Combined work/quality assurance project plan (CWQAPP)

for

Benthic Nutrient Flux Studies: 2002 -2005

Massachusetts Water Resources Authority

Environmental Quality Department
Report ENQUAD ms-077

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COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CWQAPP)

for

BENTHIC NUTRIENT FLUX STUDIES: 2002-2005

Task 16

MWRA Harbor and Outfall Monitoring Project
Contract No. S366

Submitted to

MASSACHUSETTS WATER RESOURCES AUTHORITY
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Combined Work/Quality Assurance Project Plan (CWQAPP) *for*

Benthic Nutrient Flux Studies: 2002-2005 Task 16

MWRA Harbor and Outfall Monitoring Project Contract No. S366 Concurrence and Approvals

Ms. Ellen Baptiste Carpenter Battelle Project Manager	Date
Dr. Carlton Hunt Battelle Technical Director	Date
Ms. Rosanna Buhl Battelle Project QA Officer	Date
Dr. Michael Mickelson MWRA Project Manager	Date
Mr. Ken Keay MWRA Project Area Manager	Date
Ms. Wendy Leo MWRA EM & MS Manager	Date

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Benthic Nutrient Flux Studies: 2002-2005
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

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Dr. Michael Mickelson, MWRA Harbor and Outfall Monitoring Project Manager
Mr. Kenneth Keay, MWRA Harbor and Outfall Monitoring Deputy Project Manager
Ms. Ellen Baptiste Carpenter, Battelle Project Manager for Harbor and Outfall Monitoring
Ms. Jeanine Boyle, Battelle Deputy Project Manager for Harbor and Outfall Monitoring
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Mr. Chris Gagnon, Battelle Deputy Field Manager
Ms. Deirdre Dahlen, Battelle Laboratory Manager

6.0 QUALITY ASSURANCE (QA) MANAGEMENT

Ms. Wendy Leo, MWRA EM&MS Manager
Ms. Rosanna Buhl, Battelle Project Quality Assurance Officer

7.0 PROJECT DESCRIPTION

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 data 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, nutrient fluxes from sediments, porewater nutrients, and related parameters in the vicinity of the outfall and in Boston Harbor.

- Directly measure rates of denitrification (as nitrogen gas release from the sediments) in Boston Harbor and to measure denitrification directly in the nearfield area.

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 in 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 and porewater 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 sectioned for porewater analyses. This approach, laboratory incubations of relatively undisturbed cores, is an accepted method of estimating benthic flux rates and has been used successfully in the Boston Harbor/Massachusetts Bay

system (Giblin *et al.*, 1993; 1994; 1995; Howes, 1998a; 1998b; 1998c; Tucker *et al*., 1999b; 2000; 2001; 2002).

Sediment cores will be collected during four surveys in May, July, August, and October 2002-2005 (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 40 x 40 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). 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.

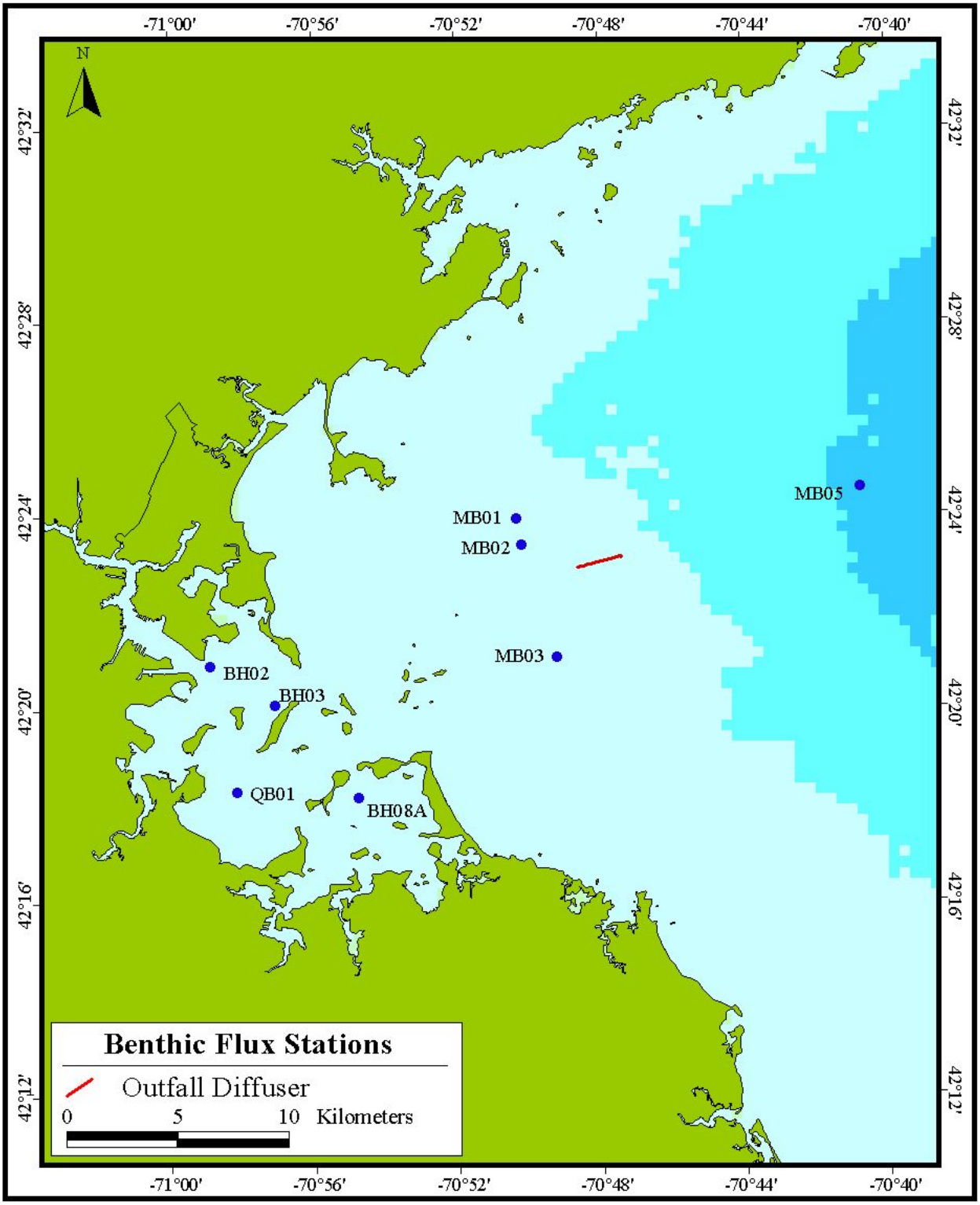

Figure 1. Benthic Flux Sampling Station Locations.

Characterization of *in situ* conditions will be accomplished using a Hydrolab Scout 2 Multiparameter Water Quality Data System to measure the O_2, temperature, and salinity of near-bottom water.

7.3.2 Laboratory Program

The flux/porewater measurements will follow methods of Giblin *et al.* (1994, 1997) for nutrients and metabolism, and the methods of Kelly and Nowicki (1993) for denitrification measurements.

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 flux	(1)
Sediment Core	6.5-cm-dia	2 or 3	Eh and pH/ Porewater/ grain size	(1), (2)
Sediment Core	2.5-cm-dia	3	Archived solids/porosity/ pigments	(1)
Sediment Core	10.1-cm-dia	2	Denitrification	(3)
Whole Seawater	Hydrolab Scout 2 Multiparameter System	1	Temperature/Salinity/Oxygen	(4)
Pumped Seawater	~15 L carboy, filtered	1	Water for incubations	(1)

(1) Giblin *et al.*, 1994; 1997.
(2) Not all parameters are measured every survey (see Section 7.4).
(3) Kelly and Nowicki , 1993.; not collected at every station or every survey (see Section 7.4).
(4) Temperature, salinity, and oxygen are measured in field.

Table 3 describes the parameters to be measured in flux and porewater samples. Cores are maintained in the dark at the *in situ* collection temperature (± 2◦C)**.** 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. Nutrient 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. Temperature, salinity, and dissolved oxygen of bottom waters will also be measured at each station. Every year, denitrification fluxes are to be carried out on cores from harbor Stations BH02 and BH03 during all four surveys, and from Stations MB02 and MB03 only during the May and October surveys, the time within our sampling season when bottom waters are typically the coolest and warmest, respectively, for the Bay. The May and October surveys may also capture the effects of the spring and fall phytoplankton blooms. The collection frequency for denitrification fluxes in years beyond 2002 will be decided before the beginning of each sampling season.

Sediment profiles of pH, Eh, TOC and TN, and chlorophyll and phaeopigments will be conducted on cores from all stations and all surveys. Porewater profiles of nutrients, alkalinity, and dissolved sulfides will be measured during only the July and August surveys, when bottom waters are warm and rates of benthic metabolism are high. Measurements made at this time will allow the midsummer peak in free sulfide to be tracked if it appears during this period of peak activity. 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 296 samples will be collected during 32 station occupations. Of this total, 88 core and 32 seawater samples will be used directly in flux measurements, 80 will be collected for use in porewater analyses, 32 will be used for pigment analyses, and 64 will be dried for solids measurements and to be archived. Cores for porewater analyses will be over-sampled to ensure an adequate number of suitable cores for these measurements and for potential ancillary measurements.

7.5 Parameter Table

Table 3 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 CW/QAPP are scheduled annually from 2002 – 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

[1]X is the last digit of the sampling year (*i.e.*, 2 – 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 three months after the completion of each survey. The due dates are August 15, October 15, November 15 and January 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
		Urea	Spectrophotometric or Rapid Flow Analyzer	µM	Price and Harrison, 1987	~5 per flux	Polyethylene bottles	<4 Months	Frozen
	10.1-cm-dia. Core (1 oxic)	N_2	GC	µmoles	Kelly and Nowicki, 1993	4 per flux	Injection in GC	NA	NA
		O_2	GC	µmoles	Kelly and Nowicki, 1993	4 per flux	Injection in GC	NA	NA
	10.1 cm-dia. Core (1 anoxic)	N_2	GC	µmoles	Kelly and Nowicki, 1993	4 per flux	Injection in GC	NA	NA
Porewater/ Solids	6.5-cm-dia. Core (1)	NH_4	Spectrophotometric	µM	Solorzano, 1969	≥6 Depth Intervals	Dilution with seawater, fixed within 1 h	24 h	NA
		NO_2 + NO_3	Flow Injection Analyzer	µM	Diamond, 1994	≥6 Depth Intervals	Polyethylene bottles	<4 Months	Frozen
		PO_4	Spectrophotometric	µM	Murphy and Riley, 1962	≥6 Depth Intervals	Acidified	<4 Months	4◦C
		Sulfide	Spectrophotometric	µM	Cline, 1969	≥6 Depth Intervals	Trapped in Zn acetate	24 h	NA
		Si	Rapid Flow Analyzer	µM	Armstrong, 1951	≥6 Depth Intervals	Polyethylene bottles	<4 Months	Frozen
		Urea	Spectrophotometric or Rapid Flow Analyzer	µM	Price and Harrison, 1987	≥6 Depth Intervals	Polyethylene bottles	<4 Months	Frozen
		Alkalinity	Titration	mE	Edmond, 1970	≥6 Depth Intervals	Immediate	NA	NA
	6.5-cm-dia. Core (1)	pH	*In situ* 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	Refrigerate
Solids	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	Elemental Analyzer	% dry weight	Kristensen and Andersen, 1987	Top 2-cm	Section, dry at 105 ◦C	<4 Months	NA
Seawater	*In situ*	O_2 Salinity Temperature	Hydrolab Multiparameter System	mg/L	Hale, 1980	Each station	Immediate	NA	NA

GC = gas chromatograph
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 Keay 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 CW/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 CWQAPP. She is also responsible for reviewing the data and synthesis reports for accuracy and completeness. Mr. Wayne Trulli is the Battelle Field Manager, responsible for the overall field program. Mr. Chris Gagnon is the Deputy Field Manager and is responsible for 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 CW/QAPP (Libby *et al.,* 2002).

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.

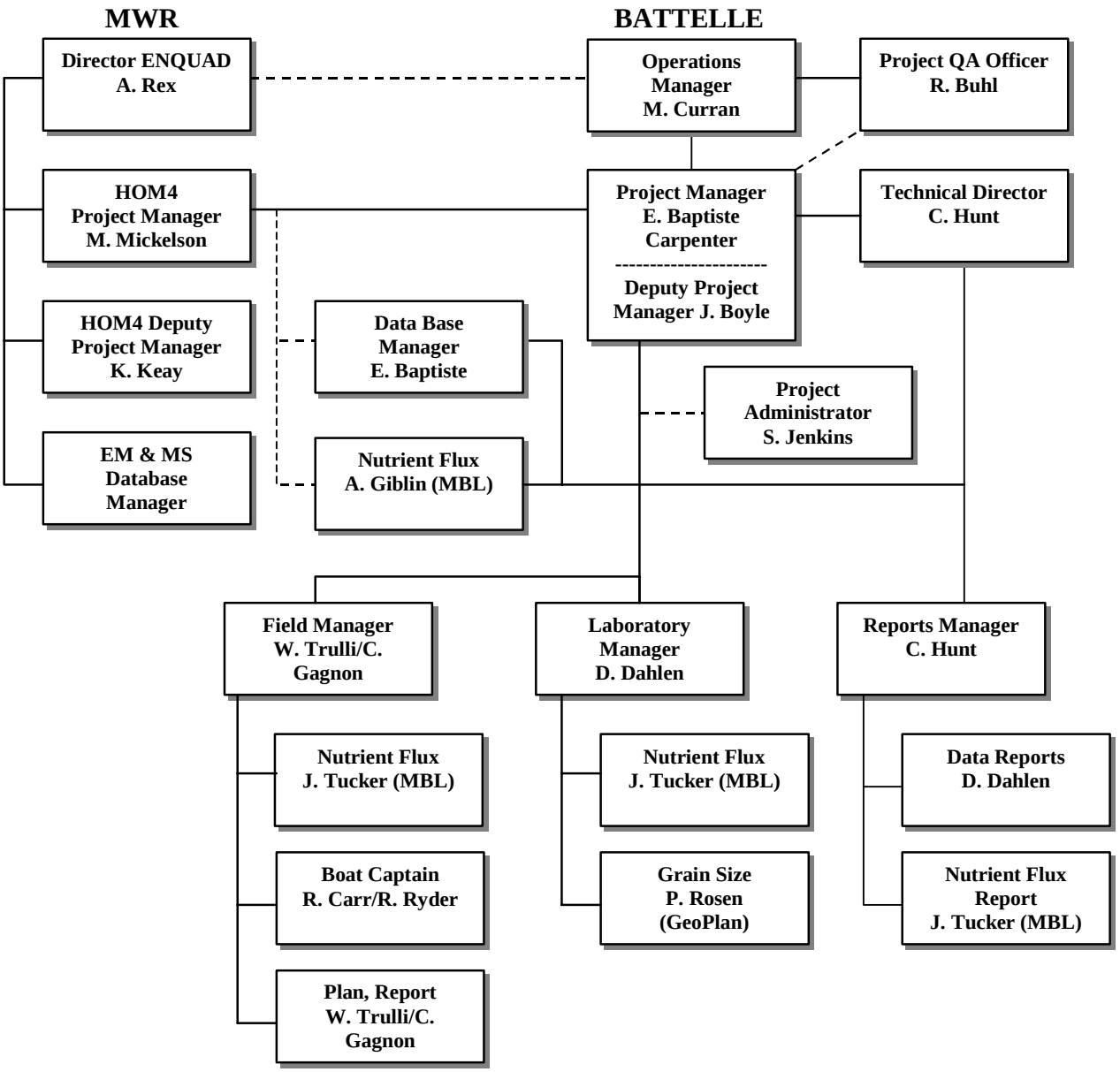

Figure 2. Flux Studies (Task 16) Organization and Analysis.

Table 5. Data Quality Objectives for Field Measurements.

Variable (Lab)	Qualifier	Detection Limits	Accuracy
Temperature (MBL)	Seawater	NA	$\pm$0.15◦C
Salinity (MBL)	Seawater	NA	$\pm$0.5 PSU
Dissolved Oxygen (MBL)	Seawater	NA	$\pm$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 six cores (two each of the 15 cm dia. cores, 10.1 cm dia. cores if required for the station, and 6.5 cm dia. cores) is obtained. If only six 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 six 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 2002-2005 (MB01, MB02, MB03 and MB05) are the same stations that have been used throughout the monitoring program, from 1992-2001. The Harbor stations (BH02, BH03, BH08A, and QB01) are the same four stations that were used during 1998-2001. 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 1998-2001 surveys, and will be visited in 2002-2005. 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 1998-2001, and will continue to be sampled in 2002-2005. 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 and incubation methods described in this CW/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). These are also identical to the methods used by Howes for 1995-1997 (Cibik and Howes, 1995) with the following exceptions:

1. Porewater nutrients will be extracted from individual 6.5 cm cores rather than from the flux cores as was done in 1995-1997. At each station, duplicate cores for porewater analyses will be taken and the better of the two, with fewest animal burrows or voids, will be used for analyses.

2. 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.

3. 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 CW/QAPP (Williams *et al.*, 2002) 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, urea, carbon dioxide, dissolved oxygen, and nitrogen gas. Porewater analyses will include measurements of sulfides, alkalinity, pigments, Eh and pH, as well as ammonia, nitrate/nitrite, phosphate, silica and urea. Solid phase analyses will be made for TOC and TN, 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. For porewaters, nutrient concentrations are relatively high and usually well above detection limits.

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.

For the denitrification studies, uncertainty (*e.g.*, confidence intervals as described in Kelly and Nowicki, 1993) in a flux estimate is expected to be in the range of 0.12 – 0.36 mmol N_2 $m^{-2}day^{-1}$. A lower detection limit for N_2 flux, a primary parameter, is ~0.12 mmol N_2 $m^{-2}day^{-1}$. The accuracy of flux measurements cannot be independently assessed. However, a descriptive measure of accuracy is provided by very good comparability between flux rates measured in Boston Harbor during 1992-1994 and 1998-2001 by this team and in 1995-1997 by Howes (1998c).

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 flux rate estimates.

Oversampling 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 will also be taken, except for total carbon dioxide (TCO_2) data, which will be collected only at the start and finish of incubations. With the exception of TCO_2, fluxes could be estimated (with less confidence) using fewer data points than planned.

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	.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, PW	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, PW	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, PW	µM	0.5	≤5%	≤5%	CRM Lab Standards Lab Duplicates	1 Verification[d] Daily 1/20 Samples	Repeat Repeat Repeat
Si	SW, PW	µM	.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
Urea	SW, PW	µM	0.2	≤5%	≤5%	Lab Standards Lab Duplicates	Daily 1/20 Samples	Repeat Repeat
Sulfide	PW	µM	2 (PW)	NA[c]	≤5%	Method Blank Lab Duplicates	2/Day Each Sample	Repeat Flag Data
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
Alkalinity	PW	mE	0.001mV[a]	≤5%	≤5%	Lab Standard Lab duplicate	≥1/survey Daily	Repeat
N_2	GAS	µmoles	2	NA	≤4%	CRM	At beginning and end of analysis run	Repeat
O_2	GAS	µmoles	2	NA	≤5%	CRM	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
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[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

For measurements of N_2 flux, the following procedures will ensure that minimum requirements for completeness are met. Denitrification rates are based on the linear flux of nitrogen gas from the oxygenated sediment cores, corrected for the background flux of nitrogen gas observed in the anoxic control cores. The rates are estimated from no fewer than four measurements (one each day) of gas sampled from a chamber. At least two replicate samples of nitrogen and oxygen will be taken from each incubation chamber on each sample day. The samples are immediately injected into the gas chromatograph and data are generated within minutes. If the gas concentrations of the replicate samples vary by more than 4%, additional samples will be taken until three samples replicate within 4%. Thus data will be reviewed for quality in "real-time", and any obvious injection or other problems will be addressed. Replicate samples taken from each chamber on at least four consecutive days will be used to generate a linear regression of nitrogen or oxygen concentrations over time. The slope of this linear regression is the rate of flux of nitrogen or oxygen from the sediments. After completion of a four-point incubation for both anoxic and oxic cores of a station, the data will be reviewed for quality, linearity of points, and reasonableness of oxic versus anoxic rates. If data are satisfactory, the incubations will be terminated. If data are unsatisfactory, a second four-point incubation series will be performed on the pair of station cores.

Collection of an extra core for Eh/pH and porewater 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. The porewater measurements provide ancillary data not required to estimate flux rates, but of interest to interpretation of sediment conditions.

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 are identical to those specified in the 1998-2001 CW/QAPP (Tucker and Giblin, 2001).

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*. 1999; 2000; 2001) in the 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 CW/QAPP (Libby *et al*., 2002) 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 40 x 40-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 ±2° 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 ±2°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. 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, silica, and urea. 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**.** Samples for nutrient analyses will be processed within 1 h according to methods presented in Table 3. Ammonium concentrations will be determined for duplicate 3-mL samples. 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 (1) nitrate/nitrite, (2) silica, and (3) urea. A duplicate determination of

NO_3 is 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). Urea will primarily be measured spectrophotometrically; however it may also be analyzed by the same method adapted for automation using the Alpkem.

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, urea (when done by hand), and sulfides (see below)] will use a Shimadzu UV-Visible Spectrophotometer (Model UV-160 or UV-1601) equipped with a flow-through "sipper" cell.

Samples for ammonia, nitrate/nitrite, phosphate, silica and urea 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 and Oxygen Flux

The two 10.1-cm-dia cores collected from each station will be used to obtain measurements of denitrification (N_2 gas release). Because oxygen concentrations are monitored simultaneously, oxygen flux will also be calculated. The methods that will be used to measure sediment denitrification and oxygen flux are fully described in Nowicki *et al.*, (1997).

Upon arrival at MBL, the rubber stoppers used to cap the cores in the field will be replaced with machined bottoms and tops that are fitted with o-rings to provide a gas tight seal. At this time the depth of the sediment contained in the core tubes may be adjusted to provide equal sediment depths for the experimental core and its anoxic control (see below) by carefully slicing off sediment from the bottom of the core. Overlying water will be replaced in the cores with filtered seawater collected at the same station as the core sample. After refilling the cores, 150-250 ml (depending on the expected fluxes) will be removed to provide a gas headspace, and measured to $\pm$ 5 ml in order to get an accurate measure of the headspace volume. The relative volumes of sediment to overlying water to headspace will be determined so as to provide enough oxygen in the overlying water of the experimental core to prevent that core from going anoxic during the incubation.

Before incubation, the headspace and the overlying water will be continuously sparged for 36-48 hours. One replicate core from a station (the experimental core) will be sparged with an 80% helium/ 20% oxygen gas mixture to remove nitrogen gas and to maintain the overlying water's ambient oxygen concentration. The second replicate core from a station will serve as the anoxic control core, treated exactly as the experimental core except that the replacement water and gas phase will be flushed of both nitrogen and oxygen with pure helium gas (without oxygen). The water in each core chamber will be

equilibrated with the gas phase by continuous stirring with a magnetic stir bar, located at the water-gas interface, and rotated by an external motor-driven magnet. Incubation of the cores will begin after the water/gas phases have been flushed of nitrogen and sufficient N_2 has been purged from the porewaters to allow accurate measurement of denitrification rates. Cores will be maintained in the dark at $\pm$2◦C of the ambient collection temperatures during the sparging/equilibration period and during incubations.

Gas samples will be withdrawn (at least once per day) through the chamber's sampling ports and analyzed for nitrogen and oxygen. Replicate 100-µl samples will be collected with a helium-flushed gastight syringe inserted through a rubber serum stopper in the sampling port. To avoid contamination by atmospheric nitrogen, the sampling port, syringe, and gas chromatography injection port will be flushed continuously with helium during sampling. The gas samples will be analyzed for nitrogen and oxygen in a Shimadzu GC-8A gas chromatograph (GC) equipped with a thermal conductivity detector. The GC uses a 1/8-in X 2-m stainless steel column packed with 5-A molecular sieve (45/60 mesh), operated at room temperature with helium as the carrier gas (35 mL/min).

Nitrogen and oxygen gas concentrations will be determined by comparison of the samples' chromatographic peak areas with those for a certified gas mixture standard (19.9% oxygen: 4.05% nitrogen: 76.05% helium). Standards are routinely run with each daily set of samples from the sealed incubation chambers.

12.3.3 Analysis of Sediment Porewaters and Archival of Solids

One 6.5-cm-dia core collected from each station will be extracted for porewater at selected core depth intervals. In a glove bag under a nitrogen atmosphere, cores will be sectioned at 1-cm intervals between 0 and 2 cm, at 2-cm intervals between 2 and 6 cm, and at 4-cm intervals to 14 cm. Each depth interval will be placed in a centrifuge tube and capped. For muddy sediments, porewater will be extracted by centrifuging the sediments for 15 min at maximum speed on a tabletop centrifuge. Sandy sediments will be centrifuged in a "split" centrifuge tube with filter support in the center of the tube. The sediment will be placed on the filter and centrifuged at high speed for 15 min.

Subsamples for sulfide, alkalinity, and nutrient analyses will be pipetted from the extracted porewater. Dissolved sulfides will be trapped in 2% zinc acetate and analyzed within 24 h according to a modified Cline (1969) method. Sulfide concentration is calculated using an algorithm based on a series of sulfide standards, after blank corrections. Alkalinity will be measured by a Gran titration (Edmond, 1970), modified for small sample sizes (using an Orion SA720 pH meter coupled to a Ross 8135 combination pH electrode). Nutrients in the porewater samples will be analyzed as described above for fluxes, including the use of reference standards in each sample run. Samples for the ammonium analysis, however, will be diluted 3- to 30-fold with clean seawater.

A second 6.5-cm-dia core from each station will be collected for pH and Eh measurements. pH will be measured with an ion sensitive field effect transistor (ISFET), stainless steel pH probe (3.5 mm dia $\times$ 20 cm length) I.Q. 200 pH/thermometer, (I.Q. Scientific Instruments) that will be progressively pushed into the sediment core. Eh will be measured in the same manner with a platinum electrode and an Orion 601A digital ionanalyzer. 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 CW/QAPP (Williams *et al*., 2002) 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 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 6) [Example: *Event ID* = NC021, *Marker No.* = 018, *Analysis Code* = NF1, *Sample ID* (Bottle ID) = NC021 018 NF1]. 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.

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	Porewater or Grainsize or Eh/pH	From first 6.5-cm core
PO2	Porewater or Grainsize or Eh/pH	From second 6.5-cm core
PO3	Porewater or Grainsize or Eh/pH	From third 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

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 and denitrification 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 CWQAPP 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 generated while in the field and the copy will be given to the Battelle Field Sample Custodian. 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** _____					
N_2 Flux (10.1 cm)	**DF1** _____	**DF2** _____					
PW (6.5 cm)	**PO1** _____	**PO2** _____	**PO3** _____				
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 _____
Via _____

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 CW/QAPP (Libby *et al*., 2002).

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.

14.2 Laboratory Equipment

Because samples for the flux studies are analyzed in real time, it is critical that the primary analytical instruments - gas chromatograph (GC) and DO sensor - are maintained and calibrated regularly.

A logbook detailing GC performance on all standards is maintained by MBL staff. The instrument will be thoroughly checked prior to a survey. Nitrogen and oxygen gas concentrations of the samples are determined by comparing chromatographic peak areas with those obtained from a reference gas mixture (approximately 20% oxygen:4% nitrogen:76% helium; each standard will vary slightly and receive a unique certification from the manufacturer). With each set of sample incubations or with each new GC column, standards will be used to check the linear response of the GC detector and column. Backup GCs are available at MBL.

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 CO_2 Analyzer used to measure CO_2 will be calibrated with bicarbonate and seawater solutions of a known carbon dioxide content (supplied by Andrew Dickson, UCSD).

Calibration procedures for the Shimadzu UV-Visible Spectrophotometer (NH_4, PO_4, urea, sulfide and chlorophyll/phaeophytin), the Lachat Flow injection analyzer (NO_2 + NO_3), and the Alpkem Rapid Flow analyzer (silica and urea) 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 Orion SA720 pH meter with Ross 8135 combination pH electrode (alkalinity and pH in porewater) and 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 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.

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 CW/QAPP for Benthic (Sea-Floor) Monitoring (Williams *et al*., 2002).

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) 508-457-1548 (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	☐	☐	☐	☐
	NC014013NF2	10/30/01 7:29:42 AM	BH02	☐	☐	☐	☐
	NC014016NF1	10/30/01 7:32:13 AM	BH03	☐	☐	☐	☐
	NC014016NF2	10/30/01 7:32:13 AM	BH03	☐	☐	☐	☐
	NC014019NF1	10/30/01 7:35:14 AM	BH08A	☐	☐	☐	☐
	NC014019NF2	10/30/01 7:35:14 AM	BH08A	☐	☐	☐	☐
	NC01401CNF1	10/30/01 7:36:57 AM	QB01	☐	☐	☐	☐
	NC01401CNF2	10/30/01 7:36:57 AM	QB01	☐	☐	☐	☐
	NC014021NF1	10/30/01 8:26:02 AM	MB03	☐	☐	☐	☐
	NC014021NF2	10/30/01 8:26:02 AM	MB03	☐	☐	☐	☐
	NC014027NF1	10/30/01 9:26:18 AM	MB02	☐	☐	☐	☐
	NC014027NF2	10/30/01 9:26:18 AM	MB02	☐	☐	☐	☐
	NC01402BNF1	10/30/01 9:55:36 AM	MB01	☐	☐	☐	☐
	NC01402BNF2	10/30/01 9:55:36 AM	MB01	☐	☐	☐	☐
	NC014034NF1	10/31/01 2:24:13 PM	MB05	☐	☐	☐	☐
	NC014034NF2	10/31/01 2:24:13 PM	MB05	☐	☐	☐	☐

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 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 CW/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:

- Flux rates of oxygen, total carbon dioxide (DIC), ammonium, nitrate + nitrite, dissolved inorganic nitrogen, phosphate, silica, and urea will be reported for each "flux-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 mmol m^{-2} day^{-1}.
- Concentrations of parameters (see Table 3), by depth interval, for each core analyzed for porewater constituents.
- Fluxes of nitrogen and oxygen gas. Fluxes for nitrogen gas will be calculated for both the oxic and anoxic core from each station. The station denitrification rate, which is the oxic core rate corrected for the anoxic core rate, will also be reported. Oxygen flux will be provided only for the one oxic core from each station. The r^2 for the regression of gas concentration over time will be reported. The temperature of the incubation will also be reported. Rates of nitrogen gas production and oxygen uptake for sediments in the sealed gas-tight chambers will be calculated as described in Kelly and Nowicki (1993) from the slopes of four-point linear regressions of dinitrogen or oxygen concentrations in the gas phase of each chamber over time. The measured rate of dinitrogen gas production or oxygen consumption will be divided by the surface area of each sediment core (0.005 m^2) to yield a flux rate in mmol N_2 $m^{-2}day^{-1}$ or mmol O_2 $m^{-2}day^{-1}$, respectively.
- The concentration of dissolved oxygen (mg L^{-1}), field temperature (°C) and salinity (psu) for each station.

Calculations
Flux rates 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 mmol m^{-2} d^{-1}.

Concentrations of NH_4, NO_3+NO_2, PO4, Si, and urea 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 mg O_2/L as read off the Orbisphere O_2 meter are converted to mmolO_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 (°K).

Sulfide concentrations are calculated from the following standard equation that was developed for a series of sulfide standards, using the method of Cline, 1969:

$$[HS^-] = (A_s - A_b)/0.542,$$

where: A_s and A_b are absorbances at 670 nm for the sample and the blank.

Alkalinity is calculated by a regression of ten points along the linear portion of a potentiometric titration that relates a mV reading to acid volume added (Edmond, 1970).

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:

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

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.

Denitrification

The calculation of N_2 and O_2 fluxes using the GC technique has several steps. The first is to calculate the concentration in samples taken from the gas headspace of the core for each sampling time. Gas standards of known concentrations are analyzed to yield a relationship of chromatographic peak area, in chart units (cu) to the concentration of the standard (after conversion to mmol/L from % using gas laws). Sample concentrations are then calculated from the relationship of cu per mmol/L from the standard to the peak area produced by the samples. The concentration in the gas headspace is used to calculate the concentration in the overlying water, which is not directly measured. This is done using solubility coefficients specific for each gas at a given temperature and salinity (Weiss, 1970). The total mass (mmoles) of gas in each phase, gas or water, is calculated by multiplying by the volume of the phase. The total mass is then divided by the surface area of the sediment in the experimental core, yielding mmol m^{-2}. This concentration for each sampling time is then regressed against time to yield mmol m^{-2} d^{-1}.

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 CWQAPP (Williams *et al*. 2002).

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

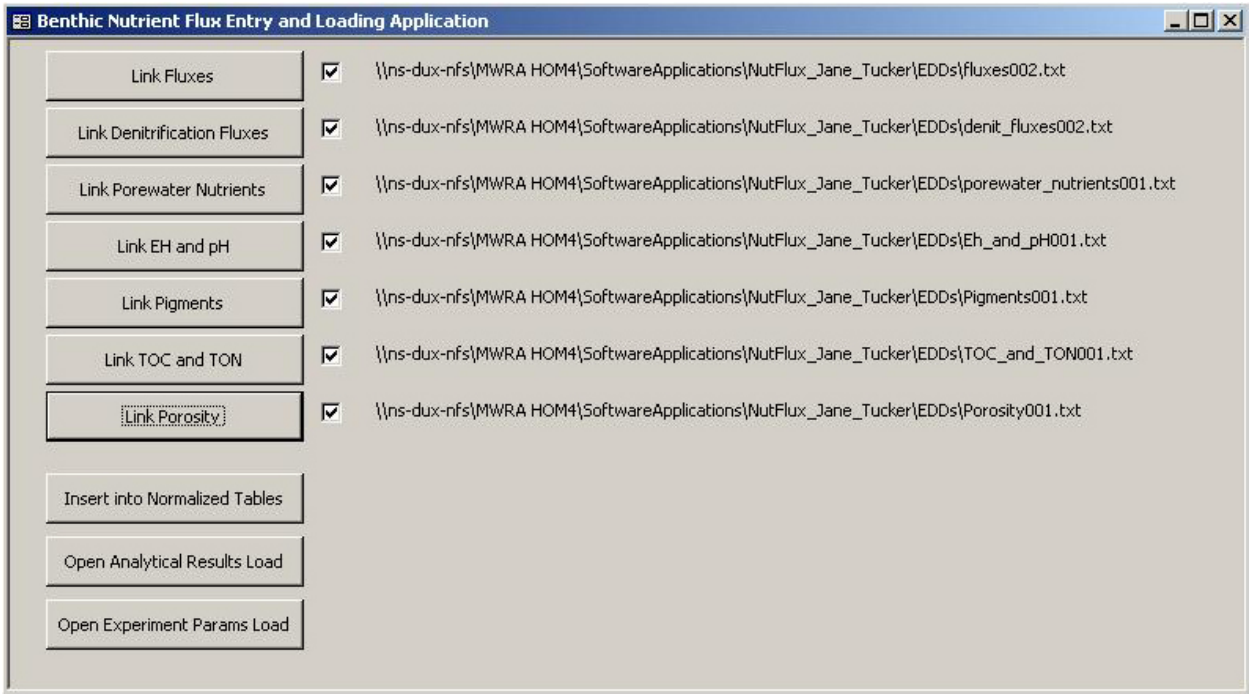

Figure 5. Benthic Nutrient Flux Entry and Loading Application.

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 CW/QAPP for Benthic (Sea-Floor) Monitoring (Williams *et al.*, 2002). 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					
Flux Measurement for DIC	DIC_FLUX	mmol/m2/d	MBL	CCO2	KEL93
r-squared of linear regression for estimation of parameter DIN_FLUX	DINFLUXR2		MBL	LATF_SPEC or RAPFL_SPEC	GIB94
Flux Measurement for DIN	DIN_FLUX	mmol/m2/d	MBL	LATF_SPEC or RAPFL_SPEC	GIB94
R Squared for NH4 Flux from Sediments	NH4FLUXR2		MBL	SPECPH	SOL69
NH4 Flux from Sediments	NH4_FLUX	mmol/m2/d	MBL	SPECPH	SOL69
r-squared of linear regression for estimation of parameter NO3_FLUX	NO3FLUXR2		MBL	LATFI	DIAM94
NO3+NO2 Flux from Sediments	NO3_FLUX	mmol/m2/d	MBL	LATFI	DIAM94
r-squared of linear regression for estimation of parameter PO4_FLUX	PO4FLUXR2		MBL	SPECPH	MURPH62
Flux Measurement for PO4	PO4_FLUX	mmol/m2/d	MBL	SPECPH	MURPH62
r-squared of linear regression for estimation of parameter UREA_FLUX	UREAFLUXR2		MBL	RAPFL	PH87
Flux Measurement for Urea	UREA_FLUX	mmol/m2/d	MBL	RAPFL	PH87
r-squared of linear regression for estimation of parameter SI_FLUX	SIFLUXR2		MBL	RAPFL	ARMS51
Flux Measurement for Silica	SI_FLUX	mmol/m2/d	MBL	RAPFL	ARMS51
R squared for O2 flux measurement	O2FLUXR2		MBL	DOPROBE	HALE80
O2 Flux from Sediments	O2_FLUX	mmol/m2/d	MBL	DOPROBE	HALE80
Temperature	TEMP	C	MBL	THER	
Denitrification Flux					
R-squared for regression of N2 flux from anoxic core against time	N2FLUXANR2		MBL	GCTCD	KEL93
R-squared for regression of N2 flux from oxic core against time	N2FLUXOXR2		MBL	GCTCD	KEL93
N2 flux from sediments in anoxic denitrification chamber	N2_FLUX_AN	mmolN2/m2/d	MBL	GCTCD	KEL93
N2 flux from sediments in oxic denitrification chamber	N2_FLUX_OX	mmolN2/m2/d	MBL	GCTCD	KEL93
N2 FLUX FROM SEDIMENTS	N2_FLUX	mmolN2/m2/d	MBL	GCTCD	KEL93
R squared for O2 flux measurement	O2FLUXR2		MBL	DOPROBE	HALE80

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
O2 Flux from Sediments	O2_FLUX	mmol/m2/d	MBL	DOPROBE	HALE80
Temperature	TEMP	C	MBL	THER	
Porewater					
Alkalinity	ALK	mE	MBL	PETTE	KEL93
Ammonium	NH4	uM	MBL	SPECPH	SOL69
Hydrogen sulfide	7783-06-4	mM	MBL	SPECPH	KEL93
Nitrate plus nitrite	NO3+NO2	uM	MBL	LATFI	DIAM94
Negative log of hydrogen ion activity	pH		MBL	PHPROBE	MIT97 EDM70
Phosphate	PO4	uM	MBL	SPECPH	MURPH62
Standard Redox Potential	EH	mV	MBL	EHPROBE	GIB94
Silicate	SIO4	uM	MBL	RAPFL	ARMS51
Urea	57-13-6	uM	MBL	SPECPH	GIB94
Redox potential discontinuity at the bottom of the bioturbation layer - where sediment is sulfidic	ARPD	cm	MBL	RULER	KEL93
Solids					
Chlorophyll a	CHLA	ug/mL	MBL	SPECPH	GIB94
Phaeophytin	PHAEO	ug/mL	MBL	SPECPH	MWRA79
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
Phi Size <-1	< -1	PCT	GOP	SVSET	FOLK74
Phi Size -1 - 0	-1 - 0	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
Seawater					
Dissolved oxygen	DISS_OXYGEN	mg/L	MBL	HYDRO-S2	HALE80
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	GCTCD	Gas Chromatograph Thermal Conductivity Detector
INSTR_CODE	LATFI	Lachat QuikChem 8000-FIA
INSTR_CODE	HYDRO-S2	Hydrolab Scout 2 Multiparameter Water Quality Data System
INSTR_CODE	PHPROBE	PH Probe and Meter
INSTR_CODE	DOPROBE	Dissolved Oxygen Probe
INSTR_CODE	EHPROBE	Eh Probe Platinum Electrode
INSTR_CODE	PE24CHN	Perkin-Elmer 2400 CHN Elemental Analyzer
INSTR_CODE	PETTE	Pipette
INSTR_CODE	RULER	Measurement by Ruler
INSTR_CODE	BAL	Balance

FIELD NAME	CODE	DESCRIPTION
INSTR_CODE	LATF_SPEC	Combination of Lachat QuikChem 8000-FIA and Spectrophotometer
INSTR_CODE	RAPFL_SPEC	Rapid flow analyzer and spectrophotometer in combination
INSTR_CODE	THER	Thermometer
INSTR_CODE	SVSET	Sieve/settling
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	mE	Milliequivalents per liter
UNIT_CODE	mM	Millimoles per liter
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	uM	Micro Moles per liter
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	KEL93	Kelly and Nowicki 1993 Benthic nut flux QA plan
METH_CODE	KA87	Kristensen & Andersen, 1987, J. Experimental MAR. BIOL. 109:15-23
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	DIAM94	Diamond 1994, Quickchem Method 31-107-04-1-C, Lachat Instruments
METH_CODE	ARMS51	Armstrong 1951, J. Marine BIOL. ASSOC. OK The UK 30:149-1160
METH_CODE	MURPH62	Murphy and Reilly. 1962 per Benthic Flux CWQAPP
METH_CODE	PH87	Price and Harrison. 1987.Marine Biology 94:307-317
METH_CODE	EDM70	Edmond 1970, Deep Sea Research 17:737-750
METH_CODE	CLINE	Cline, JD. 1969. Spectrophotometric determin of hyd. Sulfide in nat. waters. Limnol. Oceanogr. 14
METH_CODE	MIT97	Mitchell 1997, pH evolves into the silicon age, American Laboratory, June
METH_CODE	SVSET	Sieve/settling
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	s	Suspect/Invalid. Not fit for use.

FIELD NAME	CODE	DESCRIPTION
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 CW/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 flux rates) 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 CW/QAPP. A systems audit will verify the implementation of the Quality Management Plan and this CW/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 CW/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 CW/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 CW/QAPP will be included in the survey plans. One unbound, single-sided copy of each plan 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 included in the survey reports. Any deviations from this CW/QAPP, not known at the time of survey plan preparation, will be incorporated into the survey reports. One unbound, single-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.

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) flux rates by station, core, and parameter; (3) sediment pore water analyte concentrations by depth interval of each core for specified surveys; and (4) a tally of all parameters reported (the Analysis Summary). Each Flux Data Report will describe deviations from the CW/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	August 15
	July	October 15
	August	November 15
	October	January 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

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