Combined work/quality assurance project plan (QAPP)

Benthic nutrient flux studies: 2008 -2009

Massachusetts Water Resources Authority

Environmental Quality Department
Report 2008-06

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COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (QAPP)
for

BENTHIC NUTRIENT FLUX STUDIES: 2008 -2009
Task 9

MWRA Harbor and Outfall Monitoring Project

Prepared for:

MASSACHUSETTS WATER RESOURCES AUTHORITY
Environmental Quality Department
100 First Avenue
Charlestown Navy Yard
Boston, MA 02129
(617) 242-6000

Prepared by

Jane Tucker
Anne Giblin
Marine Biological Laboratory

Submitted by

Battelle Duxbury Operations
397 Washington Street
Duxbury, MA 02332
(781) 934-0571

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A. PROJECT MANAGEMENT

VERSION 0

A.1 TITLE AND APPROVALS

COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (QAPP)
for

Benthic Nutrient Flux Studies, 2008-2009

Task 9

MWRA Harbor and Outfall Monitoring Project

Prepared by:

Marine Biological Laboratory

April 29, 2008

REVIEW AND APPROVALS

Ms. Ellen Baptiste Carpenter Battelle Project Manager	Date
Mr. Scott Libby Battelle Technical Manager	4/29/2008 Date
Ms. Rosanna Buhl Battelle Project QA Officer	Date
Mr. Ken Keay MWRA Project Manager MWRA Project Area Manager	Date
Ms. Wendy Leo MWRA EM & MS Manager	Date

Quality Assurance Project Plan

REVISION HISTORY

Revision Number	Affected Sections	Effective Date	Summary of Changes	Approval (Initials/dates)

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A.3 DISTRIBUTION LIST

This document will be distributed to the following project participants once all approval signatures have been received. Recipients must copy this page and sign next to their name to indicate that they have read this document. The signed paper is returned to Battelle's QA officer.

NAME	SIGNATURE
Ms. Wendy Leo (MWRA)	
Mr. Ken Keay (MWRA)	
Dr. Anne Giblin (MBL)	
Ms. Jane Tucker (MBL)	
Mr. Sam Kelsey (MBL)	
Ms. Ellen Baptiste Carpenter (Battelle)	
Mr. Scott Libby (Battelle)	
Ms. Rosanna Buhl (Battelle)	
Mr. Greg Lescarbeau (Battelle)	
Ms. Deirdre Dahlen (Battelle)	
Mr. Matt Fitzpatrick (Battelle)	

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A.4 PROJECT AND TASK ORGANIZATION

The Benthic Nutrient Flux Monitoring tasks will be accomplished through the coordinated efforts of several organizations. Figure 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 subaccount with budget and milestones, and these accounts will be used to track costs against progress.

Dr. Andrea Rex is Director of the MWRA Environmental Quality Department. Mr. Ken Keay is the MWRA Project Manager and the Benthic Nutrient Flux Project Area Manager. They will be informed of all matters pertaining to work described in this QAPP. Ms. Wendy Leo is the MWRA EM&MS Database Manager.

Ms. Ellen Baptiste Carpenter is the Battelle Project Manager. She is responsible for ensuring that products and services are delivered in a timely and cost-effective manner that meet MWRA's expectation, and for the overall performance of this project. 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. The Battelle Quality Assurance Officer for the project is Ms. Rosanna Buhl. For this task, Ms. Buhl is responsible for reviewing data sets and QA Statements submitted by subcontractors for quality completeness and adherence to the QAPP. She is also responsible for reviewing the synthesis reports for accuracy and completeness. Mr. Matt Fitzpatrick is the Battelle Field Manager, responsible for the overall field program including all day-to-day field activities conducted by Battelle for the project. Ms. Deirdre Dahlen, Battelle's Laboratory Manager, is responsible for overseeing all laboratory activities in the contract. The key contacts at each of the supporting laboratories are shown in Figure 1. Addresses, telephone (and fax) numbers, and Internet addresses are presented in Appendix A.

Technical oversight for the Benthic Nutrient Flux Studies will be provided by the Senior Scientist, Dr. Anne Giblin (MBL). Ms. Jane Tucker, project manager, is responsible for the general management of all project activities at MBL, including field sampling, laboratory analysis, data generation and compliance with the QAPP, and data submissions. She is also responsible for reviewing data reports generated by MWRA and for writing the annual synthesis report.

The overall objective of Task 9 is to quantify the seasonal flux of oxygen, total carbon dioxide, and nutrients between the sediments and their overlying waters at selected stations in Boston Harbor and in Massachusetts Bay in the vicinity of the MWRA effluent outfall. Benthic metabolism, nutrient flux, and sediment porewater conditions are responsive to nutrient and organic matter loading, and benthic communities in shallow marine ecosystems often play a significant role in nutrient cycling and oxygen dynamics. The data obtained from the benthic nutrient flux study will continue to define these important aspects of benthic-pelagic coupling in Boston Harbor and Massachusetts Bay. Conduct of this task will provide information concerning the sixth and seventh years of monitoring following diversion of effluent discharge from Boston Harbor to the deepwater site in Massachusetts Bay.

Specific objectives of Task 9 are to determine sediment oxygen demand, nutrient fluxes, and complementary parameters (pH, Eh, etc.) by direct measurements upon or incubation of sediment cores collected in the field and taken to the laboratory. The measurements span a range of temperatures and degrees of stratification. Specific goals of Task 9 are to:

- Detect inter-annual change in rates of sediment oxygen demand, nutrient fluxes, and related parameters from sediments in the vicinity of the outfall and in Boston Harbor.

- Directly measure rates of denitrification in Boston Harbor and in the nearfield area around the Massachusetts Bay outfall.

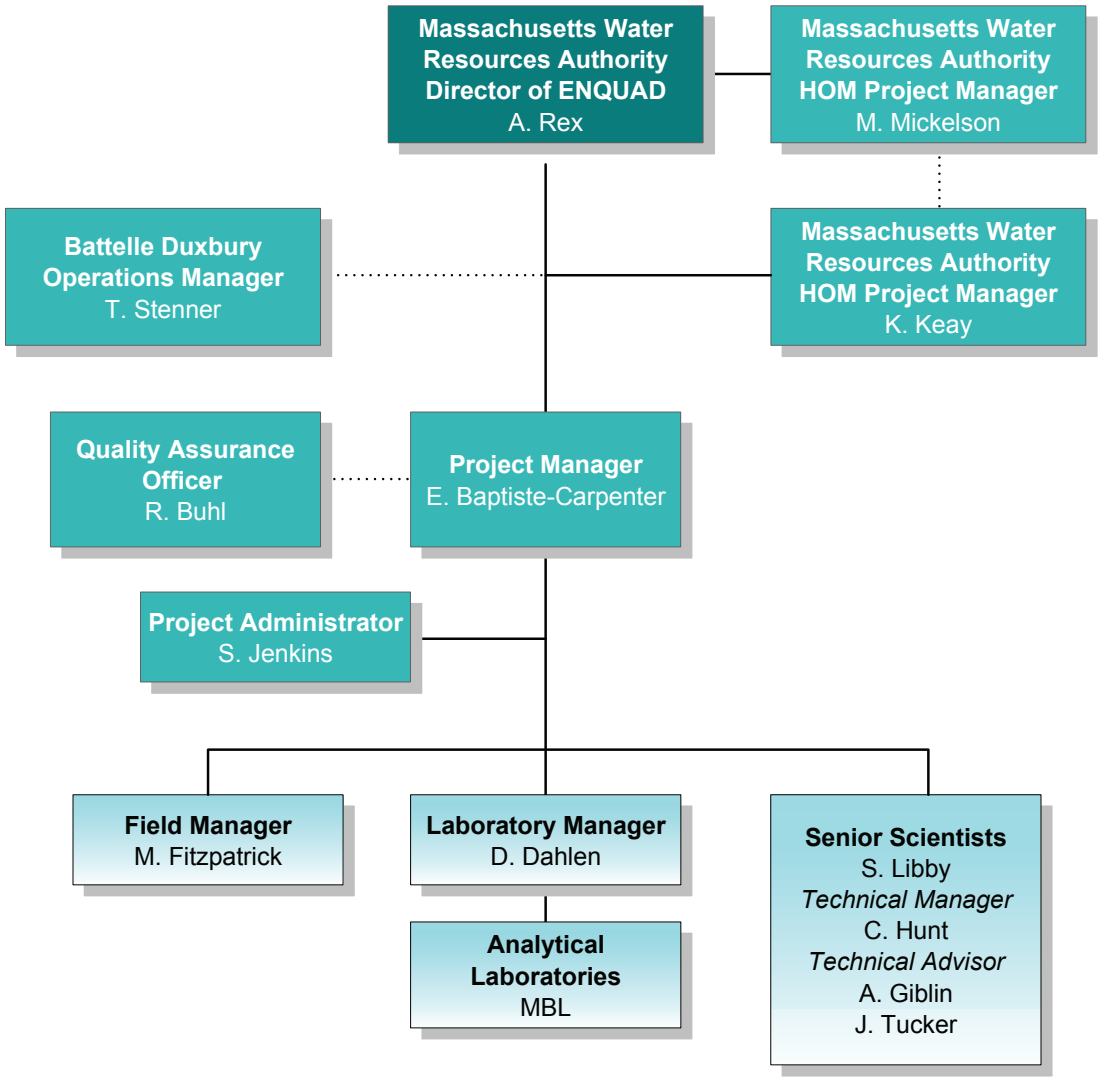

Figure A–1. Flux Studies (Task 9) Organization

A.5 PROBLEM DEFINITION/BACKGROUND

In 1992, the MWRA implemented a long-term environmental monitoring plan for the effluent outfall in Massachusetts Bay. Effluent diversion from Boston Harbor to Massachusetts Bay in September 2000 marked the end of pre-diversion baseline data collection in the Bay. The current goal is to monitor conditions in the Bay for possible changes due to the diversion, and to continue to monitor the response in Boston Harbor to this large reduction in sewage inputs. The data collected and reported for Task 9 will be added to previously collected data to increase our understanding of the ecological and biogeochemical dynamics of the soft-bottom areas of the region. They will continue to serve to describe some of the

spatial variability in fluxes, organic matter content, and redox conditions in soft-bottom areas of concern. Although no threshold parameters are measured under Task 9, post-diversion monitoring will assist in understanding system responses to the diversion, including any triggering of relevant caution and warning levels under other tasks, as listed in the MWRA Contingency Plan (MWRA, 2001). These data will also be invaluable to water quality modeling efforts as a verification data set.

At the end of 2003, after three years of post-relocation monitoring, and with the approval of the Outfall Monitoring Science Advisory Panel (OMSAP), MWRA designed a revised ambient outfall monitoring plan (MWRA, 2003, 2004). The revised plan was approved by the Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (DEP) in early 2004 (MWRA, 2004). This Quality Assurance Project Plan (QAPP) describes program methods employed under the revised plan and for the current contract years 2008-2009.

A.6 PROJECT/TASK DESCRIPTION

A.6.1 Field Program

To accomplish the objectives of Task 9, sediment cores will be collected and returned to the laboratory, where flux incubations will be performed on intact cores. Other cores will be analyzed for redox and solid phase characteristics. This approach, laboratory incubations of relatively undisturbed cores, is an accepted method of estimating benthic nutrient fluxes and has been used successfully in the Boston Harbor/Massachusetts Bay system throughout the monitoring program (Giblin *et al.* 1994; Howes 1998; Tucker *et al*. 2004, 2005, 2006, 2007).

Sediment cores will be collected during four surveys in May, July, August, and October 2008-2009 (Table A–1). This sampling strategy will provide data across the approximate annual range of bottom water temperatures in both Boston Harbor and Massachusetts Bay, as well as provide information during the critical warmer months when the Bay water column is stratified.

Table A-1. Benthic Nutrient Flux Sampling Stations.

Station	Latitude	Longitude
BH02	42°20.62'N	71°00.13'W
BH03	42°19.84'N	70°57.71'W
BH08A	42°17.46'N	70°55.33'W
QB01	42°17.61'N	70°59.27'W
MB01	42°24.18'N	70°50.24'W
MB02	42°23.55'N	70°50.06'W
MB03	42°20.88'N	70°48.92'W
MB05	42°24.99'N	70°39.12'W

Sediment sampling stations in Boston Harbor will be Stations BH02, BH03, BH08A, and QB01 (Figure A–2). Massachusetts Bay stations (Figure A–2) will be Stations MB01, MB02, MB03, and MB05 (for comparability of stations, see Section A.7.3.3). Each survey plan will include a final list of sampling stations.

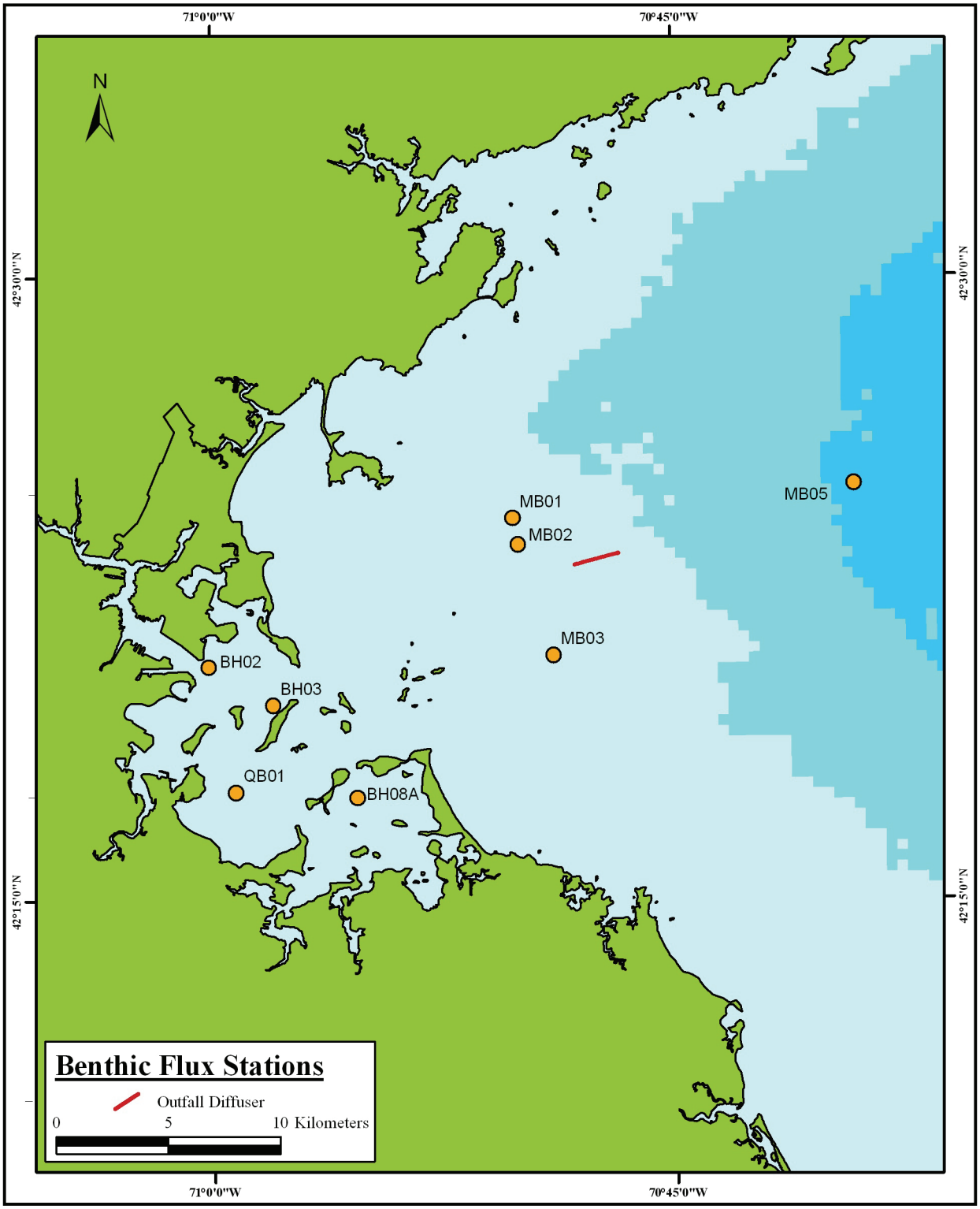

Figure A-2. Benthic Nutrient Flux Sampling Station Locations.

Stations in Boston Harbor will continue to provide data that reflect conditions in the harbor that have changed due to sewage treatment improvements, which culminated in the diversion of all effluent to the deep-water outfall in Massachusetts Bay on September 6, 2000. Three nearfield stations in Massachusetts Bay (MB01, MB02, MB03) will provide additional years of "post-diversion" data, and the Stellwagen Basin station (MB05), considered beyond the influence of the outfall, will continue to provide reference data.

Up to 10 sediment cores of four different sizes will be collected from each station (Table A–2). Cores from the Harbor stations will be collected by SCUBA divers. Each core will be carefully pushed into the sediments to approximately 15-cm depth and then capped on both ends, capturing bottom water in the headspace of the core. At stations in Massachusetts Bay, where it is too deep to dive, a box-corer will be deployed from deck to obtain a 50 x 50 x at least 15-cm core. This box core will subsequently be sub-cored on deck in a manner similar to the diver-taken cores. Cores will be held in the dark at near-ambient (± 2°C) collection temperatures while on deck, and during transport to the laboratory.

In addition to sediment samples, water samples will be collected at each station for use in the laboratory flux incubations. Seawater collected from near-bottom will be drawn through a hose by a diaphragm pump and filtered immediately through cartridges (20 and 1 µm, at minimum). The filtered water, which will be collected in carboys, will be used in the laboratory to replace the water overlying the cores collected for flux measurements.

Characterization of *in situ* conditions will be accomplished using a Hydrolab Scout 2 Multiparameter Water Quality Data System to measure the O_2, temperature, and salinity of near-bottom water. The MBL also has a YSI Model 600XLM Sonde with similar capabilities that may be used as an alternate for the Hydrolab.

A.6.2 Laboratory Program

The flux, solid phase, and redox measurements will follow methods of Giblin *et al.* (1994, 1997) and Tucker and Giblin (2001). Denitrification measurements will follow the methods of Kana *et al*. (1998).

Table A-2. Samples and Measurements at Each Survey Station.

	Type	Number	Intended Analysis or Use	Reference or Comment
Sediment Core	15-cm-dia.	2	Respiration, Nutrient and denitrification fluxes	(1), (2)
Sediment Core	6.5-cm-dia.	1	Eh, ARPD, and pH	(1)
Sediment Core	2.5-cm-dia.	3	Archived solids/porosity/ pigments	(1)
Whole Seawater	Hydrolab Scout 2 Multiparameter System or YSI 600XLM Sonde	1	Temperature/Salinity/Oxygen	(3)
Pumped Seawater	~15 L carboy, filtered	1	Water for incubations	(1)

(1) Giblin *et al.*, 1994; 1997.
(2) Kana *et al*., 1998.
(3) Temperature, salinity, and oxygen are measured in field.

Cores are maintained in the dark at the near-*in situ* collection temperature (± 2°C)**.** Table B-4 in Section B4 describes the parameters to be measured. Sampling/analytical methods are described in Sections B2 and B4, respectively.

A.7 QUALITY OBJECTIVES AND CRITERIA

A.7.1 Data Quality Objectives

The data quality objectives for HOM6 are defined by the HOM6 contract and goals for Task 9. The contract specifies the temporal and spatial boundaries for the benthic nutrient flux study and defines the methods that will provide measurement quality objectives that will meet the study goals. The analytical methods and resulting method detection limits (MDL) are selected to ensure that measurements are sensitive enough to detect inter-annual changes in flux rates within Boston Harbor and Massachusetts Bay. In addition, the general contract conditions further define the accuracy and sensitivity of geospatial (GPS) instrumentation to ensure that sampling locations are within ±30m and ±300 m of the defined station coordinates for Boston Harbor and Massachusetts Bay, respectively, in order to enable intercomparison with previous sampling results and trends analysis.

A.7.2 Measurement Quality Objectives

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

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

The application of these data quality measures is described below.

A.7.3 Field Program

A.7.3.1 Precision and Accuracy

Data quality requirements and assessments for navigational data are detailed in the Water Column Monitoring QAPP (Libby *et al.* 2008). Precision and accuracy objectives for navigation and water sampling are presented in Table A–3. Section B.4 provides details on relevant analytical procedures to ensure data quality and Section B.7 discusses instrument calibration methods.

Table A-3. Accuracy and Precision of Hydrolab Scout 2.

Parameter	Units	Range	Accuracy	Precision
Navigation: Boston Harbor	m	NA	± 30	± 30
Navigation: Mass. Bay	m	NA	± 300	± 300
Temperature	ºC	-5 to 50	± 0.15	0.01
Salinity	ppt	0 to 70	± 0.5	0.01
Dissolved Oxygen	mg/L	0 to 20	± 0.2	0.01

A.7.3.2 Completeness

For each box core brought on deck, the NavSam© operator will mark the event in the NavSam© log, which then automatically links the event with the time and location. For each Harbor SCUBA station, divers will bring cores up a buoy line marking the station. The NavSam© event marker will be logged as divers emerge at this point and pass the cores to shipboard personnel. 100% completeness for each survey is required; a station will be considered completed only if a minimum of four cores (two each of the 15 cm diameter cores, and 6.5 cm diameter cores) is obtained. If only four cores are obtained, subsamples for sediment solids to be archived will be taken from the 15 cm diameter cores after flux measurements are complete. The survey will be considered 100% complete only if four cores are obtained at the required number of stations (8) for the survey. In the event that suitable sediments cannot be located at target coordinates, alternate stations may be satisfactory provided that the MBL Senior Scientist has made reasonable efforts at attempting to complete the survey at the original stations. The MBL Senior Scientist shall notify the MWRA Project Manager of circumstances as they arise.

Seawater will be collected to replenish the overlying water in cores when flux incubations are begun. If necessary, seawater could be filtered on shore prior to use in incubations rather than on board as planned; filtration minimizes the contribution of metabolic activity in the water to the observed flux in the chambers. Given the dynamic nature and general similarity of water quality of the Bay and Harbor stations, seawater from other than the sediment collection station could be used, if needed, for the incubations without compromising the task objectives.

Temperature will be recorded to ensure that incubations are conducted under conditions that approximate *in situ* conditions. Dissolved oxygen data will establish the *in situ* conditions for comparison with conditions during incubations. Salinity, along with temperature, is needed to calculate percent oxygen saturation.

A.7.3.3 Comparability

The four Massachusetts Bay stations to be occupied in 2008 -2009 are the same stations that have been used throughout the monitoring program, starting in 1992 for the three nearfield stations MB01, MB02, and MB03, and 1993 for the farfield station MB05.

The locations of four Harbor stations to be sampled have been consistent since 1992 for stations BH02 and BH03, and since 1995 for stations BH08A and QB01. However, only station BH02 has remained unchanged since 1992. Two harbor stations, BH03 and BH08, that had been sampled during 1992-1994 were moved for the 1995-1997 sampling period and renamed BH03A and BH08A. In 1998, the decision was made to return to original station BH03; BH03 and BH03A were only about 200 meters apart, and appeared quite similar in all measured parameters (Tucker and Giblin 2001). Therefore we include the data collected at station BH03A with that collected at station BH03 as a continuous dataset that begins in 1992. In contrast, station BH08A was very different from BH08. Station BH08 was a sandy site chosen to represent erosional areas. Sediments at station BH08A are finer grained and the site was chosen to represent a depositional area (Howes 1998). Since depositional areas are more likely to show changes in inputs to the harbor, station BH08A was chosen for the ongoing sampling, and we therefore have a continuous data set for this station beginning in 1995. Station QB01 was also a new station in 1995, replacing station BH07 that was sampled in 1992-1994.

The collection methods described in this QAPP are completely comparable to studies carried out for the Boston Harbor and Massachusetts Bay surveys of 1992-1994 (Kelly *et al*. 1993) and 1998-2007 (Tucker and Giblin 2001, 2005) as well as to the methods used by Howes for 1995-1997 (Cibik and Howes 1995) with exceptions as described in Tucker and Giblin (2005).

A.7.3.4 Representativeness

Representativeness is addressed primarily through sampling design. MWRA has selected stations that are representative of areas of interest and potential impact. The DGPS readings and corrected latitude/longitude positions are representative of the actual vessel coordinates because position data are collected and reviewed at a frequency that ensures that the measured latitude/longitude positions represent the actual vessel position. The Chief Scientist has the responsibility, using professional experience, to determine whether the sediment cores are relatively undisturbed, representative of the *in situ* environment, and acceptable for laboratory measurements. Whether taken by divers or as subcores from box cores, sediment cores will be taken avoiding large disturbance features such as animal burrows. Box cores will not be accepted when there has been obvious loss of surface sediments. The Chief Scientist will instruct the NavSam© operator to note in the NavSam© log any visual observations of the core samples. The observations will be incorporated into the survey report. Water pumped to the ship will be highly representative of the near-bottom waters at each station.

A.7.4 Laboratory Program

A.7.4.1 Precision and Accuracy

For the benthic nutrient flux studies, MBL will generate data for ammonium, nitrate/nitrite, phosphate, silica, dissolved inorganic carbon (= total carbon dioxide), dissolved oxygen, and dinitrogen gas. Data for Eh and pH will also be reported. Solid phase analyses will be made for TOC and TN, chlorophyll *a* and phaeopigments, and porosity. Table A-4, Section B.4, and Table B-4 provide additional details on the quality control and analytical procedures (*e.g.*, prepared standards) that will ensure data quality, and Section B.7 describes instrument calibration methods. Fluxes are estimated from concentration changes over time and, thus, more than the precision of individual chemical analyses, the precision of flux estimates is of interest. Precision for flux estimates is determined by calculating the standard error of fluxes from replicate cores. MBL has had extensive experience with these types of measurements and has provided replicate core flux data with standard errors generally less than 30% of the mean.

A.7.4.2 Completeness

It is expected that flux measurements will be completed for all parameters in two 15-cm-diameter cores intended for flux incubations. However, 100% completion cannot be guaranteed. The task objectives will not be compromised if only one successful 15 cm diameter core from each station is successfully incubated for flux estimates.

Over-sampling for most parameters will help ensure that the minimum requirements for completion are met. Oxygen will be monitored frequently to ensure estimates of oxygen flux. A 5-point time series of samples for nutrients and N_2/Ar will also be taken. Fluxes could be estimated (with less confidence) using fewer data points than planned. Samples for dissolved inorganic carbon (DIC) data cannot be over sampled due to volume considerations; they will be collected only at the start and finish of incubations.

Collection of an extra core for Eh/pH measurements will help ensure that at least one core is completely sampled. It is expected that all specified depth intervals will be sampled, but the objectives of Task 9 would not be compromised if fewer than six depth intervals are successfully sampled and analyzed.

A.7.4.3 Comparability

Data will be directly comparable to results obtained previously at the same or similar sites in Boston Harbor and Massachusetts Bay (Giblin *et al.* 1994; Howes 1998; Tucker *et al*. 2004, 2005, 2006, 2007). Incubation and analytical techniques are identical to those specified in the 1998-2001 and 2002-2005

QAPPs (Tucker and Giblin 2001, 2005, 2006) with the following exceptions, which are detailed in the 2002-2005 QAPP:

1. After 2003, measurements for porewater nutrients, sulfides, and alkalinity were discontinued and will not be reported for 2008-2009.
2. In 2004, the method used to measure denitrification was changed to the N_2/Ar, membrane inlet mass spectrometer (MIMS) technique (Section B4.2) rather than the gas chromatography (GC) method. The N_2/Ar method will continue to be used in 2008-2009. As noted in Section B4.2, the MIMS technique is not directly comparable to the GC method, but it is considered to be more accurate (Kana *et al.* 1998).

A.7.4.4 Representativeness

Water samples will be collected, handled, and transported using procedures that will ensure the resulting data represent the sample material collected.

Deviations from the sample collection procedures described in this QAPP will be documented in the survey logbook and described in the survey report.

A.8 SPECIAL TRAINING/CERTIFICATION

It is MBL 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.

A.8.1 Technical Training

Technical training encompasses technical procedures and the associated quality control requirements. All personnel that perform technical activities must be trained to perform their assigned activities prior to conducting those procedures independently. Where available, SOPs or manuals are used as the basis of technical training. Training for a technical activity is considered complete when a staff member can perform the technical operation independently and meet the criteria of the relevant SOP.

Table A-4. Measurement Quality Objectives for Laboratory Data

Variable (Lab)	Matrix	Units	Detection Limits	Accuracy (% difference)[a]	Precision (% difference)[a]	Quality Control (QC)Sample Type	Frequency of QC Sample	Corrective Action
O_2	SW	µM	0.02mg/l[b]	≤4%	≤3%	Lab RM	1/set of measurements	Note deviation from expected
DIC (Total CO_2)	SW	µM	<0.1µgC[b]	≤5%	≤1%	CRM Lab RM	Daily 1/15 samples	Repeat Repeat
NH_4	SW	µM	0.5	≤5%	≤5%	CRM Lab Standards Check Standard Lab Duplicate	1 Verification[c] Daily 1/20 Samples Each sample	Repeat Flag Data Flag Data
$NO_2 + NO_3$	SW	µM	0.25	≤5%	≤5%	CRM Lab Standards Check Standard Blanks Lab Duplicates	1 Verification[c] 1 Set/65 Samples 1/20 Samples 1/20 Samples 1/20 Sample	Repeat Repeat Repeat Repeat Repeat
PO_4	SW	µM	0.5	≤5%	≤5%	CRM Lab Standards Lab Duplicates	1 Verification[c] Daily 1/20 Samples	Repeat Repeat Repeat
Si	SW	µM	0.5	≤5%	≤3%	CRM Lab Standards Check Standards Blanks Lab Duplicates	1 Verification[c] 1 Set/65 Samples 1/20 Samples 1/20 Samples 1/20 Samples	Repeat Repeat Repeat Repeat Repeat
pH	PW	NA	0.01[b]	≤0.05	NA	CRM (buffers)	Daily	Repeat
Eh	PW	mV	0-1400 [d]	≤5%	NA	Lab Standard	Daily	Repeat
ARPD[e]	SED	cm	NA	NA	NA	NA	NA	NA
N_2/Ar	GAS	ratio	NA	NA	≤0.05% (C.V)	Lab standard	At beginning and end of analysis run and 1/20 samples	Repeat
TOC	SED	%(w/w)	0.5%	≤5%	≤5%	Recalibration Standard Blank CRM	1/10 Samples 1/10 Samples 1/10 Samples	Repeat Repeat Repeat
TN	SED	%(w/w)	0.05%	≤10%	≤7%	Recalibration Standard Blank SRM	1/10 Samples 1/10 Samples 1/10 Samples	Repeat Repeat Repeat
Chl a	SED	µg/ml	0.1µg/mL	NA[f]	10% if > 1µg/mL	NA[f]	NA[f]	Subcore 15cm core and repeat
Phaeopigments	SED	µg/ml	0.1µg/mL	NA[f]	5%	NA[f]	NA[f]	Subcore 15-cm core and repeat
Porosity	SED	unitless	0.1g/mL[b]	≤5%	≤5%	NA[f]	NA[f]	Reanalyze

NA: Not Applicable
[a] At concentrations >5 x MDL
[b] Instrument sensitivity
[c] A CRM standard will be run to verify the Lab primary standard whenever a new primary standard stock is made.
[d] Instrument range
[e] This is a purely subjective measurement.
[f] standard reference materials are not available.

SW = Seawater
PW = Porewater
SED = Sediment
mE = milli-equivalents per liter
RM = Reference material
CRM = Certified Reference Material
SRM = Standard Reference Material
CV = Coefficient of Variation

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.*, SCUBA and boating safety). Responsibilities include:

- The Senior Scientist is ultimately responsible for the overall quality of products produced and for ensuring that appropriately qualified personnel are assigned to the tasks.
- The Task Manager is responsible for ensuring that all staff is trained in MBL quality systems and the requirements of this QAPP.
- The MBL Environmental Health and Safety Officer is responsible for general safety training.
- The Senior Scientist is responsible for any specialized training related to specific protocols.
- The MBL Diving Safety Officer is responsible for ensuring that all divers have current certification in necessary diver training and diving safety requirements.
- All divers on the project are certified by the American Academy of Underwater Sciences (AAUS).

A.9 DOCUMENTS AND RECORDS

A.9.1 Data Recording

All field and laboratory data generated by MBL must be reported to MWRA for incorporation into the Environmental Monitoring and Management System (EM&MS). Battelle data management staff will log in all data received to maintain the data audit trail. These data are processed according to Section B.10 below. All data submissions to MWRA are sent via email in the absence of the HOML application and copied to the project archive mailbox (^BCO Dux HOM6; HOM6@battelle.org). The ASCII data files are also stored on the projects file server under the HOM6 project Task 4 deliverables. This server is backed up to tape nightly. Once the HOML application goes online, electronic data submissions will be made through the system. A copy of the submission will still be sent by email to the project archive mailbox.

To ensure accurate collection of data and a permanent record of all data the following procedures will be followed.

A survey log form will be completed for each station visited during surveys. All field data will be recorded in ink on field sample data sheets and field logbooks. Station logs associated with field and laboratory custody will be kept in a survey notebook for each survey. Copies of all survey records will be provided to Battelle at the end of each survey.

All laboratory data will be recorded in a bound notebook or on standardized forms. 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. All QC data (precision, accuracy) will be recorded in laboratory notebooks. It will be the responsibility of the

laboratory manager to ensure that all data entries and hand calculations are verified in accordance with procedures described in Section D–2 (below).

All data and notes will be initially recorded either (1) electronically onto computer storage media from NavSam© or other laboratory system or (2) manually into laboratory notebooks or on established data forms. All data and notes will be written in ink. Corrections to hand-entered data will be made by drawing a single line through the incorrect entry. Corrections will be initialed, dated, and justified. Completed forms, laboratory notebooks, or other forms of hand-entered data will be signed and dated by the individual entering the data. In addition to these documentation procedures, sample logs associated with field and laboratory custody and tracking will be maintained in the project files and a copy submitted to Battelle. Manually recorded data from subcontractor laboratories will be entered by the subcontractor into PC-based MS Access databases, verified, and submitted to Battelle.

MBL will provide, along with the data submissions for each survey, a list of samples, by station, that have been archived. Any discrepancies from this QAPP will be noted.

MBL will maintain, for six years, (1) all records of calculations, (2) raw data collected during incubations, and (3) field records of DO, temperature and salinity.

A.9.2 Documents

The MWRA contract defines general conditions for reporting. These conditions apply to all reports generated for this monitoring area. Deliverables due to MWRA for Task 9 include:

- Survey Plans (one for each of the benthic flux surveys)
- Survey Reports (one for each of the benthic flux surveys)
- Benthic Nutrient Flux Data Report Review Letters

A.9.2.1 Quality Assurance Project Plan

This QAPP describes the sampling and analysis activities of MWRA's benthic nutrient flux monitoring program to be conducted under MWRA Contract S453A in 2008-09 with analysis continuing through 2010. This document is designed following EPA/QA R-5 (2001) and is based largely on benthic nutrient flux CWQAPPs of the MWRA monitoring program described in Tucker and Giblin (2002 and 2005). Benthic nutrient flux surveys will be conducted to monitor ecological and biogeochemical dynamics of the soft-bottom areas of the region. These data will serve to describe some of the spatial and temporal variability in fluxes, organic matter content, and redox conditions of these areas of concern, and assist in understanding system response to the Massachusetts Bay outfall.

A.9.2.2 Survey Plans and Survey Reports

A survey plan will be prepared for each Benthic Nutrient Flux Survey following the guidance of SOP 6-043, Contents of Survey Plans. The survey plans will describe all procedures for conducting the benthic nutrient flux sampling surveys. Any known deviations from this QAPP will be included in the survey plans. One unbound, double-sided copy of each plan on three-hole paper will submitted to MWRA in final form no later than two weeks before the start of the survey.

Survey reports will describe the survey conducted, station coverage, samples collected, measurements made, problems experienced, and general observations. A survey report is expected to be about 1-2 pages of text, with accompanying station maps and sample table. A tabular summary of stations occupied, station locations, and samples collected will be generated by MWRA and included in the survey reports. Any deviations from this QAPP, not known at the time of survey plan preparation, will be incorporated

into the survey reports. One unbound, double-sided copy of the draft survey report will submitted to MWRA no later than one month after the completion of each survey. MWRA's comments will be due two weeks after receipt of the draft report. The final survey report, addressing MWRA's comments, will be due two weeks after receipt of the comments. If MWRA does not submit comments within the two-week period, the draft survey report will be considered final.

A.9.2.3 Data Report

Four Benthic Nutrient Flux data reports will be generated by MWRA per year. Each report is final. The data reports are created directly from the EM&MS database. Benthic Nutrient Flux data reports will be submitted to Battelle for review. Included will be all sample collection information summarized from the Survey Reports for each sampling event. Data will be presented in tables containing the results of all individual sample analyses. These results will include (1) station locations and field measurement results for each survey; (2) fluxes by station, core, and parameter; (3) sediment solid phase analyte concentrations and Eh and pH by depth interval of each core; and (4) a tally of all parameters reported (the Analysis Summary).

In addition to the sample-specific raw data, data reports shall include the output of a comprehensive set of quality control checks. The set of checks could include univariate checks, multivariate checks, and property/property plots, and scatter plots, as appropriate to the data set. They will include at a minimum:

- Count of samples with non-detectable results, by parameter
- Number of null values
- List of missing samples
- Values out of range of historical data by core type and parameter

Battelle/MBL will perform a technical review and comment on the data report.

A.9.2.4 Synthesis Report

The data from all four surveys will be collated and summarized and used to develop an Annual Benthic Nutrient Flux Synthesis Report. The Report will synthesize the results of the four surveys of each calendar year and will be prepared under Task 11.3 of the Harbor and Outfall Monitoring Project. This will be submitted as a Draft and a Final Report as indicated in Table A–5.

The report for the first field year of this contract, 2008, will be an abbreviated report compared to previous reports submitted under this Task and compared to the report that will be submitted for the second field year, 2009. It will contain a brief introduction and methods section, and will consist primarily of a summary chapter describing the most noteworthy observations of the year. The report will draw on the abstract, graphs, and tables presented during the annual technical meeting and will include these materials as appendices. If a more extensive evaluation of data is warranted due to anomalous findings, the additional effort may be provided for under a separate Task Order.

The report for 2009 will be a comprehensive report and will include separate sections describing results from the Harbor and the Bay. Spatial and temporal variability of flux and porewater data will be thoroughly compared for both seasonal and inter-annual time periods. Long-term trends in denitrification rates at the two Harbor and two nearfield stations traditionally sampled for this parameter will be compared to previous years. Values for all stations will be evaluated for the period beginning in 2004, when the denitrification method changed. The authors of the benthic nutrient report will access the MWRA database for summary data on water column trends in nutrients, plankton, and metabolism to include a discussion of benthic nutrient cycling in the context of events occurring in the Harbor and the

Bay. Spatial and temporal trends will be examined and supported by statistical analyses. The report also will include an evaluation of the extent to which benthic processing of nutrients contributes to threshold exceedances, if such exceedances occur and whether the exceedances can be attributed to the MWRA discharges.

Table A–5. List of Deliverables

Deliverable	Survey Period	Due Date
Survey-Related Reports		
Survey Plans	Each survey	2 weeks prior to survey
Survey Reports – Draft	Each survey	1 month after survey
Survey Reports – Final	Each survey	14 days after receipt of comments
Data Set Submission		
Benthic Nutrient Flux Data Set Submission	May	August 15
	July	October 15
	August	November 15
	October	January 15
Data Reports		
Benthic Nutrient Flux Data Report Review Letters	May	October 15
	July	December 15
	August	January 15
	October	March 15
Synthesis or Interpretive Reports		
Benthic Nutrient Flux Report – Draft	May - October	April
Benthic Nutrient Flux Report – Final	May - October	30 days after receipt of comments

B. DATA GENERATION AND ACQUISITION

B.1 SAMPLING PROCESS DESIGN

B.1.1 Monitoring Parameters and Collection Frequency

Benthic nutrient flux surveys are conducted in May, July, August, and October. Temperature, salinity, and dissolved oxygen of bottom waters will be measured at each station. Nutrient and denitrification fluxes are conducted on cores from all eight stations visited during each of the four Benthic Nutrient Flux surveys scheduled for each year (Table B-1). Sediment profiles of pH, Eh, TOC and TN, and chlorophyll *a* and phaeopigments will also be conducted on cores from all stations and all surveys.

Table A-2 lists the samples (cores) that will be collected at each station. During the four Benthic Nutrient Flux surveys conducted in a given year, a maximum total of 256 samples will be collected during 32 station occupations. Of this total, 64 core and 32 seawater samples will be used directly in flux measurements, 64 will be collected for possible use in redox analyses (cores for redox analyses will be over-sampled to ensure a suitable core for these measurements and for potential ancillary measurements), 32 will be used for pigment analyses, and 64 will be dried for solids measurements and to be archived. The maximum total also includes 32 cores that may be used for "extra" denitrification measurements that are not required by contract but may be made available to MWRA (see Section B.4.2).

B.1.2 Schedule of Activities and Deliverables

Sampling activities associated with the Benthic Nutrient Flux Surveys (Task 9) described in this QAPP are scheduled annually from 2008 – 2009. The planned survey schedule is shown in Table B–1. Exact dates will be determined as the study progresses and will be subject to the criteria established for sampling.

Table B-1. Master Schedule for Benthic Nutrient Flux Surveys in Boston Harbor and Massachusetts Bay.

SurveyID[1]	Survey Start Date[1]
NC0X1	May-0X
NC0X2	July-0X
NC0X3	August-0X
NC0X4	October-0X

[1]X is the last digit of the sampling year (*i.e.*, 8-9)

Four Benthic Nutrient Flux Surveys will be conducted annually. These surveys will be conducted in May (following spring bloom settlement/onset of water column stratification), July (mid summer), August (stratified, warm bottom waters), and October (post stratification for the harbor, end of the stratified period for the bay). Section A.9.2 and Table A–5 define the deliverables schedule.

B.2 SAMPLING METHODS

B.2.1 Navigation

Refer to the Water Column QAPP (Libby *et al.* 2008) for a complete description of navigation procedures.

B.2.2 Field Sampling

Undisturbed sediment cores of the number and type listed in Table A-2 will be collected from Harbor stations by SCUBA divers (Dornblaser *et al*. 1989) and in Massachusetts Bay with a 50 x 50-cm box corer. Before each dive or box core deployment, core tube numbers will be recorded on the MBL station log. The box corer will be deployed with the two 15-cm-diameter cores mounted inside. After the box corer is brought on deck and it is determined that the sample is acceptable, the rest of the cores will be obtained. Core tubes will be gently pushed into the box core sample to a depth of approximately 15-cm and the ends of each tube will be capped. All core samples will be stored and later transported to the laboratory in a dark, insulated container at ±2º C of the collection temperature. The box corer will be washed clean with seawater between stations. Seawater samples will be collected and measurements will be made as described in Section B.4.

At all eight stations, near-bottom temperature, salinity, and dissolved oxygen will be measured by deploying the Hydrolab DataSonde. The Hydrolab will have been calibrated prior to the initiation of the survey, and the calibration will be checked and adjusted as needed prior to the initial deployment for each survey day. Salinity will be calibrated with a known conductivity standard and DO will be calibrated in water-saturated air. Temperature does not need calibration. If the backup sonde (YSI 600XLM) needs to be deployed, it will be calibrated in the same way.

B.3 SAMPLE HANDLING AND CUSTODY

B.3.1 Sample Handling

Upon arrival at the Woods Hole MBL facilities, the two 15-cm-diameter cores from each station will be uncapped and held in the dark at a temperature within ±2ºC of the *in situ* temperature at the station from which they were collected. The overlying water of each core will be kept aerated until flux measurements begin. Benthic flux measurements, initiated within 12-24 hours of sample collection, will be made in accordance with the procedures presented in Giblin *et al*. (1997) and will be identical to those described in Tucker and Giblin (2001, 2005).

Cores to be used for redox and solid phase analyses will also be held at ambient temperature and submerged in an aerated tank of seawater. Carboys of seawater to be used for flux incubations are held at ambient temperature until use.

B.3.2 Sample Custody

The MBL's station log is a pre-printed form (Figure B–1) that will include spaces for barcode labels generated by NavSam©, and on which all station information (Time, DO, Salinity, Temperature), core tube and carboy numbers, dive or box core records, and site descriptions will be recorded. Each core tube and carboy has a unique identifying number. These permanent numbers will be assigned one each to the unique identifiers generated by NavSam©, and will be used to track data during processing. Adhesive labels have proven unsatisfactory because they either do not stick to wet core tubes, or they stick

permanently to dry tubes, which causes confusion when the tubes are reused. Also, the ink bleeds off the labels while the cores are submerged, and they obstruct observation of sediments through clear core tubes.

Each deployment of the box core or diver will be recorded as one M*arker No* in the NavSam© system. An analysis code defined for each type of core will be concatenated to the five-character *Event ID* and three-character *Marker No* to create a unique S*ample ID* for each core (Table B-2) [Example: *Event ID* = NC061, *Marker No.* = 018, *Analysis Code* = NF1, *Sample ID* (Bottle ID) = NC061018NF1]. This ID will be stored as the S*ample ID* in EM&MS. Initially, the S*ample ID* will be the same as the *Bottle ID*. The final *Bottle IDs* for each core fraction will be defined based on processing in the laboratory. The fraction will be stored in the bottle table in the *Fraction Code* field. The in-situ data recorded at the station will be reported using the E*vent ID* and M*arker No* only.

During field collection, a separate station log form (Figure B-1) will be completed that will list each core and seawater sample, and a label generated by NavSam© will be affixed to each form, thereby creating a link between the sample and data recorded on the log. The logs will have the identification of the core that links to the bar code, NavSam© data and sample ID, ensuring the tracking of sample location and the status.

Table B-2. Analysis Codes Used in Bottle ID.

Analysis Code	Description	Laboratory
NF1	Nutrient flux rep 1	From first 15-cm core
NF2	Nutrient flux rep 2	From second 15-cm core
DE1*	Denitrification rep 1	From first 10.1-cm core
DE2*	Denitrification rep 2	From second 10.1-cm core
PO1	Eh/pH	From first 6.5-cm core
PO2	Eh/pH	From second 6.5-cm core
CN1	Porosity or Chlorophyll or CHN	From first 2.5-cm core
CN2	Porosity or Chlorophyll or CHN	From second 2.5-cm core
CN3	Porosity or Chlorophyll or CHN	From third 2.5-cm core
FS1	Filtered Seawater	From carboy

* may be used for isotope pairing method for measuring denitrification; not required.

The chief scientist will retain custody of samples during the survey. The chief scientist is responsible for verifying each sample ID vs. the chain of custody forms (COC) generated by NavSam© before the samples are removed from the ship (Figure B–2). The COC forms will be completed in the field and will accompany the samples when transferred from the field to the laboratory. All samples will be delivered to the MBL by the MBL scientific crew who will process the samples (flux cores incubated and sub-samples taken, porewater cores sectioned and extracted, etc.) before individual parameters are analyzed.

Any discrepancies between sample labels and transmittal forms, and unusual events or deviations from the project QAPP will be documented in detail on the COC form and the MBL Senior Scientist and the Battelle Field Manager will be notified. Copies of the signed COC will be faxed to the Battelle Field Sample Custodian after the survey is completed. The original COC forms will accompany MBL personnel to the laboratory and will be submitted to the Battelle Laboratory Manager with the data submission and maintained in the MWRA project files. Unique sample numbers will be used to track the samples through the laboratory; the data will be reported to the database by using the field-generated sample number.

AFFIX BAR CODE LABEL HERE

STATION LOG

MWRA Harbor and Outfall Monitoring Project

Date:	**Event ID:**
Chief Scientist:	**Station ID:**
Other Personnel:	**Time on Station:**
	LAT:
	LONG:
	Water Depth (m):

CORES: **Nut Flux (15 cm)** **NF1** _____ **NF2** _____
PW (6.5 cm) **PO1** _____ **PO2** _____
Solid Phase (2.5 cm) **CN1** _____ **CN2** _____ **CN3** _____

CARBOY: – – – – – – – – – – – – – → **FS1** _____

CORES COLLECTED BY:
DIVE # _____ **(of the day)** **BOX CORE #** _____ **(at this station)**

Divers (initials) _____ **Comments:**
Time in _____
Time out _____
ABT _____
Depth _____
Vis _____

HYDROLAB CAST:

Depth (m): _____
Temp (ºC) _____
Sal (ppt) _____
DO (mg/l) _____

OBSERVATIONS	**WEATHER**
Sediment Description:	**Air temp:**
	Wind:
	Seas:
Animals:	**Tide:**
Other:	**Other:**

Figure B–1. Example Station Log Form.

MWRA Harbor and Outfall Monitoring Program
Contract No. OP-44A
Sample Custody Form

Today's Date : 6/12/2006 9:05:08 A

Laboratory : Marine Biological Laboratory
The Ecosystems Center

Chain-of-Custody # : NC061-NF-0008
Survey ID : NC061
Analysis ID : NF
Analysis Description : Nutrient flux

Woods Hole MA 02543
Ms. Jane Tucker
508-289-7488 (Phone) 508-457-1548 (Fax)

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Depth Code:	Ck 1	Ck 2	Ck 3
	NC06100ANF1	5/4/2006 8:09:31 AM	BH08A	E	☐	☐	☐
	NC06100ANF2	5/4/2006 8:09:31 AM	BH08A	E	☐	☐	☐
	NC061010NF1	5/4/2006 8:42:49 AM	QB01	E	☐	☐	☐
	NC061010NF2	5/4/2006 8:42:49 AM	QB01	E	☐	☐	☐
	NC061015NF1	5/4/2006 9:15:06 AM	BH03	E	☐	☐	☐
	NC061015NF2	5/4/2006 9:15:06 AM	BH03	E	☐	☐	☐
	NC061019NF1	5/4/2006 9:51:52 AM	BH02	E	☐	☐	☐
	NC061019NF2	5/4/2006 9:51:52 AM	BH02	E	☐	☐	☐
	NC06102BNF1	5/8/2006 8:17:18 AM	MB03	E	☐	☐	☐
	NC06102BNF2	5/8/2006 8:17:18 AM	MB03	E	☐	☐	☐
	NC061037NF1	5/8/2006 9:25:06 AM	MB05	E	☐	☐	☐
	NC061037NF2	5/8/2006 9:25:06 AM	MB05	E	☐	☐	☐
	NC061042NF1	5/8/2006 10:34:28 AM	MB01	E	☐	☐	☐
	NC061042NF2	5/8/2006 10:34:28 AM	MB01	E	☐	☐	☐
	NC06104DNF1	5/8/2006 11:09:38 AM	MB02	E	☐	☐	☐
	NC06104DNF2	5/8/2006 11:09:38 AM	MB02	E	☐	☐	☐

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

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

Page 1 of 1

Figure B–2. Example Chain-of-Custody Form for Sediment Cores and Seawater Samples (MBL).

Field custody of electronic data will be the responsibility of the Survey Chief Scientist. The field custody of the electronic data consists of creating floppy disk or compact disk backups of all electronic data generated each day. The label on the backup media will include a survey ID, date, name of person creating the backup files, and a disk number. The data will be transferred to Battelle's data management team upon completion of the survey. The Field Manager or his designee maintains the disks until the annual archive cycle. HOM6 discs are saved for six years from the time of collection.

B.4 ANALYTICAL METHODS

Table B–3 lists all parameters and analyses, and methods, sampling frequency, holding times, reporting units, and processing.

Table B-3. Laboratory Analysis Parameter Table.

Analysis (LAB)	Sample Type (Number per Station)	Parameter	Method	Units	Reference	Frequency of Sampling	Processing	Maximum Holding Time	Preservation
Flux	15-cm-dia. Core (2)	O_2	Electrode	µM	Hale, 1980 or WTW, 2004	≥ 5 per flux	Immediate reading	NA	NA
		DIC (Total CO_2)	Coulometric CO_2 analyzer	µM	DOE, 1994	2 (Initial + Final)	Glass BOD bottles	<4 Months	Mercuric chloride, 4°C
		NH_4	Spectrophotometric	µM	Solorzano, 1969	~5 per flux	Fixed within 1 h	24 h	NA
		NO_2+NO_3	Flow Injection Analyzer	µM	Diamond, 1994	~5 per flux	Polyethylene bottles	<4 Months	Frozen
		PO_4	Spectrophotometric	µM	Murphy and Riley, 1962	~5 per flux	Acidified	<4 Months	4°C
		Si	Rapid Flow Analyzer	µM	Armstrong, 1951	~5 per flux	Polyethylene bottles	<4 Months	Frozen
		N_2/Ar	Membrane Inlet Mass Spectrophotometer	ratio	Kana *et al*, 1998	~5 per flux	12 ml glass serum vial	<4 Months	$HgCl_2$, submerged, ambient temp or 4°C
Porewater/ Sediment	6.5-cm-dia. Core (1)	pH	*In situ* Probe or Electrode	NA	Mitchell, 1997	≥6 Depth Intervals	Immediate	NA	NA
		Eh	Probe	mV	Bohn, 1971	≥6 Depth Intervals	Immediate	NA	NA
		Apparent RPD	Visual Inspection	cm		One depth per core	NA	NA	NA
Sediment	2.5-cm-dia. Core (1)	Porosity and Archive	Balance	g/mL	Giblin *et al*, 1994	1-cm intervals to 10 cm, 2-cm intervals thereafter	Section, dry in 72 hours	<4 Months	NA
	2.5-cm-dia. Core (1)	Chlorophyll/ Phaeophytin	Spectrophotometric	µg/ml	Lorenzen, 1967	1-cm intervals to 5 cm	Section into extraction tubes	<4 Months	Freeze
	2.5-cm-dia. Core (1)	TOC, TN (CHN)	CHN Elemental Analyzer	% dry weight	Kristensen and Andersen, 1987	Top 2-cm	Section, dry at 105 °C	<4 Months	NA
Seawater	*In situ* (1)	O_2 Salinity Temperature	Hydrolab Multiparameter System or YSI 600XLM Sonde	mg/L ppt °C	Hydrolab, 1991 or YSI 1999	Each station	Immediate	NA	NA

NA = not applicable

B.4.1 Measurement of Benthic Respiration and Nutrient Flux

Just prior to initiating the flux measurements, the water overlying each core will be replaced with additional filtered seawater collected at each station. In addition, two 300-mL BOD bottles of filtered water from each station will be used for analyses to correct for water column respiration. The cores will be sealed from the atmosphere with machined core tops fitted with magnetic stirrers that will gently mix the overlying water without resuspending sediments. The exact incubation time will be determined by the time required for oxygen concentrations to drop by at least 2 ppm, but not to a concentration less than 3 ppm, at which point benthic animal respiration may be impaired. The sensor from an Orbisphere 2714 dissolved oxygen measuring system, inserted into an opening in the core top, will provide at least five measurements of oxygen concentration for each core. A WTW Oxi 340i meter and electrode is available as a backup instrument.

Immediately after taking the oxygen measurements, 20-30 mL of overlying water will be withdrawn from the cores for analysis of dissolved inorganic nitrogen, phosphate, and silica. Water will be siphoned into acid-cleaned, pre-labeled bottles and simultaneously replaced in the core by gravity flow from a reservoir of filtered station water**.** Additional water will be siphoned into a 12-ml gas-tight vial and preserved for later N_2/Ar analysis (see Section B.4.2). Samples for nutrient analyses will be processed within 1 hour according to methods presented in Table B-3. Duplicate 3-ml subsamples will be analyzed immediately for ammonium (NH_4) concentrations. A 2-mL subsample will be acidified to pH 2 with 10 µL of 4.8 N HCl and held at 4°C until analyzed for phosphate. The remaining water (~12 mL) will be split and transferred to clean vials and frozen for future analyses for nitrate+nitrite (NO_3+ NO_2), and silica. Duplicate determinations of NO_3+ NO_2 and Si are made during each day's run of the instrument. Dissolved inorganic nitrogen is calculated as the sum of ammonium plus nitrate+nitrite concentrations.

The MBL has a Lachat Flow Injection Analyzer (FIA) and an Alpkem Rapid Flow Analyzer (RFA-300) available for automated nutrient analyses. Nitrate+nitrite measurements will be made by using the Lachat Flow injection analyzer (FIA), with the RFA available as a backup. Silica will be measured by using the Alpkem Rapid Flow (RFA-300) analyzer because the analysis of silica requires a heated chemistry, which the Alpkem is equipped to do (Alpkem 1986).

At the beginning and end of the core incubation period, samples of the overlying water will also be analyzed for dissolved inorganic carbon (DIC; equivalent to TCO_2, total carbon dioxide). A sample from each core will be siphoned into a 60-mL glass BOD bottle as described above. The samples will be preserved with $HgCl_2$ and stored in the dark at 4°C until the analyses are conducted. Carbon dioxide concentrations will be determined using a UIC Coulometrics CM5011 CO_2 Analyzer coupled to U.R.I. SOMMA (Single-Operator Multiparameter Metabolic Analyzer), which provides automated and very high precision introduction of the sample to the analyzer. All analyses requiring the use of a spectrophotometer (ammonium, phosphate) will use a Cary 50 or Shimadzu 160 or 1601 UV-Visible Spectrophotometer equipped with a flow-through "sipper" cell.

Samples for ammonium, nitrate/nitrite, phosphate, and silica will be analyzed against laboratory standards having nutrient concentrations bracketing those of the samples. All standards and blanks are run in duplicate.

B.4.2 Measurement of Sediment Denitrification

Denitrification is measured using a quadrupole mass spectrometer equipped with a membrane inlet (membrane inlet mass spectrometer/ MIMS) to precisely measure N_2/Argon (Ar) ratios of dissolved gases in water samples (Kana *et al*. 1998). Dinitrogen gas concentrations are affected by both biological and physical processes, whereas Ar is affected only by physical processes and can be considered conservative. Deviations from equilibrium ratios of these two gases therefore reflect biological processes acting on the N_2. The Balzers 422 quadrupole mass spectrometer is capable of measuring very small deviations in this ratio (precision of 0.05%), thereby providing a very sensitive and precise method for measuring denitrification.

Samples for dissolved gas analysis are taken from the same cores as are used for flux measurements, allowing for direct comparison of fluxes from a given core. Four to five samples are taken over the incubation time course, simultaneously with the nutrient flux samples. Samples are siphoned into 12-ml glass gas-tight vials, being careful to exclude all bubbles. Samples are quickly poisoned with 25 µl of a saturated $HgCl_2$ solution, and capped with serum caps. Samples are then held submerged and at ambient temperature or refrigerated until analysis.

An additional method for measuring denitrification, called the isotope pairing (IP) technique (Nielsen 1992), may be made using the MIMS. Although results from this technique are not required by contract, they may be made available to MWRA and so a brief description of the method is given here.

In the IP technique, overlying water of intact sediment cores is enriched with ^{15}N-labeled NO_3^- ($^{15}NO_3^-$), which then uniformly mixes with the unlabeled pool ($^{14}NO_3^-$) in the overlying water and the porewaters of the core. During incubation of the cores, denitrification may then produce N_2 that is unlabeled ($^{14}N^{14}N$), single- labeled ($^{14}N^{15}N$) or double-labeled ($^{15}N^{15}N$). These various N_2 species can be distinguished and measured using the mass spectrometer. Total denitrification is calculated by assuming random isotope pairing. In addition, the total denitrification flux may be separated into that derived from NO_3^- in the overlying water and that produced via nitrification within the sediments.

B.4.3 Analysis of Sediment Redox and Archival of Solids

A 6.5-cm-diameter core from each station will be collected for ARPD (apparent redox potential discontinuity), pH, and Eh measurements. The core is first visually inspected to determine the depth of the ARPD, which is expressed as a color change in the sediment from brown/grey to grey/black (note that this is a subjective measurement). Then, a stainless steel pH probe (3.5 mm diameter X 20 cm length) with an ion sensitive field effect transistor (ISFET), (I.Q. 200 pH/thermometer, I.Q. Scientific Instruments) is progressively pushed into the sediment core to measure pH. Measurements will be taken at 1-cm intervals from the sediment surface to 4 cm depth, by 2-cm intervals from 4-10 cm, and by 4-cm intervals through the remaining depth of the core. Eh will be measured simultaneously and in the same manner with a platinum electrode and an Orion 601A digital ion analyzer. Readings will be made at each depth after stabilization of the mV readings.

One 2.5-cm-diameter core collected from each station will be sectioned at 1-cm intervals to 10 cm, and at 2-cm intervals thereafter. The sections will be weighed wet, dried at 105°C, weighed dry, labeled, and archived. Porosity will be estimated from the difference between wet and dry weights, divided by the volume of the whole sediment section. A second 2.5-cm-diameter core will be sectioned from 0-2cm only, and used for TOC and TN analyses (note that TOC and TN are referred to together in the contract as the shorthand "CHN", taken from the name of the analyzer). The 2-cm surface section will be dried, acidified to remove carbonates and then analyzed using a Perkin Elmer 2400 CHN elemental analyzer.

A third 2.5-cm-diameter core will be sectioned by 1-cm intervals to 5 cm for analysis of sediment chlorophyll *a* and phaeopigments. Pigments will be extracted from sediment sections into cold 90% acetone. The sediment/acetone slurry will be disrupted by an ultrasonic probe and extracted overnight on ice and in the dark. Centrifuged samples will be divided into two subsamples, and the absorbance at 665nm (Shimadzu spectrophotometer) of one will be read immediately and of the other after acidification. Standard equations (Lorenzen 1967) will be used to calculate the concentrations of chlorophyll *a* and phaeopigments in the samples.

If 2.5-cm-diameter cores are not collected, one 2.5-cm-diameter core tube will be used to subcore a 15-cm-diameter core after nutrient flux measurements have been made. This subcore would be sectioned and archived as described above for the first 2.5-cm-diameter core.

B.5 QUALITY CONTROL

Certified reference materials (CRMs) are used as quality control samples for all analyses for which they are available. Otherwise, calibration standards or laboratory reference materials are used (See Table A–4).

For dissolved oxygen concentrations, the calibration standard is water-saturated air at known temperature and barometric pressure. Oxygen concentration in this standard is derived from solubility tables. The oxygen meter and electrode are calibrated to this standard at the beginning of each flux incubation. The calibration is checked daily and recorded. Oxygen readings are mathematically corrected for any deviations from expected.

Similarly, for dissolved dinitrogen gas and argon concentrations, the calibration standard is a water bath at known temperature and pressure, and at equilibrium with air. The concentrations of N_2 and Ar are calculated from solubility equations. The standard water bath is run at the beginning and end of each sample run, as well as within the run. Deviations from the expected values are used to make mathematical corrections to sample values.

For DIC (TCO_2), a CRM of seawater of known carbon dioxide concentration is available (Andrew Dickson, University of California San Diego). In addition, a lab standard of local seawater equilibrated with air and preserved with $HgCl_2$ is used.

A mixed CRM containing ammonium, nitrate (or nitrate + nitrite), and phosphate (SPEX CertiPrep) is used as the quality control sample for these nutrients. A separate CRM is used for silica analyses (SPEX CertiPrep). Primary stocks of lab standards are checked against these CRMs.

Commercial pH buffers are used as the calibration standard for pH measurements, and the pH meter/electrode combination is calibrated to these buffers once per day. For Eh, lab standard solutions are made daily from commercial pH buffers with the addition of quinhydrone (1.0 g per 100 ml buffer). Deviations from expected values are used to make mathematical corrections to sample values.

As specified by the manufacturer, acetanilide is used as the calibration standard for TOC and TN measurements. In addition, a standard reference material (ground apples leaves, NIST 1515) is analyzed as a check standard.

Sediment pigments (chlorophyll *a* and phaeopigments) are calculated from standard equations for the spectrophotometic method (Lorenzen 1967). Although CRMs exist for fluorometric methods, the concentrations of these standards are determined spectrophotometrically, using standard equations. Therefore, CRMs for the spectrophotometric method are unavailable and unnecessary.

All DI water used is 18 mohm water, produced by a combined reverse osmosis and ion exchange system, and sterilized with UV light.

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

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

B.7 INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

All data collection equipment and instruments are calibrated prior to use. Logs will be stored in the instrument files maintained by Battelle and MBL. Any deviations to this policy will be noted.

B.7.1 Navigation and Field Equipment

Details of the calibration procedures and preventative maintenance for the navigation equipment can be found in the Water Column Monitoring QAPP (Libby *et al*. 2008).

The Hydrolab probe will be calibrated in the field, prior to deployment, according to manufacturer's specifications. The O_2 sensor will be calibrated against water-saturated air, and the conductivity cell (for salinity) will be calibrated against reference conductivity standards. The thermistor does not require calibration.

B.7.2 Laboratory Equipment

All analytical equipment will be calibrated prior to use according to the manufacturers instructions. Calibration results must meet the performance standards defined by the manufacturer and/or analytical method.

The Orbisphere oxygen meter and electrode will be calibrated, according to manufacturer's specifications, against water-saturated air prior to making flux measurements. If necessary, membranes will be replaced. The meter will undergo regular checks according to manufacturer's recommendations. Additionally, calibration is checked at least daily, deviations from 100% saturation are noted, and appropriate corrections are applied to the data. The same calibration procedure and checks will be followed if the backup WTW meter is used.

Calibration of the UIC Coulometrics CM5011 CO_2 Analyzer used to measure CO_2 will be checked against a CRM (seawater solution of a known carbon dioxide content; see Section B.5).

Performance checks of the Cary or Shimadzu UV-Visible Spectrophotometer (NH_4, PO_4, and chlorophyll/phaeophytin), the Lachat Flow injection analyzer ($NO_2 + NO_3$), and the Alpkem Rapid Flow analyzer (silica) are similar. Each is checked using laboratory blanks and standards that have nutrient concentrations that bracket those of the samples. Laboratory standard concentrations will be verified against certified standard solutions each time a laboratory primary stock solution is made. Laboratory standards will be analyzed daily, checked for linearity ($r^2 > 0.99$) and for comparability to historical results. Acceptability of blanks will also be evaluated.

The ion-sensitive pH probe (sediment pH) will be calibrated each day with commercial pH buffers.

The response of the platinum electrode couple to an Orion 601A digital ion analyzer (Eh) will be checked daily against standard redox solutions made with quinhydrone and commercial pH buffers.

The Perkin Elmer 2400 CHN elemental analyzer (TOC and TN) calibration will be checked at the initiation of each run against the acetanilide commercial standard, and check standards are inserted into each sample run. The CHN elemental analyzer is serviced regularly and maintained by the technical staff of the MBL.

Table B-4. Calibration Procedures for Laboratory Instruments

Parameter	Instrument Type	Initial Calibration			Continuing Calibration			Corrective Action
		QC Sample type	Acceptance Criteria	Frequency	QC Sample type	Acceptance Criteria	Frequency	
O_2	DO meter/probe	1 Std	2% accuracy or better	Prior to initiation of flux incubation	1 std	5% accuracy or better	daily	Investigate, change membrane, recalibrate
DIC (Total CO_2)	Coulometric CO_2 analyzer	Blanks 1 CRM 2 SRMs	< 5% accuracy or better 5% precision or better	Prior to analytical run	SRM	5% precision or better	Every 15 samples	Investigate, discontinue run until problem corrected, reanalyze
NH_4	Spectrophotometer	DI blanks ≥5 stds	0 ± 0.001 $R^2 > 0.99$	Prior to analytical run	Check std	5% precision or better	Every batch	Investigate baseline, take additional samples, flag data
NO_2+NO_3	Flow Injection Analyzer	≥5 stds	$R^2 > 0.99$	Prior to analytical run	Check std	5% precision or better	Every 20 samples	Investigate, discontinue run until problem corrected, reanalyze
PO_4	Spectrophotometer	DI blanks ≥5 stds	0 ± 0.001 $R^2 > 0.99$	Prior to analytical run	Check std	5% precision or better	Every 20 samples	Investigate baseline, take additional samples, flag data
Si	Rapid Flow Analyzer	Stable baseline ≥5 stds 1 CRM	$R^2 > 0.99$ ±5% of expected	Prior to analytical run	Check std	5% precision or better	Every 20 samples	Investigate, discontinue run until problem corrected, reanalyze
N_2/Ar	Membrane Inlet Mass Spectrophotometer	≥3 stds	C.V. ≤ 0.05	Prior to analytical run	baseline check 10 min or more	C.V. ≤ 0.05	Every 20 samples	Investigate, discontinue run until problem corrected, reanalyze
pH	*In situ* Probe or Electrode	2 buffers	NA	Daily, prior to analytical run	NA	NA	NA	Investigate, recalibrate
Eh	Probe	2 buffers	NA	Daily, prior to analytical run	oxic seawater	Positive value	Prior to initiation of each profile	Investigate, clean Eh probe, reanalyze
Porosity	Balance	Calibration weights Tare balance	NA Tares to 0.000	Annually, by commercial service	Tare	Tares to 0.000	Every 15 samples	Retare
Chlorophyll/ Phaeophytin	Spectrophotometer	90% acetone blanks	0 ± 0.001	Prior to analytical run	90% acetone Blank	0 ± 0.001	Every 12 samples	Record; Rinse cell with DI, reset blank
TOC, TN (CHN)	CHN Elemental Analyzer	4 Blanks 4 Calibration Stds	Within manufacturer's specified tolerance Calibration factors ±2%	Prior to analytical run	Blank Check std	Within manufacturer's specified tolerance Calibration factors ±2%	Every 10 samples Every 10 samples	Investigate, discontinue run until problem corrected, reanalyze
Field O_2	Multi-parameter Water Quality Sonde	1 std	NA	Daily, prior to initial deployment	NA	NA	NA	Investigate, change membrane, check/ change batteries, recalibrate
Field Salinity		1 std	NA	Daily, prior to initial deployment	NA	NA	NA	Investigate, recalibrate, check/change batteries; use refractometer and pumped water as backup
Field Temperature		NA	NA	NA	NA	NA	NA	Investigate, recalibrate, check/change batteries; use digital thermometer and pumped water as backup

A calibration standard of air-saturated deionized water held at ambient sample temperature is used to calibrate the N_2/Ar output from the membrane inlet mass spectrometer (MIMS) to standardized gas solubility tables. The MIMS is serviced and maintained by the technical staff of the MBL.

Automatic pipettors used for preparing standards and pipetting samples will be checked for accuracy and recalibrated if necessary. Balances are checked, calibrated, and maintained on an annual schedule by New England Balance Service.

B.8 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

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

- Sample containers are either cleaned by the laboratory according to specifications for each analysis or purchased new.
- Field filtration equipment is cleaned by thorough rinsing with deionized water between each survey. New cartridge filters are used daily or more frequently if they become fouled. In the field, the apparatus is rinsed with station water sufficient to replace the entire volume 3 times before seawater is collected. Carboys that receive the filtered water are acid washed and DI rinsed before use in the field, and are rinsed 3 times with station water before water is collected.
- Laboratory reagents must be reagent grade or better. In the following cases, specific grades and/or suppliers are required: 1) sodium chloride used to make solutions of artificial seawater used in nutrient analyses must be analyzed for ammonium contamination before use (we have found that Mallincrodt ACS Grade meets these requirements and we specify its use for these analyses); 2) hydrochloric acid used to preserve samples for phosphate analysis must be Trace Metal grade. Reagent solutions are stored and assigned expiration dates according to analytical specifications. Sodium hypochlorite used in ammonium analyses is discarded after three months. Liquid phenol, also used in the ammonium analyses, is assigned an expiration date of 2 years or is discarded if it becomes visibly discolored. A chemical tracking inventory is maintained by the laboratory.
- Laboratory standard solutions are prepared from Primary Standard Grade reagents. Standards must be assigned an expiration date "as received" based on the manufacturer's expiration date, or a date consistent with specifications for each analysis.
- DI water is checked for purity at metered outlets in the laboratory.

B.9 NONDIRECT MEASUREMENTS

The HOM6 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-3 illustrates the benthic nutrient flux monitoring data processing strategy for data entry into the MWRA Environmental Monitoring and Management System (EM&MS) and accessing the data for various reports.

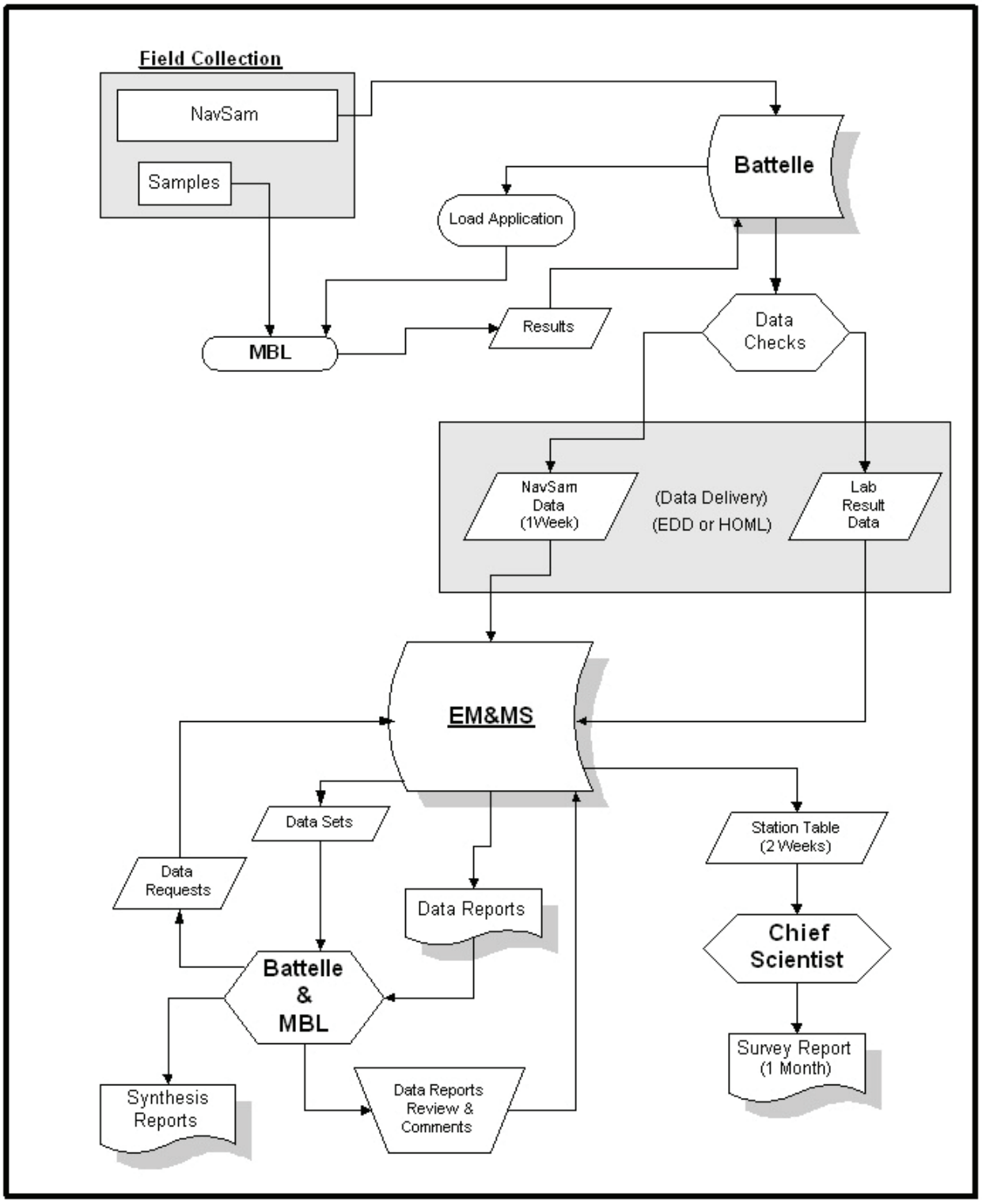

Figure B–3. Overview of the Data Management Strategy for Benthic Nutrient Flux Monitoring

B.10.1 Data Reduction

For each survey, researchers from MBL will develop PC-based spreadsheets that will contain the following data and calculations for entry into the loading application described in Section B10.2:

- Fluxes of oxygen, total carbon dioxide (DIC), dinitrogen gas, ammonium, nitrate + nitrite, dissolved inorganic nitrogen, phosphate, and silica will be reported for each "nutrient flux (NF)-rate core " collected at each station. All fluxes will normally be calculated from five data points using a linear regression (Giblin *et al*. 1995, 1997); fluxes calculated from 3 points or fewer will be assigned an appropriate qualifier and explained with a comment. The r^2 for the regression of each analyte, except for DIC, over time will also be reported. The r^2 for DIC flux is not reported because only initial and final samples are taken for this analyte; when n=2, r^2 is always 1.0 and is meaningless. The acceptability of flux measurements for a given core will depend on the linearity of the oxygen flux ($r^2 > 0.9$). (It should be understood, however, that the r^2s associated with all of these fluxes impart information about each flux as a process and may not necessarily reflect the quality of the individual data points comprising the flux. For example, burrowing animals captured in a sediment core may be active intermittently during a flux incubation; the concentrations of nutrients measured during the incubation may then show pulses rather than a linear trend, and the regression of concentration vs. time would yield a low r^2). All fluxes will be expressed as mmol m^{-2} day^{-1}. The incubation temperature will also be reported.
- Eh and pH from one "porewater (PO) core" collected at each station.
- Sediment pigments, porosity, TOC and TN from one each of the three "solid phase (CN) cores" collected at each station.
- The concentration of dissolved oxygen (mg L^{-1}), field temperature (°C) and salinity (ppt) for each station.

Calculations
Concentrations of NH_4, NO_3+NO_2, PO4, and Si are calculated from a linear standard curve that relates concentration to absorption units, which are the raw data produced from a spectrophotometer or colorimeter (Beer's Law). DIN concentration is defined as the sum of NH_4 + (NO_3+NO_2) concentrations.

Concentrations of oxygen in mg O_2/L as read off the Orbisphere O_2 meter are converted to mmol O_2/L and corrected for temperature and salinity using the following equation (Hale, 1980):

$$\alpha_s/\alpha_w + \exp\{ -[Cl^-] \cdot (-0.1288 + 53.44/T - 0.04442\ln T + 7.1145 \cdot 10^{-4} T)\},$$

where: α_s and α_w are the concentrations of oxygen in seawater and pure water, respectively
$[Cl^-]$ is the chlorinity, derived from salinity by the relationship $S = 1.80655[Cl^-]$
T is the absolute temperature (ºK).

Fluxes are calculated as a linear regression of analyte (eg. NH_4, O_2) concentration from five time points divided by the surface area of the flux core versus time to yield rates in units of mmol m^{-2} d^{-1}.

Eh values, recorded as raw mV readings, are corrected for the oxidation-reduction potential of the reference electrode, as given in tables in Lange's Handbook of Chemistry (Dean 1992).

TOC and TN, as % dry weight, reported from the Perkin-Elmer Elemental Analyzer are based on the weight of the sediment sample after it was acidified to remove carbonates. These values are corrected for the weight change by:

$$(\text{TOC or TN})_{\text{corrected}} = (\text{TOC or TN})_{\text{uncorrected}} \cdot (\text{dry weight}_{\text{acidified}}/\text{dry weight}_{\text{preacidified}})$$

Chlorophyll *a* and phaeophytin are calculated after Lorenzen, 1967:

$$\text{Chl a } (\mu g/mL) = [26.7(665_o - 665_a) \cdot v_{ex}]/(v_s \cdot l)$$
$$\text{Phaeo } (\mu g/mL) = [26.7\ ((1.7 \cdot 665_a)\text{-}665_o) \cdot v_{ex}]/(v_s \cdot l),$$

where: 665_o = absorbance at 665nm before acidification
665_a = absorbance at 665nm after acidification
v_{ex} = volume of acetone extract in mL
v_s = volume of sediment extracted in mL
l = path length of the cuvette.

The calculation of N_2 flux (denitrification) from the N_2/Ar ratios using the MIMS has several steps. The first is to calculate the expected equilibrium concentrations of N_2 and Ar in the standard calibration bath for a given temperature, salinity, and atmospheric pressure. The resulting N_2/Ar ratio is compared to the ratio output from the MIMS to derive a calibration factor that is applied to sample results. Results are also corrected for any instrument drift that occurs in the ratio. Corrected N_2/Ar values are then multiplied by the expected Ar concentration at the temperature and salinity appropriate for the sample to give the N_2 concentration (uM) of the sample. A linear regression of N_2 concentration versus time, divided by the surface area of the sediment core and with units corrected yields the N_2 flux as mmol N_2 $m^{-2}d^{-1}$. The r^2 for the regression is also reported.

B.10.2 Reporting Data to be Loaded into the Database

All field data to be loaded into the EM&MS will be submitted to Battelle in electronic format. The field data collection will be available for data loading directly off the ship. The laboratories will be supplied a loading application based on collection data that will increase data quality and data flow efficiency. These applications eliminate the need for data reporting formats and deliver many of the quality control checks upstream to the laboratories. Formats for delivering electronic data are included in the contract but these formats are subject to change and have already changed once since the contract was generated. The current delivery formats are available from the data management lead at Battelle (Greg Lescarbeau) or the data management lead at MWRA (Wendy Leo). Battelle's data management staff will process all data into the appropriate HOML format as defined in the contract. These submissions will be delivered to MWRA via email in the absence of the HOML application. Once the HOML application goes online, Battelle will submit data electronically through the application.

B.10.2.1 Navigation and Sample Collection Data

Navigation and sample collection data will be processed on-board the survey vessel and be ready for loading upon arrival at Battelle. A database application developed as part of the NavSam© system will query the on-board database tables for the fields necessary to populate the *Event, Station, Sample* and *Bottle* tables. The data will be submitted to EM&MS in the HOML format. All database constraints developed by MWRA will be applied to the tables so that the data are checked during the insert. The loading of sample collection data is detailed in SOP MWRA 006 *Loading and Reporting Benthic Nutrient Flux Data.*

B.10.2.2 Analytical and Experimental Data

B.10.2.2.1 Data Loading Applications

The data reporting for analytical and experimental data begins with the Battelle Data Management Team who will populate a loading application for MBL. Sample_ID numbers and analysis protocols will be extracted from an Access database derived from NavSam© and used to populate a database within the loading application. A separate loading application will be prepared for each data deliverable.

B.10.2.2.2 Data Entry

When MBL scientists open the flux data loading application they will be presented with a form that allows the laboratory to load the various files produced during the processing of the nutrient flux data (Figure B-4). The nutrient flux loading application will read in the various files produced by the laboratory and then process the files appropriately. MBL will populate a lookup table that relates their lab Ids to the Sample Ids from the field. The application will then assign the correct sample ID for all the various file types that are loaded with just the lab ID. All entries will be constrained by the rules of EM&MS. Errors will be caught on entry and fixed by the data contributor. Primary keys will be in place so duplication cannot occur. Entry applications will be developed for each analytical laboratory. When data entry is complete, the database will be sent back to Battelle.

The loading application will provide the laboratory with several function buttons. These include hard copy report, quality control checks, exception report, and analysis summary. The hardcopy report function button will allow the laboratory to create a hardcopy report to check for entry errors and to submit a final report to Battelle with the data deliverable. The quality control checks will be comprised of the applicable sections of EM&MS check scripts and will also perform checks for outliers. This report will provide the data contributor a chance to confirm the reasonableness of the data prior to its submission to Battelle. The exception report will check the data that were expected against the results that were loaded. The data contributor must account for any entries in the exception report. The analysis report will produce a report of the number of analyses by analyte. A copy of this report will be included with the data deliverable and with the invoice for the analyses. Within the loading application, the data entered by the laboratory will be translated into the correct codes and inserted into database tables with the same structure as the matching EM&MS table. Table B-5 shows the analytical parameters and database codes for the analytes collected under this task. Table B-6 describes the database codes to be used by the laboratory. The laboratory will have the ability to add additional codes to describe their results but the new codes will be highlighted in the exception report. Battelle will notify MWRA concerning the new qualifier and will adjust the code table in the application to agree with any changes to the EM&MS code_list table. MWRA has the responsibility for maintaining the code list for the EM&MS.

B.10.2.2.3 Submitting Analytical and Experimental Data

Data submissions from the laboratories are the final loading applications data. The submissions are logged in upon receipt and a copy is maintained on file under the login identification. Data are loaded into a temporary table space by a button on the application. A transfer script will copy the data into the proper table in Battelle's database. Data from the laboratories receive a quality assurance review prior to electronic submission to MWRA. Any issues are corrected in the database with a well-documented script that is available to MWRA upon request. A check script that verifies MWRA's business rules will be run on the database prior to export of a dataset to ensure that all data conform to quality control checks and database constraints. Project-specific SOP MWRA 006 *Loading and Reporting Benthic Nutrient Flux Data* describes these procedures.

B.10.3 Reporting Data to MWRA

The data associated with each benthic nutrient flux survey will be submitted to MWRA in the appropriate HOML format. The supporting documentation files are included with the data submission. Data deliverables will be combined only with permission from MWRA.

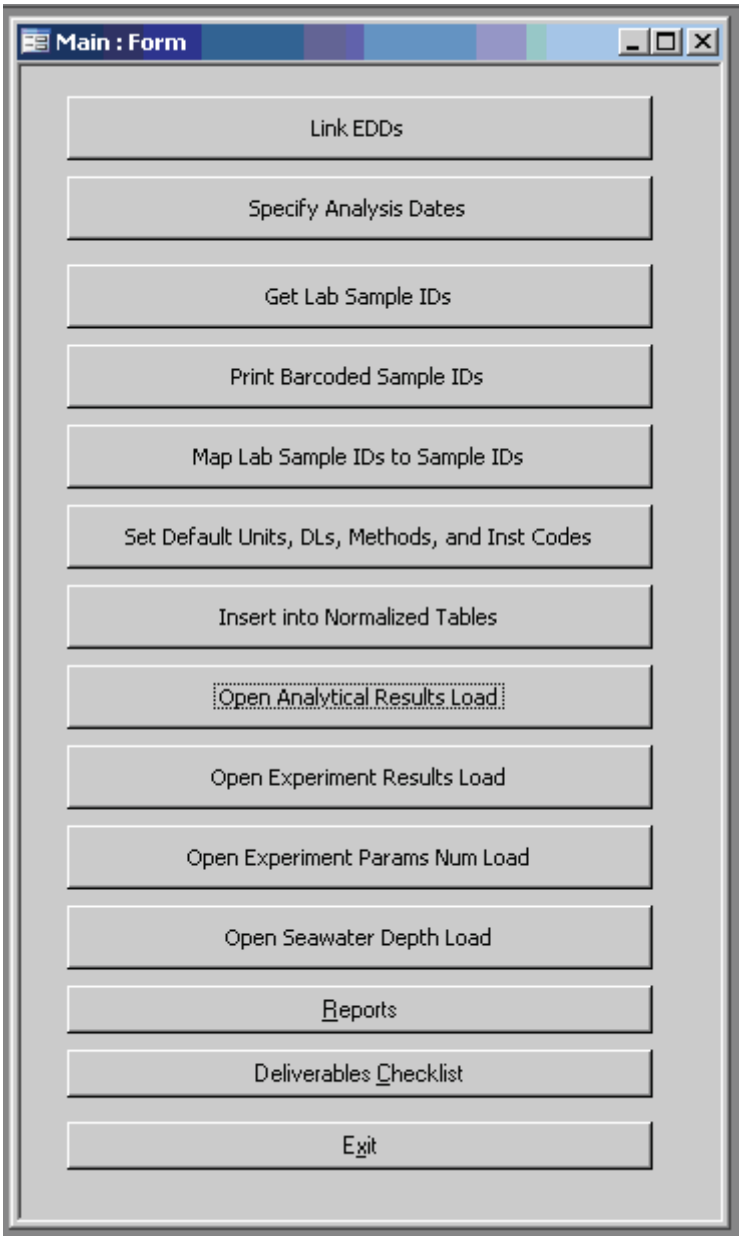

Figure B–4. Benthic Nutrient Flux Entry and Loading Application.

Table B-5. Analytical Parameters and Database Codes

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Benthic Nutrient Flux					
Efflux of dissolved inorganic carbon from sediment	DIC_FLUX	mmol/m2/d	MBL	CCO2	DOE94
Flux measurement for dissolved inorganic nitrogen	DIN_FLUX	mmol/m2/d	MBL	SPH_LTF	KEL93
R-Squared of linear regression for estimation of parameter DIN_FLUX	DINFLUXR2		MBL		
Ammonium flux from sediments	NH4_FLUX	mmol/m2/d	MBL	SPECPH	SOL69
R-Squared of linear regression for estimation of parameter NH4_FLUX	NH4FLUXR2		MBL		
Nitrate flux from sediments	NO3_FLUX	mmol/m2/d	MBL	LATFI	DIAM94
R-Squared of linear regression for estimation of parameter NO3_FLUX	NO3FLUXR2		MBL		
Flux measurement for PO4	PO4_FLUX	mmol/m2/d	MBL	SPECPH	MURPH62
R-Squared of linear regression for estimation of parameter PO4_FLUX	PO4FLUXR2		MBL		
Flux measurement for silica	SI_FLUX	mmol/m2/d	MBL	RAPFL	ARMS51
R-Squared of linear regression for estimation of parameter SI_FLUX	SIFLUXR2		MBL		
O2 flux from sediments	O2_FLUX	mmol/m2/d	MBL	DOPROBE or WTW340I	HALE80 or WTW2004
O2 flux from sediments (back-up method)	O2_FLUX	mmol/m2/d	MBL	WHOIWINK	KNAPP1990
R squared for O2 flux measurement	O2FLUXR2		MBL		
Temperature	INCUB_TEMP_FLUX	C	MBL	THER	
Denitrification Flux					
N2 flux from sediments	N2_FLUX	mmolN2/m2/d	MBL[1]	BA422QMG	MIMS
R-Squared for denitrification rate from direct (MIMS) measurement of N2/Ar ratios over time	N2FLUXR2		MBL[1]		
Temperature	INCUB_TEMP_FLUX	C	MBL[1]	THER	
Sediment					
Redox potential discontinuity at the bottom of the bioturbation layer - where sediment is sulfidic	ARPD	cm	MBL	RULER	KEL93
Chlorophyll a	CHLA	ug/mL	MBL	SPECPH	LOR67
Phaeophytin	PHAE	ug/mL	MBL	SPECPH	LOR67
Total organic carbon	TOC	PCTDRYWT	MBL	PE24CHN	KA87
Total nitrogen	MWRA47	PCTDRYWT	MBL	PE24CHN	KA87
Ratio of porewater mass to sediment volume	POROSITY	g/mL	MBL	BAL	GIB94

[1]HPL (Horn Point Laboratory) will provide backup for this analysis.

Table B-5. Analytical Parameters and Database Codes, continued

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Porewater					
Standard redox potential	EH	mV	MBL	EHPROBE	BOHN71
Negative log of hydrogen ion activity	pH		MBL	PHPROBE	MIT97
Seawater					
Dissolved oxygen	DISS_OXYGEN	mg/L	MBL	HYDRO-S2 or YSI600XLM	HYDRO91 or YSI1999
Salinity (field)	SFIELD	PPT	MBL	HYDRO-S2 or YSI600XLM	HYDRO91 or YSI1999
Temperature (field)	TFIELD	C	MBL	HYDRO-S2 or YSI600XLM	HYDRO91 or YSI1999

Table B-6. Description of Database Codes

FIELD NAME	CODE	DESCRIPTION
INSTR_CODE	CCO2	Coulometric CO2 Analyzer
INSTR_CODE	RAPFL	Rapid Flow Analyzer
INSTR_CODE	SPECPH	Spectrophotometer
INSTR_CODE	BA422QMG	Balzers 422 Quadrupole Mass Spectrometer
INSTR_CODE	LATFI	Lachat QuikChem 8000-FIA
INSTR_CODE	HYDRO-S2	Hydrolab Scout 2 Multiparameter Water Quality Data System
INSTR_CODE	YSI600XLM	YSI 600XLM Environmental Monitoring System
INSTR_CODE	DOPROBE	Dissolved Oxygen Probe (Orbishpere 2714)
INSTR_CODE	WTW340I	Dissolved Oxygen Probe (WTW Oxi 340i)
INSTR_CODE	EHPROBE	Eh Probe Platinum Electrode
INSTR_CODE	PE24CHN	Perkin-Elmer 2400 CHN Elemental Analyzer
INSTR_CODE	RULER	Measurement by Ruler
INSTR_CODE	BAL	Balance
INSTR_CODE	THER	Thermometer
INSTR_CODE	PHPROBE	pH probe and meter
INSTR_CODE	WHOIWINK	Home-made Winkler amperometric autotrator modeled after a WHOI setup
INSTR_CODE	SPH_LTF	Spectrophotometer and Lachat QuickChem 8000-FIA
UNIT_CODE	C	Degrees Celsius
UNIT_CODE	PCTDRYWT	Percent dry weight
UNIT_CODE	PPT	Parts per thousand
UNIT_CODE	cm	Centimeter
UNIT_CODE	g/mL	Grams per milliliter
UNIT_CODE	mV	Millivolts
UNIT_CODE	mg/L	Milligrams per liter
UNIT_CODE	mmol/m2/d	Millimole per meter squared per day
UNIT_CODE	mmolN2/m2/d	Millimoles of dinitrogen (N_2) per square meter per day
UNIT_CODE	ug/mL	Micrograms per milliliter
METH_CODE	BOHN71	Bohn, 1971. Soil Science 112:39-45
METH_CODE	DOE94	DOE. 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2, A.G. Dickson and C.Goyet, eds. ORNL/CDIAC-74.
METH_CODE	GIB94	Giblin et al 1994, final rept. metabolism,nut cycling and denitrif in Bos Harbr and MassBay seds 1994
METH_CODE	MIT97	Mitchell, m. 1997. ph evolves into the silicon age. american laboratory. june.
METH_CODE	KEL93	Kelly *et. al.* 1993 Benthic Nut Flux QA plan
METH_CODE	HALE80	Hale 1980, Inst. meas. of do conc. in saline water, Orbisphere Lab NJ
METH_CODE	WTW2004	WTW 2004, Instruction Manuals: Oxi 330i/340i. WTW, Weilheim, Germany
METH_CODE	SOL69	Solorzano (1969)
METH_CODE	ARMS51	Armstrong 1951, J. Marine Biol. Assoc. of the UK 30:149-1160
METH_CODE	MURPH62	Murphy and Reilly. 1962 per benthic flux CWQAPP
METH_CODE	MIMS	Kana *et al*., 1998. Membrane inlet quadrupole mass spectrometry (MIMS) for analysis of N2/Ar ratios in dissolved gases
METH_CODE	DIAM94	Diamond 1994, Quikchem method 31-107-04-1-C, Lachat Instruments
METH_CODE	KA87	Kristensen and Andersen 1987, J. Experimental Mar. Biol. 109:15-23.
METH_CODE	HYDRO91	Hydrolab. 1991. H2O Multiparameter Water Quality Data Transmitter, Operating Manual. Hydrolab Corporation, Austin, Texas, 78731.

Table B-6. Description of Database Codes, continued

FIELD NAME	CODE	DESCRIPTION
METH_CODE	YSI1999	YSI. 1999. YSI Environmental Operations Manual: 6-Series Environmental Monitoring Systems, Revision A. YSI Incorporated, Yellow Springs, Ohio, 45387.
METH_CODE	KNAPP1990	Knapp *et. al.* 1990. Automated oxygen titration and sal. determinination. WHOI Inst Tech Rpt: WHOI-90-35
METH_CODE	LOR67	Lorenzen, C.F. 1967. Determination of chlorophyll and pheo-pigments; spectrophotometric equations. Limnol. Oceanogr. 12: 343-346.
ANAL_LAB_ID	MBL	Marine Biological Laboratory – Giblin
ANAL_LAB_ID	HPL	Horn Point Laboratory – Jeffrey Cornwall
VAL_QUAL	A	Value above maximum detection limit, *e.g.*, too numerous to count or beyond range of instrument
VAL_QUAL	a	Usable non-detect result; not detected at or above the method detection limit (MDL). Database value input as null or negative. DETECT_LIMIT is the MDL.
VAL_QUAL	e	Results not reported, value given is NULL. Explanation in COMMENTS field
VAL_QUAL	f	Value reported is below method detection limit
VAL_QUAL	j	Usable result. Value estimated by method not specified in CW/QAPP. See comments.
VAL_QUAL	L	Analytical concentration reported from dilution
VAL_QUAL	o	Value out of normal range judged fit for use by principal investigator
VAL_QUAL	p	Lab sample bottles mislabeled – caution data use
VAL_QUAL	q	Possibly suspect/invalid and not fit for use. Investigation pending.
VAL_QUAL	r	Precision does not meet data quality objectives
VAL_QUAL	s	Suspect/invalid. Not fit for use. See comment.
VAL_QUAL	T	Holding time exceeded
VAL_QUAL	t	Two points used to calculate flux
VAL_QUAL	v	Arithmetic mean
VAL_QUAL	w	This datum should be used with caution, see comment field
NAVIGATION_CODE	DGPS	Differential GPS
NAV_QUAL	+/- 10m	Plus or minus 10 meters accuracy
SAMP_VOL_UNIT_CODE	L	Liter
SAMP_VOL_UNIT_CODE	cm3	Cubic centimeters
DEPTH_UNIT_CODE	m	Meters
DEPTH_UNIT_CODE	cm	Centimeters
GEAR_CODE	PUMP	Sample pumped to surface
GEAR_CODE	BC40_025	25mm diameter sub-core from 40x40 cm box core
GEAR_CODE	BC40_065	65mm diameter sub-core from 40x40 cm box core
GEAR_CODE	BC40_077	77mm diameter sub-core from 40x40 cm box core
GEAR_CODE	BC40_150	150mm diameter sub-core from 40x40 cm box core
GEAR_CODE	DIVER_025	Diver hand collected 25mm diameter sediment core
GEAR_CODE	DIVER_065	Diver hand collected 65mm diameter sediment core
GEAR_CODE	DIVER_077	Diver hand collected 77mm diameter sediment core
GEAR_CODE	DIVER_150	Diver hand collected 150mm diameter sediment core
MATRIX_CODE	SED	Sediment
MATRIX_CODE	WAT	Ambient water

C. ASSESSMENT AND OVERSIGHT

C.1 ASSESSMENT AND RESPONSE ACTIONS

C.1.1 Performance and System Audits

The Battelle QA Officer for the Harbor and Outfall Monitoring Project is Ms. Rosanna Buhl. She will direct the conduct of at least one systems audit to ensure that Task 9 is carried out in accordance with this QAPP. A systems audit will verify the implementation of this QAPP for the work conducted in the Benthic Nutrient Flux monitoring.

MBL will be responsible for audits of the data collection procedures at its laboratory. It is fully responsible for the QA of the data it submits. Data must be submitted in QAPP - prescribed formats; no other will be acceptable. During the time that work is in progress, an inspection will be conducted by the designated laboratory QA Officer to evaluate the laboratory data-production process. All data must be reviewed by the QA Officer prior to submission to the Battelle Database Manager and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted, the results, any outstanding issues that could affect data quality, and a QC narrative of activities.

Performance audits, procedures used to determine quantitatively the accuracy of the total measurement system or its components, will be the responsibility of the MBL laboratory and may include SRMs, internal performance evaluation samples, and participation in external certification programs.

C.1.2 Corrective Action

All technical personnel share responsibility for identifying and resolving problems encountered in the routine performance of their duties. Ms. Ellen Baptiste-Carpenter, Battelle's Project Manager, will be accountable to MWRA and to Battelle management for overall conduct of the Harbor and Outfall Monitoring Project, including the schedule, costs, and technical performance. She is responsible for identifying and resolving problems that (1) have not been addressed in a timely manner 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 the laboratory manager (see Figure A–1). Issues that affect schedule, cost, or performance of the benthic nutrient flux study tasks will be reported to the Task Leader, Dr. Anne Giblin, or to the Battelle Project Manager. Battelle's Technical Manager will be notified of any issues affecting data quality. The Technical Manager and Task Leader will be responsible for addressing these issues and, with the Project Manager, will be responsible for evaluating the overall impact of the problem on the project and for discussing corrective actions with the MWRA Project Management. Systematic problems identified during audits, inspections, or by project staff will be entered into the Corrective Action Logger, assigned to appropriate staff for root cause analysis, and tracked by the QA officer.

C.2 REPORTS TO MANAGEMENT

It is important that data quality issues be reported to the appropriate management level so that appropriate solutions are implemented. Data or performance quality issues are reported to Battelle management team at the monthly management meetings. Action items are discussed, assigned, and results reported at subsequent meetings. Persistent project issues that are not addressed satisfactorily during weekly meetings are reported to Battelle's Product Line Manager during monthly QA review meetings; the MWRA project is a standing agenda item for this meeting. 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 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 submission to the EM&MS database. The measurement quality objectives, sensitivity requirements, and monitoring thresholds are used to accept, reject, or qualify the environmental monitoring data generated for this project.

All data collected and analyzed as part of Task 9 will be reviewed to check for errors in transcription, calculation, or spreadsheet input. Validation procedures for data generated by Battelle or MBL will include the following:

- 100% of the data hand-entered into a database or spreadsheet will be verified for accuracy by (1) printing the spreadsheet and proofreading against the original hand entry or by (2) duplicate entry into the database and comparison of the dual entries to reveal any differences.
- Manual calculations (*e.g.*, of concentrations or fluxes) will be checked for accuracy by a second staff member.
- Electronic calculations will be checked by the technical staff member at a frequency sufficient to ensure the accuracy of the calculations. All data reduction algorithms will be verified by the subcontractor prior to final data submission.
- Electronically generated data will be reviewed in graphical form to ensure that the data are complete, accurate, and technically reasonable. The removal of all outliers, either manually or by computer algorithm, will be reviewed by the subconsultant or Battelle Senior Scientists.
- Analytical results and supporting data will be reviewed to ensure that the data are complete, accurate, and technically sound.
- Battelle database staff will ensure that all new software developed for this Task is validated prior to the entry of data.

The MBL Senior Scientist will be responsible for conducting data validation procedures to ensure that the data provided to Battelle are accurate, complete, and scientifically reasonable. Missing or suspect data will be explained by data qualifiers and comments given in the data submission. As an additional validation step, the Battelle Laboratory Manager will review all subcontractor data for completeness, internal consistency, and technical reasonableness.

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© sample IDs to sample bottle labels. Sampling documentation is verified through the review and approval of each survey log book by the field manager. Entry of field sample data in EM&MS is verified when the QA Officer audits the survey report vs. the survey log book documentation.

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

- Any data that are hand-entered (i.e., typed) are verified by qualified personnel prior to use in calculations or entry into the database.
- For each cut and paste function, the first and last data values are verified by comparison to the source data.
- 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, achieved method detection limits, instrument calibration results, and quality control sample results. The criteria for these data quality requirements are presented in Sections A.7, B.5, B.6, B.7, and B.8. Data qualifiers and comments are used to define in the database the usability of the data.

D.3 RECONCILIATION WITH USER REQUIREMENTS

Once data have been generated and compiled in the laboratory, Senior 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.

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

Final data reports developed by MWRA will be reviewed by the Project Manager (Ms. Jane Tucker) and Laboratory Manager (Ms. Deirdre Dahlen) and a data report review letter will be sent to MWRA.

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APPENDIX A

Contact List

Name	Affiliation Street Address E-mail	Telephone and Fax
	Massachusetts Water Resources Authority ENQUAD 100 First Avenue Charlestown Navy Yard Boston, MA 02129	(617) 660-7800 or 7960 (fax)
Ms. Sally Carroll	Sally.Carroll[at]mwra.state.ma.us	(617) 788-4946
Mr. Ed Caruso	Edward.Carusojr[at]mwra.state.ma.us	(617) 660-7807
Ms. Cara Seaman	Cara.Seaman[at]mwra.state.ma.us	(617) 660-7807
Ms. Kelly Coughlin	Kelly.Coughlin[at]mwra.state.ma.us	(617) 788-4943
Mr. Mike Delaney	Mike.Delaney[at]mwra.state.ma.us	(617) 660-7801
Mr. Maury Hall	Maurice.Hall[at]mwra.state.ma.us	(617) 788-4944
Dr. Doug Hersh	Douglas.Hersh[at]mwra.state.ma.us	(617) 788-4945
Mr. Ken Keay	Kenneth.Keay[at]mwra.state.ma.us	(617) 788-4947
Mr. Yong Lao	Yong.Lao[at]mwra.state.ma.us	(617) 660-7841
Ms. Wendy Leo	Wendy.Leo[at]mwra.state.ma.us	(617) 788-4948
Dr. Mike Mickelson	Mike.Mickelson[at]mwra.state.ma.us	(617) 788-4951
Dr. Andrea Rex	Andrea.Rex[at]mwra.state.ma.us	(617) 788-4940
Mr. Steve Rhode	Rhode.Steve[at]mwra.state.ma.us	(617) 660-7803
Ms. Paula Smith		(617) 788-4152
Dr. David Taylor	David.Taylor[at]mwra.state.ma.us	(617) 788-4952
Mr. Ethan Wenger	Ethan.Wenger[at]mwra.state.ma.us	(617) 660-7851
	Battelle Duxbury Operations 397 Washington Street Duxbury, MA 02332	(781) 934-0571 (operator) (781) 934-2124 (general fax)
Ms. Ellie Baptiste-Carpenter	baptiste[at]battelle.org	(781) 952-5361
Ms. Rosanna Buhl	buhl[at]battelle.org	(781) 952-5309
Ms. Deirdre Dahlen	dahlend[at]battelle.org	(781) 952-5253
Mr. Paul Dragos	dragosp[at]battelle.org	(781) 952-5357
Dr. Carlton Hunt	huntc[at]battelle.org	(781) 952-5374
Ms. Sandy Jenkins	jenkinss[at]battelle.org	(781) 952-5307
Ms. Joanne Lahey	laheyj[at]battelle.org	(781) 952-5341
Mr. Matt Fitzpatrick	fitzpatrickm[at]battelle.org	(781) 952-5329
Mr. Greg Lescarbeau	Lescarbeaug[at]battelle.org	(781) 952-5293
Ms. Stacy Pala-Abramson	abramson[at]battelle.org	(781) 952-5330
Ms. Jennifer Field	**Battelle-West Palm Beach Office** 1400 Centrepark Blvd Suite 1005 West Palm Beach, FL 33401 FieldJ[at]battelle.org	(561) 656-6303 (561) 683-0126 (fax)
Mr. Scott Libby	**Battelle-Maine Office** 153B Park Row Brunswick, ME 04011 libby[at]battelle.org	(207) 725-9572

Name	Affiliation Street Address E-mail	Telephone and Fax
Dr. Candace Oviatt	**University of Rhode Island (URI)** Graduate School of Oceanography Narragansett Bay Campus Narragansett, RI 02882-1197 coviatt[at]gso.uri.edu	(401) 874-6661 (401) 874-6613 (fax)
Dr. Aimee Keller	Mail: P.O. Box 2009 Kingston, WA 98346 FedEx: 6762 NE Wood Bay Lane Poulsbo,, WA 98370 aimee@gso.uri.edu	H- 360-697-6683 W- 206-860-3460 C- 206-795-5860
Ms. Kim Whitman Hyde Ms. Brooke Longval Mr. Matt Schult	khyde@gso.uri.edu or Kimberly.hyde@noaa.gov 42 Covington Drive Warwick, RI 02886 brooke@gso.uri.edu mschult@gso.uri.edu	(401) 874-6651 (lab) (401) 874-6108 (office) (401) 874-6657 (Brooke) (401) 874-6188 (Matt)
Dr. Jefferson Turner	1 Joshua Weeks Lane South Dartmouth, MA 02748 turner.01@comcast.net	(508) 999-8229 (office) (508) 910-6332 (Mar. lab) (508) 999-8196 (fax)
Dr. David Borkman	David Borkman 1045 Gilbert Stuart Road Saunderstown, RI 02874 University of Rhode Island Graduate School of Oceanography Narragansett, RI 02882 dborkman[at]gsosun1.gso.uri.edu	(401) 874-6686 (office) (401) 874-6160 (fax) (401) 295-7689 (home)
Dr. Anne Giblin Ms. Jane Tucker Mr. Sam Kelsey	**Marine Biological Lab (MBL)** The Ecosystems Center Woods Hole, MA 02543 agiblin[at]mbl.edu jtucker[at]mbl.edu skelsey[at]mbl.edu	(508) 289-7488 (508) 457-1548 (fax) (508) 289-7469
Dr. Rocky Geyer	**Woods Hole Oceanographic Institution** Dept. of Ocean Physics and Engineering Woods Hole, MA 02543 rgeyer[at]whoi.edu	(508) 289-2868 (508) 547-2194 (fax)
Dr. Donald Anderson	6 Arrowhead Lane Marion, MA 02738 Danderson[at]whoi.edu	(508) 289-2351 (508) 289-2745 (lab) (508) 457-2169 (fax)

Name	Affiliation Street Address E-mail	Telephone and Fax
Mr. John Dyke	**Woods Hole Oceanographic Institution** 266 Woods Hole Rd. MS 37 Woods Hole, MA 02543 jdyke@whoi.edu	(508) 289-3770 (508) 314-8013 (cell) (508) 457-2185 (fax)
Mr. Ken Houtler	**Woods Hole Oceanographic Institution** 266 Woods Hole Rd. MS 27 Woods Hole, MA 02543 jdyke@whoi.edu	(508) 289-3322 (774) 836-0054 (cell) (508) 504-8675 (fax)
Dr. Chris Werme	2838 Woosley St. Berkeley, CA 94705 werme[at]sbcglobal.net	(510) 645-8210 (510) 981-8379 (fax)
Ms. Regina Asmutis-Silvia Mr. Dave Silvia	3 Jacqueline Lane Plymouth, MA 02360 rasmutis[at]iwc.org	(508) 747-7891 (508) 830-1977 (fax) (508) 508-451-3841
Mr. Robert Carr	56 Dorothea Drive Weymouth, MA. 02188 carrlobster[at]comcast.net	(781) 953-8355 (cell) (781) 337-4886 (home) Channel 65 or 66 (*Rita C*)
Dr. Woollcott Smith	Box 86 West Tisbury, MA 02575 wksmith.stat@comcast.net	508-680-6397 (cell) 508-693-9168 (home)

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APPENDIX B

Battelle Standard Operating Procedures

Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA 02129
(617) 242-6000
http://www.mwra.state.ma.us