

# **Quality Assurance Project Plan**

*for*

## **Water Column Monitoring 2024-2026 Tasks 4-8 and 11**

**Massachusetts Water Resources Authority  
Environmental Quality Department Report  
2024-02**



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**QUALITY ASSURANCE PROJECT PLAN  
(QAPP)**

**for**

**WATER COLUMN MONITORING 2024-2026:  
Tasks 4-8 and 11**

**MWRA Harbor and Outfall Monitoring Project**

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**February 6, 2024**

**A PROJECT MANAGEMENT  
VERSION 1.0**

**A.1 TITLE AND APPROVALS**

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

**WATER COLUMN MONITORING 2024-2026:  
Tasks 4, 5, 6, 7, 8, 11**

**MWRA Harbor and Outfall Monitoring Project**

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**February 6, 2024**

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**Quality Assurance Project Plan  
REVISION HISTORY**

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

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## APPENDICES

Appendix I	MWRA Standard Operating Procedures
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Appendix III	HOM12 Sample Collection Requirements
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## ACRONYMS AND ABBREVIATIONS

µL	microliter
µm	micrometer
AHA	Activity Hazard Analysis
ARRS	<i>Alexandrium</i> Rapid Response Study
BOD	biological oxygen demand
BOSS	Battelle Ocean Sampling System
CCS	Center for Coastal Studies
CTD	conductivity–temperature–depth
dGPS	differential global positioning system
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nutrients
DLS	Department of Laboratory Services
DMF	Division of Marine Fisheries
DO	dissolved oxygen
DOC	dissolved organic carbon
EMMS	Environmental Monitoring and Management System
EPA	U.S. Environmental Protection Agency
HCl	hydrochloric acid
HgCl <sub>2</sub>	mercuric chloride
HOM	Harbor and Outfall Monitoring
HOML	Harbor and Outfall Monitoring Loading
HPLC	high-performance liquid chromatography
Hz	Hertz
ID	identification
IDL	instrument detection limit
L	liter
LIMS	Laboratory Information Management System
L/L	latitude-longitude
m	meter
m/s	meters per second
MA DEP	Massachusetts Department of Environmental Protection
MDL	method detection limit
MITSG	Massachusetts Institute of Technology Sea Grant
mL	milliliter
MQO	method quality objective
MWRA	Massachusetts Water Resource Authority
NH <sub>4</sub>	ammonia
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
OMO	Outfall Monitoring Overview
PAR	photosynthetically active radiation
PCN	particulate carbon and particulate nitrogen
PP	particulate phosphorus
PSP	paralytic shellfish poisoning
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	quality control

QMP	Quality Management Plan
RPD	relative percent difference
RSD	relative standard deviation
SCM	subsurface chlorophyll maximum
SEIS	Supplemental Environmental Impact Statement
SOP	Standard Operating Procedure
SRM	standard reference material
TDNP	total dissolved nitrogen and phosphorus
TSA	technical systems audit
TSS	total suspended solids
UMD	University of Massachusetts Dartmouth Campus
WHOI	Woods Hole Oceanographic Institution

### 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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Chris Werme (independent subcontractor)	

#### A.4 PROJECT AND TASK ORGANIZATION

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

Dr. Betsy Reilley is the Director of the Massachusetts Water Resource Authority (MWRA) Environmental Quality Department.

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

Mr. Chris Goodwin is the MWRA Water Column Monitoring Technical Manager. He has primary oversight of data quality and interpretation under the project. He will be informed of all technical matters pertaining to work described in this Quality Assurance Project Plan (QAPP).

Dr. Doug Hersh is the MWRA Environmental Monitoring and Management System (EMMS) Database Manager and Quality Assurance (QA) Lead.

Dr. Jennifer Rogers manages the Water Quality Modeling contract and provides technical support to the MWRA HOM Water Column Monitoring program.

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 expectations, generating project management reports, and for the overall performance of this project. She is supported by Battelle Environmental Solutions Acting Division Manager Carolyn Scala who oversees operations at the Norwell site and by Ms. Clare Larson, who supports the corporate business office.

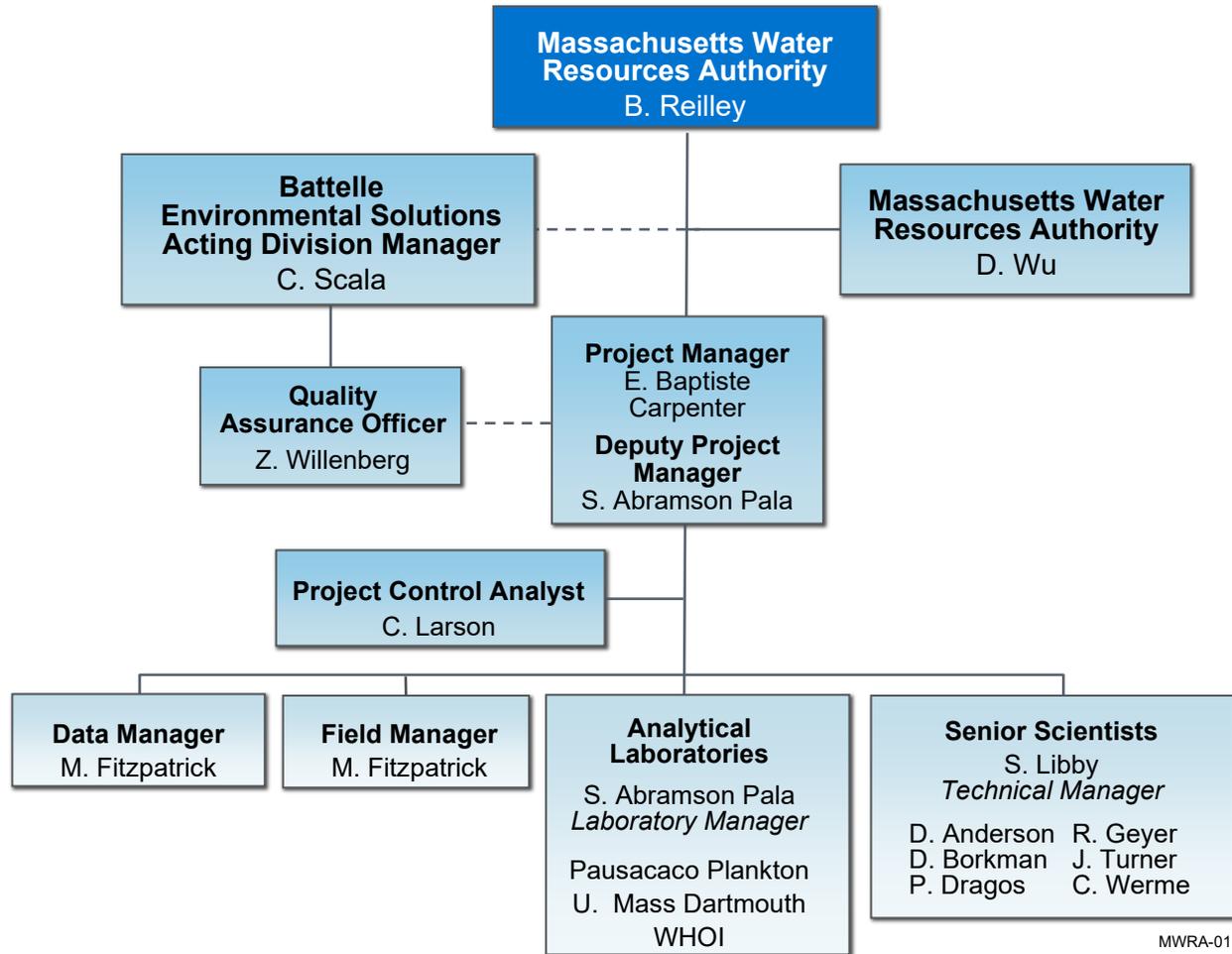
Ms. Stacy Abramson Pala is the Deputy Project Manager. Ms. Pala will work closely with Ms. Baptiste Carpenter to monitor project activities, including managing the project tracking database (*Planisware*) and generating management reports.

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

Mr. Matt Fitzpatrick is the Battelle Field Manager and is responsible for the overall field program and for all day-to-day field and laboratory activities conducted by Battelle for the project. Mr. Fitzpatrick is also the Battelle Data Manager and is responsible for day-to-day management of the database and loading data into MWRA's Harbor and Outfall Monitoring Loading (HOML).

Mr. Zachary Willenberg is the Battelle Project Quality Assurance Officer (QAO). Mr. Willenberg 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. He is also responsible for reviewing the synthesis reports for accuracy and completeness.

The senior scientists on Battelle's team are experts in the respective fields and provide technical support to the program: Drs. Don Anderson and Rocky Geyer (WHOI), Dr. Dave Borkman (Pausacaco), Mr. Paul Dragos (Battelle), Dr. Jeff Turner (UMD), and Dr. Chris Werme. They are primarily responsible for data analysis, interpretation, and synthesis.

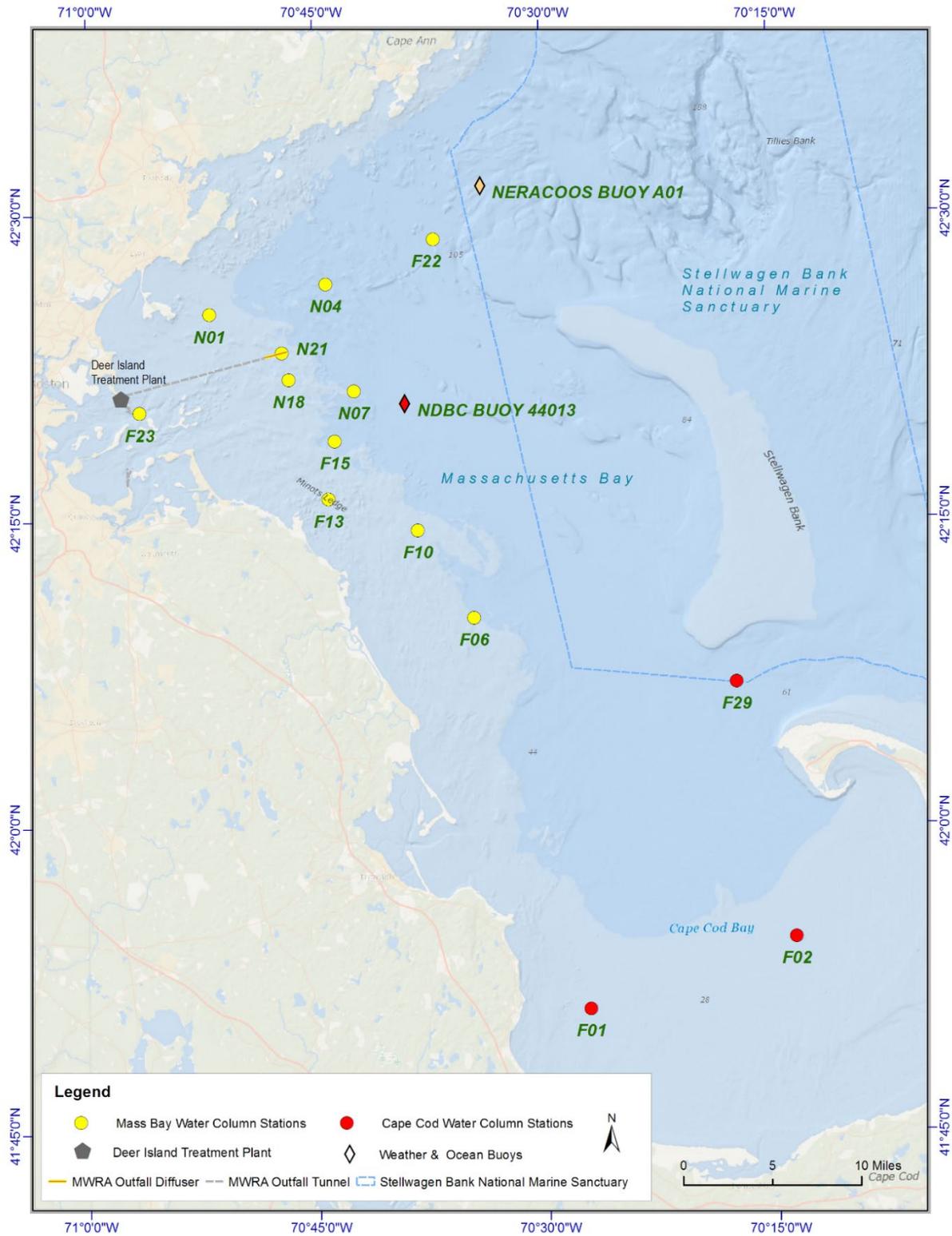


MWRA-01

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

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

The MWRA has implemented a long-term marine environmental monitoring plan (MWRA 1991, 1997, 2004, 2010, 2021) for its treated-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/MA DEP 2000). The EPA Supplemental Environmental Impact Statement (SEIS) for the outfall (EPA 1988) determined that there would be no significant water quality or biological impacts associated with the outfall. Even so, the SEIS recommended a monitoring program be implemented for assessing compliance with the NPDES permit, assessing unacceptable impacts, and collecting data useful for outfall management considerations (MWRA 1990). 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 associated Ambient Monitoring Plan, public, scientific, and



**Figure A-2. Location of MWRA Effluent Outfall and Water Column Monitoring Stations in Massachusetts and Cape Cod Bays**

regulatory areas of concern were identified following guidance for coastal monitoring (*i.e.*, NRC 1990). The program is designed to assess the potential environmental impact of the effluent discharge into Massachusetts Bay and evaluate compliance with the discharge permit. It includes measurements that facilitate evaluations required by a Contingency Plan (MWRA 1997, as updated in MWRA 2001) component of the Ambient Monitoring Plan.

The primary objective of water column monitoring is to detect changes in the water column of Massachusetts and Cape Cod Bays that may be caused by relocating the effluent outfall. The main concern is that discharged nutrients will be detrimental. The rationale for the work is discussed in the Outfall Monitoring Plan (MWRA 1991, 1997, 2004, 2010, 2021). The monitoring is focused on detecting changes in physical water properties, nutrient concentrations, dissolved oxygen (DO), phytoplankton biomass, and phytoplankton and zooplankton community composition in Massachusetts Bay and Cape Cod Bay. To date no substantial change has been observed in the bays related to the outfall diversion (Libby et al. 2019).

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

In 2009-2010, a second round of data evaluation and monitoring plan revisions was conducted. The second revision to the Ambient Monitoring Plan (MWRA 2010) was submitted to EPA in July 2010 and officially approved by EPA on December 6, 2010. The changes were detailed in the QAPP for Water Column Monitoring: 2011-2013 (Libby et al. 2011) and included a reduction in surveys, stations, and analytical parameters. The number of surveys was reduced from six nearfield only and six combined nearfield/farfield surveys to nine Massachusetts Bay surveys per year. The number of water column stations was reduced from 32 to 14. A total of 11 stations are sampled in Massachusetts Bay by Battelle. Three additional stations in Cape Cod Bay and Stellwagen National Marine Sanctuary are being sampled synoptically under a separate contract by the Center for Coastal Studies (CCS, [coastalstudies.org](http://coastalstudies.org)). Biogenic silica, total suspended solids (TSS), dissolved organic carbon (DOC), primary production, and respiration analyses were dropped from the program based on diminished importance to the program or completion of associated special studies.

Minor changes to the MWRA QAPP have occurred over the past 10 years. In 2014, the sample collection depths for extracted chlorophyll and phaeophytin analysis were modified to improve the calibration of the intensive in situ fluorescence data collected on the HOM surveys (Libby et al. 2014). In 2015, MWRA was approached by researchers at Massachusetts Institute of Technology Sea Grant (MITSG) to partner with them on an ocean acidification study. The measurement of in situ pH was added as an amendment to Libby et al. (2014) and, in 2017, additional ocean acidification-related sample collection (dissolved inorganic carbon [DIC], and total alkalinity) were added (Libby et al. 2018). Recent changes in phytoplankton nomenclature for the species of *Alexandrium* found in Gulf of Maine waters from *Alexandrium fundyense* to *Alexandrium catenella* (Litaker et al. 2018) were implemented by MWRA in 2018 and have been incorporated in this QAPP. In February 2018, EPA approved MWRA dropping *Phaeocystis* from the Contingency Plan thresholds. MWRA continues to identify and enumerate *Phaeocystis* as one of many species of phytoplankton observed in the whole water phytoplankton samples

collected in Massachusetts Bay. In 2021, Winkler dissolved oxygen analysis was terminated based upon Seabird Electronics recommendations to not self-calibrate the sensor (Libby et al. 2023).

## A.6 PROJECT/TASK DESCRIPTION

The HOM project water column surveys have been conducted since 1992 and are scheduled to continue through 2026. This QAPP describes activities specific to the nine scheduled Massachusetts Bay water column surveys and any *Alexandrium* Rapid Response Study (ARRS) Surveys conducted each year from 2024 through 2026. The contract for this 3-year period is referred to as HOM12, as it is the 12<sup>th</sup> in the series. Physical and meteorological data collected by stationary moorings and satellites may supplement data collected during the water column surveys. Under the water quality monitoring program, in situ hydrographic data are collected and samples for the laboratory measurement of water quality parameters, nutrient and biomass concentrations, and phytoplankton and zooplankton communities are collected and analyzed. The study objectives are described below.

- **Task 4 Data Quality Control and Data Set Submission:** Convert raw electronic data into useful data; load data generated by the project, including survey/sample collection data, into the database; and maintain data quality.
- **Task 5 Water Column Surveys:** Develop a three-dimensional picture of seasonal variability of water column properties in Massachusetts Bay; identify factors affecting the seasonal pattern of plankton abundances and species composition and the seasonal decline of DO concentrations in Massachusetts Bay; describe the broad-scale interaction of water from Boston Harbor and the Gulf of Maine with Massachusetts Bay.
- **Task 6.1 Alexandrium Rapid Response Study Surveys:** Characterize and understand the distribution and dynamics of *Alexandrium catenella* blooms triggering the ARRS thresholds in Massachusetts Bay and northern Cape Cod Bay and to evaluate the potential influence (impact) of outfall discharge on the bloom (e.g., localized and downstream, change in magnitude of bloom, etc.).
- **Task 8 Plankton Analysis:** Characterize the phytoplankton and zooplankton communities and describe changes in community structure within Massachusetts Bay.
- **Task 11 Synthesis Reports:** Report the results of the sampling and analytical tasks in survey reports, data reports, and synthesis reports.

## A.7 QUALITY OBJECTIVES AND CRITERIA

### A.7.1 DATA QUALITY OBJECTIVES

The data quality objectives for HOM12 are defined by the outfall discharge permit (EPA and MA DEP 2000) and the Contingency Plan thresholds (MWRA 2001). Threshold limits are described in a set of MWRA Standard Operating Procedures (SOPs; Appendix I). The low method detection limits (MDLs) achieved by the MWRA analytical methods are more than sufficient to distinguish whether results are above or below the thresholds and are sensitive enough to detect even subtle effects of the outfall. The general contract conditions define the accuracy and sensitivity of geospatial instrumentation to ensure that sampling locations are within 300 meters (m) of the defined station coordinates to enable inter-comparison 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 dataset can be compared to another.
- **Representativeness** is the degree to which data accurately and precisely represent a characteristic of a population.

The application of these data quality measures is described below.

### A.7.3 NAVIGATIONAL AND HYDROGRAPHIC DATA

#### A.7.3.1 PRECISION AND ACCURACY

Manufacturer precision and accuracy objectives for navigation and hydrographic sampling are presented in Table A-1. Section B.5 provides details on sampling procedures established to ensure data quality. Sections B.6 and B.7 contain instrument calibration methods and specifications. Navigational accuracy of 10 m is required for this program.

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

Sensor	Model	Units	Range	Accuracy	Precision
Pressure	Sea-Bird SBE-29	decibels (db)	0 to 600	0.1%	0.1
Temperature	Sea-Bird SBE-3	degrees Celsius (°C)	-5 to +35	0.001	0.01
Conductivity	Sea-Bird SBE-4	microseimens/ centimeter (mS/cm)	0 to 70	0.03	0.01
Dissolved Oxygen	Sea-Bird SBE-43	milligram/liter (mg/L)	0 to 15	0.50	0.05
pH	Sea-Bird SBE-18	unit less	0 to 14	0.1	0.1
Fluorometer (chlorophyll a)	WET Labs WETStar	microgram (µg)/L	0.03 to 75	0.03	0.01
Transmissometer	WET Labs 25 cm C-star	m <sup>-1</sup>	0 to 40	0.20	0.01
In situ irradiance	Biospherical QSP-200PD	micro Einstein (µE) m <sup>-2</sup> s <sup>-1</sup>	0.14 to 5000	10	1
On-Deck irradiance	Biospherical QSR-2200/-2240	µE m <sup>-2</sup> s <sup>-1</sup>	0.14 to 5000	10	1
Altimeter	Data Sonic PSA-916	m	0-99.9	0.1	0.025
Echosounder (depth)	Furuno DFF-3D	m	0 to 200	2	0.1
Navigation	Furuno GP330B/NavNet TZtouch2	Degree	World	<3 m	<3 m

### **A.7.3.2 COMPLETENESS**

Battelle's navigation software system outputs navigation positions at an interval of 1 second. The software system will display all position fixes and save these fixes in an electronic file during hydrocasts and sampling operations. The project time interval requirement for obtaining positions during sampling is 1 minute. Thus, even if a few bad data streams from the differential global positioning system (dGPS) 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 5 minutes.

Because hydrographic data are acquired electronically and monitored in real time, no loss of data is expected. With the sampling rates of the conductivity–temperature–depth (CTD; 4 Hertz [Hz]) and navigation systems (1-second intervals), sufficient data will be acquired to locate the depth of the pycnocline (boundary between a less-dense shallower layer and more-dense deeper layer). 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 dGPS at these stations. The station locations are targets and sampling will be conducted within 300 m of the targets as visualized on the Battelle Ocean Sampling System (BOSS) navigation display (NavSam<sup>®</sup>).

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, 1998; Bowen et al. 1998; Libby et al. 2002, 2005, 2006, 2009, 2010, 2011, 2014, 2018, 2020, 2021, and 2023). Except for chlorophyll fluorescence sensor values, the instrumentation data reduction methods are based on laboratory or vendor calibrations. To improve the representativeness of the in situ chlorophyll fluorescence values, the electronic data are post-calibrated by MWRA using the laboratory-determined values for this parameter collected during each survey.

### **A.7.3.4 REPRESENTATIVENESS**

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

## **A.7.4 WATER SAMPLING AND ANALYSIS**

### **A.7.4.1 PRECISION AND ACCURACY**

Precision and accuracy of water sampling procedures are quantified by the collection of field blanks and duplicates and are also ensured by the collection procedures. Quality control (QC) procedures to assess precision and accuracy of laboratory data are detailed in Section B.5. 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 identification [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 protocols presented in Section B.2.5 and detailed in Battelle SOP 8-266, *Nutrient Sample Processing*.

#### **A.7.4.2 COMPLETENESS**

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

#### **A.7.4.3 COMPARABILITY**

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

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

#### **A.7.4.4 REPRESENTATIVENESS**

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

### **A.8 SPECIAL TRAINING AND CERTIFICATION**

It is Battelle policy that all management and technical personnel involved in conducting work must be qualified to perform their assigned activity and that training be documented. This objective is achieved by identifying personnel at all levels who have the education and/or experience needed to perform an assigned task, and by encouraging professional development through continual practical training and providing opportunities for professional growth. Battelle requirements for personnel qualifications and training are detailed in the Quality Management Plan (QMP; Battelle 2021). Specific requirements from this QMP which relate to HOM12 activities are summarized below.

#### **A.8.1 TECHNICAL TRAINING**

Technical training encompasses technical procedures and the associated QC requirements. All personnel that perform technical activities must be trained to perform their assigned activities prior to conducting those procedures independently. Where available, SOPs or manuals are 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. Chief scientists for the MWRA surveys must complete the training outline in Battelle SOP MWRA 009. All Battelle personnel conducting

activities for HOM12 will have documented training in the appropriate SOPs. The training records for each staff member are maintained in Battelle training management database, SuccessFactors Learning Management System. The Battelle Project QAO is responsible for ensuring that the technical and management staff members are familiar with both the site and HOM12 specific procedures. All Battelle and subcontractor staff will receive training in QAPP requirements for documentation, version control, records management, and data review procedures.

### **A.8.2 SAFETY TRAINING**

Basic safety training is provided to each employee during orientation sessions. Other specific safety training sessions are conducted with staff whose responsibilities expose him or her to potential risk or hazard (*e.g.*, boating safety). The Field Manager and the employee's manager are responsible for identifying the need for specific safety training. The managers are responsible for ensuring that safety training is conducted. Safety training is detailed in the Battelle Environmental, Health, and Safety Plan. An Activity Hazard Analysis (AHA) has been prepared for the MWRA field program. It identifies potential hazards and mitigation and preventive actions to minimize injury. The AHA will be distributed to field staff at the beginning of the field season and used as part of the safety training for any personnel participating in the HOM12 field surveys.

### **A.8.3 RESPONSIBILITIES**

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

The Project QAO is responsible for ensuring that all staff are trained in Battelle quality systems and the requirements of the QMP and this QAPP. Each individual is responsible for ensuring that his/her training records are documented in SuccessFactors, any certificates are uploaded to the Battelle Field Resources Teams Channel and for updating his/her curriculum vitae as needed. The Battelle Environmental, Safety and Health Officer, Emma Corell, 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 NavSam<sup>®</sup> or other laboratory systems or (2) manually into bound logbooks or onto established data forms. All notes will be written in black ink. Corrections to hand-entered data will be initialed, dated, and justified. Corrections to electronically captured data (*e.g.*, electronic "spikes") will be documented on a hard-copy plot of the data. Completed data forms or other types of hand-entered data will be signed and dated by the individual entering the data. Direct-entry and electronic data entries will indicate the person collecting or entering the data. It is the responsibility of the senior scientists or their delegates at Battelle, Pausacaco Plankton, UMD, and WHOI to ensure that all data entries and hand calculations are verified in accordance with procedures described in Sections D.1, D.2, and D.3 below. In addition to these documentation procedures, station logs associated with field and laboratory custody and tracking will be kept in the survey logbook for each survey. Survey logbooks will be stored at Battelle under the supervision of the Field Manager.

All field and laboratory data generated by Battelle must be reported to MWRA for incorporation into the EMMS. Battelle data management staff will log in all data received for loading to maintain the data audit trail. These data are processed per Section B.10 below. The data files are stored on the projects file server under the HOM12 project Task 4 deliverables. This server is automatically backed up to a server at Battelle Columbus nightly. Data submissions will be made through MWRA's HOML application web

site. Copies of the data files used for submission to the HOML web site are e-mailed to Battelle's Records Management Office (recordsmgmt@battelle.org).

## A.9.2 DOCUMENTS

A total of nine water column surveys will be conducted each year from 2024 to 2026. For each water column survey, one Survey Plan, one Survey Summary, and one Survey Report will be prepared. Details on each are provided below.

Collection data from water column surveys (Task 5), ARRS surveys (Task 6.1), in situ data processing (Task 4), data loading and QA (Task 4), and plankton sample analysis (Task 8) are reported to MWRA in various forms as defined in the HOM12 contract. Tasks 5 and 6 collection data will be reported in survey reports while Task 8 (Plankton Analysis) will be reported in data sets used to generate Plankton Data Reports (Section A.9.3). Data synthesis reports (Task 11) are described in Section A.9.4. Survey-related deliverables that will be generated under this QAPP include:

### Task 5

- 27 Survey Plans (one for each of the water column surveys)
- 27 Survey Summaries (including the rapid phytoplankton and *Alexandrium* results; one for each of the water column surveys)
- 27 Survey Reports (one for each of the water column surveys)
- Report any notable whale or floatables observations in the Survey Summary (Task 5.7), Survey Report (Task 5.8), and associated tables that are delivered with the hydrographic data (Task 4).

### Task 6.1

- Up to 9 Survey Summaries (including the *Alexandrium* results; one for each of the ARRS surveys that need to be conducted)
- 3 Survey Reports (one for all surveys per sampling year that ARRS surveys are triggered)

### Task 7

- 9 Nutrients / Water Quality Data Report Review letters (three per year)

### Task 8

- 9 Plankton Data Report Review letters (three per year)

Draft and final reports will be submitted electronically as Microsoft® Word (draft reports) and pdf (final reports) files. Cover letters will be submitted as a separate file and will be copied to the Battelle project manager and Battelle's Records Management Office (recordsmgmt@battelle.org). The final pdf documents will contain all text, tables, and figures suitable for loading onto the Internet. Documents greater than 3 megabytes will be submitted via Box.com.

### 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-466 in 2024, 2025, and 2026, with data analysis and interpretation continuing through 2027. This document is designed following EPA/QA R-5 and is based largely on water quality QAPPs of the MWRA monitoring program described in Libby et al. (2002, 2005, 2006, 2009, 2010, 2011, 2014, 2018, 2020, 2021, and 2023). The QAPP will be reviewed and revised

annually by Battelle if directed to do so by MWRA based on significant changes to the procedures and requirements defined in this document or changes in MWRA's NPDES permit. A history of QAPP modifications will be documented in the Revision History Form located at the front of the document.

### **A.9.2.2 SURVEY PLANS**

Survey Plans will be prepared for each water column survey conducted. Each Survey Plan will follow Battelle SOP 8-043 *Preparation, Distribution, and Implementations of Field Survey Plans* that is based on the guidelines established by EPA for use of its vessels. Each Survey Plan will be submitted electronically as a pdf file at least 1 week prior to the start of the survey and will include the following information:

- Survey title, logistics, and contact information
- Schedule of operations
- Survey background, justification, rationale, and objectives
- 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 SUMMARY**

**Water Column Surveys (Task 5):** A Survey Summary will be delivered to MWRA via e-mail within 1 week of completion of each water column survey. This e-mail will include a summary of the survey operational dates, weather conditions, stations not sampled and reason, summary of preliminary water quality observations, deviations from survey scope, results of the rapid phytoplankton and *Alexandrium* analyses, observations from marine mammal sightings, notable anthropogenic debris seen, and identify technical problems encountered and resolutions. These summaries will also include satellite images of chlorophyll distribution from the day of the survey (if available) to make a comparison to the in situ observations. This summary will also highlight any potential exceedance of monitoring thresholds, or conditions, which if continued, might lead to exceedances. If available, the rapid response phytoplankton and *Alexandrium* results will be sent to MWRA via e-mail prior to the Survey Summary.

**ARRS Surveys (Task 6.1):** Battelle will report the results of the *Alexandrium* counts to MWRA within approximately 5 days of the survey. These results are used by MWRA, along with MA Division of Marine Fisheries (DMF) paralytic shellfish poisoning (PSP) toxicity data, to determine if a subsequent ARRS survey is required (within a week) or if values are below the threshold and the rapid response effort can end.

#### **A.9.2.4 SURVEY REPORTS**

**Water Column Surveys (Task 5):** Survey Reports will describe how the survey was conducted, stations occupied, measurements made, samples collected, problems experienced, and general observations from in situ sensor data, observations of visible anthropogenic debris, and summarize observations made by the certified whale observer. Unusual observations of environmental conditions, especially those with implications for the later testing of contingency plan thresholds, will be emphasized. Survey Reports will include a text narrative with accompanying station maps and survey tracklines, a complete sample collection table, a station data table, a floatables table, and a preliminary data summary table. The sample collection table will be a tabular summary of stations occupied, station locations, and samples collected versus planned. The station data table will be generated by MWRA data management staff and will include data on each station and depth sampled including arrival time, coordinates, depth, sample ID, and others. Any deviations from this QAPP, not known at the time of survey plan preparation, will also be incorporated into the Survey Reports. The Survey Report will be submitted to MWRA electronically as a pdf file no later than 3 weeks after the completion of each survey. MWRA's comments on the report will be due to Battelle 2 weeks after receipt of the report. The final electronic Survey Report in pdf format, addressing MWRA's comments, will be due to MWRA 2 weeks after receipt of the comments. If MWRA does not submit comments within the 2-week period, the survey report will be considered final.

**ARRS Surveys (Task 6.1):** Within 4 weeks of the final ARRS survey, a detailed survey report will be submitted for MWRA's approval. The ARRS survey report will include data about each ARRS survey (where and when samples were collected) and summarize hydrographic results and *Alexandrium* counts. The full set of survey data, hydrographic data, and *Alexandrium* data from all ARRS surveys conducted in a given year will also be submitted within 4 weeks of the final ARRS survey.

#### **A.9.3 DATA REPORT REVIEW AND COMMENT**

Three Nutrients/Water Quality Data Reports (Task 7) and three Plankton Data Reports (Task 8) will be generated by MWRA for each monitoring year (2024-2026), corresponding to the Winter/Spring, Summer, and Fall periods. The data reports are created directly from the EMMS database. Battelle will perform a technical review and comment on each of the data reports prepared by MWRA.

#### **A.9.4 SYNTHESIS REPORTS (TASK 11)**

The data delivered above will be used in the Water Column Summary Report and Outfall Monitoring Overview (OMO) prepared under Task 11. MWRA comments on the reports will be provided to Battelle within 4 weeks of report receipt. The final reports, addressing MWRA comments, will be due to MWRA within 2 weeks of comment receipt. The OMO has an additional step with submission of an outline. Schedules for all activities, including this report, are provided in Table A-2.

##### **A.9.4.1 WATER COLUMN SUMMARY REPORT (TASK 11.1)**

All data for the annual Water Column Summary Report will come from the EMMS database. Authors will request data extracts. The annual Water Column Summary Reports will provide a synthesis of results from water column monitoring activities conducted under Tasks 5 through 8 during each monitoring year (2024-2026). The report will describe the status of the ecosystem, including spatial and temporal patterns within Massachusetts and Cape Cod Bays (e.g., the distribution of the MWRA effluent plume as described by ammonia [NH<sub>4</sub>] concentrations). It will have abbreviated introduction and method sections and primarily focus on presenting the most noteworthy observations made during the year. The summary report will draw heavily upon the presentations at the Annual Technical Meeting (Task 10).

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

<b>Deliverable</b>	<b>Survey Period</b>	<b>Due Date</b>
<b>Task 4 Data Quality Control and Data Set Submission</b>		
Survey Data Set (collection information)	Each survey	1 week after survey
Hydrographic Data Set (including marine mammal and floatables tables)	Each survey	2 weeks after survey
Plankton Data Set	Each survey	60 days after survey
<b>Task 5 Water Column Surveys</b>		
Survey Plan	Each survey	1 week prior to survey
Survey Summary	Each survey	1 week after survey
Survey Report – Draft	Each survey	3 weeks after survey
Survey Report – Final	Each survey	2 weeks after receipt of comments
<b>Task 6 Harmful Algal Bloom Response Surveys</b>		
ARRS Survey Summary	Each survey	Within 1 week of survey
ARRS Survey Report	Per sampling year	4 weeks after final ARRS survey each year
Letter report on <i>Pseudo-nitzschia australis</i> gene probe test	February – June 2024	June 30, 2024
<b>Task 7. Hydrography/Nutrients Data Report Review</b>		
Review Comments for Data Report Nutrients/Water Quality	February – April	August 15
	May – August	December 15
	September – October	February 15 of following year
<b>Task 8. Plankton Data Report Review</b>		
Review Comments for Data Report – Plankton	February – April	August 15
	May – August	December 15
	September – October	March 15 of following year
<b>Task 11 Synthesis Reports</b>		
Water Column Summary – Draft	February – October	June 2025, 2026, 2027
Water Column Summary – Final		August 2025, 2026, 2027
Outfall Monitoring Overview – Outline	February – October	May 2025, 2026, 2027
Outfall Monitoring Overview–Draft		August 2025, 2026, 2027
Outfall Monitoring Overview– Final		October 2025, 2026, 2027

**A.9.4.2 OUTFALL MONITORING OVERVIEW (TASK 11.2)**

This report will summarize key findings of the previous year’s monitoring findings and related findings about Massachusetts and Cape Cod Bays including any special studies and threshold violations. The OMO Report will follow the “Results” format established in 2007, when the report was split into two separate reports (“Results” and “Background”) (Werme et al. 2008; Werme and Hunt 2008). The overview will include any data collected from contractors conducting sampling in Cape Cod Bay and Stellwagen Bank to ensure consistency in the report. The report will be written toward the general public, regulators, and interested scientists.

## **B DATA GENERATION AND ACQUISITION**

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

#### **B.1.1 MASSACHUSETTS BAY SURVEYS**

##### **B.1.1.1 WATER COLUMN SURVEYS (TASK 5)**

Water column sampling will be conducted nine times per year in 2024, 2025, and 2026 (Table B-1) using the WHOI R/V *Tioga* or equivalent vessel as the sampling platform. Figure A-2 shows the location of the water column stations. Sampling under this contract will be conducted at the 11 stations in Massachusetts Bay. The stations include five nearfield stations and six farfield stations as designated based on distance from the bay outfall. Three additional stations are noted on Figure A-2 in Cape Cod Bay and Stellwagen National Marine Sanctuary that will be sampled concurrently by a different contractor (CCS).

##### **B.1.1.2 ALEXANDRIUM RAPID RESPONSE STUDY (ARRS) SURVEYS (TASK 6.1)**

If the trigger thresholds outlined in Libby et al. (2013) are exceeded, ARRS sampling will be conducted up to three times per year in 2024, 2025, and 2026 under this task. If additional ARRS surveys are required MWRA will issue a task order request under Task 9. The ARRS surveys will be conducted using the WHOI R/V *Tioga* or equivalent vessel as the sampling platform. Figure B-1 shows the location of the ARRS stations. The ARRS surveys cover the 10 water column stations where *Alexandrium* are regularly sampled (i.e., all stations except N21), plus nine additional stations.

### **B.1.2 SAMPLING LOCATIONS AND FREQUENCY**

##### **B.1.2.1 WATER COLUMN SURVEYS (TASK 5)**

Table B-2 identifies the location for each of the water column monitoring stations. The five nearfield stations are located within 5 kilometers of the outfall. The six farfield stations are located beyond the nearfield to (1) cover regional-scale oceanographic processes in Massachusetts Bay; (2) broadly characterize reference areas; and (3) verify that impacts by the outfall plume are not found beyond the nearfield. Table B-3 shows sub-sampling by analysis type and sample depth. The main differences in sample collection between stations is that no plankton samples will be collected at station N21, ocean acidification (DIC and total alkalinity) samples will be collected from stations F06, F22, N01, and N07, and an additional sample for rapid phytoplankton analysis will be collected at station N18.

Each water column survey will be conducted in a single day. Battelle will be in close communication with scientists at CCS to coordinate sampling in Massachusetts and Cape Cod Bays. The water column surveys are scheduled to be conducted monthly (February through October) with target dates provided in Table B-1. Note that the early September surveys (WN248, WN258, and WN268) must fall in September so that they are within the autumn season as defined for seasonal threshold calculations (September-December).

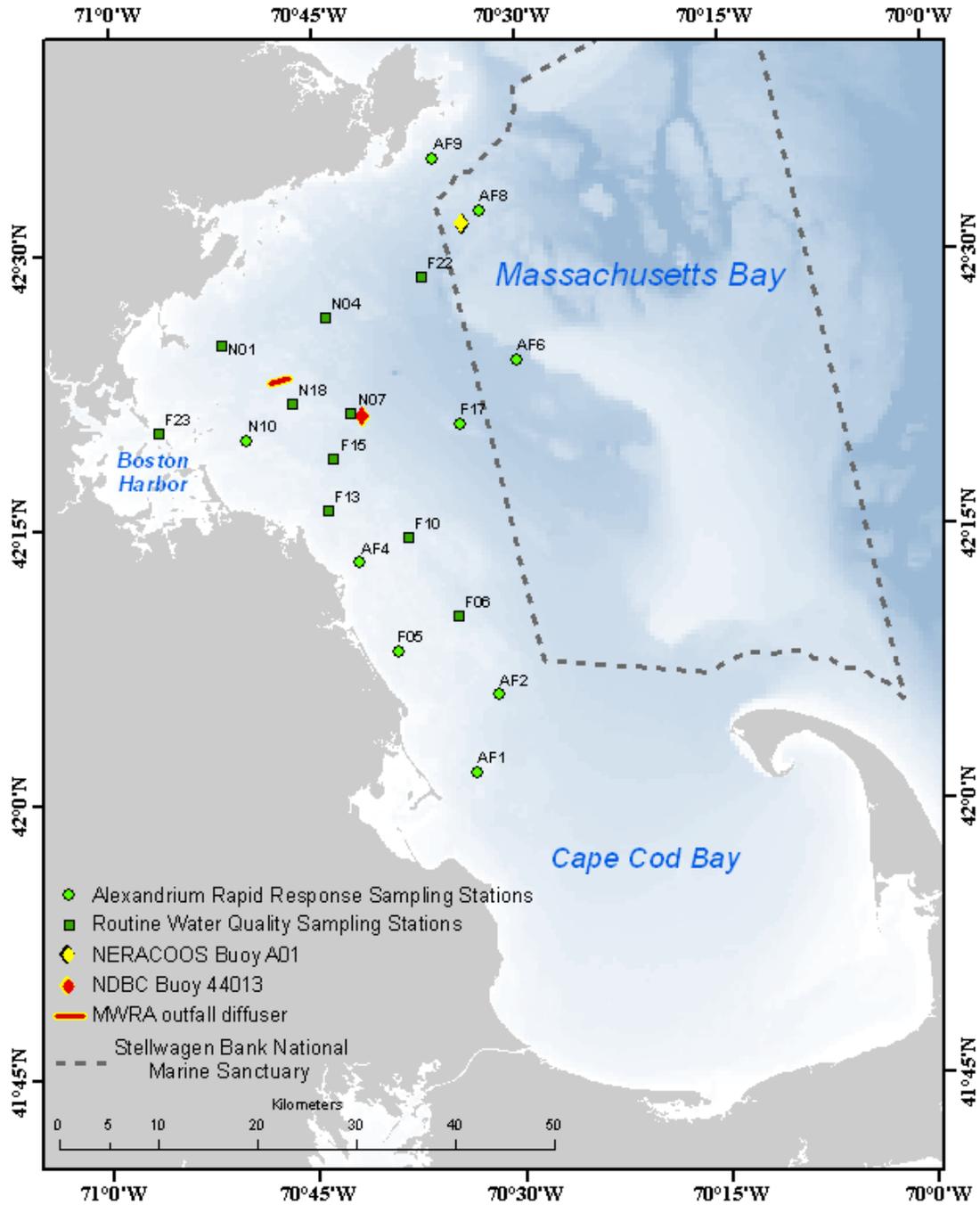
##### **B.1.2.2 ALEXANDRIUM RAPID RESPONSE STUDY (ARRS) SURVEYS (TASK 6.1)**

Table B-4 identifies the location for each of the ARRS monitoring stations. These stations include eight farfield stations, five nearfield stations, and six additional stations. Table B-5 shows sub-sampling and sample depth for each station. Dissolved inorganic nutrient and *Alexandrium* samples will be collected at all 19 stations. In addition, chlorophyll will be collected at a subset of stations for calibration of the in situ sensors.

**Table B-1. HOM12 Water Column Survey and Survey Related Deliverables Schedule**

Survey ID	Target Date	Survey Plan	Survey Summary	Survey Report
WN241	02/06/24	01/30/24	02/13/24	02/27/24
WN242	03/19/24	03/12/24	03/26/24	04/09/24
WN243	04/09/24	04/02/24	04/16/24	04/30/24
WN244	05/14/24	05/07/24	05/21/24	06/04/24
WN245	06/18/24	06/11/24	06/25/24	07/09/24
WN246	07/23/24	07/16/24	07/30/24	08/13/24
WN247	08/20/24	08/13/24	08/27/24	09/10/24
WN248	09/04/24	08/27/24	09/10/24	09/24/24
WN249	10/22/24	10/15/24	10/29/24	11/12/24
WN251	02/04/25	01/28/25	02/11/25	02/25/25
WN252	03/18/25	03/11/25	03/25/25	04/08/25
WN253	04/08/25	04/01/25	04/15/25	04/29/25
WN254	05/13/25	05/06/25	05/20/25	06/03/25
WN255	06/17/25	06/10/25	06/24/25	07/08/25
WN256	07/22/25	07/15/25	07/29/25	08/12/25
WN257	08/19/25	08/12/25	08/26/25	09/09/25
WN258	09/03/25	08/26/25	09/09/25	09/23/25
WN259	10/21/25	10/14/25	10/28/25	11/11/25
WN261	02/03/26	01/27/26	02/10/26	02/24/26
WN262	03/17/26	03/10/26	03/24/26	04/07/26
WN263	04/07/26	03/31/26	04/14/26	04/28/26
WN264	05/12/26	05/05/26	05/19/26	06/02/26
WN265	06/16/26	06/09/26	06/23/26	07/07/26
WN266	07/21/26	07/14/26	07/28/26	08/11/26
WN267	08/18/26	08/11/26	08/25/26	09/08/26
WN268	09/01/26	08/25/26	09/08/26	09/22/26
WN269	10/20/26	10/13/26	10/27/26	11/10/26

Note that survey WN2X8 must be conducted in September to meet threshold testing requirements.



**Figure B-1. ARRS Survey Station Locations in Massachusetts Bay.**

Note: Both the “*Alexandrium* rapid response sampling stations” and the “routine water quality sampling stations” are included in the ARRS surveys. When appropriate, additional stations in Cape Cod and Boston Harbor may be sampled.

**Table B-2. Water Column Sampling Stations**

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

**Table B-3. Water Column Subsamples by Analysis Type and Sample Depth Class**

							Total	
Number of Stations		1	1	1	2	3	3	11
Analysis Type	Sample Depth Codes	Number Depths Collected					Number Samples Collected	
Dissolved inorganic nutrients (NH <sub>4</sub> , NO <sub>3</sub> , NO <sub>2</sub> , PO <sub>4</sub> , and SiO <sub>4</sub> ) <sup>a</sup>	ABCDE	5	5	5	5	5	5	55
Other nutrients (TDNP, PCN, PP) <sup>b</sup>	ABCDE	5	5	5	5	5	5	55
Chlorophyll <sup>c</sup>	ACE		3	3	3			33
	ABC	3				3	3	
Zooplankton	Z		1	1	1	1	1	10
Whole water phytoplankton	AC		2	2	2	2	2	20
Alexandrium	AC		2	2	2	2	2	20
Rapid analysis phytoplankton <sup>d</sup>	C		1					1
DIC and total alkalinity <sup>e</sup>	ACE			3		3		12

<sup>a</sup> NH<sub>4</sub> = ammonium, NO<sub>3</sub> = nitrate, NO<sub>2</sub> = nitrite, PO<sub>4</sub> = phosphate, and SiO<sub>4</sub> = silicate.

<sup>b</sup> TDNP = total dissolved nitrogen and phosphorous, PCN = particulate carbon and nitrogen, and PP = particulate phosphorous.

<sup>c</sup> Chlorophyll samples collected at A, C and E depths at four stations (F22, F23, N04, and N18) and at A, B and C depths at seven stations (F06, F10, F13, F15, N01, N07, and N21)

<sup>d</sup> Rapid sample collected at station N18 only.

<sup>e</sup> DIC and total alkalinity are sampled at four stations (F06, F22, N01, and N07)

**Table B-4. ARRS Sampling Stations**

Station	Latitude	Longitude	Station	Latitude	Longitude
AF1	42.02788	-70.55467	N18	42.36583	-70.77767
AF2	42.09879	-70.52724	F05	42.13867	-70.65000
AF4	42.21997	-70.69553	F06	42.17067	-70.57667
AF6	42.40335	-70.50163	F10	42.24233	-70.63733
AF8	42.54019	-70.54553	F13	42.26833	-70.73500
AF9	42.58754	-70.60224	F15	42.31550	-70.72767
N01	42.41933	-70.86450	F17	42.34583	-70.57050
N04	42.44383	-70.73650	F22	42.47983	-70.61767
N07	42.35633	-70.70617	F23	42.33917	-70.94200
N10	42.33150	-70.83400			

**Table B-5. ARRS Subsamples by Sample Depth**

Analysis		Chlorophyll	Dissolved Inorganic Nutrients	<i>Alexandrium</i>	Number of Samples Collected
Analysis Code		CH	DIN	AL	
Sample Depth Codes		A10m20m E	A10m20m E	A10m	
Station	Depth (m)	Number of Depths Collected			
AF1	28.5	4	4 + Dup <sup>a</sup>	3 <sup>b</sup>	12
AF2	41		4	2	6
AF4	25		4	2	6
AF6	92.5		4	2	6
AF8	59.5		4	2	6
AF9	46		4	2	6
F05	17.5		4	2	6
F06	34		4	2	6
F10	33		4	2	6
F13	25	4	4 + Dup <sup>a</sup>	3 <sup>b</sup>	12
F15	38		4	2	6
F17	78		4	2	6
F22	81	4 + Dup <sup>a</sup>	4 + Dup <sup>a</sup>	3 <sup>b</sup>	22
F23	25		4	2	6
N01	30		4	2	6
N04	52	4	4	3 <sup>b</sup>	11
N07	52		4	2	6
N10	26.5		4	2	6
N18	27	4 + Dup <sup>a</sup>	4 + Dup <sup>a</sup>	3 <sup>b</sup>	22
Total Samples		22	80	43	145

<sup>a</sup> Duplicate sample collected at 10 m depth.

<sup>b</sup> Additional *Alexandrium* sample collected at 20 m depth.

Each ARRS survey will be conducted in a single day. The additional station coverage is feasible within one day because the ARRS surveys measure a subset of the water column parameters, shortening time on station, the principal measurement being *Alexandrium* cell abundance. Up to three ARRS surveys per year may be conducted under Task 6. Any additional ARRS surveys that are required will be conducted under Task 9 (Supporting Studies). The ARRS surveys supplement the nine regular water column monitoring surveys. Because the water column surveys follow a set schedule and are about a month apart, they are not designed to adequately describe the development of a short-lived, seasonal bloom of a single species such as *Alexandrium*. The ARRS surveys supplement the water column surveys by providing information between them. The ARRS has a set of thresholds based on cell abundance and PSP toxicity that trigger the need to conduct an *Alexandrium* response survey. Libby et al 2013 details this process, the requirements for the ARRS survey, and when the surveys can be terminated.

### **B.1.3 HYDROCASTS AND SENSOR MEASUREMENTS**

Hydrographic data will be collected at all water column and ARRS stations. At each station, a hydrocast will be conducted with an underwater unit consisting of a CTD system, various sensors (DO, pH, chlorophyll fluorescence, optical beam transmittance, light irradiance, 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 to 2 m) to within approximately 3 to 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 (PAR) at the sea surface, navigational position, and time will be recorded concurrently with the hydrocast measurements.

### **B.1.4 WATER COLLECTION AND ZOOPLANKTON NET TOWS**

#### **B.1.4.1 WATER COLUMN SURVEYS (TASK 5)**

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

On deck, water from the Rosette bottles will be subsampled for analysis of dissolved inorganic nutrients and other analytes. Samples for extracted chlorophyll and phaeophytin analyses are collected at two different sets of sampling depths. To reduce potential error in the field, samples for extracted chlorophyll analysis will be collected at A, B, C and E depths at all 11 stations. For stations F22, F23, N04, and N18, Battelle will send MWRA samples from the A, C and E depths. For stations F06, F10, F13, F15, N01, N07, and N21, Battelle will send samples from A, B and C depths. Phytoplankton and *Alexandrium* samples will be collected from the rosette bottles and vertical net tows to collect zooplankton will be conducted at all stations except station N21 (Table B-3). A detailed listing of samples collected at each station during the water column surveys is provided in Appendix III.

#### **B.1.4.2 ALEXANDRIUM RAPID RESPONSE STUDY (ARRS) SURVEYS (TASK 6.1)**

Discrete water samples will be collected at four depths: surface, ~10 meters, ~20 meters and near bottom at each station and subsampled as described in Table B-5. Once the Rosette system is onboard, subsamples will be obtained for each of the parameters being measured. All samples will be processed for analysis according to procedures outlined in Section B.1.6. Dissolved inorganic nutrient samples will be collected at each discrete water depth sampled. Chlorophyll samples will be collected at three depths at five of the stations for calibration of the in situ fluorescence sensor – stations AF1, F13, N04, N18, and F22. Duplicate samples will be collected from the 10 m sample depth at stations F22 and N18 for dissolved inorganic nutrients (DIN) and chlorophyll; DIN duplicates will also be collected from this depth as stations AF1 and F13. The 20-micrometer ( $\mu\text{m}$ ) screened water *Alexandrium* samples will be collected at two depths (surface and 10 m) at all 19 stations with additional samples collected at 20 m at stations AF1, F13, N04, N18, and F22. The screened samples will be analyzed using the fluorescent gene-probe technique for *Alexandrium* identification and enumeration (Anderson et al. 2005). The nutrient and chlorophyll samples will be transferred to MWRA upon completion of the survey. The screened *Alexandrium* samples will be transferred directly to WHOI (Don Anderson/Dave Kulis) within 24 hours of collection.

#### **B.1.5 WHALE AND FLOATABLES OBSERVATIONS**

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

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

#### **B.1.6 SHIPBOARD PROCESSING OF DISCRETE WATER SAMPLES**

Sample aliquots for nutrient analyses are removed from the Rosette sampling bottles and are processed aboard ship per Battelle SOP 8-266, *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.

Samples for DIC and alkalinity analyses are collected together in a 300-milliliter (mL) biological oxygen demand (BOD) bottle before all other subsamples. The sample bottle is overflowed one full bottle volume, and the tube used to fill the bottle is pinched and removed, allowing for sufficient headspace for preservation. Samples are fixed with 50 microliter ( $\mu\text{L}$ ) saturated mercuric chloride ( $\text{HgCl}_2$ ) solution provided by MITSG, making sure the pipette or repipettor tip does not touch the sample.

#### **B.1.7 LABORATORY PROGRAM**

Water samples collected during the surveys will be analyzed by MWRA Department of Laboratory Services (DLS) to determine concentrations of dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate); dissolved and particulate organic nutrients (carbon, nitrogen, and phosphorus); chlorophyll a and phaeophytin. Scientists from Pausacaco and UMD will analyze phytoplankton and

zooplankton community structure, respectively. *Alexandrium* counts will be conducted by scientists at WHOI. The sample analyses conducted by the Battelle team are summarized in Table B-6. Sampling and analytical methods are described in Sections B.2 and B.4, respectively.

Water samples collected during the surveys will be provided to MITSG by Battelle. MITSG researchers are responsible for the analysis of DIC and total alkalinity samples. These samples are not a formal component of the MWRA HOM12 monitoring program and do not appear in Table B-6.

### B.1.8 MONITORING PARAMETERS AND COLLECTION FREQUENCY

Table B-6 lists analytical parameters and in situ hydrographic measurements generated by Battelle and Table B-3 presents the collection frequency of each. Sample collection plans for the water column and ARRS surveys are presented in Appendix III.

### B.1.9 SCHEDULE OF ACTIVITIES AND DELIVERABLES

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

**Table B-6. Water Column Sample Analyses**

Parameter	Lab	Units	Instrument	Reference
<b>Laboratory Measurements</b>				
Whole-water phytoplankton	Pausacaco	E6Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Borkman (1994), Borkman et al. (1993), Turner et al. (1995)
<i>Alexandrium catenella</i>	WHOI	Cells/L	Zeiss epifluorescence microscope with filter sets complementary to the probe/fluorochrome combination used.	Anderson et al. (2005)
Rapid phytoplankton	Pausacaco	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)
<b>In situ Measurements</b>				
Conductivity	Battelle	mS/cm	Sea-Bird SBE-4	SBE-25 CTD Manual/ Battelle SOP 8-183
Temperature	Battelle	C	Sea-Bird SBE-3	SBE-25 CTD Manual/ Battelle SOP 8-183
Pressure	Battelle	db	Sea-Bird SBE-29	SBE-25 CTD Manual/ Battelle SOP 8-183
Dissolved oxygen	Battelle	mg/L	Sea-Bird SBE 43	Weiss (1970)/Battelle SOP 8-180
Chlorophyll fluorescence	Battelle	µg/L	WET Labs WETStar	WET Labs WETStar Manual/Battelle SOP 8-163
pH	Battelle	unit less	SeaBird SBE-18	SBE-18 App. Note/ Battelle SOP 8-183
Transmissivity	Battelle	m <sup>-1</sup>	WET Labs C-Star (25-mm pathlength)	WET Labs C-Star Manual/Battelle SOP 8-174
In situ irradiance	Battelle	µEm <sup>-2</sup> sec <sup>-1</sup>	Biospherical QSP-200PD	Biospherical Manual/ Battelle SOP 8-127
Surface irradiance	Battelle	µEm <sup>-2</sup> sec <sup>-1</sup>	Biospherical QSR-2200 & -2240	Biospherical Manual/ Battelle SOP 8-127
Altimeter	Battelle	m	Data Sonic PSA-916	Data Sonic Manual
Bottom depth <sup>1</sup>	Battelle	m	Furuno DFF-3D	Furuno Manual
Navigational position <sup>1</sup>	Battelle	Degree	Furuno GP330B/NavNet TZtouch2	Furuno Manual
Sigma-t (calculated)	Battelle	unit less	Calculated based upon conductivity, temperature and pressure	SBE-25 CTD Manual/ Battelle SOP 8-183
Salinity (calculated)	Battelle	PSU	Calculated based upon conductivity, temperature and pressure	SBE-25 CTD Manual/ Battelle SOP 8-183

<sup>1</sup> Bottom depth and navigational position data will be collected using R/V *Tioga* on-board equipment.

## **B.2 SAMPLING METHODS**

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

### **B.2.1 NAVIGATION**

Vessel positioning during sampling operations will be accomplished with Battelle's NavSam<sup>®</sup> system. This system consists of the Furuno NavNet TZtouch2 (mounted) equipped with GP330B dGPS antennae which are interfaced to the NavSam<sup>®</sup> computer. The Furuno dGPS is capable of locking on up to 12 satellites.

### **B.2.2 VESSEL HANDLING**

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

At each sampling station, the vessel will be positioned upwind/upcurrent of the target station position with distance dependent upon wind/current strength and expected drift. The objective is to sample as close to the nominal station coordinates as possible, but at no more than 300 m off the station. The vessel heading will be selected such that the underwater unit will be deployed on the side of the boat facing the sun and relative to the prevailing seas. The vessel will maintain this position during the cast. If a vessel positioning or safety issue causes shading of the CTD, the shading incident will be noted in the station log and shading will be qualified during post-processing.

### **B.2.3 HYDROGRAPHIC PROFILES**

The hydrographic profile sampling equipment and data acquisition equipment consists of the following apparatus and instruments. Hydrographic profile data are collected per Battelle SOP 8-275 *At Sea Collection of Hydrographic Data using CTD and Rosette System*.

- 9-L Rosette sampling bottles (e.g., Go-Flo or Niskin)
- Sea-Bird 32 Carousel Water Sampling System
- Sea-Bird SBE-25 CTD system (one additional SBE-25 serves as backup; Battelle SOP 8-367) mounted on the Rosette and equipped with the following:
  - Sea-Bird SBE-43 DO sensor (intake at same depth as the pressure sensor) produces an oxygen-dependent electrical current and incorporates a thermistor for determining membrane temperature (three additional SBE-43 serve as backups).

- Sea-Bird SBE-4 Conductivity sensor (shared intake with the DO sensor) provides in situ measurements of water conductivity so that salinity and sigma-T can be calculated (three additional SBE-4 serve as backups).
  - Sea-Bird SBE-3 Temperature sensor (shared intake with the DO sensor) provides in situ measurements of water temperature which also contributes to salinity and sigma-T calculations (three additional SBE-3 serve as backups).
  - Sea-Bird SBE-29 Pressure sensor provides in situ measurements of water pressure which is converted to sensor depth in meters and also contributes to salinity and sigma-T calculations (one additional SBE-29 serves as backup).
  - WET Labs C-Star 25 cm-pathlength transmissometer that provides in situ measurements of optical beam transmission (related to the concentration of suspended matter in the water over the sensor's 25-cm pathlength; the sensor is located mid-Niskin bottle about 20 cm above the pressure sensor).
  - WET Labs WETStar chlorophyll fluorometer (intake at same depth as the pressure sensor)
  - Biospherical QSP-200PD spherical quantum scalar irradiance sensor that measures underwater photosynthetically active radiation (PAR) – mounted 1 m above the pressure sensor.<sup>2</sup>
  - Sea-Bird SBE-18 pH sensor will be mounted upright on the Rosette sampler (two Sea-Bird SBE-18 pH sensors will serve as back-up).
- Data Sonic PSA 916 altimeter provides a measurement of underwater unit height from the bottom – mounted level with the pressure sensor
  - Biospherical QSR-2200 or QSR-2240 reference hemispherical quantum scalar irradiance sensor that measures on-deck radiation conditions (*e.g.*, due to atmospheric conditions)
  - Furuno DFF-3D multibeam and transducer depth sounder is shown on the Furuno NavNet TZtouch2 system's TZTL12F display unit and provides a NMEA-0183 output to NavSam<sup>®</sup> of bathymetric measurements during vertical and horizontal profiling operations aboard the R/V *Tioga*
  - Computer with custom data-acquisition software (NavSam<sup>®</sup>)
  - Color printer
  - Navigation:
    - Furuno NavNet TZtouch2 system equipped with GP330B dGPS antenna aboard the R/V *Tioga* (Note: there are two separate GP330B dGPS on the R/V *Tioga*) provides a NMEA-0183 position output to NavSam<sup>®</sup>.

Battelle's software, NavSam<sup>®</sup> acquires data from all profile electronic-sampling-systems and navigation systems at the rate of four times per second. Once per second the software displays all of the information on a color monitor. The screen is split to show sensor data on the left and navigation data on the right (Figure B-2). Once the data are acquired, they are automatically written to a data file and logged 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. Setup of NavSam<sup>®</sup> for survey operations is described in SOP 8-029 *Survey Set-up and Sample Tracking Using NavSam<sup>®</sup> Software*.

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<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).

During hydrocast operations, position fixes will be electronically recorded at 1-second intervals. During transit between stations, position fixes and deck irradiance (upon request) will be electronically recorded at 4 Hz. Additionally, between stations, position fixes will be stored at 5-minute intervals. Irradiance measurements will be conducted from one-half hour before sunrise to one-half hour after sunset. Weather and waves permitting, the vessel will be oriented to avoid shading of the light sensors.

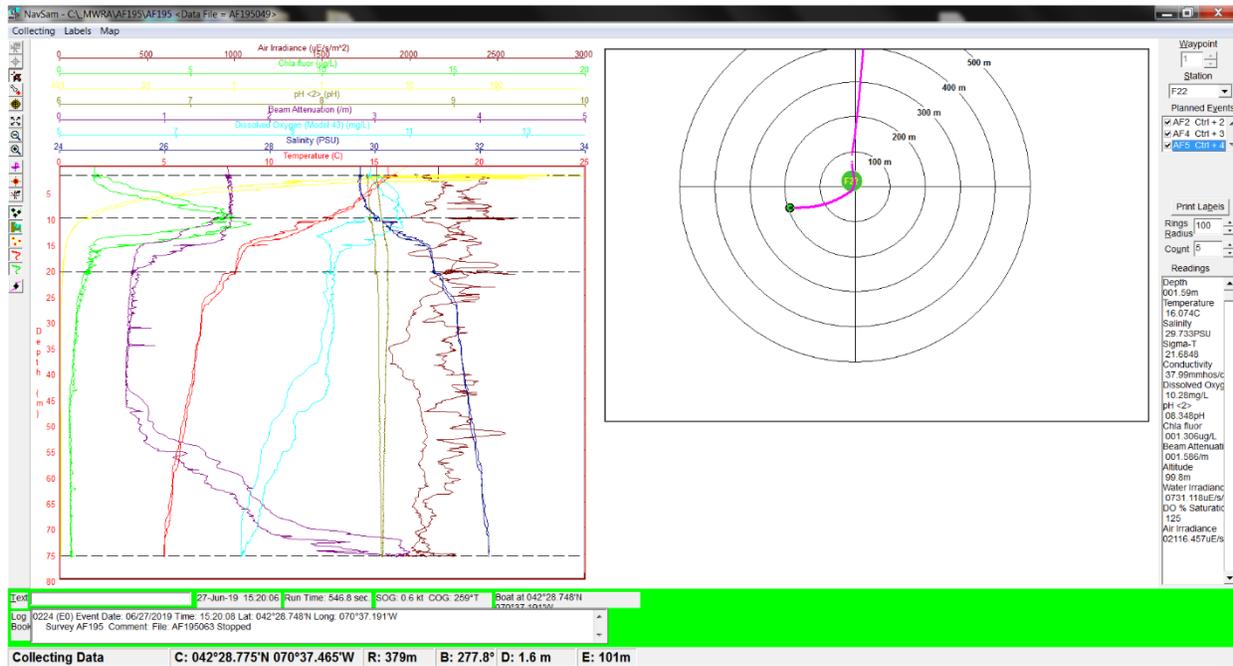


Figure B-2. Sample NavSam<sup>®</sup> Data Acquisition Screen

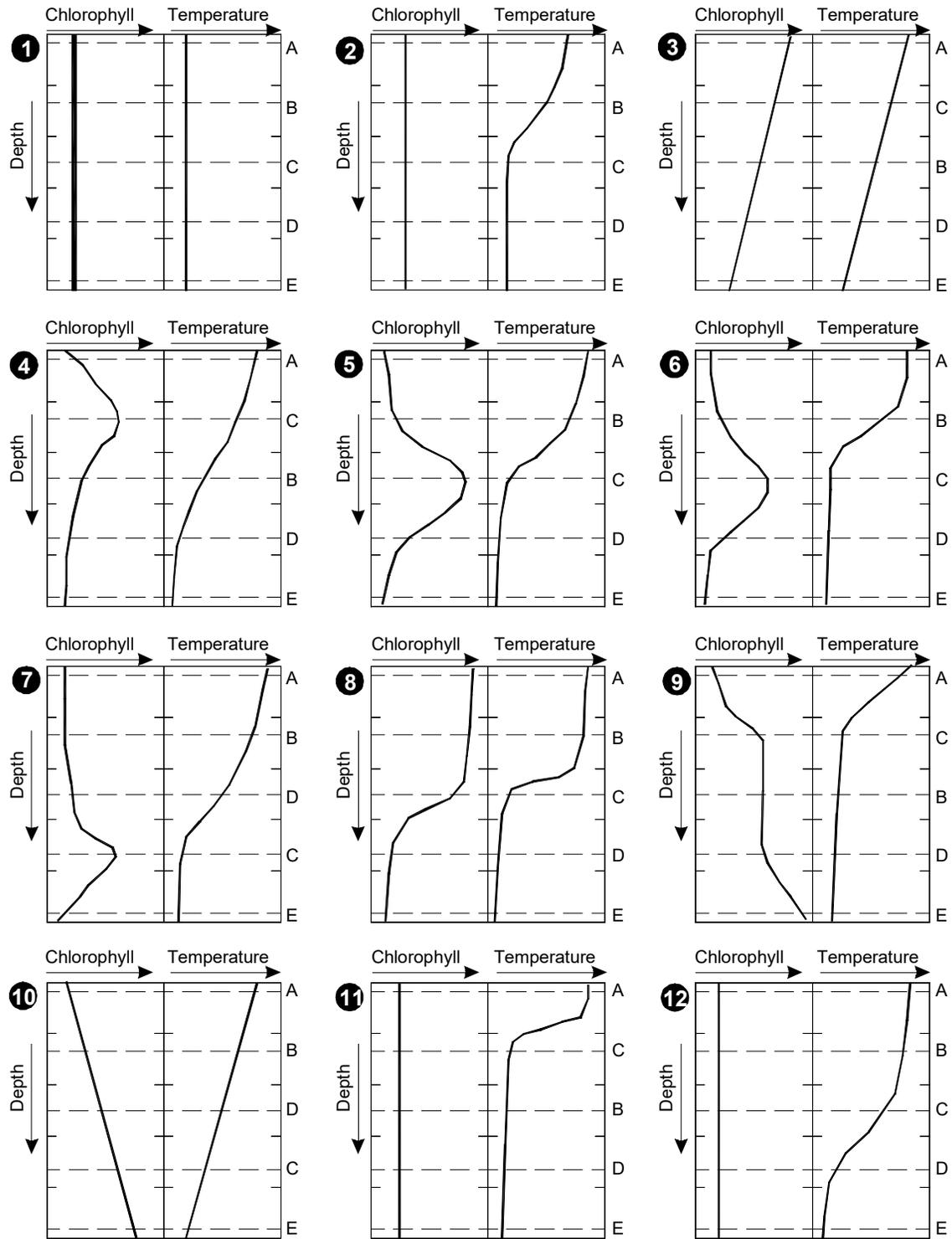
## B.2.4 WATER SAMPLING

Water samples for dissolved inorganic nutrients, dissolved organic nutrients, particulate nutrients, chlorophyll *a*, DIC, total alkalinity, 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 versus surface irradiance, beam attenuation less than 0.5/m). Prior to the first deployment of the day, the pressure sensor will be used to adjust the depth offset based on atmospheric pressure.
3. After a successful on-deck check out, the underwater unit will be lowered into the water to a depth of approximately 5 meters and held in this position.
4. The Rosette will be held at this depth for at least 1 minute while sensors equilibrate (*e.g.*, stable salinity, DO, and temperature readings) and the pump evacuates air from the plumbing, the rosette will be returned to the surface (remaining submerged), and it will then be lowered

(downcast) at a descent rate of about 0.5 meters per second (m/s) to within 3 to 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 Task 5 Water Column survey water-sampling depths for the upcast. These water column survey sampling depths are based on defined locations relative to a subsurface chlorophyll maximum detected by in situ fluorometer. The five water column sampling depths are designated surface (A), mid-surface (B), mid-depth (C), mid-bottom (D), bottom (E), although actual sampling depths would not necessarily be evenly spaced. At all stations, the C-depth sample will represent the chlorophyll maximum. Depending on the depth of chlorophyll maximum, the mid-surface and mid-depth or mid-bottom and mid-depth levels can be exchanged. In these cases, the C-depth can be switched to a shallower (B-depth) or deeper (D-depth) to represent the subsurface chlorophyll maximum, as deemed appropriate by the chief scientist. For example, scenario 4 of Figure B-3 shows an intense and shallow chlorophyll maximum. In this case, the sampling protocol for the mid-depth and mid-surface would be exchanged so that the chlorophyll maximum would receive the full suite of analyses usually allocated to the water column mid-depth. If the chlorophyll maximum is at the surface, the C depth code is assigned to a subsurface maximum. Scenario 7 of Figure B-3 shows an intense and deep chlorophyll maximum, thus the protocols for mid-depth and mid-bottom would be exchanged. In scenarios 9 and 11, the switch of C and B depths is driven by the importance of sampling at the pycnocline as fluorescence was consistent over these depths. The Task 6.1 ARRS survey water samples will be collected at four depths during the upcast: near bottom, ~20 m, ~10 m, and surface.
6. During the upcast, the unit will be maintained at each of the selected depths until the sensor readings stabilize (*i.e.*, little fluctuation in the instrument readings), typically this is 20 to 30 seconds (may be longer in summer under strongly stratified conditions). Water will be collected by closing one or more Rosette sampling bottles, depending on the water volume needed for analysis. When the Rosette deck unit indicates that the bottles are closed, this 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, pH, 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 Bottle IDs provided by DLS as Laboratory Information Management System (LIMS) sample numbers that are entered into NavSam<sup>®</sup> prior to the survey according to Battelle MWRA SOP 008, *Integrating MWRA Client ID Numbers into the NavSam<sup>®</sup> Survey Database*. Onboard processing is described in Section B.2.5.
7. After collecting the surface water sample, the operator will close the data cast file, the rosette will be brought on board, and the Niskin bottles will be subsampled for processing.
8. NavSam<sup>®</sup> will be put into navigation mode with a file created for transit to the next station.



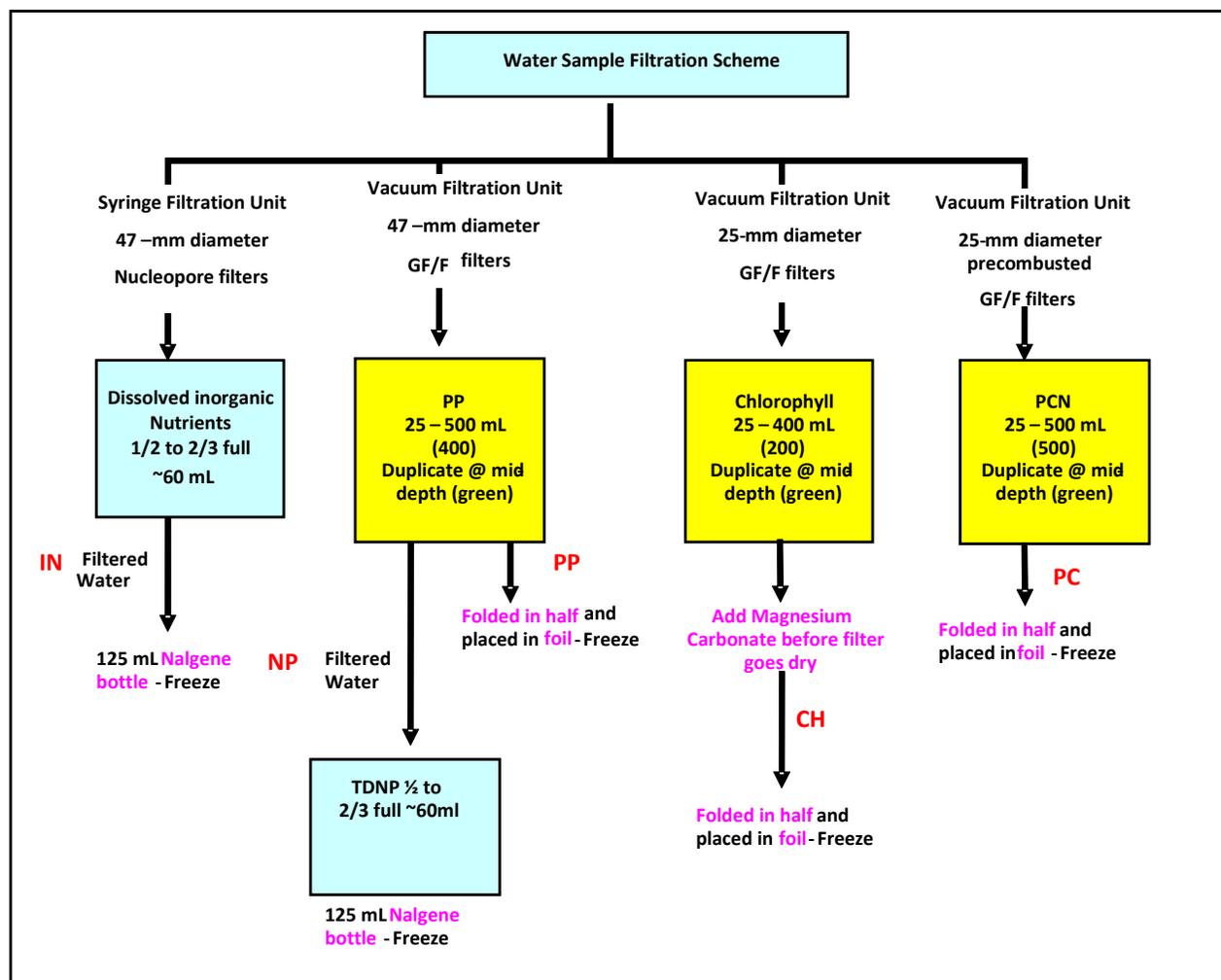
Notes:  
- Mid-depth 'C' must be less than 30 meters and cannot be the bottom

**Figure B-3. Twelve Scenarios for Selecting Water Column Sample Depths**

### B.2.5 ONBOARD SAMPLE PROCESSING

Depending on the subsampling requirements at each station, some or the entire following onboard sample processing procedures will be conducted. Appendix III tables lay out the required subsampling required for the Task 5 water column surveys and the Task 6.1 ARRS surveys.

Water from the Rosette sampling bottles is transferred to 1-Liter (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% hydrochloric acid (HCl) at the beginning of the survey day and with deionized water between sampling stations. The filtrate sample bottles will be rinsed three times with filtrate prior to filling. Figure B-4 summarizes the onboard processing of the dissolved and particulate nutrient subsamples from the 1-L opaque polyethylene jars (Battelle SOP 8-266, *Nutrient Sample Processing*). Sample volumes, containers, and storage conditions are listed in Table B-7.



**Figure B-4. Onboard Filtration and Processing Flow Chart**  
 (Note: analysis codes for Bottle IDs and labels are shown in red – see Table B-7 for definitions).

**Table B-7. Sample Volumes, Containers, and Processing for Field Samples**

Parameter	Sample Volume (Target) (mL)	Sample Containers <sup>b</sup>	Shipboard Processing/ Preservation <sup>b</sup>	Maximum Holding Time to Analysis
Hydrographic Profiles <sup>a</sup>	NA	NA	Record data to CD.	NA
<b>Subsamples from PVC Rosette Bottles</b>				
Dissolved inorganic nutrients	60	125-mL polyethylene bottle	Pass through a Nucleopore membrane filter. Freeze until analysis.	28 days
Total dissolved phosphorus and nitrogen	60	125-mL polyethylene bottle	Pass sample through a GF/F. Freeze filtrate until analysis.	28 days
Particulate carbon and nitrogen	25-500 (500)	Whatman GF/F in foil	Pass through a GF/F. Freeze filter until analysis.	28 days
Particulate phosphorus	25 – 500 (400)	Whatman GF/F in foil	Pass sample through a GF/F. Freeze filter until analysis.	28 days
Chlorophyll <i>a</i> and phaeopigments	25 – 400 (200)	Whatman GF/F in foil	Pass through GF/F filter. Fix with a saturated MgCO <sub>3</sub> solution. Freeze filter until analysis.	4 weeks
DIC and Alkalinity	300	300 ml glass BOD	Fix samples and transfer to MITSG personnel. Chill in the dark.	30 days
Phytoplankton (whole water)	800	1000 mL HDPE bottle	Preserve with Utermöhl's solution.	6 months
<i>Alexandrium</i>	4000	15 mL centrifuge tube	Strain through a 20-µm mesh netting; wash retained organisms into centrifuge tube. Preserve with formalin. Store upright in the dark on ice.	24 hours until transfer to methanol; 1 week <sup>c</sup>
Rapid phytoplankton	4000	1000-mL HDPE bottle	Strain through a 20-µm mesh netting; wash organisms into bottle; preserve with formalin and store in the dark.	6 days
<b>Sample from vertical net tow</b>				
Zooplankton	800	1000-mL HDPE bottle	Wash with screened seawater into jar. Preserve with formalin.	6 months

HDPE: High-density polyethylene

GF/F: pre-ashed glass fiber filter

<sup>a</sup> Conductivity, temperature, pressure, dissolved oxygen, chlorophyll *a* fluorescence, transmissivity, in situ irradiance, pH, surface irradiance, bottom depth, navigational position, date/time

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

<sup>c</sup>Although 24 hours is the optimal time frame, it is expected that the fluorescent probes will provide acceptable results on samples stored up to 1 week in formalin and on ice (Libby et al. 2013).

### B.2.5.1 DISSOLVED INORGANIC NUTRIENTS

Samples for dissolved inorganic nutrients will be processed according to Battelle SOP 8-266, *Nutrient Sample Processing*. A 60-mL syringe will be used to inject sample water from a transfer jar, through an in-line filter (Nucleopore 47-mm-diameter, 0.4-µm-membrane-fiber filter) and into a 125-mL white polyethylene (Nalgene) bottle. At the start and end of each survey day the 60-mL syringe is rinsed with 10% HCl solution then with Milli-Q. Additionally, the syringe is rinsed with Milli-Q between each station. The sample processing begins with the syringe receiving a triple rinse with site water. The bottle is then rinsed three times with filtered site water and 60 mL of site water is filtered into the bottle for analysis. The sample bottle will be labeled, and the sample will be frozen. The samples will remain frozen until analyzed. For the Task 5 Water Column surveys, a duplicate sample will be collected from the mid-depth (SCM) at stations F22, F23, N04, and N18 (1 duplicate analysis per 20 samples is required by DLS

[Constantino et al. 2017]). For the Task 6.1 ARRS surveys, a duplicate sample will be collected from the 10-m depth at stations AF1, F13, F22, and N18 (Libby et al 2013).

### **B.2.5.2 TOTAL DISSOLVED NITROGEN AND PHOSPHORUS**

Samples for total dissolved nitrogen and phosphorus (TDNP) will be processed according to Battelle SOP 8-266, *Nutrient Sample Processing*. A 60-mL aliquot will be obtained from the particulate phosphorus filtrate. The sample will be passed through a Whatman 47-mm-diameter GF/F and collected in a polysulfon filtration flask. A 125-mL high density polyethylene (Nalgene) bottle will be rinsed three times with filtrate, shaken to remove excess sample and then filled with approximately 60 mL of filtrate. Samples will be stored upright and frozen until analysis. A duplicate sample will be collected from the mid-depth (SCM) at stations F22, F23, N04, and N18 (1 duplicate analysis per 20 samples is required by DLS [Constantino et al. 2017]).

### **B.2.5.3 PARTICULATE CARBON AND NITROGEN**

Samples for particulate carbon and particulate nitrogen (PCN) will be processed according to Battelle SOP 8-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample will be filtered<sup>3</sup>, depending on particulate density. The samples will be collected on a precombusted 25-mm GF/F filter (nominal pore size 0.7 µm) using a vacuum-filter system. Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. A duplicate sample will be collected from the mid-depth (SCM) at each station. The second filter is for duplicate analysis (1 duplicate analysis per 20 samples is required by DLS [Constantino et al. 2017]).

### **B.2.5.4 PARTICULATE PHOSPHORUS**

Samples for particulate phosphorus (PP) will be processed according to Battelle SOP 8-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample<sup>3</sup> will be collected on 47-mm GF/F using a vacuum-filter system. Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. A duplicate sample will be collected from the mid-depth (SCM) at each station. The second filter is for duplicate analysis (1 duplicate analysis per 20 samples is required by DLS [Constantino et al. 2017]).

### **B.2.5.5 CHLOROPHYLL A AND PHAEOPHYTIN**

Samples for chlorophyll *a*/phaeophytin determination will be processed according to Battelle SOP 8-266, *Nutrient Sample Processing*. Between 25 and 400 mL sample<sup>3</sup> for chlorophyll *a* analysis will be collected on Whatman 25-mm-diameter GF/F using a vacuum-filter system. The final volume should result in a light green/brown residue on the filter and will be noted on the sample label. A saturated solution of MgCO<sub>3</sub> will be added to the sample during filtration to aid retention and buffer the sample against low pH (which converts chlorophyll to phaeophytin). Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. For the Task 5 Water Column surveys, a duplicate sample will be collected from the mid-depth (SCM) at each station. The second filter is for duplicate analysis (1 duplicate analysis per 20 samples is required by DLS [Constantino et al. 2017]). For the Task 6.1 ARRS surveys, a duplicate sample will be collected from the 10-m depth at stations F22 and N18 (Libby et al 2013).

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

### **B.2.5.6 DIC AND TOTAL ALKALINITY**

Water will be collected in a 300-mL BOD bottle at each of three depths (surface, mid-depth, and bottom) at stations F22, F23, N04 and N18. Using a hose (about 50-cm long) attached to the outlet on the Rosette sampling bottle, the BOD bottle will be filled from the bottom up with a minimum of bubbles and turbulence. After filling the sample bottles, the DIC/total alkalinity samples will be fixed with mercuric chloride (50  $\mu$ L of saturated HgCl<sub>2</sub> solution) as described in Dickson et al. (2007). The sample bottles will be kept cool and in the dark until the samples are analyzed. The samples will be transferred to MITSG for analysis.

### **B.2.5.7 WHOLE-WATER PHYTOPLANKTON**

Water from the Rosette sampling bottle will be poured into a graduated cylinder that has been cut at the 800-mL mark. Before filling the cylinder to 800 mL, it is rinsed twice with water from the Rosette sampling bottle. The filled cylinder is then poured into a 1-L bottle containing 8 mL of Utermöhl's solution preservative. The preserved samples are stored at ambient temperature and in the dark until analysis. The Utermöhl's solution is prepared as described in Guillard (1973): 100 g potassium iodide, 50 g iodine, and 50 g sodium acetate each are dissolved incrementally in distilled water to a final volume of 1 L. Sampling procedures are detailed in SOP 8-280 *Phytoplankton and Zooplankton Sample Collection*. The whole-water sample will be transferred to Pausacaco for analysis.

### **B.2.5.8 ALEXANDRIUM CATENELLA**

The *Alexandrium* samples will be collected as 4-liter 20- $\mu$ m screened samples from the surface and mid-depth waters. Each sample will be rinsed into a 15-mL centrifuge tube with filtered seawater (a funnel may be used), then the appropriate volume of formalin will be added. For example, if there are 14 mL of sample, 1 mL concentrated formalin (37% formaldehyde) will be added. *Alexandrium* samples are stored upright on ice and in the dark. The *Alexandrium* samples will be transferred to WHOI within 24 hours of the survey for processing and analysis. Although 24 hours is the optimal time frame, it is expected that the fluorescent probes will provide acceptable results on samples stored up to 1 week in formalin (Libby et al. 2013).

### **B.2.5.9 RAPID-ANALYSIS PHYTOPLANKTON**

For the rapid analysis samples, a 4-L graduated cylinder is rinsed twice and filled (to 4-L) with sample water from the Rosette sampling bottle. The water from the filled cylinder is passed through a 20- $\mu$ m-mesh screen. Using a squeeze bottle containing seawater that has passed through the 20- $\mu$ m-mesh screen, the seawater is squirted back through the screen to wash the retained plankton into a 1-L sample bottle and the sample will be preserved with enough formalin to produce a 5% formalin to seawater solution (e.g., 5 mL:100 mL). The plankton sample will be stored at ambient temperatures in the dark until analyzed. Sampling procedures are detailed in SOP 8-280 *Phytoplankton and Zooplankton Sample Collection*. The rapid analysis sample will be transferred to Pausacaco for immediate analysis.

## **B.2.6 ZOOPLANKTON SAMPLING**

A vertical-oblique zooplankton tow will be conducted with a 0.5-m diameter 102  $\mu$ m-mesh net equipped with a flow meter. Sampling procedures are detailed in SOP 8-280 *Phytoplankton and Zooplankton Sample Collection*. Tows will be in a vertical-oblique manner, 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 to 1500 turns. The initial reading will be subtracted from the final reading and recorded on the log sheet to confirm that this range has been met. If the reading does not fall within this range, the tow will be repeated, as above. The flow meter will not be 'rezeroed' between stations. This will provide a cross-check of the flow meter readings (i.e., the final reading from the previous station should be the initial reading of the current station). When the net does not clog and a sample is collected successfully, the material retained by the net will be transferred to a jar as described below. The flow meter reading before and after the tow, the tow time, and the depth of the tow will be recorded on the zooplankton measurement log (Figure B-5).

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

### **B.2.7 WHALE AND FLOATABLES OBSERVATIONS**

During water column surveys, a trained whale observer will conduct sighting watches while on station and during transit between stations. The sighting operations will occur during daylight hours. The observer will scan the ocean surface by eye for a minimum of 40 minutes every hour. The horizon will be swept 180° during transit between stations ( $\pm 90^\circ$  of heading) and 360° while on station. All sightings will be recorded on standardized marine mammal field sighting logs (Figure B-6). Header fields for sighting logs will include observer name and position on vessel; date; survey number; chief scientist, Captain, and vessel name. Data fields on sighting logs will include: time, vessel position and heading (every 10 minutes), sighting 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. The marine mammals observations will be submitted via HOML within one week of the survey. Although reporting of sightings of healthy right whales is voluntary for all vessels, reasonable effort will be made to report sightings within 12 hours by calling 866-755-6622, which reaches the North Atlantic Right Whale Sighting Advisory System (<http://www.nefsc.noaa.gov/psb/surveys/SAS.html>).

The whale observer and Battelle team field personnel will also observe the sea surface in the vicinity of the boat at each station and while underway and note the presence of anthropogenic debris/floatables (e.g., paper, plastics, and floating bits of fat), especially those potentially associated with wastewater (e.g., tampon applicators) in the station log. Particular attention will be paid while in the vicinity of stations N01, N18, and N21 (note that station N21 is above the outfall) and any notable observations at these three stations will be documented in the floatables table (Table B-8). These observations include visible plume, seagulls feeding along the diffuser line, fat particles visible (with a description), and other wastewater related or anthropogenic debris. No entry will be made if nothing is observed. The data table will be submitted to MWRA along with the hydrographic data. The observations will also be reported in the survey summary and survey report as described in Section B.1.5.

<h2 style="margin: 0;">Zooplankton Measurement Log</h2> <p style="margin: 0; font-size: small;">For Zooplankton Tow data for MWRA Nearfield Surveys</p> <p style="margin: 0; font-size: x-small;">Project Name: Harbor and Outfall Monitoring OP468    MWRA Project No. N00372</p>	
<p><b>Survey ID: WN241</b></p> <p>Station: F23</p> <p style="text-align: center; margin-top: 20px;">Label Here</p>	<p style="text-align: center;"><b>Protocol ID: ZO</b></p> <p>Ending Flowmeter Reading _____</p> <p>Starting Flowmeter Reading: _____</p> <p>Total Revolutions: _____</p> <p>Tow Time (mm:ss.ss) _____</p> <p>Depth of Tow (M) _____</p> <p>Formalin added (ml) _____</p> <p>Date: _____      Recorded by: _____</p>
<p>Station: N01</p> <p style="text-align: center; margin-top: 20px;">Label Here</p>	<p>Ending Flowmeter Reading _____</p> <p>Starting Flowmeter Reading: _____</p> <p>Total Revolutions: _____</p> <p>Tow Time (mm:ss.ss) _____</p> <p>Depth of Tow (M) _____</p> <p>Formalin added (ml) _____</p> <p>Date: _____      Recorded by: _____</p>
<p>Station: N04</p> <p style="text-align: center; margin-top: 20px;">Label Here</p>	<p>Ending Flowmeter Reading _____</p> <p>Starting Flowmeter Reading: _____</p> <p>Total Revolutions: _____</p> <p>Tow Time (mm:ss.ss) _____</p> <p>Depth of Tow (M) _____</p> <p>Formalin added (ml) _____</p> <p>Date: _____      Recorded by: _____</p>
<p>Station: F22</p> <p style="text-align: center; margin-top: 20px;">Label Here</p>	<p>Ending Flowmeter Reading _____</p> <p>Starting Flowmeter Reading: _____</p> <p>Total Revolutions: _____</p> <p>Tow Time (mm:ss.ss) _____</p> <p>Depth of Tow (M) _____</p> <p>Formalin added (ml) _____</p> <p>Date: _____      Recorded by: _____</p>
<p>Station: N18</p> <p style="text-align: center; margin-top: 20px;">Label Here</p>	<p>Ending Flowmeter Reading _____</p> <p>Starting Flowmeter Reading: _____</p> <p>Total Revolutions: _____</p> <p>Tow Time (mm:ss.ss) _____</p> <p>Depth of Tow (M) _____</p> <p>Formalin added (ml) _____</p> <p>Date: _____      Recorded by: _____</p>
<p>Station: N07</p> <p style="text-align: center; margin-top: 20px;">Label Here</p>	<p>Ending Flowmeter Reading _____</p> <p>Starting Flowmeter Reading: _____</p> <p>Total Revolutions: _____</p> <p>Tow Time (mm:ss.ss) _____</p> <p>Depth of Tow (M) _____</p> <p>Formalin added (ml) _____</p> <p>Date: _____      Recorded by: _____</p>

**Figure B-5. Example of a Zooplankton Measurement Log**



analyzed by DLS (e.g., plankton, and DIC and total alkalinity), Bottle IDs will be generated by concatenating the NavSam<sup>®</sup> *Sample ID* with the analysis code (Table B-9) 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 WN201 with “WN” indicating that it is a water column survey, “20” indicating the survey year, and “1” signifying the first survey of the year. 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.

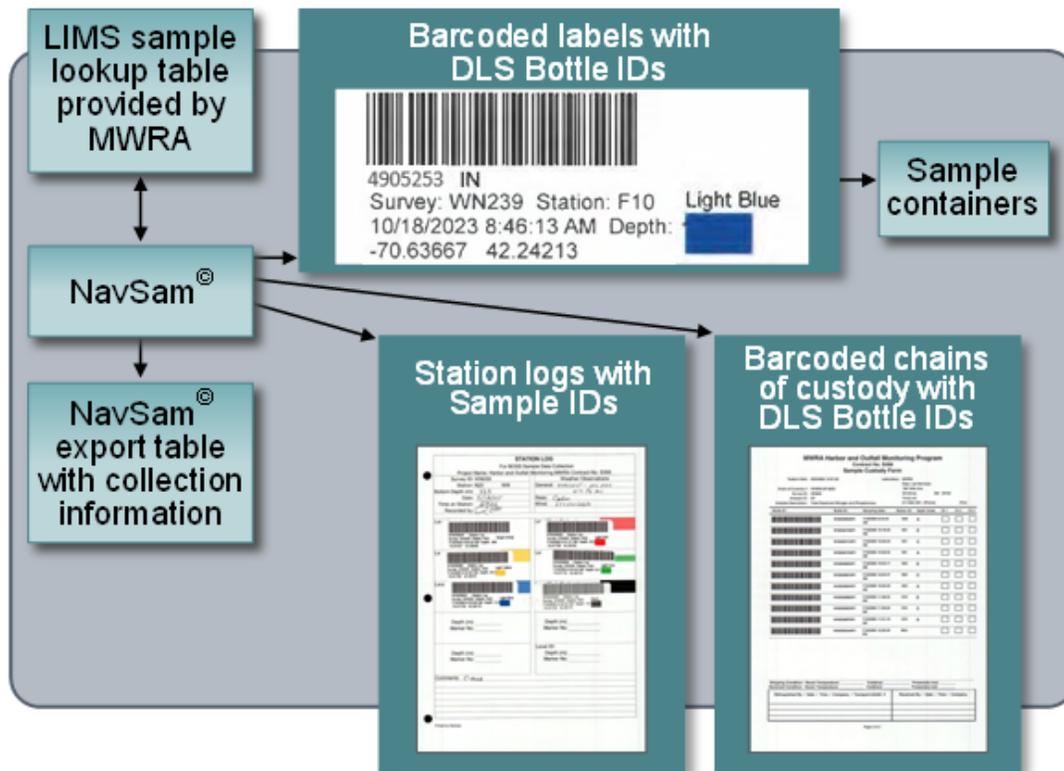


Figure B-7. Depiction of Linkage from DLS LIMS to NavSam<sup>®</sup>

Table B-9. Analysis Codes Used in Bottle ID or Used as Label Abbreviations

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

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

Battelle SOP 8-055 describes general sample chain-of-custody (custody) procedures; custody begins immediately upon sample collection:

- The chief scientist assumes custody of the samples and confirms that samples are stored at the QAPP-defined temperature while held on the survey vessel.
- Each sample bar code label is scanned following field collection as the sample is packed into laboratory specific coolers, and chain-of-custody forms are generated by NavSam<sup>®</sup> and printed. Custody forms document the project name, station ID, sample-type designation, DLS LIMS Bottle ID or NavSam<sup>®</sup> Bottle ID, sample date and time, and other pertinent sample information (Figure B-8, Figure B-9, and Figure B-10).
- The NavSam<sup>®</sup> Custody File is compared to the sample bottles and any discrepancies are resolved.
- When the custody of samples is transferred, the custody form will be signed by both the staff member that relinquishes custody and the staff member assuming custody for the samples.
- The relinquishing staff member will retain a photocopy of the signed chain.
- Upon receipt at the laboratory, the laboratory custodian compares bottle IDs to the chain-of-custody forms, verifies sample integrity and temperature, signs and dates the "Received By" section of the custody form, and logs the samples into the laboratory sample tracking system.

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

<b>STATION LOG</b> For BOSS Sample Data Collection Project Name: Harbor and Outfall Monitoring MWRA Contract No. OP466	
Survey ID: <u>WN241</u> Station: _____ Bottom Depth (m): _____ Date: _____ Time on Station: _____ Recorded by: _____	<b>Weather Observations</b> General: _____ Visibility: _____ Seas: _____ Wind: _____
Level ID: _____ Depth (m): _____ Marker No: _____	Level ID: _____ <span style="background-color: red; display: inline-block; width: 20px; height: 15px; vertical-align: middle;"></span> Depth (m): _____ Marker No: _____
Level ID: _____ <span style="background-color: yellow; display: inline-block; width: 20px; height: 15px; vertical-align: middle;"></span> Depth (m): _____ Marker No: _____	Level ID: _____ <span style="background-color: green; display: inline-block; width: 20px; height: 15px; vertical-align: middle;"></span> Depth (m): _____ Marker No: _____
Level ID: _____ <span style="background-color: blue; display: inline-block; width: 20px; height: 15px; vertical-align: middle;"></span> Depth (m): _____ Marker No: _____	Level ID: _____ <span style="background-color: black; display: inline-block; width: 20px; height: 15px; vertical-align: middle;"></span> Depth (m): _____ Marker No: _____
Level ID: _____ <span style="background-color: orange; display: inline-block; width: 20px; height: 15px; vertical-align: middle;"></span> Depth (m): _____ Marker No: _____	Level ID: _____ Depth (m): _____ Marker No: _____
Level ID: _____ Depth (m): _____ Marker No: _____	Level ID: _____ Depth (m): _____ Marker No: _____
Comments: _____ _____ _____ _____ _____	

Figure B-8. Example Station Log

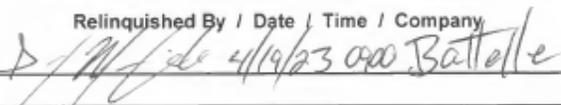
### MWRA Harbor and Outfall Monitoring Program Project No. 100041494 Sample Custody Form

Today's Date : 4/18/2023 4:36:14 PM      Laboratory : MWRA  
 Chain-of-Custody # : WN233-NP-0004      Dept. Lab Services  
 Survey ID : WN233      190 Tafts Ave  
 Analysis ID : NP      Winthrop MA 02152  
 Yong Lao  
 Analysis Description : Total Dissolved Nitrogen and Phosphorous      617-660-7841 (Phone)      (Fax)

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	4802564	4/18/2023 6:40:33 AM	BB1		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802568	4/18/2023 4:33:30 PM	BK3		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802569	4/18/2023 10:35:43 AM	BK2		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802570	4/18/2023 6:42:26 AM	BK1		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802635	4/18/2023 3:12:35 PM	F06	A	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802639	4/18/2023 3:11:49 PM	F06	B	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802646	4/18/2023 3:11:03 PM	F06	C	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802649	4/18/2023 3:10:10 PM	F06	D	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802652	4/18/2023 3:09:20 PM	F06	E	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802656	4/18/2023 2:30:20 PM	F10	A	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802660	4/18/2023 2:28:05 PM	F10	B	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802667	4/18/2023 2:29:30 PM	F10	C	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802670	4/18/2023 2:26:52 PM	F10	D	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802673	4/18/2023 2:25:54 PM	F10	E	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802677	4/18/2023 4:19:29 PM	F13	A	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	4802681	4/18/2023 4:18:03 PM	F13	B	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Shipping Condition - Room Temperature: \_\_\_\_\_ Cold(ice): \_\_\_\_\_ Frozen(ice):

Received Condition - Room Temperature: \_\_\_\_\_ Cold(ice): \_\_\_\_\_ Frozen(ice): \_\_\_\_\_

Relinquished By / Date / Time / Company 	Received By / Date / Time / Company  

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

## MWRA Harbor and Outfall Monitoring Program

### Project No. 100041494

### Sample Custody Form

Today's Date : 10/18/2023 1:58:20 PM

Laboratory : University of Massachusetts, Dartmouth

Chain-of-Custody # : WN239-ZO-0011

Survey ID : WN239

Analysis ID : ZO

Analysis Description : Zooplankton

Biology Department

285 OldWestport Road

North Dartmouth MA 02747-230

Dr. Jefferson Turner

508-999-8229 (Phone) 508-999-8197 (Fax)

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	WN239026ZO1	10/18/2023 8:17:57 AM	F06	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN239037ZO1	10/18/2023 8:46:13 AM	F10	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN239045ZO1	10/18/2023 9:16:50 AM	F15	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN239053ZO1	10/18/2023 9:39:32 AM	N07	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN239066ZO1	10/18/2023 10:06:12 AM	N18	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN239084ZO1	10/18/2023 11:20:18 AM	F22	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN239092ZO1	10/18/2023 11:51:01 AM	N04	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN2390A0ZO1	10/18/2023 12:21:54 PM	N01	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN2390AEZO1	10/18/2023 12:49:39 PM	F23	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	WN2390BCZO1	10/18/2023 1:35:52 PM	F13	Z	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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

Relinquished By / Date / Time / Company <i>C. Swangle</i> 10/19/23 11:00	Received By / Date / Time / Company <i>Jefferson Turner</i> 10/20/23

Figure B-10. Example of Custody Form with NavSam<sup>®</sup> generated IDs

### **B.3.2 CUSTODY OF ELECTRONIC DATA**

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

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

The DIC and total alkalinity data are not formal components of the MWRA HOM12 monitoring program and will remain in the custody of MITSG. These samples will be identified by the unique sample IDs, which will allow MITSG researchers to request associated data from the MWRA EMMS database.

### **B.3.3 CUSTODY OF WATER SAMPLES**

Following field collection, NavSam<sup>®</sup> will create chain-of-custody forms from the sample table used to generate sample labels, thereby creating a link between the sample and data recorded on the chain of custody form. The chain of custody forms will have the same Bottle ID (LIMS or NavSam<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 and is responsible for verifying each Bottle ID versus the custody forms generated by NavSam<sup>®</sup> prior to delivering the samples to the laboratory.

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

Upon receipt of the samples at each laboratory, the designated sample custodian will examine the samples, verify that sample-specific information recorded on the chain is accurate and that the sample

integrity is uncompromised, log the samples into the laboratory tracking system, complete the custody forms, and sign the chain form so that transfer of custody of the samples is complete. Any discrepancies between sample labels and transmittal forms, and unusual events or deviations from the project QAPP will be documented in detail on the chain and the Battelle Field Manager will be notified. The designated sample custodian at each laboratory will then sign and keep the original chain-of-custody forms. Copies of the signed chain of custody will be e-mailed to the Battelle Field Manager within 24 hours of receipt. The original chain forms will be submitted with the data submission and maintained in the Sample Custody Logbook. 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 (Constantino et al. 2017) for nutrient, and chlorophyll analyses for outfall monitoring:

- Dissolved inorganic nutrients
- Total dissolved nitrogen and phosphorus
- Particulate carbon and nitrogen
- Particulate phosphorus
- Chlorophyll *a* and phaeophytin

### **B.4.1 WHOLE-WATER PHYTOPLANKTON**

The methods discussed below have been used for the identification and enumeration of phytoplankton species during HOM3 through HOM11 and will continue to be used on HOM12. At the laboratory, Utermöhl's-preserved whole seawater samples will be prepared for analysis by concentrating the sample by gravitational settling as described by Borkman (1994), Borkman et al. (1993), and Turner et al. (1995). The method is similar to the methods of Hasle (1959), Iriarte and Fryxell (1995), and Sukhanova (1978). Samples will be settled in graduated cylinders with no more than a 5-to-1 height-to-width ratio.

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

$$[1 \text{ cell}/4 \text{ paths} * 48 \text{ paths} / 1\text{ml S-R} * 50\text{ml settling volume}] / 0.8 \text{ L seawater} = 750 \text{ cells L}^{-1}.$$

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

#### **B.4.2 ALEXANDRIUM SAMPLES**

The *Alexandrium* samples will be identified, counted, and quantified using a fluorescent probe technique. These methods have been used during the ARRS surveys during HOM4 through HOM11 (Libby et al. 2013) and will continue to be used on HOM12. The samples will be delivered to WHOI typically within 24 hours of the survey where the sample will be centrifuged and the formalin removed by aspiration leaving the pellet intact. The pellet will then be resuspended with 100% cold methanol for analysis and storage. For optimal results, this process should occur within 24 hours after fixation in formalin. The sample cannot tolerate long time periods in formalin because the rRNA signal in the cell is lost due to excessive cross-linking of the nucleic acids by the formalin. Although 24 hours is the optimal time frame, it is expected that the fluorescent probes will provide acceptable results on samples stored up to 1 week in formalin (Libby et al. 2013).

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

#### **B.4.3 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 catenella*, *Dinophysis* spp., *Karenia mikimotoi*, *Margalefidinium* spp., *Phaeocystis pouchetii*, *Pseudo-nitzschia* spp.). Within 6 days of sample receipt at the counting laboratory, an aliquot of this sample will be qualitatively analyzed using the Sedgwick-Rafter counting cell and viewed through an Olympus BH-2 compound microscope (phase-contrast optics) to quickly verify the presence or absence of nuisance species. The analysis will also produce a qualitative impression of the types and abundance of dominant taxa. These results will be reported in the Survey Summary and Survey Report, as well as by e-mail prior to the Survey Summary if possible.

#### **B.4.4 ZOOPLANKTON**

The methods discussed below have been used for the identification and enumeration of zooplankton species during HOM3 through HOM11 and will continue to be used on HOM12. At the lab, each sample for zooplankton is transferred to 70% ethanol solution to prevent inhalation of formalin fumes during counting. Samples are reduced to aliquots of at least 250 animals with a Folsom plankton splitter, and animals are counted under a dissecting microscope and identified to the lowest possible taxon. In most cases, this will be to species; adult copepods will be additionally characterized by sex. Counts of all copepodite stages of a given copepod genus will be combined. Copepod nauplii will not be identified to genus or species because nauplii species cannot be reliably identified to those levels by using a dissecting microscope. Meroplankters cannot be identified to genus or species in most cases, and such organisms will be identified to the lowest reliable taxon, such as barnacle nauplii, fish eggs, or gastropod veligers.

The concentrations of total zooplankton and all identified taxa are calculated based on the number of animals counted, multiplied by the aliquot concentration factor, and divided by the volume of filtered by the net. For instance, if 400 animals were counted in a 1/256 split, and the volume filtered was 4.2 cubic meters, then the calculation would be  $400 \times 256 = 102,400$ , and  $102,400$  divided by  $4.2 = 24,381$  animals per cubic meter.

## **B.5 QUALITY CONTROL**

### **B.5.1 FIELD PROGRAM**

Field QC samples are defined in Table B-10 (Water Column surveys) and Table B-11 (ARRS surveys). 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-10 and B-11.

### **B.5.2 DECONTAMINATION**

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

### **B.5.3 FIELD BLANKS**

Field blank processing for dissolved parameters follows the same procedures used for sample processing, but with Milli-Q water in place of seawater. Milli-Q water is supplied by DLS. For dissolved inorganic nutrients, field blanks are collected using syringes and filter cartridges. TDNP field blanks are collected from the PP filtration flasks after processing Milli-Q through a glass fiber filter like a regular sample. Filter blanks are collected for PCN, PP, and chlorophyll by placing a new, unused filter directly into the appropriate sample container (foil packet). Tables B-10 and B-11 detail the collection of field blank samples. All samples will be labeled with a bar-coded label produced by NavSam<sup>®</sup> and then stored in the freezer. In addition to the processed field blanks, bottle blanks will be collected at the same time as the morning field blank for dissolved inorganic nutrients and TDNP. The bottle blank is used to evaluate non-processing elements of contamination (e.g., Milli-Q, sample containers, etc.). The bottle blank will consist of a clean, unused sample bottle filled with the Milli-Q water supplied by DLS without a triple rinse. These samples will be labeled with a bar-coded label produced by NavSam<sup>®</sup> and stored in the freezer. A duplicate label for each field blank is pasted into the survey logbook. MWRA will use the results of the field blanks to assess the impact of field and laboratory-related contamination on water samples.

### **B.5.4 FIELD REPLICATES**

Field replicates are taken at several stations each day. Replicates consist of the processing of a second sample from the upcast in the exact manner as the primary sample. Replicates provide information regarding the variability of samples processed in the field. Table B-10 and B-11 detail the collection of field replicate samples.

**Table B-10. QA/QC Samples for Water Column Surveys.**

Analysis Type	Quantity	Depths	Stations
<b>Field Replicates</b>			
Dissolved inorganic nutrients	1	Mid-depth	F22, F23, N04, and N18
TDNP	1	Mid-depth	F22, F23, N04, and N18
Chlorophyll, PP, PCN	1	Mid-depth	All stations
DIC and total alkalinity	1	Mid-depth	F22 and N01
<b>Blanks</b>			
Filter Blank: Chlorophyll, PCN, PP	2/day/parameter	NA	Collected at the beginning and end of the sampling day.
Field Blank: Dissolved inorganic nutrients, 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. Mid-day blanks will typically be collected between N21 and F22.
Bottle Blank: Dissolved inorganic nutrients, TDNP	1/day	NA	One blank per container type at the beginning of each day

**Table B-11. QA/QC Samples for ARRS Surveys.**

Analysis Type	Quantity	Depths	Stations
<b>Field Replicates</b>			
Dissolved inorganic nutrients	1	10 m	AF1, F13, F22, N18
Chlorophyll	1	10 m	F22, N18
<b>Blanks</b>			
Filter Blank: Chlorophyll	2/day/parameter	NA	Collected at the beginning and end of the sampling day.
Field Blank: Dissolved inorganic nutrients	3/day/parameter	NA	One blank for each analysis will be collected at the beginning of the day, mid-day, and at the end of the day. Mid-day blanks will typically be collected between N21 and F22.
Bottle Blank: Dissolved inorganic nutrients	1/day	NA	One blank per container type at the beginning of each day

### B.5.5 LABORATORY PROGRAM

Section B.4 details the analytical procedures that will ensure data quality; Section B.6 describes instrument calibration methods.

### B.5.6 PRECISION AND ACCURACY

Precision and accuracy of DLS laboratory procedures are assessed through the analysis of QC samples including procedural/filter blanks, prepared standards, standard reference materials (SRMs), laboratory replicates and field replicates, as applicable. Measures of precision and accuracy for analysis performed by DLS are described in Constantino et al. (2017). The QC procedures used to assess accuracy and precision of phytoplankton and zooplankton methods are described below.

### **B.5.6.1 WHOLE-WATER PHYTOPLANKTON**

Based on a study conducted by Guillard (1973), counts of 400 phytoplankton cells will provide a precision of  $\pm 10\%$  of the mean. Following the analytical protocols described in Section B.4.1, for this program, a minimum of 400 entities (solitary single cells, chains, or colonies) will be tallied for each sample. Unicellular forms (e.g., *Cryptomonas* spp., microflagellates), aggregate forms (e.g., *Phaeocystis pouchetii*), and chained forms (e.g., *Skeletonema* spp.) will each count as one entity towards the 400-entities-counted-per-sample minimum tally. To increase precision of the abundance estimates for the most abundant taxa, when practical at least 75 entities of each of the three most abundant taxa will be counted in each sample. The overall goal is to enumerate a minimum of 400 entities total and the 3 most abundant taxa to at least 75 entities each. An additional data quality procedure will be performed on the whole water phytoplankton samples. A subset of samples will be counted in duplicate by a different taxonomist or as a blind recount by the same taxonomist to provide an estimate of the variability in the analysis and quantify the accuracy and comparability of the results. One whole water sample from each of the water column surveys will be analyzed in duplicate. The results, as relative percent difference (RPD), will be included in the data submission to Battelle as an estimate of the variability in the analysis. The precision method quality objective (MQO) for the total and the single most dominant species is  $\leq 20\%$ . If the RPD is greater than 20 a second aliquot will be counted and the three results used to calculate the relative standard deviation [RSD; (standard deviation  $\times$  100)/average)], which should be  $\leq 20\%$ . If the RSD is  $> 20\%$ , then the Technical Manager will assess the impact and a comment will be added to the database, as appropriate.

### **B.5.6.2 ALEXANDRIUM**

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

### **B.5.6.3 ZOOPLANKTON**

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

## **B.5.7 COMPLETENESS**

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

### **B.5.8 COMPARABILITY**

Data will be directly comparable to results obtained previously at the same or similar sites in Massachusetts Bay and to those of similar studies conducted in Cape Cod Bay (Albro et al. 1993; Bowen et al. 1998; Libby et al. 2002, 2005, 2006, 2009, 2010, 2011, 2013, 2014, 2018, 2020, 2021, and 2023), because field program design and analytical procedures are similar or identical. In addition, the use of written standardized procedures ensures that sample preparation and analyses will be comparable throughout the project and with other projects. Specific, potential comparability issues are addressed in Albro et al. (1998).

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

### **B.5.9 REPRESENTATIVENESS**

Representativeness is addressed primarily in sampling design. The laboratory measurements that will be made during the water quality monitoring task have already been used in many systems to characterize eutrophication effects on the water column and are, therefore, considered to yield data representative of the study area. Representativeness will also be ensured by proper handling, storage (including appropriate preservation and holding times), and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

Deviations from the analytical scheme described in this QAPP will be noted in the laboratory records associated with analytical batches and in the QA statements provided to MWRA with the data. Significant deviations will be discussed in the quarterly QA/QC Corrective Action reports.

### **B.5.10 SENSITIVITY**

Sensitivity is the capability of methodology or instrumentation to discriminate among measurement responses for quantitative differences of a parameter of interest. The MDL and instrument detection limit (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 (Constantino et al. 2017).

## **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 recalibration. See the following sections for the appropriate calibration frequencies. 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 setup files. The setup and verification will be documented in the survey logbooks.

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

## **B.6.1 HYDROGRAPHIC PROFILING EQUIPMENT**

### **B.6.1.1 PRESSURE (DEPTH) SENSOR**

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

### **B.6.1.2 TEMPERATURE AND CONDUCTIVITY**

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

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

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

### **B.6.1.3 ALTIMETER**

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

### **B.6.1.4 pH**

The software gain and offset of the pH sensors (Sea-Bird Model 18) will be calibrated annually at Sea-Bird. The calibration settings may be changed thereafter using manufacturer software in conjunction with results from benchtop calibrations using factory supplied standards. The pH 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, soak in deionized water for at least 2 hours, and then stored in 4-Molar potassium chloride buffer saturated with silver chloride.

### **B.6.1.5 DISSOLVED OXYGEN**

The software gain and offset of the DO sensors (Sea-Bird Model 43) will be calibrated at Sea-Bird. Calibration and pre-survey checks of the DO sensor will be conducted in a water-saturated air

environment as described in Battelle SOP 8-180. If the readings are more than  $\pm 5\%$  from 100% saturation, the probe will be examined and replaced if necessary, prior to sampling. Sensors that cannot meet this criterion will be sent back to Sea-Bird for inspection and recalibration. The sensor check file confirming the DO results are  $\pm 5\%$  from 100% saturation will be stored with the NavSam survey data. 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.6.1.6 TRANSMISSOMETER**

The WET Labs C-Star transmissometer is calibrated 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 and calibrations will be conducted as specified in Battelle SOP 8-174.

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.6.1.7 IN SITU CHLOROPHYLL A FLUOROMETER**

The WETStar fluorometer is sent to the manufacturer for maintenance and recalibration as specified in Battelle SOP 8-163. A review of the calibration coefficients for this instrument indicates it is stable from year to year. The factory calibration is based on instrument response in distilled water and a 0.5 mg/L coproporphyrin standard solution (fluorescence signal equivalent to 50  $\mu\text{g/L}$  chlorophyll in a *Thalassiosira weissflogii* phytoplankton culture). The fluorometer data, displayed with the NavSam<sup>®</sup> program, will approach 0.0  $\mu\text{g/L}$  when the instrument is on deck. The on-deck reading will be checked prior to each survey day. Then, when the CTD is in the water, the reading will again be checked for a reasonable value. Errant readings will instigate corrective action. All errant readings and resultant corrective actions will be noted in the survey logbook. As daily maintenance, the fluorometer will be rinsed with deionized water. The in situ fluorescence readings will be calibrated by MWRA (Hersh and Leo 2012) using the chlorophyll *a* data measured in the laboratory from discrete bottle samples.

#### **B.6.1.8 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-2200 and QSR-2240 (On-deck Irradiance Sensor)**

The Biospherical Instruments Solar Reference Scalar Irradiance Sensors QSR-2200 and QSR-2240 are virtually identical except for model number. The QSR-2200/-2240 are 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-2200/-2240 sensor measures the sunlight in air to provide the reference ambient irradiance and the QSP-200PD underwater sensor measures the sunlight penetrating the water column at depth.

The QSR-2200/-2240 sensor is calibrated by Biospherical Instruments Inc as specified in Battelle SOP 8-127. In addition, this instrument should be checked every 2 to 3 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  $\mu\text{E m}^{-2}\text{sec}^{-1}$  depending upon the time of year. Any deviation of >40% is strong evidence of a problem. Whenever the instrument's calibration is in question for any reason, the instrument will be returned to Biospherical Instruments for recalibration and examination. Additionally, prior to each survey the sensor will be capped (dark), and an average of at least 20 readings will be recorded in the survey electronic files. The average reading should be  $0 \pm 10 \mu\text{E m}^{-2}\text{sec}^{-1}$ .

The Teflon<sup>®</sup> collector sphere of the QSR-2200/-2240 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 to 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<sup>®</sup> sphere. A qualified technician will conduct maintenance. Battelle SOP 8-127 for Biospherical Irradiance Sensors provides a complete description of the setup, use, calibration and maintenance of the QSR-2200/-2240 On-deck Irradiance Sensor.

#### **QSP-200PD (Underwater Irradiance Sensor)**

The Biospherical Instruments Logarithmic Output Oceanographic Light Transducer (QSP-200PD) is calibrated using a National Institute of Standards and Technology traceable 1000-watt type FEL Standard of Spectral Irradiance. Biospherical Instruments Inc. performs instrument calibration. The Battelle Calibration Results Check Sheet for Biospherical Irradiance Sensor QSP-200PD 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-2200/-2240 surface irradiance sensor. The values from the QSP-200PD sensor should be close to zero for the dark reading and approximately 40 to 50% higher than the surface irradiance sensor for the uncovered reading on deck. The difference in the readings between the two sensors is caused by field-of-view differences and a correction factor is applied to the underwater sensor to account for its lower collection efficiency when immersed. Calibration data are stored in the field equipment files (initial) or the survey log (daily survey check). The capped readings will be entered into the NavSam<sup>®</sup> calibration coefficient entry form as an offset, which will bring the on deck dark readings close to zero.

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

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

The QSP-200PD 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.6.1.9 NAVIGATION EQUIPMENT**

Once the Furuno GP330B dGPS has been switched on and plugged into the NavSam<sup>®</sup> computer, 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 checks will be performed by Battelle's NavSam operator twice per day (start and end of survey operations) as follows:

1. An absolute position is obtained for a land-based calibration point (published positions or repeat visits with multiple dGPS readings). Alternatively, if a land-based calibration point is not available and a second GPS is available, the coordinates from the second GPS can be used for the absolute position. (Note that there are two separate Furuno GP330B dGPS on the R/V *Tioga* that are used for this cross calibration.)
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, NavSam<sup>®</sup> will save a screen capture to the program files directory.

### **B.6.1.10 ROSETTE SAMPLING BOTTLES**

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

### **B.6.1.11 NETS AND FLOWMETER**

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

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

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 (Constantino et al. 2017).

## **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 survey or before analysis begins. Supplies and consumables consist of sample containers, filters, filtration apparatus, preservation solutions (*e.g.*, formalin, Utermöhl's solution), deionized water, laboratory reagents, and standards.

- Sample containers are either cleaned by the laboratory or purchased new. Containers must be cleaned according to SOPs prior to use and must be rinsed three times with station water prior to being filled with sample. Field blanks assess potential contamination of containers and sampling equipment.

- All filtering equipment (the filtering apparatus and graduated cylinders) are cleaned daily prior to use. The equipment gets a 10% HCl rinse in the morning followed by a triple rinse of Milli-Q water. Between stations the equipment gets a triple rinse with Milli-Q.
- Filters for chlorophyll and dissolved nutrients are used directly from the manufacturer and are not cleaned or treated. Filters for particulate carbon and nitrogen are precombusted and supplied by MWRA.
- Preservation solutions must be prepared using at least reagent grade chemicals and high-performance liquid chromatography (HPLC) grade solvents. Solutions must be assigned an expiration date of 1 year.
- Milli-Q water must be collected into cleaned containers and refreshed prior to each survey.
- Laboratory reagents must be at least reagent grade. Dry reagents must be assigned an expiration date of no more than 5 years; be stored in a clean, desiccated environment, away from light, and be traceable to receipt and certificate of analysis. Reagent solutions must be assigned an expiration date of no more than 1 year and be stored appropriately. Each laboratory must maintain a chemical tracking inventory.

## **B.9 NONDIRECT MEASUREMENTS**

The HOM12 monitoring program utilizes data from previous programs, other Massachusetts Bay monitoring programs, satellite imagery and mooring data, in order to continually assess the state of Boston Harbor and Massachusetts Bay. These secondary data are used “as received” and not censored.

## **B.10 DATA MANAGEMENT (TASK 4)**

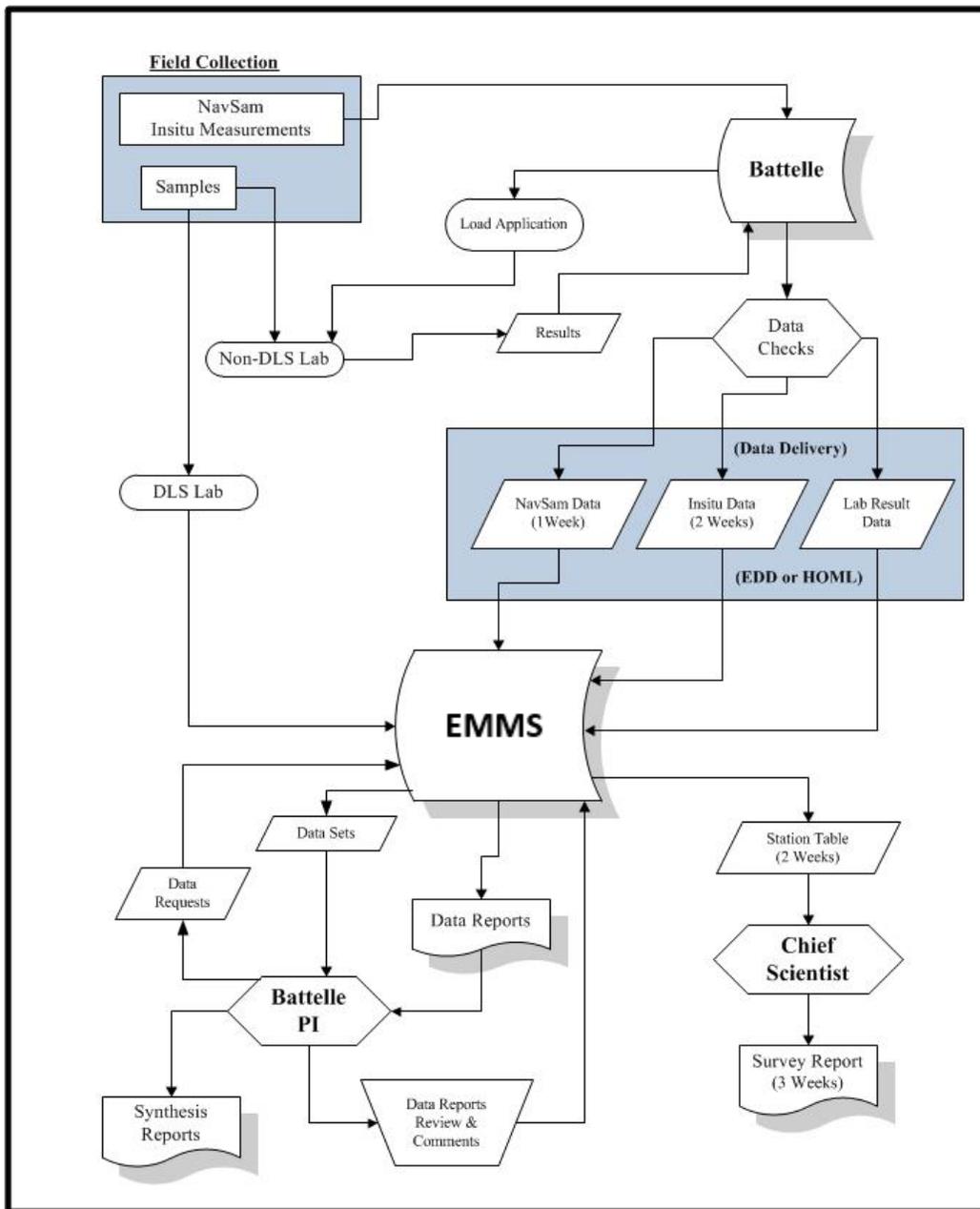
Figure B-11 illustrates the water-column-monitoring data processing strategy for data entry into the MWRA EMMS and accessing the data for various reports. The data from the program will be compared by MWRA to the caution and warning threshold parameters included in the MWRA Contingency Plan (MWRA 2001).

### **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, pH, fluorescence, transmissivity, underwater light levels, total incident radiation, and bathymetry. The NavSam<sup>®</sup> 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. Salinity and density are calculated from temperature, conductivity and depth using the equations of Fofonoff and Millard (1983), and DO percent saturation is calculated from DO concentration, temperature, and salinity using the equations of Weiss (1970). The station arrival time is marked 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 or another method will be used to visually review the profiles and mark any data as bad or suspect as appropriate. (If an alternative method is used, it will be documented in the deliverable letter submitted with the Oracle<sup>®</sup> export). After the editing is complete, the profile upcast data recorded during discrete water sample collection will be processed. NavSam<sup>®</sup> post-processing will result in two tables. The first will contain the downcast data that excludes the ship’s upward motions and is averaged to 0.5-m depth bins. The second table will average the upcast data corresponding to discrete samples (data within  $\pm 2.5$  seconds of the moment of bottle closing). These files will serve as the export file to the EMMS database.



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

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

### **B.10.1.2 LABORATORY DATA**

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

### **B.10.2 REPORTING DATA TO BE LOADED INTO THE DATABASE**

Before being loaded into EMMS, all field and non-DLS laboratory data 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 with a loading application based on collection data that will increase data quality and data flow efficiency. These applications eliminate the need for data reporting formats and deliver many of the QC checks upstream to the laboratories. Formats for delivering electronic data are included in the contract but these formats are subject to change. The current delivery formats are available from the data management lead at Battelle (Matt Fitzpatrick) or the data management lead at MWRA (Doug Hersh). Battelle's data management staff will process all data into the appropriate HOML format as defined in the contract. These submissions will be delivered electronically through MWRA's HOML web application.

#### **B.10.2.1 NAVIGATION AND SAMPLE COLLECTION DATA**

Navigation and sample collection data will be processed onboard 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 EMMS 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 Battelle's project-specific MWRA SOP 001: *Post-Survey CTD Water Column Data Processing*.

#### **B.10.2.2 HYDROGRAPHIC DATA**

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

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

A database application will be used to load the hydrographic data from the processing database directly into Battelle's database. Table B-12 shows the database codes for the hydrographic parameters. Database constraints will be in place to provide an initial check of the data integrity and validity.

**Table B-12. Database Codes for Hydrographic Parameters**

Parameter	Param_Code	Unit_Code	Instr_Code <sup>1</sup>	Meth_Code
Conductivity	CONDTVY	mS/cm	SB4 ( <i>Serial Number</i> )	BOSS
Dissolved oxygen	DISS_OXYGEN	mg/L	DO3 ( <i>Serial Number</i> )	BOSS
Raw fluorescence (not calibrated)	FLU_RAW	ug/L	WS ( <i>Serial Number</i> )	BOSS
in situ Irradiance level	LIGHT	uEm-2sec-1	LIG4 ( <i>Serial Number</i> )	BOSS
Salinity	SAL	PSU	SB4 ( <i>Serial Number</i> )	BOSS
Density as measured by sigma-t	SIGMA_T		SB4 ( <i>Serial Number</i> )	BOSS
Surface irradiance level	SURFACE_IRRAD	uEm-2sec-1	LIG2 ( <i>Serial Number</i> )	BOSS
Temperature	TEMP	C	SB3 ( <i>Serial Number</i> )	BOSS
pH	PH		SB18 ( <i>Serial Number</i> )	BOSS
Transmissivity	TRANS	m-1	T1R25 ( <i>Serial Number</i> )	BOSS
Dissolved oxygen percent saturation	PCT_SAT	PCT	DO3 ( <i>Serial Number</i> )	BOSS

<sup>1</sup> Instrument codes: (*Serial Number*) indicates unique probe serial number; in the case of DO\_3, the membrane thickness may also be included for instrument serial number 448

### B.10.2.3 ANALYTICAL AND EXPERIMENTAL DATA

The data reporting for analytical and experimental data begins with the Battelle Data Management Team who will populate a loading application that is then sent to each non-DLS laboratory for their data entry. As defined above, the collection data from field activities are delivered to the data manager as an Access database. Sample IDs and analysis protocols are extracted from this database and used to populate a table within the laboratory loading application. A separate loading application is prepared for each data deliverable. Data contributors open the database and are presented with a form that already contains the Sample IDs and analyte list for their data submittal (Figure B-12). The laboratory enters the results and other supporting information such as qualifiers. All entries are constrained by the rules of EMMS. 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 1 day of training on the application prior to their first set of samples. When data entry is complete, the loading application is sent back to Battelle.

The loading application provides the laboratory many available functions (Figure B-13), including hardcopy report, QC checks, exception report, and analysis summary. The hardcopy report function allows the laboratory to create a hardcopy report to check for entry errors and to submit a final report to Battelle with the data deliverable. The QC checks are comprised of the applicable sections of EMMS 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 are translated into the correct codes and inserted into database tables with the same structure as the matching EMMS table. Table B-13 shows the qualifiers to be used by the laboratory. Database codes for plankton taxonomy and species qualifiers are presented in Table B-14 and Table B-15, respectively.

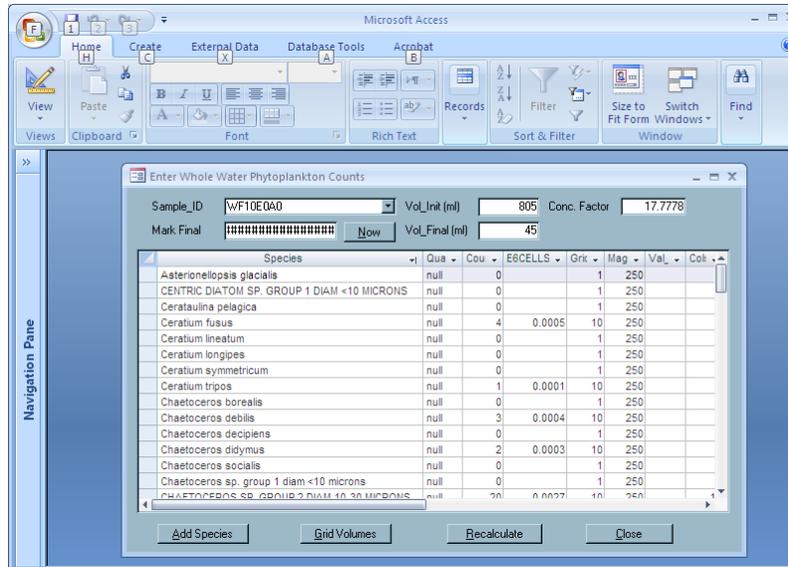


Figure B-12. Example of Loading Application Data Entry Form

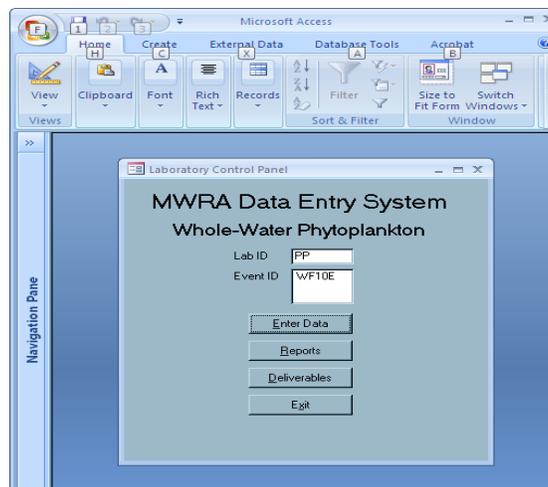


Figure B-13. Loading Application Main Menu

Database code descriptions are provided in Table B-16. 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 EMMS code list table. MWRA has the responsibility for maintaining the code list for the EMMS. A laboratory submission is not accepted as complete unless it includes the QA statement, QA/QC corrective action log, electronic data, hardcopy data report, exceptions report, and analysis summary. Processing of laboratory data is further described in MWRA SOP 004, *Loading and Reporting Water Column Data*.

**Table B-13. Laboratory Qualifiers**

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

**Table B-14. Database Codes for Plankton Taxonomy**

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

### **B.10.3 LOADING ANALYTICAL AND EXPERIMENTAL DATA INTO THE EMMS DATABASE**

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

### **B.10.4 REPORTING DATA TO MWRA**

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

**Table B-15. Database Codes for Species Qualifiers**

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

**Table B-16. Description of Database Codes**

<b>Field Name</b>	<b>Code</b>	<b>Description</b>
ANAL LAB ID	BOS	Battelle, Norwell, MA
ANAL LAB ID	DIL	MWRA Department of Laboratory Services, Winthrop, MA
ANAL LAB ID	UMD	University of Massachusetts, Dartmouth, MA
ANAL LAB ID	PP	Pausacaco Plankton, Saunderstown, RI
ANAL LAB ID	WHO6	Woods Hole Oceanographic, Woods Hole, MA (D. Anderson)
DEPTH UNIT CODE	m	Meters
INSTR_CODE	DO3 <i>(Serial Number)</i>	Sea-Bird D.O. probe, model SBE-43
INSTR_CODE	LIG2 <i>(Serial Number)</i>	Biospherical model QSR-2200 or QSR-2240 hemispherical scalar irradiance sensor
INSTR_CODE	LIG4 <i>(Serial Number)</i>	Biospherical Instruments QSP-200PD: quantum scalar irradiance profiling sensor
INSTR_CODE	S18 <i>(Serial Number)</i>	SeaBird pH sensor, model SBE-18, serial number <i>(Serial Number)</i>
INSTR_CODE	SB3 <i>(Serial Number)</i>	Sea-Bird temperature sensor, model SBE-3
INSTR_CODE	SB4 <i>(Serial Number)</i>	Sea-Bird conductivity sensor, model SBE-4C
INSTR_CODE	T1R25 <i>(Serial Number)</i>	WET Labs C-Star 25cm transmissometer 660 nm fixed wavelength
INSTR_CODE	TOC_1010	OI model 1010 TOC analyzer
INSTR_CODE	WS <i>(Serial Number)</i>	WETStar miniature fluorometer, model ws-3-mf-p
METH_CODE	BOSS	Battelle Ocean Sampling System
METH_CODE	COU_WW	Enumeration method for whole-water phytoplankton (Libby et al. 2002)
METH_CODE	COU_ZO	Enumeration method for zooplankton (Libby et al. 2002)
METH_CODE	NA1	Enumeration of <i>Alexandrium</i> (Anderson et al. 2005)
SAMP_VOL_UNIT_CODE	L	Liter
UNIT_CODE	C	Degrees Celsius
UNIT_CODE	CELLS/L	Cells per liter
UNIT_CODE	db	Decibars
UNIT_CODE	E6CELLS/L	Millions of cells per liter
UNIT_CODE	ind/m3	Individuals per cubic meter
UNIT_CODE	m-1	Inverse meters
UNIT_CODE	mg/L	Milligrams per liter
UNIT_CODE	PSU	Practical salinity units
UNIT_CODE	uEm-2sec-1	Micro-Einsteins per square meter per second
UNIT_CODE	ug/L	Micrograms per liter
UNIT_CODE	mS/cm	Millisiemens per centimeter
UNIT_CODE	PCT	Percent

## **C ASSESSMENT AND OVERSIGHT**

### **C.1 ASSESSMENTS AND RESPONSE ACTIONS**

#### **C.1.1 PERFORMANCE AND SYSTEM AUDITS**

The Battelle QAO for the HOM12 Project is Mr. Zachary Willenberg. He will direct the conduct of at least one technical systems audit (TSA) to ensure that Tasks 4, 5, and 7 are carried out in accordance with this QAPP. A systems audit will verify the implementation of the Battelle QMP and this QAPP.

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

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

In addition to the TSA, the Battelle QAO will conduct laboratory and field inspections as needed to assess compliance with the QMP and this QAPP.

#### **C.1.2 CORRECTIVE ACTION**

All technical personnel share responsibility for identifying and resolving problems encountered in the routine performance of their duties. Ms. Ellen Baptiste Carpenter, Battelle's Project Manager, will be accountable to MWRA and to Battelle management for overall conduct of the HOM12 project, including the schedule, costs, and technical performance. She is responsible for identifying and resolving problems that (1) have not been addressed timely or successfully at a lower level, (2) influence multiple components of the project, (3) necessitate changes in this QAPP, or (4) require consultation with Battelle management or with MWRA. Mr. Scott Libby is the Battelle Technical Manager and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise.

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

### **C.2 REPORTS TO MANAGEMENT**

It is important that data quality issues be reported to the appropriate management level so that appropriate solutions are implemented. Data or performance quality issues are reported to Battelle management team in real time via e-mail. Action items are discussed, assigned, and results reported to the QAO. Persistent project issues that are not addressed satisfactorily by the project manager are reported to Battelle's

Environment Division Manager during QA review meetings. In addition, data quality and performance issues are reported in the corrective action log submitted to MWRA each quarter and are discussed during the monthly management meetings, as necessary.

## **D DATA VALIDATION AND USABILITY**

### **D.1 DATA REVIEW, VERIFICATION, AND VALIDATION**

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

### **D.2 VALIDATION AND VERIFICATION METHODS**

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

Field sampling data are verified through the chain-of-custody process that compares NavSam<sup>®</sup> Bottle IDs to sample bottle labels. Sampling documentation is verified through the review and approval of each survey logbook by the field manager. Entry of field sample data in EMMS is verified when the QA Officer audits the survey report versus the survey logbook 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.
- Calculations performed by software are verified at a frequency sufficient to ensure that the formulas are correct, appropriate, and consistent, and that calculations are accurately reported. All modifications to data reduction algorithms are verified prior to submission of data to MWRA.

Data validation is performed by reviewing holding times, instrument calibration results, and QC sample results. The criteria for these data quality requirements are presented in Sections A.7, B.5, B.6, B.7, and B.8. Data qualifiers (Table B-13) and comments are used to define in the database the usability of the data.

### **D.3 RECONCILIATION WITH USER REQUIREMENTS**

Several procedures are used to assess the usability of the data. During generation of the data reports, MWRA will run QC checks of the EMMS 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.

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

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**Appendix I**  
**MWRA SOPs**

**Appendix I**  
MWRA Standard Operating Procedures

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

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

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

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

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

SOP-27 Calculation methods for seasonal threshold values for *Pseudo-nitzschia multiseries*

## **Appendix II**

### **Battelle SOPs**

**Appendix II**  
Battelle Standard Operating Procedures

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

MWRA SOP 004: Loading and Reporting Water Column Data

MWRA SOP 008: Integrating MWRA Client ID Numbers into the NavSam<sup>®</sup> Survey Database

MWRA SOP 009: Chief Scientists on Field Surveys

SOP 8-029: Survey Set-up and Sample Tracking Using NavSam<sup>®</sup> Software

SOP 8-043: Preparation, Distribution, and Implementation of Field Survey Plans

SOP 8-055: Sample Custody, Receipt, and Handling

SOP 8-127: Biospherical Irradiance Sensors

SOP 8-163: WETStar Fluorometer

SOP 8-174: Operation and Maintenance of the WET Labs C-Star Transmissometer

SOP 8-180: Sea-Bird Electronics Model 43 Dissolved Oxygen Sensor

SOP 8-183: Sea-Bird Electronics SBE-25 Sealogger CTD System

SOP 8-266: Nutrient Sample Processing

SOP 8-275: At Sea Collection of Hydrographic Data using CTD and Rosette System

SOP 8-280: Phytoplankton and Zooplankton Sample Collection

SOP 8-367: Sea-Bird Electronics SBE-25plus Sealogger and SBE-32 Carousel Water Sampler System

Electronic copies of the Battelle SOPs referenced in this document were provided to MWRA with the Final QAPP.

## **Appendix III**

### **HOM12 Survey Sample Collection Requirements**





**Table III-2. ARRS Sampling Plan.**

StationID	Depth (m)	Level Code/Depth	Total Volume at Depth (L)	Number of 9-L Niskin Bottles	Dissolved Inorganic Nutrients	Total Dissolved Nitrogen and Phosphorous	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Chlorophyll a	Dissolved Inorganic Carbon & Alkalinity	Rapid Analysis Phytoplankton	Whole Water Phytoplankton	Alexandrium	Zooplankton	Comments
		Protocol Code			IN	NP	PC	PP	CH	AK	RP	WW	AL	ZO	
		Volume (L)			1	0	1	1	1	1	4	1	4	1	
AF1	28.5	AF1 E	2	2	1				1						CH Dup IN 20m Alex
		AF2 20m	6	2	1				1				1		
		AF4 10m	7	2	2				1				1		
		AF5 A	6	2	1				1				1		
AF2	41	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1								1		
AF4	25	AF5 A	5	2	1								1		
		AF1 E	1	2	1										
		AF2 20m	1	2	1										
AF6	92.5	AF4 10m	5	2	1								1		
		AF5 A	5	2	1								1		
		AF1 E	1	2	1										
AF8	59.5	AF2 20m	1	2	1										
		AF4 10m	5	2	1								1		
		AF5 A	5	2	1								1		
AF9	46	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1								1		
F05	17.5	AF5 A	5	2	1								1		
		AF1 E	1	2	1										
		AF2 20m	1	2	1										
F06	34	AF4 10m	5	2	1								1		
		AF5 A	5	2	1								1		
		AF1 E	1	2	1										
F10	33	AF2 20m	1	2	1										
		AF4 10m	5	2	1								1		
		AF5 A	5	2	1								1		
F13	25	AF1 E	2	2	1				1						CH Dup IN 20m Alex
		AF2 20m	6	2	1				1				1		
		AF4 10m	7	2	2				1				1		
		AF5 A	6	2	1				1				1		

StationID	Depth (m)	Level Code/Depth	Total Volume at Depth (L)	Number of 9-L Niskin Bottles	Dissolved Inorganic Nutrients	Total Dissolved Nitrogen and Phosphorous	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Chlorophyll a	Dissolved Inorganic Carbon & Alkalinity	Rapid Analysis Phytoplankton	Whole Water Phytoplankton	Alexandrium	Zooplankton	Comments
		Protocol Code			IN	NP	PC	PP	CH	AK	RP	WW	AL	ZO	
		Volume (L)			1	0	1	1	1	1	4	1	4	1	
F15	38	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1								1		
		AF5 A	5	2	1								1		
F17	78	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1								1		
		AF5 A	5	2	1								1		
F22	81	AF1 E	2	2	1				1						CH w/ dup Dup IN 20m Alex
		AF2 20m	6	2	1				1				1		
		AF4 10m	8	2	2					2				1	
		AF5 A	5	2	1					1				1	
F23	25	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1									1	
		AF5 A	5	2	1									1	
N01	30	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1									1	
		AF5 A	5	2	1									1	
N04	52	AF1 E	2	2	1				1						CH 20m Alex
		AF2 20m	6	2	1				1					1	
		AF4 10m	6	2	1					1				1	
		AF5 A	6	2	1					1				1	
N07	52	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1									1	
		AF5 A	5	2	1									1	
N10	26.5	AF1 E	1	2	1										
		AF2 20m	1	2	1										
		AF4 10m	5	2	1									1	
		AF5 A	5	2	1									1	
N18	27	AF1 E	2	2	1				1						CH w/ dup Dup IN 20m Alex
		AF2 20m	6	2	1				1					1	
		AF4 10m	8	2	2					2				1	
		AF5 A	6	2	1					1				1	
Total Samples				80					22			43			
Bottle Blanks				1											
Blanks				3					2						

**Appendix IV**  
**QA Statements**

Quality Assurance Statement

**I. Description of Audit and Review Activities:**

**II. Accuracy:**

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

**III. Completeness:**

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

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

---

Signature of Reviewer/Date

---

Signature of Task Leader/Date

MWRA HOM12

Project Task Number/Title: Task 4 Alexandrium catenella

Event of Data Set or Deliverable: WN24#

---

QA/QC Corrective Action Log

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

---

Signature of Reviewer/Date

---

Signature of Task Leader/Date

MWRA HOM12

Project Task Number/Title: Task 4 Hydrographic Data

Event of Data Set or Deliverable: WN24#

---

Quality Assurance Statement

**I. Description of Audit and Review Activities:**

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

**II. Accuracy:**

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

**III. Completeness**

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

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

---

Signature of Reviewer/Date

---

Signature of Task Leader/Date

QA/QC Corrective Action Log

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

\_\_\_\_\_  
Signature of Reviewer/Date

\_\_\_\_\_  
Signature of Task Leader/Date

Project Task Number/Title: Task 4 Zooplankton

Event of Data Set or Deliverable: WN24#

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Quality Assurance Statement

**I. Description of Audit and Review Activities:**

**II. Accuracy:**

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

**III. Completeness:**

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

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

---

Signature of Reviewer/Date

---

Signature of Task Leader/Date

MWRA HOM12

Project Task Number/Title: Task 4 Zooplankton

Event of Data Set or Deliverable: WN24#

---

QA/QC Corrective Action Log

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

---

Signature of Reviewer/Date

---

Signature of Task Leader/Date

Quality Assurance Statement

**I. Description of Audit and Review Activities:**

**II. Accuracy:**

	1. Custody of All samples were transferred properly and maintained except as described in part IV.
	2. All of the samples on the COC were received and all required test performed except as described in part IV.
	3. QC samples and calibration standards were analyzed according to the CW/QAPP and the acceptance criteria were met. Corrective action for exceedances was taken.
	4. Samples were analyzed according to the procedures specified in the CW/QAPP.
	5. 100% hand-entered and/or calculated data were checked for accuracy.
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	10. Results of QC data and activities defined in WC/QAPP Section 5.6 are attached and percent differences or recoveries calculated

**III. Completeness:**

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

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

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Signature of Reviewer/Date

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Signature of Task Leader/Date





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