

**Quality assurance project plan
(QAPP)**

**Benthic Nutrient Flux Studies:
2004 -2005**

Massachusetts Water Resources Authority

**Environmental Quality Department
Report ENQUAD 2005-10**



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**QUALITY ASSURANCE PROJECT PLAN
(QAPP)**

BENTHIC NUTRIENT FLUX STUDIES: 2004 -2005

Task 16

**MWRA Harbor and Outfall Monitoring Project
Contract No. S366**

Submitted to

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

**Benthic Nutrient Flux Studies: 2004-2005
Task 16**

**MWRA Harbor and Outfall Monitoring Project
Contract No. S366
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TABLE OF CONTENTS

1.0	PROJECT NAME.....	1
2.0	PROJECT REQUESTED BY	1
3.0	DATE OF REQUEST.....	1
4.0	DATE OF PROJECT INITIATION	1
5.0	PROJECT MANAGEMENT.....	1
6.0	QUALITY ASSURANCE (QA) MANAGEMENT.....	1
7.0	PROJECT DESCRIPTION.....	2
7.1	Objective and Scope	2
7.2	Data Usage	2
7.3	Technical Approach	3
7.3.1	Field Program.....	3
7.3.2	Laboratory Program	6
7.4	Monitoring Parameters and Collection Frequency.....	6
7.5	Parameter Table.....	7
8.0	PROJECT FISCAL INFORMATION.....	7
9.0	SCHEDULE OF ACTIVITIES AND DELIVERABLES	7
10.0	PROJECT ORGANIZATION AND RESPONSIBILITIES.....	8
11.0	DATA QUALITY REQUIREMENTS AND ASSESSMENTS	9
11.1	Field Program.....	9
11.1.1	Precision and Accuracy	9
11.1.2	Completeness.....	11
11.1.3	Comparability.....	11
11.1.4	Representativeness	12
11.2	Laboratory Program	13
11.2.1	Precision and Accuracy	13
11.2.2	Completeness.....	13
11.2.3	Comparability.....	15
11.2.4	Representativeness	15
12.0	SAMPLING AND ANALYTICAL PROCEDURES.....	15
12.1	Navigation	15
12.2	Field Sampling	15
12.3	Laboratory Sample Processing and Analysis	16
12.3.1	Measurement of Benthic Respiration and Nutrient Flux.....	16
12.3.2	Measurement of Sediment Denitrification and Oxygen Flux.....	17
12.3.3	Analysis of Sediment Porewaters and Archival of Solids.....	18
12.3.4	Grain-Size Analysis.....	19
13.0	SAMPLE CUSTODY PROCEDURES	19
14.0	CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE	22
14.1	Navigation and Field Equipment.....	22
14.2	Laboratory Equipment.....	22

15.0 DOCUMENTATION, DATA REDUCTION, AND REPORTING	25
15.1 Documentation	25
15.1.1 Data Recording Requirements.....	25
15.1.2 Data Collection Procedures	25
15.2 Data Reduction.....	26
15.3 Data Entry, Loading and Reporting	28
15.3.1 Navigation and Sample Collection Data	28
15.3.2 Analytical and Experimental Data.....	28
15.3.2.1 Data Loading Applications	28
15.3.2.2 Data Entry.....	28
15.3.2.3 Loading Analytical and Experimental Data into the Project Database.....	29
15.3.3 Reporting Laboratory Data to the EM & MS Database	30
16.0 DATA VALIDATION.....	33
17.0 PERFORMANCE AND SYSTEMS AUDITS.....	34
18.0 CORRECTIVE ACTION	34
19.0 REPORTS	35
19.1 Survey Plans and Survey Reports	35
19.2 Data Report.....	35
19.3 Synthesis Report.....	36
20.0 REFERENCES	37

LIST OF TABLES

Table 1. Benthic Flux Sampling Stations.	3
Table 2. Samples and Measurements at Each Survey Station.....	6
Table 3. Master Schedule for Benthic Nutrient Flux Surveys in Boston Harbor and Massachusetts Bay. .	7
Table 4. Laboratory Analysis Parameter Table.....	8
Table 5. Data Quality Objectives for Field Measurements.....	11
Table 6. Data Quality Objectives for Laboratory Measurements.	14
Table 7. Analysis Codes Used in Bottle ID.	20
Table 8. Analytical Parameters and Database Codes.....	30
Table 9. Description of Database Codes.....	32
Table 10. List of Deliverables.....	36

LIST OF FIGURES

Figure 1. Benthic Flux Sampling Station Locations.....	5
Figure 2. Flux Studies (Task 16) Organization and Analysis.....	10
Figure 3. Example Station Log Form	21
Figure 4. Chain-of-Custody Form for Sediment Cores and Seawater Samples.....	24
Figure 5. Benthic Nutrient Flux Entry and Loading Application	29

1.0 PROJECT NAME

Benthic Nutrient Flux Studies: 2004-2005
Task 16
MWRA Harbor and Outfall Monitoring Project

2.0 PROJECT REQUESTED BY

Massachusetts Water Resources Authority

3.0 DATE OF REQUEST

November 28, 2001

4.0 DATE OF PROJECT INITIATION

November 28, 2001

5.0 PROJECT MANAGEMENT

Dr. Andrea Rex, MWRA Director of Environmental Quality Department
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6.0 QUALITY ASSURANCE (QA) MANAGEMENT

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7.0 PROJECT DESCRIPTION

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). The revised plan was approved by the Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (DEP) in early 2004 (MWRA, 2004). In the Benthic Nutrient Flux Studies program, the following changes were implemented in 2004:

1. Urea flux measurements were discontinued.
2. Porewater nutrient (NH_4^+ , $\text{NO}_3^- + \text{NO}_2^-$, PO_4^- , Si), sulfide, and alkalinity measurements were discontinued.
3. The method for measuring denitrification was changed.

This Quality Assurance Project Plan (QAPP) describes program methods employed in 2004 and 2005. Methods for urea and porewater nutrient measurements are described in the previous QAPP (Tucker and Giblin 2002), and the new denitrification method is described here (see Section 12.3.2).

7.1 Objective and Scope

The overall objective of Task 16 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 second through fifth years of monitoring following diversion of effluent discharge from Boston Harbor to the deep water site in Massachusetts Bay.

Specific objectives of Task 16 are to specify the measurements of sediment oxygen demand, nutrient fluxes, and complimentary 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 16 are to:

- Detect inter-annual change in rates of sediment oxygen demand and nutrient fluxes from sediments
- Detect inter-annual changes in parameters related to organic matter content of sediments, such as redox, organic carbon content, and chlorophyll content
- Directly measure rates of denitrification in Boston Harbor and in the nearfield area of Massachusetts Bay

7.2 Data Usage

The MWRA has 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 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 final reduction in sewage inputs. The data collected and reported for Task 16 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 16, 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.

7.3 Technical Approach

7.3.1 Field Program

To accomplish the objectives, 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 fluxes and has been used successfully in the Boston Harbor/Massachusetts Bay system throughout the monitoring program (Giblin *et al.*, 1993; 1994; 1995; Howes, 1998a; 1998b; 1998c; Tucker *et al.*, 1999b; 2000; 2001; 2002; 2003, 2004).

Sediment cores will be collected during four surveys in May, July, August, and October 2004-2005 (Table 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.

Sediment sampling stations in Boston Harbor will be Stations BH02, BH03, BH08A, and QB01 (Figure 1). Massachusetts Bay stations (Figure 1) will be Stations MB01, MB02, MB03, and MB05 (for comparability of stations, see Section 11.1.3). Each survey plan will include a final list of sampling stations.

Table 1. Benthic Flux Sampling Stations.

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

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 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 ($\pm 2^{\circ}\text{C}$) 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). 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.

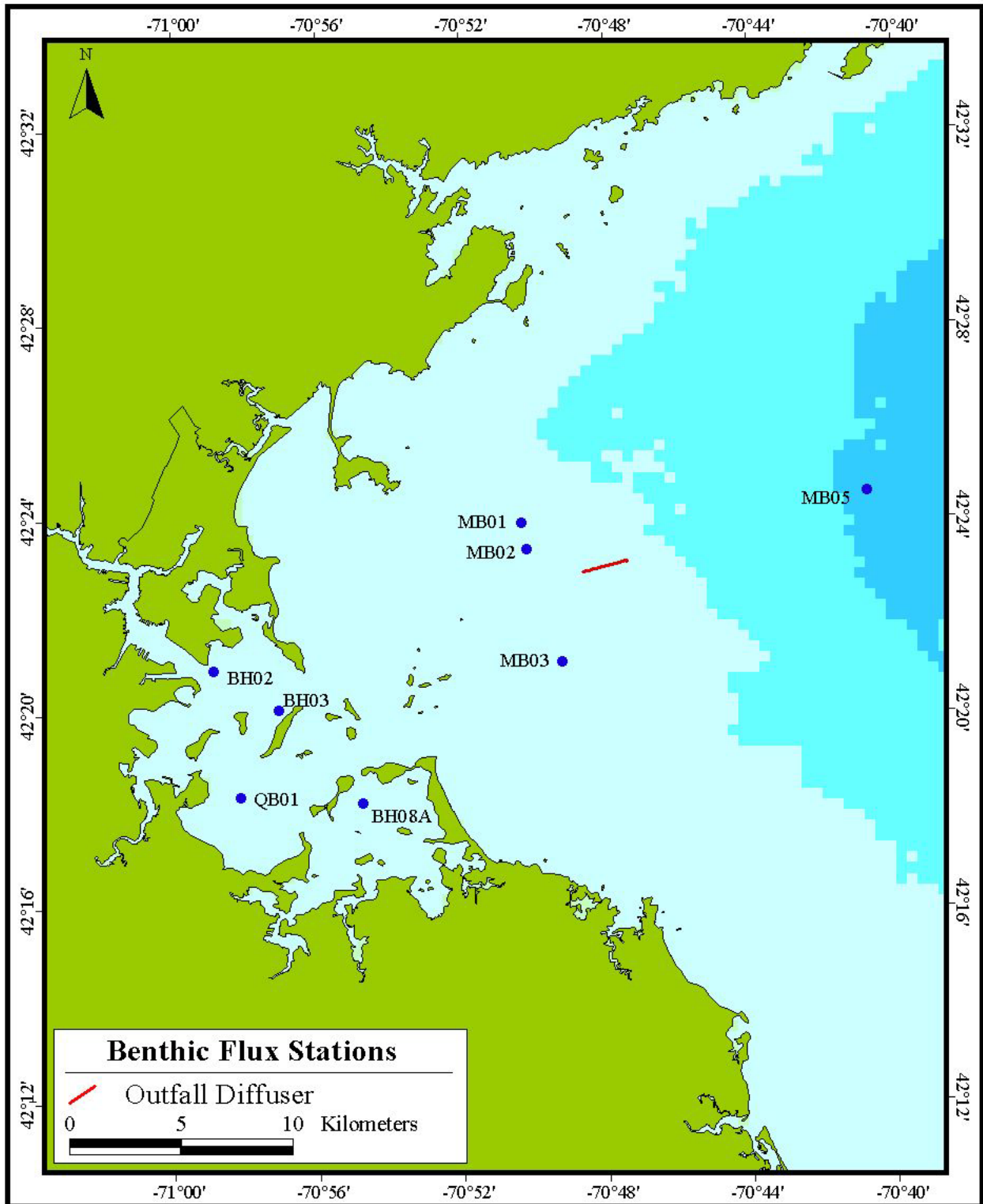


Figure 1. Benthic Flux Sampling Station Locations.

Characterization of *in situ* conditions will be accomplished using a Hydrolab Scout 2 Multiparameter Water Quality Data System to measure the O₂, temperature, and salinity of near-bottom water.

7.3.2 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 2. Samples and Measurements at Each Survey Station.

	Type	Number	Intended Analysis or Use	Reference or Comment
Sediment Core	15-cm-dia	2	Nutrient and denitrification flux	(1), (2)
Sediment Core	6.5-cm-dia	1	Eh and pH / grain size	(1)
Sediment Core	2.5-cm-dia	3	Archived solids/porosity/ pigments	(1)
Whole Seawater	Hydrolab Scout 2 Multiparameter System	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 *in situ* collection temperature ($\pm 2^\circ\text{C}$). Table 4 describes the parameters to be measured. Sampling/analytical methods are described in Section 12.

7.4 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 (Table 1) during each of the four Benthic Nutrient Flux surveys scheduled for each year. Sediment profiles of pH, Eh, TOC and TON, and chlorophyll and phaeopigments will also be conducted on cores from all stations and all surveys. Samples will be taken for grain size analyses in May and October.

Table 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 12.3.2).

7.5 Parameter Table

Table 4 lists all parameters and analyses, and methods, sampling frequency, holding times, reporting units, and processing.

8.0 PROJECT FISCAL INFORMATION

Task 16 is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S366) between MWRA and Battelle Duxbury Operations.

9.0 SCHEDULE OF ACTIVITIES AND DELIVERABLES

Sampling activities associated with the Benthic Nutrient Flux Surveys (Task 16) described in this QAPP are scheduled annually from 2004 – 2005. The planned survey schedule is shown in Table 3. Exact dates will be determined as the study progresses and will be subject to the criteria established for sampling.

Table 3. 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

¹X is the last digit of the sampling year (*i.e.*, 4 – 5)

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). A Survey Plan will be delivered to MWRA two weeks before each survey. Draft Survey Reports will be delivered within one month after the completion of each survey.

Benthic Nutrient Flux Data Reports will be prepared and delivered to MWRA within four months after the completion of each survey. The due dates are September 15, November 15, December 15 and February 15. An Annual Synthesis Report will be prepared and delivered to MWRA in April of the year following the survey year. Details of the contents of all reports are described in Section 19.0.

Table 4. 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	≥ 5 per flux	Immediate reading	NA	NA
		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	μM	Kana <i>et al</i> , 1998	~5 per flux	12 ml glass serum vial	<4 Months	HgCl ₂ , submerged, ambient temp or 4°C
Porewater/ Solids	6.5-cm-dia. Core (1)	pH	<i>In situ</i> Probe or Electrode		Mitchell, 1997 or Edmond, 1970	≥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
		Grain Size	Stacked sieves on Fritsch Analysette vibrating table and pipette/settling procedures	% dry weight	Folk, 1974	Top 2-cm	Section and refrigerate	<4 Months	Freeze
Solids	2.5-cm-dia. Core (1)	Porosity and Archive	Balance	g/mL	Giblin <i>et al</i> , 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, TON	Elemental Analyzer	% dry weight	Kristensen and Andersen, 1987	Top 2-cm	Section, dry at 105 °C	<4 Months	NA
Seawater	<i>In situ</i> (1)	O ₂ Salinity Temperature	Hydrolab Multiparameter System	mg/L	Hale, 1980	Each station	Immediate	NA	NA

NA = not applicable

10.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The Benthic Nutrient Flux Monitoring tasks will be accomplished through the coordinated efforts of several organizations. Figure 2 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. Battelle's Project Management Plan describes the management policies that will be applied to all HOM 4 activities (Battelle, 2002).

Dr. Andrea Rex is Director of the MWRA Environmental Quality Department. Dr. Michael Mickelson is the MWRA Project Manager. Mr. Ken Key is the MWRA Deputy 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. Dr. Carlton Hunt is the Battelle Technical Director and is

responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise. Ms. Jeanine Boyle is the Battelle Deputy Project Manager. The Battelle Quality Assurance Officer for the project is Ms. Rosanna Buhl. For this task, Ms. Buhl is responsible for reviewing data reports and QA Statements submitted by subcontractors for quality completeness and adherence to the QAPP. She is also responsible for reviewing the data and synthesis reports for accuracy and completeness. Mr. Alex Mansfield 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. Ms. Ellie Baptiste-Carpenter is also Battelle's Database Manager for this project. The key contacts at each of the supporting laboratories are shown in Figure 2. Addresses, telephone (and fax) numbers, and Internet addresses, as well as specific project roles and responsibilities, are presented in the HOM 4 Program Management Plan.

Technical oversight for the Benthic Nutrient Flux Studies will be provided by the Senior Scientist, Dr. Anne Giblin (MBL).

11.0 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

11.1 Field Program

Data quality requirements and assessments for navigational data are detailed in the Water Column Monitoring QAPP (Libby *et al.*, 2005).

11.1.1 Precision and Accuracy

Precision and accuracy objectives for navigation and water sampling are presented in Table 5. Section 12 provides details on relevant analytical procedures to ensure data quality and Section 14 discusses instrument calibration methods.

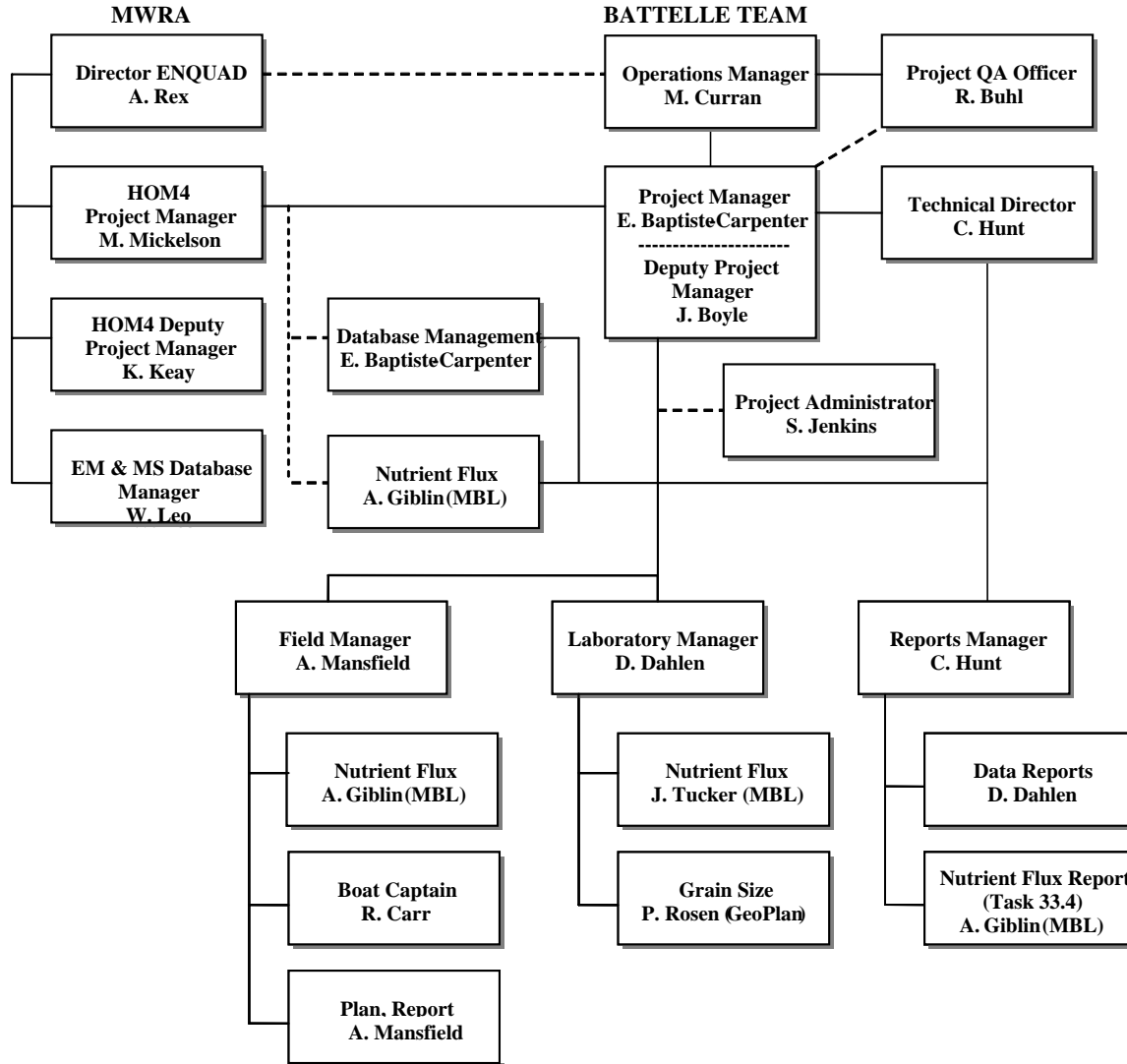


Figure 2. Flux Studies (Task 16) Organization

Table 5. Data Quality Objectives for Field Measurements.

Variable (Lab)	Qualifier	Detection Limits	Accuracy
Temperature (MBL)	Seawater	NA	±0.15°C
Salinity (MBL)	Seawater	NA	±0.5 PSU
Dissolved Oxygen (MBL)	Seawater	NA	±0.2 mg L ⁻¹

NA: Not Applicable

11.1.2 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. A station will be considered completed only if a minimum of four cores (two each of the 15 cm dia. cores, and 6.5 cm dia. cores) is obtained. If only four cores are obtained, subsamples for sediment solids to be archived will be taken from the 15 cm dia. 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.

Seawater will be collected to replenish the overlying water in cores that will be incubated. If necessary, seawater could be filtered on shore 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. Water column surveys in the study area will be conducted within one week of each benthic flux survey; water column surveys could be used to provide data on *in situ* bottom water conditions without compromising the task objectives.

11.1.3 Comparability

The four Massachusetts Bay stations to be occupied in 2004 -2005 (MB01, MB02, MB03 and MB05) are the same stations that have been used throughout the monitoring program, from 1992-2003. The Harbor stations (BH02, BH03, BH08A, and QB01) are the same four stations have been sampled since 1998. However, there have been some changes made to harbor station locations during the monitoring program.

Harbor stations were not comparable between 1992-1994 and 1995-1997. In 1995 the locations of BH03 and BH08 were changed and the stations became BH03A and BH08A. Stations BH03 and BH03A are only about 200 meters apart, and appear quite similar in all measured parameters: benthic fluxes of oxygen and nutrients are high at both these stations, as are benthic amphipod abundances (Giblin *et al.* 1993; 1994; 1995; Howes, 1998a, 1998b, 1998c). Both sites seem to represent the former sludge disposal area. However, BH03 is the station that is sampled for benthic infauna, and long-term data on metals (Zago and Giblin, 1994) and stable isotopes (Tucker *et al.*, 1999a) have been collected from this site. Therefore, to provide continuity with these analyses, Station BH03 rather than BH03A was used during

the 1998-2003 surveys, and will be visited in 2004-2005. Station BH08A is very different from BH08. Station BH08 was a sandy site chosen to represent erosional areas. Sediments at BH08A are finer grained than sediments at BH08 and the site was chosen to represent a depositional area (Howes 1998a). Depositional areas are more likely to show changes in inputs to the harbor, so BH08A was sampled in 1998-2003, and will continue to be sampled in 2004-2005. Station QB01 was a new station in 1995, replacing Station BH07 that was sampled in 1992-1994. Station BH02 has remained unchanged since 1992.

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 1998-2001 (Tucker and Giblin, 2001) as well as to the methods used by Howes for 1995-1997 (Cibik and Howes, 1995) with the following exceptions:

1. All cores will be transported back to MBL for flux incubations and other analyses; in 1995-1997, flux incubations were conducted in Boston. Before transportation, cores will be capped with no air in the headspace. This eliminates sloshing of the water in the cores tubes and minimizes sediment disturbances. Cores will be examined for obvious disturbance before the flux measurements are made. It should be noted that even if the cores were incubated in Boston they would still experience the disturbance of box coring, subsampling from the box corer, and transportation from the boat. A comparison with the data taken from the Massachusetts Bay station in 1992-1994 to that taken in 1995-1997 showed that the data were completely comparable. Year to year variation between the stations was about 20% and no systematic difference between the data take in 1992-1994, when cores were transported to Woods Hole, from that of 1995-1997, when the cores were incubated in Boston, was evident in the data. The excellent temperature control capability at MBL, combined with MBL's ability to make some chemical measurements immediately and avoid possible preservation artifacts, outweigh any transportation problem.
2. Dissolved oxygen concentrations, temperature, and salinity will be measured at depth in the water column using a Hydrolab Scout 2 Multiparameter Water Quality Data System. In 1995-1997, a Niskin bottle was used to collect bottom water. DO was measured by Winkler titration, temperature by thermometer, and salinity by refractometer. Salinity and temperature data from the Hydrolab will be more accurate than that obtained from a refractometer and field thermometer; however, a calibrated refractometer and thermometer will serve as backup to the Hydrolab.

11.1.4 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.

11.2 Laboratory Program

Refer to the Benthic (Sea-Floor) Monitoring QAPP (Williams *et al.*, 2005) for a description of the data quality requirements for the grain-size analysis.

11.2.1 Precision and Accuracy

For the benthic nutrient flux studies, MBL will generate data for ammonia, nitrate/nitrite, phosphate, silica, 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 TON, chlorophyll *a* and phaeopigments, porosity, and grain size analysis. Precision of these analyses for replicate samples is shown in Table 6. Section 12 provides additional details on the analytical procedures (*e.g.*, prepared standards) that will ensure data quality, and Section 14 describes instrument calibration methods. Fluxes are estimated from concentration changes over time and, thus, precision is, in this context, of more concern than accuracy. 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.

11.2.2 Completeness

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

Oversampling for most parameters will help ensure that the minimum requirements for completion are met. Oxygen will be frequently monitored to ensure estimates of oxygen flux. A 5-point time series of samples for nutrients and N₂/Ar will also be taken. Fluxes could be estimated (with less confidence) using fewer data points than planned. Samples for total carbon dioxide (DIC) data cannot be oversampled due to volume considerations; they will be collected only at the start and finish of incubations.

Table 6. Data Quality Objectives for Laboratory Measurements.

Variable (Lab)	Matrix	Units	Detection Limits	Accuracy (% difference) ^f	Precision (% difference) ^f	Quality Control (QC) Sample Type	Frequency of QC Sample	Corrective Action
O ₂	SW	μM	0.02mg/l ^a	≤4%	≤3%	Lab RM	1/set of measurements	Note deviation from expected
Total CO ₂	SW	μM	<0.1μgC ^a	≤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 ^d ≥1 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 ^d 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 ^d Daily 1/20 Samples	Repeat Repeat Repeat
Si	SW	μM	0.5	≤5%	≤3%	CRM Lab Standards Check Standards Blanks Lab Duplicates	1 Verification ^d 1 Set/65 Samples 1/20 Samples /20 Samples 1/20 Samples	Repeat Repeat Repeat Repeat Repeat
pH	PW	NA	0.01 ^a	≤0.05	NA	CRM (buffers)	Daily	Repeat
Eh	PW	mV	0-1400 ^b	≤5%	NA	Lab Standard	Daily	Repeat
N ₂ /Ar	GAS	ratio	NA	NA	≤0.05% (C.V)	Lab standard	At beginning and end of analysis run	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
TON	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 ^c	10% if > 1μg/mL	NA ^c	NA ^c	Subcore 15cm core and repeat
Phaeopigments	SED	μg/ml	0.1μg/mL	NA ^c	5%	NA ^c	NA ^c	Subcore 15-cm core and repeat
Porosity	SED	NA	0.1g/mL ^a	≤5%	≤5%	NA ^c	NA ^c	Reanalyze
Grain Size	SED	Modal phi interval	NA	NA	≤20% ^e	Lab Triplicates	5% of samples	Document; justify deviations

NA: Not Applicable

^a Instrument sensitivity

^b Instrument range

^c standard reference materials are not available.

^d A CRM standard will be run to verify the Lab primary standard whenever a new primary standard stock is made.

^e If the component is >5% of the sample

^f At concentrations >5 x MDL

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

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 16 would not be compromised if fewer than six depth intervals are successfully sampled and analyzed.

11.2.3 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.*, 1993; 1994; 1995; Howes, 1998a; 1998b; 1998c; Tucker *et al.*, 1999b; 2000; 2001). Incubation and analytical techniques, with the following exceptions, are identical to those specified in the 1998-2001 and 2002-2005 QAPPs (Tucker and Giblin, 2001; 2002):

1. In 2004 and 2005, porewater nutrients, sulfides, and alkalinity will not be reported.
2. In 2004 and 2005, denitrification measurements will be made using the N₂/Ar, membrane inlet mass spectrometer (MIMS) technique (Section 12.3.2) rather than by gas chromatography (GC).
3. As noted in section 12.3.2, the MIMS technique is not directly comparable to the GC method, but it is more accurate (Kana *et al.*, 1998)

11.2.4 Representativeness

Representativeness is addressed primarily through sampling design. In addition, evaluation of previous studies has helped ensure that the sampling sites selected for the Harbor and Outfall Monitoring Project are representative of the Boston Harbor/Massachusetts Bay system. Flux measurements of the type that will be made during the conduct of Task 16 have been used since 1992 (Giblin *et al.*, 1993; 1994; 1995; Howes, 1998a; 1998b; 1998c; Tucker *et al.*, 1999b; 2000; 2001; 2002; 2003; 2004) in Boston Harbor and Massachusetts Bay and are considered to yield rates representative of the Boston Harbor/Massachusetts Bay system.

12.0 SAMPLING AND ANALYTICAL PROCEDURES

12.1 Navigation

Refer to the Water Column QAPP (Libby *et al.*, 2005) for a complete description of navigation procedures.

12.2 Field Sampling

Undisturbed sediment cores of the number and type listed in Table 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-dia. 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 $\pm 2^{\circ}$ 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 7.

12.3 Laboratory Sample Processing and Analysis

12.3.1 Measurement of Benthic Respiration and Nutrient Flux

Upon arrival at the Woods Hole MBL facilities, the two 15-cm-dia cores from each station will be uncapped and held in the dark at a temperature within $\pm 2^{\circ}\text{C}$ 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 h 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; 2002). These methods are summarized below.

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.

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 12.3.2). Samples for nutrient analyses will be processed within 1 h according to methods presented in Table 4. Duplicate 3-ml subsamples will be analyzed immediately for ammonium 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, and silica. Duplicate determinations of NO_3 and Si are made during each day's run of the instrument. Dissolved inorganic nitrogen is calculated as the sum of ammonium, and 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 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 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 ammonia, 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.

12.3.2 Measurement of Sediment Denitrification

From 1992 through 2003, a method developed by Barbara Nowicki at the University of Rhode Island was used to measure denitrification. A detailed description of sampling and measurement methods for this technique is given in Nowicki *et al.* (1997) and in an earlier QAPP (Tucker and Giblin, 2002).

Briefly, for each estimate of N₂ flux, two sediment cores were incubated at ambient temperature. Prior to the flux incubation, the overlying water and headspace in one core (the oxic core) was sparged with a mixture of 80% Helium (He):20% O₂ in order to maintain an oxic environment while lowering the background level of N₂ within the core. The overlying water and headspace in the other core (the anoxic core) was sparged with 100% He to remove both O₂ and N₂. The anoxic core provided an abiotic control for N₂ diffusing from the porewater and conditions under which coupled nitrification/denitrification were prevented. During the incubation, N₂ gas within the headspace of both cores was monitored by drawing off samples of the headspace and analyzing it on a gas chromatograph with a thermal conductivity detector. Denitrification was calculated as the difference in N₂ production in the oxic and anoxic cores.

In 2004 and after, a new technique for measuring denitrification will be used. This method uses a quadrupole mass spectrometer equipped with a membrane inlet (membrane inlet mass spectrometer/MIMS) to precisely measure N₂/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 N₂. The mass spectrometer is capable of measuring very small deviations in this ratio, thereby providing a very sensitive and precise method for measuring denitrification. Whereas gas chromatography offers a precision of measurement for gas concentrations on the order of 0.3-1%, the mass spectrometer yields a precision of 0.05% for gas ratios.

Importantly for our benthic flux studies in Boston Harbor and Massachusetts Bay, 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 HgCl₂ solution, and capped with serum caps. Samples are then held submerged and at ambient temperature or refrigerated until analysis.

In 2003, we used both techniques. Results indicate that the two techniques are not directly comparable. Most of the GC results were higher than N₂/Ar results. For a number of reasons, the GC technique may be expected to have higher or more variable results than the MIMS technique. One reason is that bio-irrigation by benthic invertebrates leads to faster abiotic degassing of N₂ from sediments in the oxic core than in the anoxic core (in which the animals would have been killed). Another reason is that during the long incubations used for the GC technique (typically 5 days), NH₄⁺ builds up in both the porewater and

the overlying water. Higher porewater ammonium leads to higher nitrification, which in turn leads to higher coupled nitrification/denitrification (Giblin, unpublished data). The N₂/Ar method has a shorter incubation time of 1-2 days (the same as the nutrient flux cores), which results in less build-up of NH₄⁺ over the course of the incubation.

The GC technique was labor intensive, and therefore limited the number of measurements that were made. Measurements were made at only four of the eight benthic flux stations, two from Boston Harbor (BH02 and BH03) and two from the Massachusetts Bay (MB02 and MB03). In addition, measurements from Bay cores were made only in May and October. The N₂/Ar technique allows us to take measurements at all eight stations, and during all surveys.

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.

The overlying water of intact sediment cores is enriched with ¹⁵N-labeled NO₃⁻ (¹⁵NO₃⁻), which then uniformly mixes with the unlabeled pool (¹⁴NO₃⁻) in the overlying water and the porewaters of the core. During incubation of the cores, denitrification may then produce N₂ that is unlabeled (¹⁴N¹⁴N), single-labeled (¹⁴N¹⁵N) or double-labeled (¹⁵N¹⁵N). These various N₂ 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 NO₃⁻ in the overlying water and that produced via nitrification within the sediments.

12.3.3 Analysis of Sediment Redox and Archival of Solids

A 6.5-cm-dia core from each station will be collected for pH and Eh measurements. A stainless steel pH probe (3.5 mm dia. X 20 cm length) with an ion sensitive field effect transistor (ISFET), (I.Q. 200 pH/thermometer, I.Q. Scientific Instruments) will be 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 2cm 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. After the pH and Eh measurements are completed, the top 0-2 cm of this core will be sectioned and frozen wet for later grain size analysis by GeoPlan Associates.

One 2.5-cm-dia 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-dia. core will be sectioned from 0-2cm only, and used for TOC and TON analyses. 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-dia 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-dia cores are not collected, one 2.5-cm-dia. core tube will be used to subcore a 15-cm-dia core after nutrient flux measurements have been made. This subcore would be sectioned and archived as described above for the first 2.5-cm-dia core.

12.3.4 Grain-Size Analysis

Refer to the Benthic (Sea-Floor) Monitoring QAPP (Williams *et al.*, 2005) for a description of grain-size analysis procedures.

13.0 SAMPLE CUSTODY PROCEDURES

The MBL's station log will be a pre-printed form (Figure 3) 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 *Marker 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 *Sample ID* for each core (Table 7) [Example: *Event ID* = NC021, *Marker No.* = 018, *Analysis Code* = NF1, *Sample ID* (Bottle ID) = NC021 018 NF1]. This ID will be stored as the *Sample ID* in EM&MS. Initially, the *Sample 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 *Event ID* and *Marker No* only.

Table 7. 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	Grainsize or Eh/pH	From first 6.5-cm core
PO2	Grainsize or 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.

During field collection, a separate station log form (Figure 3) 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.

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. 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 principal investigator 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.

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 EM & MS database upon completion of the survey. The Field Manager or his designee maintains the disks until the annual archive cycle. HOM 4 discs are saved for six years from the time of collection.

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) _____
Time in _____
Time out _____
ABT _____
Depth _____
Via _____

Comments:

HYDROLAB CAST:

Depth (m): _____
Temp (°C) _____
Sal (psu) _____
DO (mg/l) _____

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

Figure 3. Example Station Log Form.

14.0 CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

Logs of maintenance, calibrations, 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.

14.1 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.*, 2005).

The Hydrolab probe will be calibrated in the field, prior to deployment, according to manufacturer's specifications. The O₂ 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.

14.2 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 UIC Coulometrics CM5011 CO₂ Analyzer used to measure CO₂ will be calibrated with bicarbonate and seawater solutions of a known carbon dioxide content (supplied by Andrew Dickson, UCSD).

Calibration procedures for the Cary or Shimadzu UV-Visible Spectrophotometer (NH₄, PO₄, and chlorophyll/phaeophytin), the Lachat Flow injection analyzer (NO₂ + NO₃), and the Alpkem Rapid Flow analyzer (silica) are similar. Each is calibrated using laboratory 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 acceptability of blanks.

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 TON) calibration will be checked at the initiation of each run against a 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.

A calibration standard of air-saturated deionized water held at ambient sample temperature is used to calibrate the N₂/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.

Calibration for the grain-size analysis equipment is described in the QAPP for Benthic (Sea-Floor) Monitoring (Williams *et al.*, 2005).

MWRA Harbor and Outfall Monitoring Program
Contract No. S366
Chain-of-Custody Form

Today's Date : 3/19/02 12:27:44 PM

Laboratory : Marine Biological Laboratory
 The Ecosystems Center

Chain-of-Custody # : NC014-NF-0008

Survey ID : NC014

















Analysis ID : NF

Analysis Description : Nutrient flux

Woods Hole MA 02543

Dr. Anne Giblin

508-289-7488 (Phone) 508-457-1648 (Fax)

Bottle ID :	Bottle ID :	Sampling Date :	Station ID :	Ck 1	Ck 2	Ck 3	Ck 4
	NC014013NF1	10/30/01 7:29:42 AM	BH02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014013NF2	10/30/01 7:29:42 AM	BH02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014016NF1	10/30/01 7:32:13 AM	BH03	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014016NF2	10/30/01 7:32:13 AM	BH03	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014019NF1	10/30/01 7:35:14 AM	BH08A	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014019NF2	10/30/01 7:35:14 AM	BH08A	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC01401CNF1	10/30/01 7:36:57 AM	QB01	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC01401CNF2	10/30/01 7:36:57 AM	QB01	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014021NF1	10/30/01 8:26:02 AM	MB03	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014021NF2	10/30/01 8:26:02 AM	MB03	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014027NF1	10/30/01 9:26:18 AM	MB02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014027NF2	10/30/01 9:26:18 AM	MB02	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC01402BNF1	10/30/01 9:55:36 AM	MB01	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC01402BNF2	10/30/01 9:55:36 AM	MB01	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014034NF1	10/31/01 2:24:13 PM	MB05	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	NC014034NF2	10/31/01 2:24:13 PM	MB05	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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

Figure 4. Chain-of-Custody Form for Sediment Cores and Seawater Samples (MBL).

15.0 DOCUMENTATION, DATA REDUCTION, AND REPORTING

15.1 Documentation

15.1.1 Data Recording Requirements

All documentation will conform to the Battelle HOM 4 Quality Management Plan. The specific types of documentation that will be maintained for Task 16 include:

- A survey log form will be generated for each station visited during surveys. Completed survey logs will be maintained in Field Record Books.
- Laboratory Record Books will document laboratory information related to sample tracking and analysis.
- COC Forms will document complete sample collection information and identify the individual who will have custody of the samples. Completed COC forms are maintained in the Sample Log Book.
- Corrective Action Log, maintained by the Project and Subcontractor QA Officers, will summarize QA activities associated with the project.

15.1.2 Data Collection Procedures

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 managers to ensure that all data entries and hand calculations are verified in accordance with procedures described in Section 16 (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 spreadsheets, 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 and GeoPlan will maintain, for six years, (1) all records of calculations, (2) raw data collected during incubations, and (3) field records of D.O, temperature and salinity.

15.2 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 15.3:

- 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 be calculated from five data points using a linear regression (Giblin *et al.*, 1995; 1997). 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 incubation temperature will also be reported. The acceptability of flux measurements for a given core will depend on the linearity of oxygen flux ($r^2 > 0.9$). All fluxes will be expressed as $\text{mmol m}^{-2} \text{day}^{-1}$.
- Eh and pH from one “porewater (PO) core” collected at each station.
- Sediment pigments, porosity, TOC and TON from one each of the three “solid phase (CN) cores” collected at each station.
- The concentration of dissolved oxygen (mg L^{-1}), field temperature ($^{\circ}\text{C}$) and salinity (psu) for each station.

Grain Size data will be entered into a loading application by the analytical laboratory and submitted directly to Battelle.

Calculations

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

Concentrations of NH_4 , NO_3+NO_2 , PO_4 , 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).

Concentrations of oxygen in $\text{mg O}_2/\text{L}$ as read off the Orbisphere O_2 meter are converted to $\text{mmol O}_2/\text{L}$ and corrected for temperature and salinity using the following equation (Hale, 1980):

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

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 $S = 1.80655[\text{Cl}]$
T is the absolute temperature ($^{\circ}\text{K}$).

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 TON, 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:

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

Chlorophyll and phaeophytin are calculated after Lorenzen, 1967:

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

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 (μM) 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 $\text{mmol N}_2 \text{ m}^{-2} \text{ d}^{-1}$. The r^2 for the regression is also reported.

15.3 Data Entry, Loading and Reporting

15.3.1 Navigation and Sample Collection Data

Navigation and sample collection data will be processed on-board the survey vessel and be ready for loading into EM&MS 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 loaded into the EM&MS database by clicking a button. All database constraints developed by MWRA will be applied to the tables so that the data are checked during the insert.

15.3.2 Analytical and Experimental Data

15.3.2.1 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 each laboratory. 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. Entry applications will be developed for each analytical laboratory. Laboratory staff will receive one day of training on use of the application prior to analysis of the lab's first set of samples.

15.3.2.2 Data Entry

Entry of grain size data into the loading applications is described in the Benthic QAPP (Williams *et al.* 2005).

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 5). 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. Laboratory staff receive one day of training on the application prior to analysis of the lab's first set of samples. 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 script 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 was 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 8 shows the analytical parameters and database

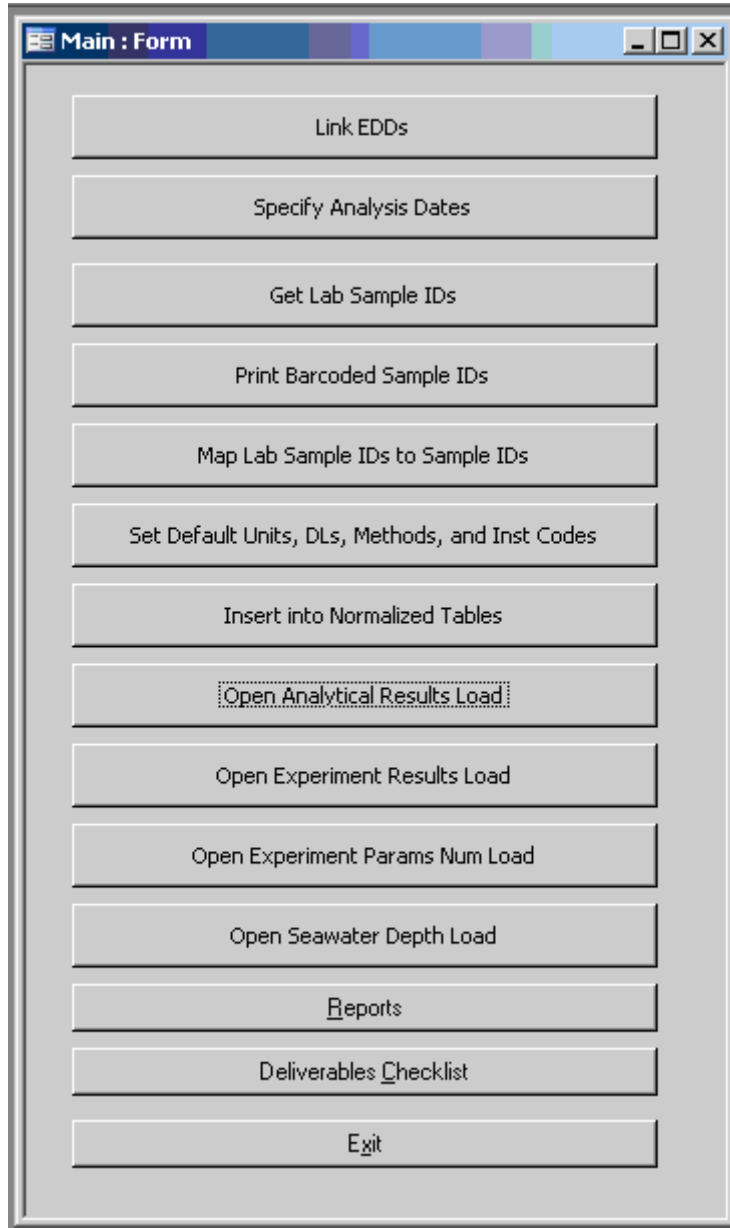


Figure 5. Benthic Nutrient Flux Entry and Loading Application.

codes for the analytes collected under this task. Table 9 describes the database codes to be used by the laboratories. The laboratories 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.

15.3.2.3 Loading Analytical and Experimental Data into the Project Database

Data submissions from the laboratory will consist of the final loading applications. The submissions will be logged in upon receipt and a copy of the login will be maintained on file under the login id. Data will be loaded into a temporary table by striking a button on the application. A transfer script will copy the

data into the proper table in Battelle’s copy of the EM&MS. Data from the laboratories will receive a quality assurance review by Battelle after the data have been synthesized into a data report. Any issues will be corrected in the database and the script output will be available to MWRA. The MWRA check script will be run on the database prior to export. Any issues will be sent to the Battelle Data Manager via email. Any irresolvable issues in the database as a result of quality control checks (for example, stations more than specified distance from target) will also be submitted to MWRA with the data export. Grain-size data reduction and reporting are as described in the QAPP for Benthic (Sea-Floor) Monitoring (Williams *et al.*, 2005). Processing of data and development of data reports are defined in MWRA SOP 006-01 *Loading and Reporting Benthic Nutrient Flux Data*.

15.3.3 Reporting Laboratory Data to the EM & MS Database

Every data deliverable must be accompanied by the following reports:

- QA Statement
- QA/QC Corrective Action Log
- Signed, Original Chain of Custody
- Electronic Data
- Hardcopy Data Report
- Exceptions Report (hardcopy – only applicable to those laboratories that receive loading applications)
- Analysis Summary (hardcopy – only applicable to those laboratories that receive loading applications)

All field and laboratory data to be loaded into the EM&MS will be submitted to Battelle in electronic format. The field data will be available for data loading directly off the ship. The laboratories will be supplied a loading application that will increase data quality and efficiency. These applications eliminate the need for data reporting formats and deliver many of the quality control checks upstream to the laboratories.

Table 8. Analytical Parameters and Database Codes.

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Nutrient Flux					
Efflux of dissolved inorganic carbon from sediment	DIC_FLUX	mmol/m2/d	MBL	CCO2	KEL93
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	SPH_LTF	KEL93
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	SPECPH	SOL69
Nitrate flux from sediments	NO3_FLUX	mmol/m2/d	MBL	LATFI	KLU83
R-Squared of linear regression for estimation of parameter NO3_FLUX	NO3FLUXR2		MBL	LATFI	KLU83

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
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	SPECPH	MURPH62
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	RAPFL	HALE80
O2 flux from sediments	O2_FLUX	mmol/m2/d	MBL	DOPROBE or WHOIWINK	HALE80 or KNAPP1990
R squared for O2 flux measurement	O2FLUXR2		MBL	DOPROBE or WHOIWINK	HALE80 or KNAPP1990
Temperature	TEMP	C	MBL	THER	
Denitrification Flux					
N2 flux from sediments	N2_FLUX	mmolN2/m2/d	MBL	BA422QMG	MIMS
R-Squared for denitrification rate from direct (MIMS) measurement of N2/Ar ratios over time	N2FLUXR2		MBL	BA422QMG	MIMS
Temperature	TEMP	C	MBL	THER	
Solids					
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	LO186
Phaeophytin	PHAE	ug/mL	MBL	SPECPH	LO186
Total organic carbon	TOC	PCTDRYWT	MBL	PE24CHN	KP93TOC
Total nitrogen	MWRA47	PCTDRYWT	MBL	PE24CHN	STFP-V-EE
Ratio of porewater mass to sediment volume	POROSITY	g/mL	MBL	BAL	GIB94
Phi size <-1	<-1	PCT	GOP	SVSET	FOLK74
Phi size -1 - 0	-1	PCT	GOP	SVSET	FOLK74
Phi size 0 - 1	0 - 1	PCT	GOP	SVSET	FOLK74
Phi size 1 - 2	1 - 2	PCT	GOP	SVSET	FOLK74
Phi size 2 - 3	2 - 3	PCT	GOP	SVSET	FOLK74
Phi size 3 - 4	3 - 4	PCT	GOP	SVSET	FOLK74
Percent by weight of sediment clay fraction	CLAY	PCTDRYWT	GOP	SVSET	FOLK74
Percent by weight of sediment gravel fraction	GRAVEL	PCTDRYWT	GOP	SVSET	FOLK74
Percent by weight of sediment sand fraction	SAND	PCTDRYWT	GOP	SVSET	FOLK74
Percent by weight of sediment silt fraction	SILT	PCTDRYWT	GOP	SVSET	FOLK74
Porewater					
Standard redox potential	EH	mV	MBL	EHPROBE	BAG78
Negative log of hydrogen ion activity	pH		MBL	PHPROBE	EDM70
Seawater					
Dissolved oxygen	DISS_OXYGEN	mg/L	MBL	RTL	QP1239
Salinity (field)	SFIELD	PPT	MBL	HYDRO-S2	HALE80
Temperature (field)	TFIELD	C	MBL	HYDRO-S2	HALE80

Table 9. 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	DOPROBE	Dissolved Oxygen Probe
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	SVSET	Sieve/settling
INSTR_CODE	PHPROBE	pH probe and meter
INSTR_CODE	RTL	Radiometer Titralab titrator
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
UNIT_CODE	PCT	Percent
METH_CODE	GIB94	Giblin et al 1994, final rept. metabolism,nut cycling and denitrif in Bos Harbr and MassBay seds 1994
METH_CODE	LO186	Lambert and Oviatt (1986)
METH_CODE	KEL93	Kelly <i>et. al.</i> 1993 Benthic Nut Flux QA plan
METH_CODE	FOLK74	Folk 1974, Petrology of Sedimentary Rock, Hemphills, Austin, TX
METH_CODE	HALE80	Hale 1980, Inst. meas. of do conc. in saline water, Orbisphere Lab NJ
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 <i>et al.</i> , 1998. Membrane inlet quadrupole mass spectrometry (MIMS) for analysis of N2/Ar ratios in dissolved gases
METH_CODE	KP93TOC	TOC analysis, Kropp <i>et. al.</i> 1993 softbottom QA plan
METH_CODE	STFP-V-EE	Secondary treatment facilities plan, vol. V, appendix EE-QA plans
METH_CODE	KNAPP1990	Knapp <i>et. al.</i> 1990. Automated oxygen titration and sal. determination. WHOI Inst Tech Rpt: WHOI-90-35
METH_CODE	KLU83	Klump and Martens. 1983. Benthic nitrogen regeneration. Nitrogen in Marine Env. Acad Press
METH_CODE	QP1239	Bowen <i>et. al.</i> 1996, water quality mon. qapp, section 12.4.9

FIELD NAME	CODE	DESCRIPTION
METH_CODE	EDM70	Edmond 1970, Deep Sea Research 17:737-750
METH_CODE	BAG78	Bagander and Niemisto. 1978. an eval of use of redox measurements. Est Coast Mar Sci 6
ANAL_LAB_ID	GOP	GeoPlan Assoc
ANAL_LAB_ID	MBL	Marine Biological Laboratory – GIBLIN
VAL_QUAL	A	Value above maximum detection limit, e.g., too numerous to count or beyond range of instrument
VAL_QUAL	a	Not detected – value reported as negative or null
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	Estimated value
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.
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

16.0 DATA VALIDATION

A primary component of data validation is compliance with the quality assurance program defined in the specified Quality Management Plan developed specifically for the Harbor and Outfall Monitoring Project (Battelle, 2002) and outlined in Section 11.0 (Data Quality Requirements and Assessments) of this QAPP.

All data collected and analyzed as part of Task 16 will be reviewed to checks for errors in transcription, calculation, or spreadsheet input. Validation procedures for data generated at Battelle or by the subcontractors 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 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.

17.0 PERFORMANCE AND SYSTEMS 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 16 is carried out in accordance with this QAPP. A systems audit will verify the implementation of the Quality Management Plan and this QAPP for the work conducted in the Benthic monitoring.

MBL and GeoPlan will be responsible for audits of the data collection procedures at their laboratories. Each 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 subcontractor QA Officer or their designee to evaluate the laboratory data-production process. All data must be reviewed by the subcontractor QA Officer prior to submission to the Battelle Database Manager and must be accompanied by a signed QA statement (a copy of the statement can be found in the Quality Management Plan; Battelle, 2002) 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 subcontractor laboratory and may include SRMs, internal performance evaluation samples, and participation in external certification programs.

18.0 CORRECTIVE ACTION

Identification of problems regarding technical performance is the responsibility of all staff members working on this project. Responsibility for overall conduct of the project, including schedule, costs, and technical performance lies with the Battelle Project Manager. The Project Manager is responsible for identifying and resolving problems that (1) have not been addressed promptly or successfully at a lower level, (2) influence other components of the project, (3) require changes in this QAPP, or (4) require consultation with Battelle management or with MWRA.

Technical problems relating to sample collection in the field (schedule changes, modifications to the sampling plan, etc.) will be resolved through discussion with the MWRA Project Area Manager, the Battelle Field Manager, and the Project Senior Scientists. Problems relating to the overall successful completion of the project will be reported to the MWRA Program and Project Area Manager in a timely manner for discussion and resolution between the Battelle and MWRA managers.

Identification of problems and corrective action at the laboratory level will be resolved by the laboratory staff. Issues that affect schedule, cost, technical performance, or data quality will be reported to the

Battelle Laboratory Manager or the Battelle Project Manager. They will be responsible for evaluating the overall impact to the project and for discussing corrective actions with the MWRA Project Manager.

A QA/QC Corrective Action Log will be maintained by the Project QA Officer and submitted to MWRA at quarterly intervals. The log will include documentation of QA/QC activities, descriptions of the methods and procedures recommended to prevent the problem from reoccurring, and verification that these actions have corrected the problem.

19.0 REPORTS

The MWRA contract defines general conditions for reporting. These conditions are incorporated into the HOM 4 Quality Management Plan, Appendix 1, and apply to all reports generated for this monitoring area. Deliverables due to MWRA for Task 16 include:

- Survey Plans (one for each of the benthic flux surveys)
- Survey Reports (one for each of the benthic flux surveys)
- Sediment Flux Data Reports

19.1 Survey Plans and Survey Reports

Each survey plan will follow the guidelines established by the U.S. Environmental Protection Agency for the use of the *OSV Anderson* and 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, single-sided copy of each plan will be 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 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. Two unbound, double-sided copies of the draft survey report will be 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.

19.2 Data Report

A Benthic Flux Data Report will be prepared and submitted to MWRA for each of the four surveys in a calendar year (see Table 10). Each report will include tables of results including (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). Each Flux Data Report will describe deviations from the QAPP. All data presented in the data reports are available in the EM&MS database at Battelle and will be provided as an export at the same time as the data report.

19.3 Synthesis Report

The data from all four surveys will be collated and summarized and used to develop an Annual Benthic Flux Report. The Report will synthesize the results of the four surveys of each calendar year and will be prepared under Task 33.4 of the Harbor and Outfall Monitoring Project. This will be submitted as a Draft and a Final Report as indicated in Table 10.

The Annual Benthic Nutrient Synthesis Report (Task 33.4) will include separate sections describing results from the Harbor and the Bay for each type of measurement. Spatial and temporal variability of flux and porewater data will be thoroughly compared for both seasonal and inter-annual time periods. Trends in denitrification rates at the Harbor stations sampled for this parameter will be compared to previous years. Massachusetts Bay denitrification rates will be directly compared to measurements made in previous years. 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. Prior to preparation of the draft, an outline will be prepared and delivered to MWRA. Draft and final versions of the report will be prepared. The schedule for preparation of the report is listed in Section 9.0.

Table 10. 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 Reports and Exports		
Nutrient Flux Data Reports	May	September 15
	July	November 15
	August	December 15
	October	February 15
Synthesis or Interpretive Reports		
Benthic Nutrient Flux Report – Outline	May - October	March
Benthic Nutrient Flux Report – Draft	May - October	April
Benthic Nutrient Flux Report – Final	May - October	30 days after receipt of comments

20.0 REFERENCES

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