

- Calculate the mean bottom dissolved oxygen for each station on each day to average replicate casts if any.
- Calculate the linear regression of station-day bottom-water DO averages versus time for each year, including y-intercept, slope, R<sup>2</sup>, and P value. The independent variable for the regression is the Julian day for the station-day minus the Julian day for May 31 of the year. This is to ensure that the y-intercepts approximate to the DO at setup of stratification (i.e., June 1). The absolute value of the slope is the yearly bottom-water DO depletion rate.

#### Baseline Calculation:

• The average of the eight yearly bottom-water oxygen depletion rates (the absolute value of the slope, see table below) is the baseline mean (0.0244 mg/L/day).

Year	N	Y_intercept(day)	Slope (mg/L/day)	$R^2$	P
1992	125	11.7	-0.030	0.87	< 0.001
1993	168	11.1	-0.024	0.80	< 0.001
1994	162	9.9	-0.028	0.80	< 0.001
1995	142	9.8	-0.023	0.76	< 0.001
1996	135	9.9	-0.017	0.70	< 0.001
1997	153	9.9	-0.018	0.61	< 0.001
1998	146	11.5	-0.032	0.81	< 0.001
1999	176	9.3	-0.024	0.74	< 0.001

Table 2. Statistical summary of linear regression on bottom-water dissolved oxygen

- Caution threshold is 1.5\* baseline mean.
- Warning threshold is 2\*baseline mean.

#### Threshold Testing:

• For each post-discharge year, the nearfield bottom-water oxygen depletion rate from June to October is compared against the caution and warning thresholds in table 1. If the DO decline is faster than the threshold, there is an exceedance for that year.

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	Wendy Leo	Date
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Responsible for Water		
Column Data:	Mike Mickelson	Date



MWRA ENQUAD EM&MS SOP TH.5.1

To: Wendy Leo, Mike Mickelson, Andrea Rex

From: Joe LoBuglio, Suh Yuen Liang

Date: December 3, 2001

Subject: Calculation methods for seasonal threshold values for *Phaeocystis pouchetii* and

Pseudonitzschia multiseries.

# **Revision History:**

Revision 1: September 21, 2004 - Reduced survey sets used in revised monitoring program (MWRA, 2004), are now used to calculate baseline and post-discharge results.

There are three seasonal caution-level threshold tests for each of two nuisance algae: *Phaeocystis pouchetii* and *Pseudonitzschia multiseries*. This memo summarizes the methods used to calculate these seasonal averages and the baseline values against which they are compared.

The surveys included in the calculation include those falling in the following time periods (not every year has surveys during each of these times):

- early February - late July

- late February - late August

- mid-March (surveys in1992-94 only) - early to mid-Sept - late March - late September

- early April - mid-October

- late May - late October/early November

- mid-June

Surveys **excluded** include late April, early/mid-July, mid-August, late November/early December, and mid-December.

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			Caution Level		
Algae	Threshold ID	Season	(million cells/liter)	Baseline Years	Baseline Method
Phaeocystis pouchetii	WNSPHSPR	Winter/ Spring	2.02	1992-2000 (detected only in 1992, 1994, 1996, 1997 and 2000)	95th percentile of annual means using Solow method for nondetect correction.
	WNSPHSUM	Summer	0.000357	1992-2000 (detected only in 1994 and 1997)	95th percentile of annual means using Solow method for nondetect correction.
	WNSPHAUT	Autumn	0.00254	1992-1999 (detected only in 1993)	Use the only nonzero value measured.
Pseudo- nitzschia multiseries (Pseudonitzschia pungens, Pseudonitzschia cf. pungens, and Pseudonitzschia spp.)	WNSPSSPR	Winter/ Spring	0.021	1992-2000	95th percentile of log- transformed annual means.
	WNSPSSUM	Summer	0.0431	1992-2000	95th percentile of annual means.
	WNSPSAUT	Autumn	0.0247	1992-1999	95th percentile of annual means.

Table 1: Nuisance Algae Thresholds.

# Data Source (Data from EM&MS database):

- Whole water cell counts and sample information are obtained from the ABUNDANCE and SAMPLE tables via the view PWW\_AVG\_VALUE\_PER\_STAT\_DAY. This view performs the first three data aggregation steps listed below.
- "Nearfield" and "Farfield" days are specified in the BWQM DAY table.
- Depth classification is obtained from ordered depth code in the DEPTH CLASS table.

# Data To Be Used In The Analysis:

- Only data collected on "Nearfield" and "Farfield" days are included in the averages.
- Baseline calculations are performed on nearfield and farfield stations (station IDs beginning with 'N' or 'F'.)
- Post-discharge seasonal averages for threshold testing only include data from nearfield stations (stations having identifiers beginning with 'N').
- Seasonal averages are calculated for the following periods, except that for autumn 2000, the date begins on September 6 (the day after the Outfall went on line) and ends on December 31.

Season	Dates to include for a given year
Winter/Spring	Jan 1 – Apr 30
Summer	May 1 – Aug 31
Autumn	Sep 1 – Dec 31

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• In order to make the results from the reduced survey set starting in 2004 comparable to the pre-discharge baseline – so as not to change the likelihood of exceeding a threshold – surveys dropped from the monitoring program are not included in the threshold calculation. The surveys excluded are late April, early/mid-July, mid-August, late November/early December, and mid-December.

- Data qualified as suspect/invalid (VAL\_QUAL contains 's') or under investigation (VAL\_QUAL contains 'q') are not used.
- Whole water samples are identified in the ABUNDANCE database table by METH\_CODE = 'COU WW'.

# Data Aggregation:

- The following three steps describe the data aggregation in the view PWW AVG VALUE PER STAT DAY.
- For each species code, bottle (or subsample) averages are generated by averaging analytical replicates. Since only species which are seen are recorded in the abundance table, the averaging requires summing individual species concentrations over all replicates for a bottle and dividing by the number of replicates for that bottle. For example, there are species A, B, and C with abundance 4, 2, and 7 in replicate 1 and species B and C with abundance 4 and 3 in replicate 2. The bottle averages for the species is the sum of replicate 1 and 2 divided by 2 (two replicates). The bottle averages for species A, B, and C are therefore 2, 3, and 5.
- Sample averages are generated by averaging the bottle averages. As with the bottle averages, this requires summing the bottle average concentrations for each species for a sample and dividing by the number of bottles for that sample.
- Daily station averages are calculated for each depth by averaging the sample averages for each station, day and depth. As with the bottle averages, this requires summing the sample average concentrations for each species for a station, day, and depth and dividing by the number of samples taken at a particular station, day and depth.
- Fill in zero for each station at each depth on each station day where the whole-water samples were taken but *Phaeocystis pouchetii* or any of the three congeners of *Pseudonitzshia* were absent. The species codes that identify these species are listed below. These records are joined with the view PWW AVG VALUE PER STAT DAY for further calculations.

Species	Species Code	Taxa Description
Phaeocystis pouchetii	0603020101	Phaeocystis pouchetii
Pseudonitzschia	0703100113	Pseudonitzschia pungens
multiseries	0703100113CF	Pseudonitzschia cf. pungens
	07031001PSEUSPP	Pseudonitzschia spp.

- The sum of the three congeners of *Pseudonitzschia* is taken as the computed value for *Pseudonitzschia multiseries* for each station day at each depth.
- For each station and date, the average value over all depths is computed for *Phaeocystis* pouchetii and *Pseudonitzschia multiseries*.
- For each season, the average value over all daily station averages is computed for *Phaeocystis pouchetii* and *Pseudonitzschia multiseries*.

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#### Baseline Calculation:

#### Pseudonitzschia

• There were detections of *Pseudonitzschia* each year and for every season, so the eight or nine seasonal values were used to calculate the 95th percentile. The summer and autumn thresholds were determined to be normal using Kolmogorov-Smirnov (Lilliefors Significance Correction) and Shapiro-Wilk tests for normality so the 95th percentiles for these thresholds were calculated using: Threshold = baseline mean + 1.64\*(baseline standard deviation). The winter-spring threshold was log-normal according to the same tests, so the 95th percentile was calculated using: Threshold = 10<sup>[baseline log mean + 1.64\*(baseline log std. dev.)]</sup>

#### Phaeocystis

 As shown in Table 1, there were several years when *Phaeocystis* was not detected. For the winter-spring and summer thresholds an alternative method outlined by Andrew Solow (Solow, personal communication 2000) was used for nondetect correction, as described below.

N = Total number of baseline years (years with observations)

 $N_a$ = Number of years with zero mean

y = Mean of all non-zero years

sd = Standard deviation of all non-zero years

The fraction of zero years is

$$f = N_a/N$$

and the probability at the  $95^{th}$  percentile is

$$p = (0.95-f)/(1-f)$$
.

If NORMSINV(p) is a function that returns the inverse of the standard normal cumulative distribution then the 95th percentile is calculated as:

$$Threshold = y + NORMSINV(p)*sd$$

• There was only one year with a nonzero Autumn average concentration. Since there were not enough data on which to base a distribution, the nonzero value was used as the threshold. Since this value was observed only once in eight years, it should represent a number closer to the 88th percentile, resulting in a more stringent threshold.

#### Threshold Testing:

• For each post-discharge season, the average concentration is compared against the caution threshold in table 1. If the seasonal average exceeds the threshold, there is an exceedance for that season.

#### References:

MWRA. 2004. Massachusetts Water Resources Authority effluent outfall ambient monitoring plan Revision 1, March 2004. Boston: Massachusetts Water Resources Authority. Report ms-092. 65 p.

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MWRA ENQUAD EM&MS SOP TH.6.1

To: Wendy Leo, Mike Mickelson, Andrea Rex

From: Joe LoBuglio, Suh Yuen Liang

Date: December 21, 2001

Subject: Calculation methods for threshold values for *Alexandrium*.

#### **Revision History:**

Revision 1: November 9, 2005 – Include analyses by alternative method – DNA probe, and include Alexandrium Rapid Response study. Also include *Alexandrium fundyense* specifically (no longer always lumped with *A. tamarense*.)

This memo summarizes the methods used to calculate the *Alexandrium* threshold (WNSAL). For each post-discharge event, the *Alexandrium* concentration for each sample is compared against the caution threshold of 100 cells/liter. If any sample exceeds the threshold, there is an exceedance for that event.

# Data Source (Data from EM&MS database):

- Species concentrations from screened water and probe samples are obtained from the ABUNDANCE and SAMPLE tables via the view
   PK\_AVG\_VALUE\_PER\_SAMPLE\_METH. This view performs the two steps of the data aggregation discussed below.
- Depth classification is obtained from the ORDERED DEPTH CLASS table.

#### Data To Be Used In The Analysis:

- Data from nearfield stations (station identifier beginning with "N") are used in the threshold calculation. Data from farfield stations (those with identifiers beginning with "F" or any other stations) are used in calculations that provide auxiliary information.
- Three *Alexandrium* taxa are included in the threshold:
  - *Alexandrium fundyense* the the toxic form
  - Alexandrium tamarense is likely to actually be the toxic form A. fundyense
  - *Alexandrium spp.* may include the toxic form.

(SPECIES\_CODE = '12041008FUND' or '12041008TAMA' or '12041008SPP'). The less-toxic form *A. ostenfeldii* is not included in the total count of potentially toxic *Alexandrium* cells.

- Samples from all depths are used.
- Data qualified as suspect/invalid (VAL QUAL contains 's') are not used.
- Screened samples are identified in the ABUNDANCE database table by METH\_CODE = 'SCR20U'; probe samples by 'NA1'. Whole water samples are not included because the data are potentially not comparable, at least at low populations of *Alexandrium*.

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#### Data Aggregation:

- The following three steps describe the data aggregation in the view PK AVG VALUE PER SAMPLE METH.
- For each species code and method combination, bottle (or subsample) averages are generated by averaging analytical replicates. Since only species which are seen are recorded in the abundance table, the averaging requires summing individual species concentrations over all replicates for a bottle and method and dividing by the number of replicates for that bottle and method. For example, there are species A, B, and C with abundance 4, 2, and 7 in replicate 1 and with abundance 0, 4 and 3 in replicate 2 (*i.e.* no record for species A in replicate 2). The bottle averages for each species and method combination is the sum of replicate 1 and 2 divided by 2 (two replicates). The bottle averages for species A, B, and C are therefore 2, 3, and 5.
- Sample averages are generated by averaging the bottle averages. As with the bottle averages, this requires summing the bottle average concentrations for each species and method combination for a sample and dividing by the number of bottles for that sample which were analyzed with that method.
- Each method is considered separately, that is, analyses of the same sample with two methods are not averaged because the methods may not give completely comparable results.
- The threshold script WNSAL.SCP sums the three target SPEC\_CODEs for each station-visit-depthclass-method combination.

#### Baseline Calculation:

There is no baseline calculation for this threshold. The threshold was recommended by EPA based on the observed maximum of 163 cells/l in baseline samples.

#### Threshold Testing:

• For each post-discharge event, the *Alexandrium* concentration for each nearfield sample is compared against the caution threshold of 100 cells/liter. If any sample exceeds the threshold with **either** analysis method, there is an exceedance for that event.

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To: Wendy Leo, Ken Keay, Mike Mickelson

From: Suh Yuen Liang, Joe LoBuglio

Date: May 29, 2001

Subject: Calculation method for baseline and test values for water column bottom

dissolved oxygen and percent saturation at the nearfield and Stellwagen

Basin.

## **Revision History:**

Contingency plan threshold comparisons for both the nearfield and Stellwagen Basin for bottom-water dissolved oxygen (mg/L) and percent oxygen saturation (%) are performed for each event occurring from June through October. The mean event values are compared to the threshold and background values to determine if there is an exceedence (event means below the threshold values can trigger an exceedence). The comparisons for these parameters are unusual in that there is no threshold exceedence unless the event mean is below both the threshold value (caution or warning) and the background value. The background values are calculated from data gathered during the baseline period (summers of 1992 through 1999).

The table below shows the caution, warning, and background values for each parameter and location.

Parameter	Location	Caution	Warning	Background
Dissolved Oxygen	Nearfield	6.5	6.0	5.75
(mg/L)	Stellwagen Basin	6.5	6.0	6.2
Percent Oxygen	Nearfield	80	75	64.3
Saturation (%)	Stellwagen Basin	80	75	66.3

This memo describes how event means are calculated, how background values are calculated, and how the threshold comparison is performed.

Data Source (Data from EM&MS database):

- Data for bottom-water dissolved oxygen and percent saturation are from the water column upcast data (calibrated sensor reading from the PROFILE table).
- "Nearfield" and "Farfield" days are specified in the BWQM DAY table.
- Bottom depth classification is obtained from the ORDERED\_DEPTH\_CLASS table.

Data To Be Used In The Analysis:

- Dissolved oxygen data (PARAM\_CODE = 'DISS\_OXYGEN', UNIT\_CODE = 'mg/L') or percent saturation data (PARAM\_CODE = 'PCT\_SAT', UNIT\_CODE = 'PCT').
- Data qualified as suspect/invalid ('s'), under investigation ('q'), and missing ('e') are not used.
- Non-detects will be treated as zeros if they occur. (There are currently no non-detects ('a' qualified values) in the database.)
- Only data from June 1st to October 31st is included in calculations.
- Stations and event days:

Nearfield: Nearfield stations on "Nearfield" days.

Stellwagen Basin: Stations F12, F17, F19, and F22 on all event days.

- Only bottom depth (ORDERED\_DEPTH\_CODE='E') are included. Obtaining the bottom depths necessitates joining the PROFILE table with a view of the SAMPLE and ORDERED\_DEPTH\_CLASS tables; this is done in such a way as to insure no duplication of profile data when multiple samples are taken. However, profile data without a corresponding sample are not included. There were no such exclusions in the background calculation. There is currently one nearfield station where the bottom measurement would be excluded (N21 on 06-July-2000) but it occurs after the last complete background summer and before the first post-discharge survey on October of 2000.
- If there are no valid PROFILE oxygen data for a survey, the discrete bottom sample dissolved oxygen laboratory measurements for that survey are used instead (true? example?)

## Data Aggregation:

- Calculate the mean bottom dissolved oxygen and percent saturation for each station on each day to remove double casts.
- Calculate the station mean for each event to combine measurements taken over more than one day.
- Calculate the event mean by averaging station means of the event. The stations for the nearfield and Stellwagen basin are as specified in "Data to be used in the analysis" above.

#### Background Calculation:

- Find the lowest event mean for each of the eight years (1992 through 1999) for all months.
- Fit a normal distribution to the eight annual minimum event means. All data for bottom dissolved oxygen and percent saturation at the nearfield and Stellwagen Basin are normally distributed as shown by a Kolmogorov-Smirnov test and a Shapiro-Wilk test.
- Take the 5<sup>th</sup> percentile of this fitted distribution.

  Baseline of bottom dissolved oxygen or percent saturation = mean 1.645\*Standard deviations.

#### Threshold Testing:

- Compare the event mean to the threshold value (caution or warning) and to the background value. If it is below the background value and the threshold value then there is an exceedence. If the mean is not below both values then there is no exceedence.
- The results of the comparisons are recorded in the database table THRESHOLD\_TEST.

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MWRA. 2004. Massachusetts Water Resources Authority effluent outfall ambient monitoring plan Revision 1, March 2004. Boston: Massachusetts Water Resources Authority. Report ms-092. 65 p.

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Appendix D

**Battelle SOPs** 

# Appendix D Battelle Standard Operating Procedures

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



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