Combined work/quality assurance project plan (CW/QAPP) revision 1

for

Benthic Nutrient Flux Studies: 1998-2001

Massachusetts Water Resources Authority

Environmental Quality Department
Report ENQUAD MS-51 Revision 1

Citation: Tucker, J. and A. Giblin. 2001. Combined Work/Quality Assurance Plan (CW/QAPP) Revision 1 for Benthic Nutrient Flux Studies: 1998-2001. Boston: Massachusetts Water Resources Authority. Report ENQUAD MS-51 Revision 1. 36 p.

COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CW/QAPP)
REVISION 1

for

BENTHIC NUTRIENT FLUX STUDIES: 1998-2001

Task 16

MWRA Harbor and Outfall Monitoring Project
Contract No. S274

Submitted to

MASSACHUSETTS WATER RESOURCES AUTHORITY
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February 2001

MS-51 Revision 1

COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CW/QAPP) REVISION 1

for

BENTHIC NUTRIENT FLUX STUDIES: 1998-2001

MWRA Harbor and Outfall Monitoring Project Contract No. S274

Concurrences and Approvals

_____	_____
Dr. Carlton Hunt Battelle Project Manager	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: 1998-2001
Task 16
MWRA Harbor and Outfall Monitoring Project

2.0 PROJECT REQUESTED BY

Massachusetts Water Resources Authority

3.0 DATE OF REQUEST

November 5, 1997

4.0 DATE OF PROJECT INITIATION

November 5, 1997

5.0 PROJECT MANAGEMENT

Dr. Andrea Rex, MWRA Director of Environmental Quality Department
Dr. Michael J. Mickelson, MWRA Harbor and Outfall Monitoring Project Manager
Mr. Ken Keay, MWRA Harbor and Outfall Monitoring Deputy Project Manager and Benthic Nutrient Flux Project Area Manager

Dr. Carlton D. Hunt, Harbor and Outfall Monitoring Battelle Project Manager
Ms. Jeanine Boyle, Harbor and Outfall Monitoring Battelle Deputy Project Manager
Mr. Wayne Trulli, Harbor and Outfall Monitoring Battelle Field Manager
Ms. Deirdre Dahlen, Harbor and Outfall Monitoring Battelle Laboratory Manager
Dr. Anne E. Giblin, Marine Biological Laboratory Senior Scientist

6.0 QUALITY ASSURANCE (QA) MANAGEMENT

Ms. Wendy Leo, MWRA EM&MS Manager
Ms. Rosanna Buhl, Battelle Project QA 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 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. Conduct of this task provided monitoring data for the three years before MWRA discharged the effluent directly into Massachusetts Bay and will provide data for one year after. Sediment 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 this important aspect of the current benthic-pelagic coupling as well as document conditions after discharge into Massachusetts Bay begins.

Specific objectives of Task 16 are the following:

- Monitor nutrient flux and metabolism throughout the year at selected sediment stations that may be influenced by changes in MWRA effluent discharge practices.

- Concomitantly determine porewater nutrient concentrations and other geochemical factors within the surface sediments that may be influenced by changes in MWRA effluent discharge practices.

- Through these measurements and auxiliary data on water quality, monitor conditions in sediment-water exchange rates of nutrients and dissolved gases in the Boston Harbor/Massachusetts Bay region of concern.

7.2 Data Usage

The MWRA has implemented a long-term environmental monitoring plan for the effluent outfall Massachusetts Bay. A goal of this monitoring is to continue to acquire baseline data until effluent is diverted to the ocean outfall in Massachusetts Bay in November 1998, and thereafter to monitor conditions for possible changes due to the diversion. The data collected and reported for Task 16 in 1998 – August 2000 will add to the baseline data previously collected and increase our understanding of the ecological and biogeochemical dynamics of the region. These data will be invaluable to water quality modeling efforts as a verification/calibration data set, and will serve to describe some of the baseline spatial variability in fluxes and porewater conditions in soft-bottom areas of concern. No threshold parameters are measured under Task 16, however 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, 1997; MWRA in prep).

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, 1998).

Sediment cores will be collected during four surveys each year in May, July, August, and October (Table 1). In 1998, only Boston Harbor stations will be sampled, whereas in 1999, 2000, and 2001 both Harbor and Massachusetts Bay stations will be sampled. 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	Years to be Sampled
BH02	42°20.62'N	71°00.13'N	1998, 1999, 2000, 2001
BH03	42°19.84'N	70°57.71'N	1998, 1999, 2000, 2001
BH08A	42°17.46'N	70°55.33'N	1998, 1999, 2000, 2001
QB01	42°17.61'N	70°59.27'N	1998, 1999, 2000, 2001
MB01	42°24.18'N	70°50.24'N	1999, 2000, 2001
MB02	42°23.55'N	70°50.06'N	1999, 2000, 2001
MB03	42°20.88'N	70°48.92'N	1999, 2000, 2001
MB05	42°24.99'N	70°39.12'N	1999, 2000, 2001

Data from Boston Harbor will provide a continuation of data reflecting conditions during the ongoing recovery of the harbor. They will also provide data as conditions change after the effluent was diverted through the deep-water outfall. Stations in Massachusetts Bay will provide data that will continue to describe variability in soft-bottom sites near the outfall and monitor conditions once the outfall is on line.

Although only eight cores from each station are required for the laboratory studies, up to 11 cores will be collected from each station (Table 2). Cores from the Harbor stations will be collected by SCUBA divers. At stations in Massachusetts Bay, a 40 x 40-cm box corer will be used to obtain relatively undisturbed cores. Each core will be carefully pushed into the sediments to approximately 15-cm depth and then capped on both ends. 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.

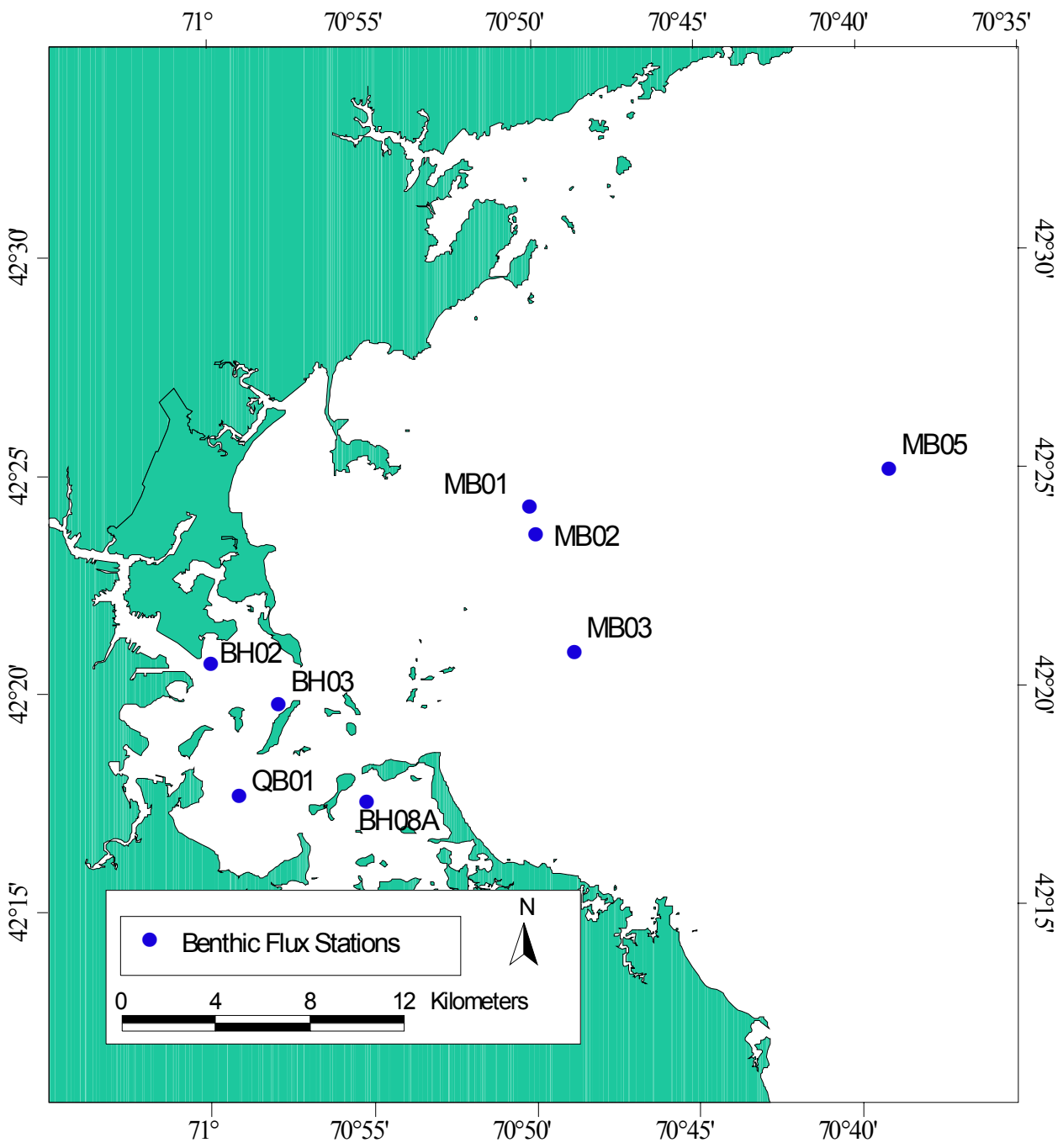

Figure 1. Benthic Flux Sampling Station Locations.

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/metabolism	(1)
Sediment Core	6.5-cm-dia	3	Porewater	(1)
Sediment Core	2.5-cm-dia	3	Archived solids/porosity/ pigments	(1), (2)
Sediment Core	10.1-cm-dia	2	N_2/O_2	(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)Subsampling 15-cm-dia cores after completion of flux measurements would be performed only if needed.
(3)Kelly and Nowicki , 1993.
(4)Temperature, salinity, and oxygen are measured in field.

Table 3 describes the parameters to be measured in flux and porewater samples. Cores will be 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 of every survey year. Nutrient fluxes will be conducted on cores from all stations visited (Table 1) during each of the 16 Benthic Nutrient Flux surveys scheduled for 1998-2001. Temperature, salinity, and dissolved oxygen of bottom waters will also be measured at each station. Denitrification fluxes were carried out on cores from Stations BH02 and BH03 during all four surveys in 1998. In 1999 and 2000, denitrification fluxes were measured during the May and August surveys on sediments from BH02 and BH03, and in May and October on sediments from the Bay stations MB02 and MB03. In 2001, denitrification measurements will be made for stations BH02 and BH03 during all four surveys, and for MB02 and MB03 in May and October. When measurements are not performed during all surveys, they are done during the surveys with the coolest (May) and warmest bottom water temperatures for the sites (August for the Harbor and October for the Bay). The May survey is also intended to capture the effects of the spring phytoplankton bloom.

Sediment profiles of pH, Eh, TOC and TN 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. Sediment chlorophyll and phaeopigments will be sampled during the

May and October surveys to look for sedimenting fresh carbon from the spring and fall blooms. Grain size will also be analyzed at this time to add to "summer" (August) data previously collected from these stations.

Table 2 lists the samples (cores) that will be collected at each station. During the 16 Benthic Nutrient Flux surveys conducted in 1998-2001, a maximum total of 856 samples will be collected during 112 station occupations. Of this total, 296 will be used directly in flux measurements, 280 will be collected for use in porewater analyses, 56 will be used for pigment analyses, and 224 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. S274) between MWRA and Battelle Duxbury Operations.

9.0 SCHEDULE OF ACTIVITIES AND DELIVERABLES

Benthic Nutrient Flux Survey (Task 16) activities will span the period from the date of project initiation (November 5, 1997) until April 2002, when the last annual synthesis report is due. Activities include field sampling and laboratory analyses, with deliverables consisting of associated survey plans, survey reports, and synthesis reports (prepared under Task 33).

Four Benthic Nutrient Flux Surveys will be conducted in 1998, 1999, 2000, and 2001. 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.

A Benthic Nutrient Flux Data Report will be prepared and delivered to MWRA within three months after the completion of each survey. An Annual Synthesis Report will be prepared and delivered to MWRA in April 1999, 2000, 2001,and 2002. Details of the contents of all reports are described in Section 19.0.

Table 3. Laboratory Analysis Parameter Table.

Analysis (LAB)	Sample Type (Number per Station)	*Parameter*	Method	Units	Reference	Frequency of Sampling	Processing	Maximum Holding Time	Preservation
Flux	15-cm-dia. Core (2)	O_2	Probe	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	6.5-cm-dia. Core (3)	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
		pH	Probe *In situ* Probe		Edmond, 1970 Mitchell, 1997	≥6 Depth Intervals	Immediate	NA	NA
		Eh	Probe	mV	Bohn, 1971	≥6 Depth Intervals	Immediate	NA	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
		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 (3)	Porosity and Archive	Balance	NA	Giblin *et al*, 1995	1-cm intervals to 10 cm, 2-cm intervals thereafter	Section, dry in 72 hours	<4 Months	NA
		Chlorophyll/ Phaeophytin	Spectrophotometric*	μg/ml	Lorenzen, 1967	1-cm intervals to 5 cm	Section into extraction tubes	<4 Months	Freeze
		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
* Change made as of first survey. See Exceptions Report for NC981.

10.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

Figure 2 presents the Project Management structure for the Benthic Nutrient Flux Study (Task 16). This represents the major tasks necessary to complete the scope of work.

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 MWRA's EM & MS database manager.

Dr. Carlton Hunt is the Battelle Project Manager and is responsible for the overall performance of this project. 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 MBL for completeness and adherence to the CW/QAPP. An initiation audit consisting of a review of laboratory procedures and personnel qualifications will be performed. The need for laboratory inspection will be based on the results of this audit. Mr. Wayne Trulli is the Battelle Field Manager responsible for all Battelle field collections. Ms. Deirdre Dahlen, Battelle's Laboratory Manager, is responsible for overseeing all laboratory activities in the contract. Ms. Ellie Baptiste-Carpenter is Battelle's Database Manager.

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

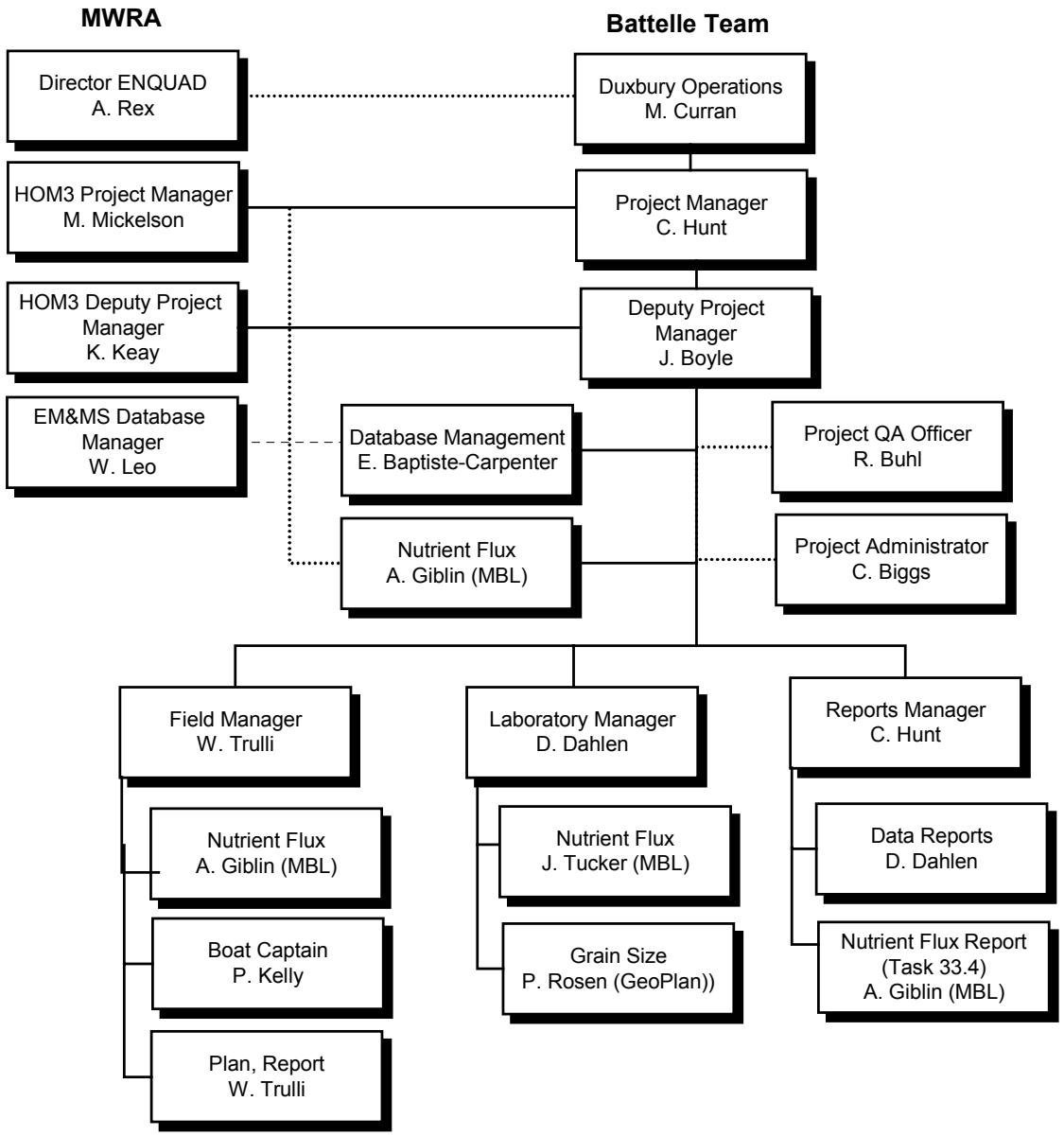

Figure 2. Flux Studies (Task 16) Organization and Analysis.

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 (Albro *et al.,* 1998).

11.1.1 Precision and Accuracy

Precision and accuracy objectives for navigation and water sampling are presented in Table 4. Section 12 provides details on relevant analytical procedures to ensure data quality, and Section 14 discusses instrument calibration methods.

Table 4. Data Quality Objectives for Field Measurements.

Variable (Lab)	Qualifier	Lower Detection Limits	Accuracy
Temperature (MBL)	Seawater	NA	$\pm$0.15°C
Salinity (MBL)	Seawater	NA	$\pm$0.2 PSU
Dissolved Oxygen (MBL)	Seawater	NA	$\pm$0.2 mg L^{-1}

NA: Not Applicable

11.2 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, 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 (4 or 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.

11.3 Comparability

The four Massachusetts Bay stations (MB01, MB02, MB03 and MB05) are the same stations that were used both in the 1992-1994 surveys and in the 1995-1997 surveys. These will be sampled in 1998-2001. The Harbor stations were not comparable between 1992-1994 and 1995-1997. In 1995 the locations of BH03 and BH08 were changed and the stations are now designated BH03A and BH08A. Station BH03A appears to be very similar to BH03, benthic fluxes of oxygen and nutrients are high at both these stations and benthic amphipod abundances fluctuate but can be extremely high (Giblin *et al*. 1993; 1994; 1995; Howes, 1997). Although the locations are slightly different 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*., submitted) have been collected from this site. Therefore, to provide continuity with these analyses, Station BH03 rather than BH03A will be visited during the 1998-2001 surveys. 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 1997). Depositional areas are more likely to show changes in inputs to the harbor, so BH08A will continue to be sampled in 1998-2001.

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. These are also identical to the methods reported by Howes for 1995-1997 with the following exceptions. The core sizes (6.5 and 10.1 cm) previously used (1992-1994) for porewater measurements and denitrification fluxes, respectively will be used. A number of cores will be taken and cores with obvious, large burrows from infauna will be discarded. The cores will be transported back to MBL for analysis. 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. Before transportation, cores will be capped with no air in the headspace. This eliminates sloshing of the water in the cores tube and minimizes sediment disturbances. A comparison with the data taken from the Massachusetts Bay station in 1992-1994 to that taken in 1995-1997 showed that the data are completely comparable. Year to year variation between the stations is 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. It should be noted that even if the cores are incubated in Boston they still experience the disturbance of box coring, subsampling from the box corer, and transportation from the boat. Cores will be examined for obvious disturbance before the flux measurements are made.

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. Dissolved oxygen concentrations measured by the Hydrolab probe will be compared to Winkler titrations (Culberson and Huang, 1987; Knapp *et al.*, 1998) to assure comparability. Salinity and temperature data will be more accurate than that obtained from a refractometer and field thermometer. A calibrated refractometer and thermometer will serve as backup to the Hydrolab.

11.4 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. Cores will not be accepted if they contain such features or large animals themselves. 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 to be prepared within one month of the survey. Water retrieved by Niskin bottle or pumped to the ship will be highly representative of the near-bottom waters at each station.

11.5 Laboratory Program

Refer to the Benthic (Sea-Floor) Monitoring CW/QAPP (Kropp and Boyle, 1998) for a description of the data quality requirements for the grain-size analysis.

11.5.1 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 5-15 μMol N_2 $m^{-2}h^{-1}$. A lower detection limit for N_2 flux, a primary parameter, is ~5 μMol N_2 $m^{-2}h^{-1}$. 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 Massachusetts Bay during 1992-1994 by this team and in 1995 by Howes (1997).

11.5.2 Completeness

It is expected that flux measurements will be completed for all parameters in two 15-cm-dia cores and two 10.1-cm-dia cores (one oxic, one anoxic) 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. If one successful estimate of N_2 flux is obtained (10.1 cm dia. cores), the relevant objectives will be met fully.

Table 5. Data Quality Objectives for Laboratory Measurements.

Variable (Lab)	Matrix	Units	Lower 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	1 per batch 1/15 samples	Repeat Repeat
NH_4	SW, PW	µM	0.5	≤5%	≤5%	CRM Lab Standards Lab Duplicate	Quarterly 1 Set/Batch 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/Batch 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] 1 Set/Batch 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/Batch 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	1 Set/Batch 1/20 Samples	Repeat Repeat
Sulfide	PW	µM	2 (PW)	NA[c]	≤5%	Method Blank Lab Duplicates	2/Batch Each Sample	Repeat Flag Data
pH	PW	NA	0.01[a]	≤0.05	≤1%	CRM (buffers)		Repeat
Eh	PW	mV	0-±1400 [b]	≤5%	≤5%	Lab Standard	1/batch	Repeat
Alkalinity	PW	mE	0.001mV[a]	≤5%	≤5%	Lab Standard	1/batch	Repeat
N_2	GAS	µmoles		NA	≤4%	CRM	At beginning and end of analysis run	Repeat
O_2	GAS	µmoles		NA	≤1%	CRM	At beginning and end of analysis run	Repeat
TOC	Sed	%(w/w)	0.5%	≤5%	≤2%	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	0.05µg/mL	NA	NA	NA	NA	NA
Phaeopigments	Sed	µg/ml	0.1µg/mL	NA	NA	NA	NA	NA
Porosity	Sed	NA	0.1mg[a]	≤5%	≤5%	NA	NA	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

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.

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. 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%, a third sample will be taken. Replicate samples taken from each chamber on 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, including obvious injection problems, obvious sample or chamber contamination, 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 extra cores for 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 five depth intervals are successfully sampled and analyzed. The porewater measurements provide ancillary data not required to estimate flux rates, but only of interest to interpretation of sediment conditions.

11.5.3 Comparability

Data will be directly comparable to results obtained previously at the same or similar sites in Boston Harbor and Massachusetts Bay (Giblin, 1993; 1994; 1995; Howes, 1997) because the incubation and analytical techniques are identical or comparable. Exceptions are noted below. In addition, direct measurements of sediment denitrification based on nitrogen gas flux can be compared to calculated indirect estimates of denitrification activity from stoichiometric analyses of sediment dissolved nitrogen and carbon flux.

A high precision coulometric system will be used to measure total carbon dioxide (TCO_2). This is the method that was chosen for the global oceanic inorganic carbon survey that has been made in conjunction with the World Ocean Circulation Experiment-World Hydrographic program (WOCE-WHP) and the Joint Global Ocean Flux Study (JGOES) programs (Johnson *et al.,* 1993; DOE, 1994). This is the same method used to measure TCO_2 in the 1992-1994 surveys but is different from the technique used by Howes in 1995-1997. The two techniques are not directly comparable, but the coulometric technique is considered to have higher precision and accuracy due to the combination of the coulometric method with a single-operator multiparameter metabolic analyzer (SOMMA), which introduces a very accurately measured volume of sample to the coulometer (Johnson *et al*., 1993). A comparison of the data from 1992-1994 to that taken in 1995-1997 indicates that the values between the two data sets are not nearly as close for DIC as they are for oxygen and nutrients. In 1994, for example, there is a strong correlation between oxygen uptake and DIC flux between stations. The respiratory quotient (RQ) for MB stations in

1992-1994 usually fell between 1 and 2 with an average of about 1.5. In 1997 more than half the stations had RQ values over 2.0, with several RQ values falling above 4.0. Values for the RQ of Harbor stations between 1992-1994 and 1995 were more similar. The difference between the data sets is probably due, at least in part, to the problem of measuring extremely low DIC fluxes at the Bay stations with the less precise IR method. In any case, we feel, a return to the more precise technique is warranted.

Sediment pH will be measured using an *in-situ* probe (Mitchell, 1997) on the same porewater core that is used for Eh measurements. *In-situ* measurements and measurements on extracted porewaters during one sampling survey (when porewater profiles are specified) will be performed. The *in-situ* method is inherently better because gaseous carbon dioxide can be lost to the headspace of the centrifuge tube during the time it takes to separate the porewater from the sediment. Loss of carbon dioxide causes the pH to rise. The difference in pH in marine porewaters is usually quite small and should not appreciably affect the comparability of the data. However, getting very accurate pH values, at times when alkalinity is also being measured, will help resolve questions of carbonate dissolution.

Sediment profiles of nutrients, alkalinity, and dissolved sulfides will be made at 6 depth intervals to a minimum of 10 cm core depth. The intervals will be divided to maximize resolution in the top few centimeters of sediment but reach a depth below the influence of bioturbation by amphipods. Normally, the porewater core will be sectioned by 1-cm intervals to a depth of 2 cm, by 2-cm intervals to a depth of 6 cm, and by 4-cm intervals to a depth of 14 cm.

11.5.4 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, 1997) 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 (Albro *et al*., 1998) 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 ±2ºC of the *in situ* temperature at the station from which they were collected. The overlying water of each core will be kept aerated until flux measurements begin. Benthic flux measurements, initiated within 12-24 h of sample collection, will be made in accordance with the procedures presented in Giblin *et al*. (1997). 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 and regeneration. 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 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 approximately 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, nitrate, and 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 by hand; 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 CO2 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.

Samples for ammonia, nitrate/nitrite, phosphate, silica and urea will be analyzed against laboratory standards having nutrient concentrations bracketing those of the samples. Laboratory standard concentrations will be verified against certified standard solutions each time a laboratory primary standard stock solution is made. Laboratory standards will be analyzed daily, and checked for linearity (r^2 >0.99) and acceptability of blanks. All standards and blanks are run in duplicate. 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.

The high-precision coulometric carbon dioxide analyzer will be calibrated with bicarbonate and seawater solutions of a known carbon dioxide content (supplied by Andrew Dickson, UCSD). The dissolved oxygen meter will be calibrated against air-saturated water and the calibration will be checked prior to each oxygen measurement. Deviations from 100% saturation will be noted and appropriate corrections will be applied to the data following the manufacturer's manual.

12.3.2 Measurement of Sediment Denitrification and Oxygen Flux

Two of the 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 also 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 ± 1 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. 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. Cores will be maintained in the dark at ±2°C of the ambient collection temperatures during this sparging/equilibration period.

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). 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. Incubations will be conducted in the dark and at ambient temperatures.

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

The methods that will be used for porewater sampling and analysis are detailed in Giblin *et al*. (1997). Briefly, 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.

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. The electrode response will be checked daily against standard redox solutions. 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.

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. Dissolved sulfides will be trapped in 2% zinc acetate and analyzed within 24 h according to a modified Cline (1969) method. Sulfide concentration is determined by running blanks and samples and is calculated using an algorithm based on a series of sulfide standards. Alkalinity, recorded immediately after pH readings, will be measured by a Gran titration (Edmond, 1970) modified for small sample sizes. Alkalinity and pH are measured by using an Orion SA720 pH meter coupled to a Ross 8135 combination pH electrode. The probe will be calibrated each day with commercial pH buffers.

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 weighings. A subsample of the dried sediment from the surface section will be acidified to remove carbonates and then analyzed for TOC and TN using a Perkin Elmer 2400 CHN elemental analyzer. Instrument calibration is checked

at the initiation of each run against a commercial standard, and check standards are inserted into each sample run.

A second 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 (Kropp and Boyle, 1998) 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* = NC981, *Marker No.* = 018, *Analysis Code* = NF1, *Sample ID* (Bottle ID) = NC981 018 NF1]. This ID will be stored as the S*ample ID* in EM&MS. The S*ample ID* will be the same as the *Bottle ID*. *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 6. 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 CHM	From first 2.5-cm core
CN2	Porosity or Chlorophyll or CHM	From second 2.5-cm core
CN3	Porosity or Chlorophyll or CHM	From third 2.5-cm core
FS1	Filtered Seawater	From carboy

During field collection, station log forms (Figure 3) will be completed and labels will be affixed to the forms, 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 sample ID, ensuring the tracking of sample location and the status.

The samples will remain in the custody of the Field Sample Custodian (designated for each survey) while in the field. COC forms (Figure 4) will be completed in the field and will accompany the samples when transferred from the field to the laboratory. All samples will be distributed to the appropriate laboratory personnel by hand or by Federal Express. When samples arrive at each of the laboratory, custody will be relinquished to the Laboratory Custodian. Upon receipt of the samples at Battelle or its subcontractors, the Sample Custodian will examine the samples, verify that sample-specific information recorded on the COC is accurate and that the sample integrity is uncompromised, log the samples into the laboratory tracking system, complete the custody forms, and sign the COC form so that transfer of custody of the samples is complete. Any discrepancies between sample labels and transmittal forms, and unusual events or deviations from the project will be documented in the survey report.

Field custody of electronic data will be the responsibility of the survey chief scientist. This person will be identified for each survey. The field custody of the electronic data consists of creating floppy-disk backups of all electronic data generated each day. Each floppy disk label will include a survey ID, date, name of person creating the backup files, and a disk number. When the equipment is returned to Battelle, a second complete backup, labeled as "Set 2", will be generated on floppy disks. The backup will be in the custody of Mr. Wayne Trulli. The survey chief scientist maintains the original.

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 (ºC) _____
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 (Albro *et al*., 1998).

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/probe will be calibrated, according to manufacturer's specifications, against air-saturated water 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 prior to each oxygen measurement, deviations from 100% saturation are noted, and appropriate corrections are applied to the data.

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. The CHN elemental analyzer is serviced regularly and maintained by the technical staff of the MBL.

Calibration for the grain-size analysis equipment is described in the CW/QAPP for Benthic (Sea-Floor) Monitoring (Kropp and Boyle, 1998).

MWRA Harbor and Outfall Monitoring Program

Contract No. S274

Chain-of-Custody Form

Today's Date : 6/16/98 12:04:49 PM

Laboratory : Marine Biological Laboratory
The Ecosystems Center

Chain-of-Custody # : NC981-NF-0188
Survey ID : NC981
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
	NC981005NF1	5/18/98 9:00:47 AM	BH02				
	NC981005NF2	5/18/98 9:00:47 AM	BH02				
	NC981006NF1	5/18/98 10:45:53 AM	BH03				
	NC981006NF2	5/18/98 10:45:53 AM	BH03				
	NC981007NF1	5/18/98 11:34:32 AM	BH08A				
	NC981007NF2	5/18/98 11:34:32 AM	BH08A				
	NC981009NF1	5/18/98 12:29:02 PM	QB01				
	NC981009NF2	5/18/98 12:29:02 PM	QB01				

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

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

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

15.0 DOCUMENTATION, DATA REDUCTION, AND REPORTING

15.1 Documentation

The specific types of documentation that will be maintained for Task 16 include:

- Laboratory Record Books - document pertinent field information related to sample collection.
- COC Forms - 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; summarizes QA activities associated with the project.

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 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. It will be the responsibility of the laboratory managers to ensure that all data entries and hand calculations are verified. In addition to these documentation procedures, sample logs associated with field and laboratory custody and tracking will be maintained in the project files. Manually recorded data from subcontractor laboratories will be entered by the subcontractor into PC-based spreadsheets, verified, and submitted to Battelle.

15.2 Data Reduction and Reporting

15.2.1 Battelle

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.

15.2.1.1 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.

15.2.1.2 Analytical Data

Battelle will work with the Marine Biological Laboratory to create a data report format for their final nutrient flux and porewater spreadsheets. The laboratory will have to meet their own internal laboratory format and satisfy the basic QC checks for the data to load successfully.

Data deliverables will include a hardcopy report, exception report, and analysis summary. The hardcopy report allows the laboratory to check for entry errors and serves as a final data report to Battelle with deliverable. The exception report checks the data that was expected against the results loaded. This report gives the data contributor a chance to confirm the reasonableness of their data prior to submission to Battelle. The data contributor must account for any entries in the exception report. The analysis summary report produces a report of the number of analyses by analyte. A copy of this report is included with the data deliverable and with the invoice for the analyses.

Data entered by the laboratory is translated by Battelle into the correct codes and inserted into database tables with the same structure as the matching EM&MS table. The laboratory will have the ability to add additional codes to describe their results but the new qualifiers will be highlighted in the exception report. Battelle will notify MWRA concerning the new qualifier. MWRA has the responsibility for maintaining the code list for the EM&MS.

Table 7 shows the analytical parameters and related database codes for the benthic nutrient flux surveys. The description of each database code is provided in Table 8. The Study_ID for all benthic nutrient flux, surveys is "BBNF".

15.2.2 MBL

For each survey, researchers from MBL will develop PC-based spreadsheets that will contain the following data for entry into the MWRA Harbor Studies Database and for use in analyzing Task 16 data:

- Flux rates of oxygen, total carbon dioxide (DIC flux), ammonium, nitrate + nitrite, dissolved inorganic nitrogen, phosphate, silica, and urea for each "flux-rate core" collected at each station. 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 and sparge gas mixture used for the dentrification measure will be reported.

- 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 coefficient of determination for the regression of gas concentration over time will be reported. The temperature of the incubation will also be reported.

- The concentration of dissolved oxygen (mg L^{-1}) for each station.

Table 7. 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	DOE94
R Squared for Flux Measurement for DIN	DINFLUXR2		MBL	NA	GIB94
Flux Measurement for DIN	DIN_FLUX	mmol/m2/d	MBL	NA	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 for NO3+NO2 Flux from Sediments	NO3FLUXR2		MBL	LATFI	DIAM94
NO3+NO2 Flux from Sediments	NO3_FLUX	mmol/m2/d	MBL	LATFI	DIAM94
R Squared for Flux Measurement for PO4	PO4FLUXR2		MBL	SPECPH	MURPH62
Flux Measurement for PO4	PO4_FLUX	mmol/m2/d	MBL	SPECPH	MURPH62
R Squared for Flux Measurement for Urea	UREAFLUXR2		MBL	RAPFL or SPECPH	PH87
Flux Measurement for Urea	UREA_FLUX	mmol/m2/d	MBL	RAPFL or SPECPH	PH87
R Squared for Flux Measurement for Silica	SIFLUXR2		MBL	RAPFL	ARMS51
Flux Measurement for Silica	SI_FLUX	mmol/m2/d	MBL	RAPFL	ARMS51
R Squared for O2 Flux from Sediments	O2FLUXR2		MBL	RAPFL	ARMS51
O2 Flux from Sediments	O2_FLUX	mmol/m2/d	MBL	DOPROBE	HALE80
Temperature of incubation	TEMP	C	MBL	NA	NA
Denitrification Flux					
R Squared for N2 Flux from sediments in oxic denitrification chamber	N2_FLUX_OXR2		MBL	GCTCD	KEL93
N2 Flux from sediments in oxic denitrification chamber	N2_FLUX_OX	mmol N2/m2/d	MBL	GCTCD	KEL93
R Squared for N2 Flux from sediments in anoxic denitrification chamber	N2_FLUX_ANR2		MBL	GCTCD	KEL93
N2 Flux from sediments in anoxic denitrification chamber	N2_FLUX_AN	mmol N2/m2/d	MBL	GCTCD	KEL93
Denitrification rate as N2 Flux	N2_FLUX	mmol N2/m2/d	MBL	GCTCD	KEL93
R Squared for O2 Flux from Sediments	O2_FLUXR2		MBL	GCTCD	KEL93
O2 Flux from Sediments	O2_FLUX	mmol/m2/d	MBL	GCTCD	KEL93
Temperature of incubation	TEMP	C	MBL	NA	NA
Porewater					
Alkalinity	ALK	mE	MBL	PETTE	EDM70
Ammonium	NH4	uM	MBL	SPECPH	SOL69
Hydrogen sulfide	7783-06-4	mM	MBL	SPECPH	CLINE
Nitrate plus nitrite	NO3+NO2	uM	MBL	LATFI	DIAM94
pH	pH		MBL	PHPROBE	EDM70
Phosphate	PO4	uM	MBL	SPECPH	MURPH62
Standard Redox Potential	EH	mV	MBL	EHPROBE	GIB94
Silica	SIO4	uM	MBL	RAPFL	ARMS51
Urea	57-13-6	uM	MBL	RAPFL or SPECPH	PH87
Apparent RPD	ARPD	cm	MBL	RULER	KEL93
Solids					
Chlorophyll a	CHLA	ug/mL	MBL	SPECPH	LOR67
Phaeopigments	PHAEO	ug/mL	MBL	SPECPH	LOR67
Total Organic Carbon	TOC	PCTDRYWT	MBL	PE24CHN	KA87
Total Nitrogen	MWRA47	PCTDRYWT	MBL	PE24CHN	KA87
Porosity	POROSITY	g/mL	MBL	BAL	GIB94
Phi Size	< -1	PCT	GOP	SVSET	FOLK74
Phi Size	-1 - 0	PCT	GOP	SVSET	FOLK74
Phi Size	0 - 1	PCT	GOP	SVSET	FOLK74
Phi Size	1 - 2	PCT	GOP	SVSET	FOLK74

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Phi Size	2 - 3	PCT	GOP	SVSET	FOLK74
Phi Size	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 8. 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	Ruler
INSTR_CODE	BAL	Balance
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	mmolN/m2/d	Millimoles nitrogen per sq.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 et al 1993 Benthic nut flux QA plan
METH_CODE	KA87	Kristensen & Andersen, 1987 Determination of organic carbon in marine sediments: A comparison of two CHN-analyzer methods
METH_CODE	DOE94	DOE 1994 Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water
METH_CODE	FOLK74	Folk 1974
METH_CODE	HALE80	Hale, JM. 1980. Instrumental Measurements of Dissolved Oxygen Concentrations in Saline Water.
METH_CODE	SOL69	Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method.
METH_CODE	DIAM94	Diamond, DH. 1994. Determination of nitrate + nitrite in brackish or seawater by flow injection analysis colorimetry.
METH_CODE	ARMS51	Armstrong, FAJ. 1951. The determination of silicate in seawater.
METH_CODE	MURPH62	Murphy and Reilly. 1962 per Benthic Flux CWQAPP
METH_CODE	PH87	Price and Harrison. 1987. Comparison of methods for the analysis of dissolved urea in seawater.
METH_CODE	EDM70	Edmond, JM. 1970. High precision determination of titration alkalinity and total carbon dioxide content of seawater by potentiometric titration.
METH_CODE	CLINE	Cline, JD. 1969. Spectrophotometric determin of hyd. Sulfide in nat. waters. Limnol. Oceanogr. 14
FIELD NAME	**CODE**	**DESCRIPTION**

METH_CODE	LOR67	Lorenzen, "C.F. 1967. Determination of chlorophyll and pheo-pigments: spectrophotometric equations. Limnol. Oceanogr. 12.
ANAL_LAB_ID	GOP	GeoPlan
ANAL_LAB_ID	MBL	Marine Biological Laboratory
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	aL	Below MDL; value reported as negative or null, analytical conc. reported from dilution
VAL_QUAL	aLs	Not detected, analytical conc. reported from dilution, suspect/invalid, not fit for use.
VAL_QUAL	aLT	Not detected, analytical conc. reported from dilution, holding time exceeded
VAL_QUAL	aq	Not detected - value reported as negative or null. May be invalid, under investigation (Do not use).
VAL_QUAL	As	Value above maximum detection limit and suspect/invalid, not fit for use
VAL_QUAL	as	Not detected - value reported as negative or null, and not fit for use
VAL_QUAL	asT	Not detected - value reported as negative or null, not fit for use, and holding time exceeded
VAL_QUAL	aT	Not detected - value reported as negative or null, and holding time exceeded
VAL_QUAL	E	Calibration Level Exceeded
VAL_QUAL	e	Results not reported, value given is NULL. Explanation in COMMENTS field
VAL_QUAL	ELs	Calibration exceeded, concentration reported from dilution, suspect/invalid, not fit for use
VAL_QUAL	eq	Not reported, may be invalid, under investigation (Do not use).
VAL_QUAL	Es	Calibration exceeded, suspect/invalid, not fit for use
VAL_QUAL	f	Value reported is below method detection limit
VAL_QUAL	fL	Value reported is between zero and MDL, analytical conc. reported from dilution
VAL_QUAL	fq	VALUE reported is below method detection limit. May be invalid, under investigation (Do not use).
VAL_QUAL	fs	VALUE reported is below method detection limit,not fit for use
VAL_QUAL	fsT	Reported value is below MDL, suspect/invalid, not fit for use, and holding time is exceeded
VAL_QUAL	fT	Reported value below MDL and holding time is exceeded
VAL_QUAL	g	Recovery outside data objectives
VAL_QUAL	gq	Recovery outside data objectives. May be invalid, under investigation (Do not use).
VAL_QUAL	h	Below the standard curve 0
VAL_QUAL	j	Estimated value
VAL_QUAL	jp	Estimated value and bottles mislabeled
VAL_QUAL	L	Analytical Concentration Reported From Dilution
VAL_QUAL	LE	Analytical concentration reported from dilution, calibration level exceeded
VAL_QUAL	Lq	Analytical concentration reported from dilution. May be invalid, under investigation (Do not use).
VAL_QUAL	Ls	Analytical concentration reported from dilution, suspect/invalid, not fit for use
VAL_QUAL	Lsx	Diluted, matrix interference, suspect/invalid, not fit for use
VAL_QUAL	LT	Analytical concentration reported from dilution, holding time exceeded
VAL_QUAL	o	Value out of normal range judged fit for use by principal investigator
VAL_QUAL	p	Lab sample bottles mislabeled - caution data use
VAL_QUAL	q	Possibly suspect/invalid and not fit for use. Investigation pending.
VAL_QUAL	r	Precision does not meet data quality objectives
VAL_QUAL	s	Suspect/Invalid. Not fit for use.
VAL_QUAL	sT	Suspect/invalid, not fit for use and holding time is exceeded
VAL_QUAL	sv	Value is suspect/invalid and not fit for use, arithmetic mean of multiple results
VAL_QUAL	T	Holding time exceeded
VAL_QUAL	t	Two points used to calculate flux
VAL_QUAL	v	Arithmetic mean
VAL_QUAL	w	Use with caution

All fluxes will be calculated from five data points using a linear regression (Giblin *et al*., 1995; 1997). 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}. All records of calculations and raw data collected during incubations will be maintained by MBL and GeoPlan for six years.

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 nitrogen or oxygen concentrations in the gas phase of each chamber over time. The measured rate of nitrogen 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 mMoles $m^{-2}day^{-1}$.

Grain-size data reduction and reporting are as described in the CW/QAPP for Benthic (Sea-Floor) Monitoring (Kropp and Boyle, 1998).

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) BOD-bottle oxygen data.

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, 1998) 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 similar 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, 1998) 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 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

Deliverables due to MWRA under 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

Each survey plan will follow the new guidelines established by the U.S. Environmental Protection Agency for the use of the *OSV Anderson*. 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 two weeks after the completion of each survey. MWRA's comments will be due two weeks after receipt of the draft report. The final survey report, addressing MWRA's comments, will be due two weeks after receipt of the comments. If MWRA does not submit comments within the two-week period, the draft survey report will be considered final.

A Benthic Flux Data Report will be prepared and submitted to MWRA for each of the four surveys in a calendar year (see Table 9). Each report will include tabular listings 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 in a QAQC data report, a Corrective Action Log, and an Exceptions Report. All data presented in the data reports are available in the EM&MS database at Battelle and will be provided as an export within 30 days of the data 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 9.

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 measured in 1998 through 2001 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 violations, if such violations occur and whether the violations 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 9. 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
	July	October
	August	November
	October	January
Synthesis or Interpretive Reports		
Benthic Nutrient Flux Report – Outline	May - October	March
Benthic Nutrient Flux Report – Draft	May - October	April
Benthic Nutrient Flux Report – Final	May - October	30 days after receipt of comments

20.0 REFERENCES

Albro, C., H. Trulli, J. Boyle, S. Sauchuk, C. Oviatt, C. Zimmermann, J. Turner, D. Borkman, and J. Tucker. 1998. Combined work quality assurance plan for baseline water quality monitoring : 1998-2001. MWRA Enviro. Quality Dept. Misc. Rpt. No. ms-48. Massachusetts Water Resources Authority, Boston, MA. Draft.

Alpkem. 1986. Nitrate and nitrite in water and seawater. RFA Method Number A303-S171. Alpkem Corporation, Clackamas, OR.

Armstrong, F.A.J. 1951. The determination of silicate in seawater. *Journal of the Marine Biological Association of the U.K.* 30:149-1160.

Battelle. 1998. Quality management plan for Massachusetts Water resources Authority Harbor and Outfall Monitoring Project (HOM) III. 28 pp.

Bohn, H.L. 1971. Redox potentials. *Soil Science* 112:39-45.

Cibik, S.J. and B.L. Howes. 1995. Combined work/quality assurance plan for benthic nutrient flux study: 1995-1997. MWRA Envir. Quality Dept. Misc. Rpt. No. ms-36. Massachusetts Water Resources Authority, Boston, MA. 50pp

Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography* 14:454-458.

Culberson, C.H. and S. Huang. 1987. Automated amperometric oxygen titration. *Deep-Sea Research* 34: 875-830.

Diamond, D.H. 1994. Determination of nitrate + nitrite in brackish or seawater by flow injection analysis colorimetry. QuikChem Method 31-107-04-1-C. Lachat Instruments.

DOE (1994). Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2, A.G. Dickson and C. Goyet, eds. ORNL/CDIAC-74.

Dornblaser, M.M., J. Tucker, G.T. Banta, K.H. Foreman, M.C. O'Brien, and A.E. Giblin. 1989. Obtaining undisturbed sediment cores for biogeochemical process studies using SCUBA. Pages 97-104 In: M.A. Lang and W.C. Jaap (Eds.), *Proceedings of the American Academy of Underwater Science, 9th Annual Diving Symposium.*

Edmond, J.M. 1970. High precision determination of titration alkalinity and total carbon dioxide content of seawater by potentiometric titration. *Deep Sea Research* 17:737-750.

Giblin, A.G., J. Tucker, and C. Hopkinson. 1993. Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments. MWRA Environmental Quality Department Technical Report Series, No. 93-2. Massachusetts Water Resources Authority, Boston, MA. 46 pp.

Giblin, A.G., C.S. Hopkinson, J. Tucker, B. Nowicki, and J.R. Kelly. 1994. Metabolism and nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments in 1993. Massachusetts Water Resources Authority Environmental Quality Department Technical Report. Series No. 94-5. Massachusetts Water Resources Authority, Boston, Massachusetts.

Giblin, A.G., C.S. Hopkinson, J. Tucker, B. Nowicki, and J.R. Kelly. 1995. Metabolism and nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments in 1994. Massachusetts Water Resources Authority Environmental Quality Department Technical Report. Series No. 95-13. Massachusetts Water Resources Authority, Boston, Massachusetts.

Giblin, A.G., C.S. Hopkinson, and J. Tucker. 1997. Benthic Metabolism and Nutrient Cycling in Boston Harbor, Massachusetts. *Estuaries* 20: 346-364.

Hale, J.M. 1980. Instrumental Measurements of Dissolved Oxygen Concentrations in Saline Water. Technical Notes. Orbishpere Laboratories, NJ.

Howes, B.L. 1998. Sediment metabolism within Massachusetts Bay and Boston Harbor: relating to sediment-water column exchanges of nutrients and oxygen in 1995. MWRA Environmental Quality Department Technical Report Series, No. 1998-02. Massachusetts Water Resources Authority, Boston, MA. 70 pp.

Johnson, K.M., K.D. Wills, D.B. Butler, W.K. Johnson, and C.S. Wong. 1993. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and Coulometric detector. *Marine Chemistry* 44: 167-187.

Kelly, J.R. and B.L. Nowicki. 1993. Direct measurements of denitrification in Boston Harbor. MWRA Environmental Quality Department Technical Report Series, No. 93-3. Massachusetts Water Resources Authority, Boston, MA. 39 pp.

Knapp, G.P., M.C. Stalcup, and R.J. Stanley. 1990. Automated Oxygen Titration and Salinity Determi nation. Woods Hole Oceanographic Institution Technical Report , WHOI-90-35. Woods Hole Oceanographic Institution, Woods Hole, MA. 22pp.

Kristensen, E. and F.Ø. Andersen. 1987. Determination of organic carbon in marine sediments: A comparison of two CHN-analyzer methods. *Journal of Experimental Marine Biology and Ecology* 109: 15-23.

Kropp, R.K. and J.D. Boyle. 1998. Combined work/quality assurance plan for benthic monitoring: 1998-2000. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-50. 72p.

Lorenzen, C.F. 1967. Determination of chlorophyll and pheo-pigments; spectrophotometric equations. Limnol. Oceanogr. 12:343-346.

Mitchell, M.L. 1997. PH evolves into the silicon age. Application Note. American Laboratory. June 1997. P.10.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analitica Chimica Acta* 27:31-36.

MWRA. 1997. Contingency Plan. Massachusetts Water Resources Authority, Boston, MA. 40 pp.

MWRA. In Prep. Procedures for calculation and testing of Contingency Plan thresholds. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-064.

Nowicki, B.L, J.R. Kelly, E. Requintina, D. Van Keuren. 1997. Nitrogen Losses Through Sediment Denitrification in Boston Harbor and Massachusetts Bay. Estuaries. 20:626-639.

Price, N.M. and P.J. Harrison. 1987. Comparison of methods for the analysis of dissolved urea in seawater. *Marine Biology* 94:307-317.

Ramette, R.W. 1981. Chemical equilibrium and analysis. Chapter 13 In: *Limitations of Experimental Measurements.* Addison-Wesley Publishing Co., Reading, MA.

Seitzinger, S., S. Nixon, M.E.Q. Pilson, and S. Burke. 1980. Denitrification and N_2O production in near-shore marine sediments. *Geochimica et Cosmochimica Acta* 44:1853-1860.

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. *Limnology and Oceanography* 14:799-801.

Strickland, J.D.H. and T.R. Parsons. 1972. A practical handbook of seawater analysis. Fisheries Research Board of Canada. Bulletin 167.

Tucker, J., N. Sheats, A.E. Giblin, C.S. Hopkinson, and J.P. Montoya. 1999. Using stable isotopes to trace sewage derived material through Boston Harbor and Massachusetts Bay. *Marine Environmental Research* 48:353-375.

Zago, C., and A.E. Giblin. 1994. Analysis of Acid Volatile Sulfide and Metals to Predict the Toxicity of Boston Harbor Sediments. *Biol. Bull.* 187: 290-291.

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