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

for

BENTHIC NUTRIENT FLUX STUDIES: 1993-1994

Task 19
MWRA Harbor and Outfall Monitoring Project

submitted to

MASSACHUSETTS WATER RESOURCES AUTHORITY
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Concurrences and Approvals

Battelle Project Manager	Carlton D Hunt Dr. Carlton Hunt	4/12/93 Date
Battelle Project QA Officer	Bruna L Dahl for S. Anderson Ms. Sandra Anderson	4-12-93 Date
MWRA Project Manager	Michael J. Mickelson Dr. Michael Mickelson	4/20/93 Date

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MWRA Harbor and Outfall Monitoring Project

2. PROJECT REQUESTED BY

Massachusetts Water Resources Authority

3. DATE OF REQUEST

December 3, 1992

4. DATE OF PROJECT INITIATION

December 3, 1992

5. PROJECT MANAGEMENT

Dr. Michael Connor, MWRA Director of Environmental Quality Department
Dr. Michael Mickelson, MWRA Harbor and Outfall Monitoring Project Manager

Dr. Carlton Hunt, Battelle Project Manager for Harbor and Outfall Monitoring
Dr. Jack Kelly, Battelle Technical Director and Task Leader
Dr. Anne Giblin, Marine Biological Laboratory Subcontractor Project Manager
Dr. Barbara Nowicki, University of Rhode Island Subcontractor Project Manager

6. QUALITY ASSURANCE (QA) MANAGEMENT

Ms. Sandra Anderson, Battelle Project QA Officer
Ms. Rosanna Buhl, Battelle Task QA Officer

7. PROJECT DESCRIPTION

7.1 Objective and Scope

The overall objective of Task 19 is to quantify the seasonal flux of oxygen, total carbon dioxide, several forms of inorganic nitrogen, and phosphate between the sediments and their overlying waters at selected stations in Boston Harbor and Massachusetts Bay in the vicinity of the proposed MWRA effluent outfall. Benthic metabolism, nutrient flux, and sediment porewater conditions are responsive to nutrient and organic matter loading. Conduct of this task will provide baseline data before MWRA discharges the effluent directly into Massachusetts Bay. Sediment communities in shallow marine ecosystems often play a significant role in nutrient cycling and oxygen dynamics, and the data obtained from the benthic nutrient flux study will help to define this important aspect of the present benthic-pelagic coupling.

Specific objectives of Task 19 are the following:

- Determine 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, characterize baseline conditions and variability 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 is implementing Phase I of a long-term environmental monitoring plan for the effluent outfall currently under construction in Massachusetts Bay. A goal of Phase-I monitoring is to provide baseline data that may be used to assess potential environmental impact of effluent discharge into the Bay. The data collected and reported for Task 19 will be useful in understanding 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.

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 some intact cores and 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 if laboratory conditions can simulate *in situ* environmental conditions.

To determine the seasonal variability in benthic fluxes, cores will be collected during five surveys each year (Table 1). This sampling strategy will provide data across the approximate annual range of bottom water temperatures in both Boston Harbor and Massachusetts Bay, as well as provide information during the critical warmer months when the Bay water column is stratified.

Selection of the sediment sampling stations has not been finalized. The stations referenced in MWRA (1991) are not all suitable for coring and studies conducted in 1992 indicated that other station locations may be preferable for monitoring. A tentative station sampling plan is provided in Table 1. However, each survey plan will include a final list of sampling stations. In accordance with MWRA's request, six stations will be sampled in February, May, and October, and eight stations will be sampled in July and August.

Table 1. Benthic Flux Sampling Stations

Month of Survey	***Target Stations****	
	Boston Harbor	***Massachusetts Bay***
February	T2, T3, T8	W1, G8, 11
May	T3	W1, G8, 11, G9, one additional station
July	T2, T3, T8	W1, G8, 11, G9, one additional station
August	T3	W1, G8, 11, G9, three additional stations
October	T3	W1, G8, 11, G9, one additional station

* Stations refer to those of Kelly and Nowicki (1993).

In general, stations in Boston Harbor will provide baseline data reflecting not only conditions of enrichment before cessation of effluent discharge, but also the conditions of the current transition period when recovery from sludge abatement (stopped December 1991) may be occurring. Stations in Massachusetts Bay will provide baseline data that will help describe variability in soft-bottom sites near the proposed outfall.

Although only six cores from each station are required for the laboratory studies, 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 40x40-cm box corer will be used to obtain relatively undisturbed cores. Cores will be carefully pushed into the sediments to approximately 15-cm depths 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.

Table 2. Samples and Measurements at Each Survey Station.

Type	*Qualifier*	*Number*	*Laboratory*	*Intended Analysis or Use*	*Reference or Comment*
Sediment Core	15-cm-dia	2	MBL	Nutrient flux/ metabolism	(1)
Sediment Core	6.5-cm-dia	3	MBL	Porewater	(1)
Sediment Core	2.5-cm-dia	3	MBL	Archived solids/ porosity	(1), (2)
Sediment Core	7.7-cm-dia	3	URI	N_2/O_2	(3)
Whole Seawater	5-L Niskin	1	MBL/URI	Temperature (MBL) Salinity (MBL) Oxygen (URI)	(4)
Pumped Seawater	~15 L carboy, filtered	2	MBL/URI	Water for incubations	(1)

(1) Giblin *et al.*, 1993.
(2) Previous studies (Giblin *et al.*, 1993) have gathered small cores in the field and this practice will be continued. Subsampling 15-cm-dia cores after completion of flux measurements would be performed only if needed.
(3) Kelly and Nowicki (1993); two of three cores will be used; collection of an extra core will help ensure completion of work.
(4) Temperature and salinity are measured in field; oxygen samples are fixed in field.

In addition to sediment samples, water samples will be collected at each station to characterize *in situ* conditions and for use in the laboratory flux incubations. A 5-L Niskin bottle will be used to collect samples of near-bottom water. The temperature and salinity of the bottom water drawn from the Niskin will be measured by a calibrated field thermometer and refractometer, respectively. Two 300-mL BOD bottles will be filled by siphoning from the Niskin bottle. The BOD bottle samples will be fixed for analysis of dissolved oxygen and returned to the laboratory.

At each station, seawater will be collected from near-bottom water 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 and stored at collection temperatures ($\pm$ 2°C), will be used in the laboratory to replace the water overlying the cores collected for flux measurements.

7.3.2 Laboratory Program

The flux/porewater measurements will follow methods of Giblin *et al.* (1993) for nutrients and metabolism, and the methods of Kelly and Nowicki (1993) for denitrification measurements. 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 ($\pm$ 2°C). Sampling/analytical methods are described in Section 12.

7.4 Monitoring Parameters and Collection Frequency

Table 2 lists the samples that will be collected at each station. During the 10 total surveys in 1993-1994, 34 stations will be occupied to provide a total of 374 samples (34 x 11 cores). Of this total, 136 (34 x 4) will be used directly in flux measurements, 102 (34 x 3) will be used for porewater analyses, and 34 (34 x 1) will be dried for solids and archived. The remaining 102 samples (34 x 3) will result from oversampling to ensure an adequate number of suitable cores for denitrification estimates and for potential ancillary measurements (e.g., porosity and additional solid archival/analysis).

7.5 Parameter Table

Table 3 lists all parameters and analyses, as well as related information.

Table 3. Laboratory Analysis Parameter Table

Analysis (LAB)	Sample Type (Number per Station)	Parameter	Method	Units	Reference or Comment	Frequency of Sampling	Processing	Maximum Holding Time	Preservation
Flux	15-cm-dia. core (2)	O_2	Probe	μM	(1)	Continuous	Immediate reading	NA	—
		Total CO_2	Coulometric CO_2 analyzer	μM	(1)	1 (Initial + Final)	Glass BOD bottles	Months	Mercuric chloride, 4°C
		NH_4	Spectrophotometric	μM	(1)	~5 per flux	Fixed within 1 h	24 h	—
		NO_2+NO_3	Rapid Flow Analyzer	μM	(1)	~5 per flux	Polyethylene bottles	Months	Frozen
		PO_4	Spectrophotometric	μM	(1)	~5 per flux	Acidified	Months	4C°
Flux	7.7-cm-dia. core (1 oxic)	N_2	GC	Micromoles	(2)	4 per flux	Injection in GC	NA	—
		O_2	GC	Micromoles	(2)	4 per flux	Injection in GC	NA	—
	7.7 cm-dia. core (1 anoxic)	N_2	GC	Micromoles	(2)		Injection in GC	NA	
Porewater	6.5-cm-dia. core (2)	NH_4	Spectrophotometric	μM	(1)	≥5 Depth Intervals	Dilution with seawater, fixed within 1 h	24 h	—
		$NO_2 + NO_3$	Rapid Flow Analyzer	μM	(1)	≥5 Depth Intervals	Polyethylene bottles	Months	Frozen
		PO_4	Spectrophotometric	μM	(1)	≥5 Depth Intervals	Acidified	Months	4°C
		Sulfide	Spectrophotometric	μM	(1)	≥5 Depth Intervals	Trapped in Zn acetate	24 h	—
		pH	Probe	mV	(1)	≥5 Depth Intervals	Immediate	NA	—
		Eh	Probe	mV	(1)	≥5 Depth Intervals	Immediate	NA	—
		Alkalinity	Titration	mEq	(1)	≥5 Depth Intervals	Immediate	NA	—
Archived solids	2.5-cm-dia. core (1)	Archive	Section	—	(1)	1 cm intervals to 10 cm, 2 cm intervals thereafter	Section, dry in 72 hours	Months	—
Seawater	300 mL-BOD bottle (2)	O_2	Winkler	mg/L	(3)	Each station	Fixed immediately	24 h	—

(1) Giblin *et al.*, 1993; (2) Kelly and Nowicki, 1993; (3) Kelly *et al.*, 1992.

8. PROJECT FISCAL INFORMATION

Task 19 is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S138) between MWRA and Battelle Ocean Sciences.

9. SCHEDULE OF ACTIVITIES AND DELIVERABLES

The tentative schedule for Task 19 is presented in Table 4.

10. PROJECT ORGANIZATION AND RESPONSIBILITIES

10.1 Project Management

Task 19 will be carried out in accordance with the project organization shown in Figure 1. Dr. Jack Kelly is Battelle's Technical Director and will serve as Task Leader for the benthic nutrient flux studies. Dr. Anne Giblin is Subcontractor Project Manager for MBL and Dr. Barbara Nowicki is Subcontractor Project Manager for URI.

10.2 Field Program

Battelle will schedule the vessels and the box corer. For each survey, Battelle will also provide a staff member trained in BOSS navigation and sample tracking procedures. This person will be in custody of all samples on the vessel and will be responsible for recording all required station sampling data on survey forms. Battelle will provide the Niskin bottles (with messenger), navigation, sample labels, and chain-of-custody (COC) forms. In the event that MBL is unable to provide all three SCUBA divers for a survey, Battelle will provide a backup diver. The Task Leader will designate a Chief Scientist for each survey, who will communicate with the Task Leader as needed and will be responsible for ensuring the technical quality of the field sampling program.

Dr. Anne Giblin normally will serve as Chief Scientist. She will be assisted by Dr. Chuck Hopkinson and Ms. Jane Tucker of MBL. MBL will provide the MBL cores, the filtration system for seawater, carboys, field thermometer, and refractometer, and will be responsible for sediment and seawater collection. MBL will also measure temperature and salinity in the field and preserve the dissolved oxygen samples.

Table 4. Task 19 (Benthic Nutrient Flux) Deliverables		
Survey/Associated Deliverable	***Scheduled Finish***	***Survey Event ID***
BNF Survey (2/93)	**02/26/93**	**B9301**
BNF Survey Plan 2/93	02/11/93	
BNF Survey Report 2/93 (Draft)	03/19/93	
BNF Survey Report 2/93 (Final)	04/16/93	
BNF Data Report 2/93 (Draft)	05/26/93	
BNF Survey (5/93)	**05/21/93**	**B9302**
BNF Survey Plan 5/93	05/06/93	
BNF Survey Report 5/93 (Draft)	06/21/93	
BNF Survey Report 5/93 (Final)	07/19/93	
BNF Data Report 5/93 (Draft)	08/21/93	
BNF Survey (7/93)	**07/14/93**	**B9303**
BNF Survey Plan 7/93	06/29/93	
BNF Survey Report 7/93 (Draft)	08/11/93	
BNF Survey Report 7/93 (Final)	09/08/93	
BNF Data Report 7/93 (Draft)	10/14/93	
BNF Survey (8/93)	**08/14/93**	**B9304**
BNF Survey Plan 8/93	07/29/93	
BNF Survey Report 8/93 (Draft)	09/13/93	
BNF Survey Report 8/93 (Final)	10/11/93	
BNF Data Report 8/93 (Draft)	11/14/93	
BNF Survey (10/93)	**10/21/93**	**B9305**
BNF Survey Plan 10/93	10/05/93	
BNF Survey Report 10/93 (Draft)	11/18/93	
BNF Survey Report 10/93 (Final)	12/16/93	
1993 Data Report for Completed Surveys		
BNF Flux Report 1993 (Draft)	01/21/94	
BNF Flux Report 1993 (Final)	02/18/94	
BNF Survey (2/94)	**02/15/94**	**B9401**
BNF Survey Plan 2/94	01/30/94	
BNF Survey Report 2/94 (Draft)	03/18/94	
BNF Survey Report 2/94 (Final)	04/16/94	
BNF Data Report 2/94 (Draft)	05/15/94	
BNF Survey (5/94)	**05/15/94**	**B9402**
BNF Survey Plan 5/94	04/29/94	
BNF Survey Report 5/94 (Draft)	06/15/94	
BNF Survey Report 5/94 (Final)	07/14/94	
BNF Data Report 5/94 (Draft)	08/15/94	
BNF Survey (7/94)	**07/15/94**	**B9403**
BNF Survey Plan 7/94	06/29/94	
BNF Survey Report 7/94 (Draft)	08/15/94	
BNF Survey Report 7/94 (Final)	09/13/94	
BNF Data Report 7/94 (Draft)	10/15/94	
BNF Survey (8/94)	**08/15/94**	**B9404**
BNF Survey Plan 8/94	07/30/94	
BNF Survey Report 8/94 (Draft)	09/16/94	
BNF Survey Report 8/94 (Final)	10/14/94	
BNF Data Report 8/94 (Draft)	11/15/94	
BNF Survey (10/94)	**10/15/94**	**B9405**
BNF Survey Plan 10/94	09/30/94	
BNF Survey Report 10/94 (Draft)	11/16/94	
BNF Survey Report 10/94 (Final)	12/14/94	
1994 Data Report for Completed Surveys		
BNF Flux Report 1994 (Draft)	01/21/95	
BNF Flux Report 1994 (Final)	02/18/95	

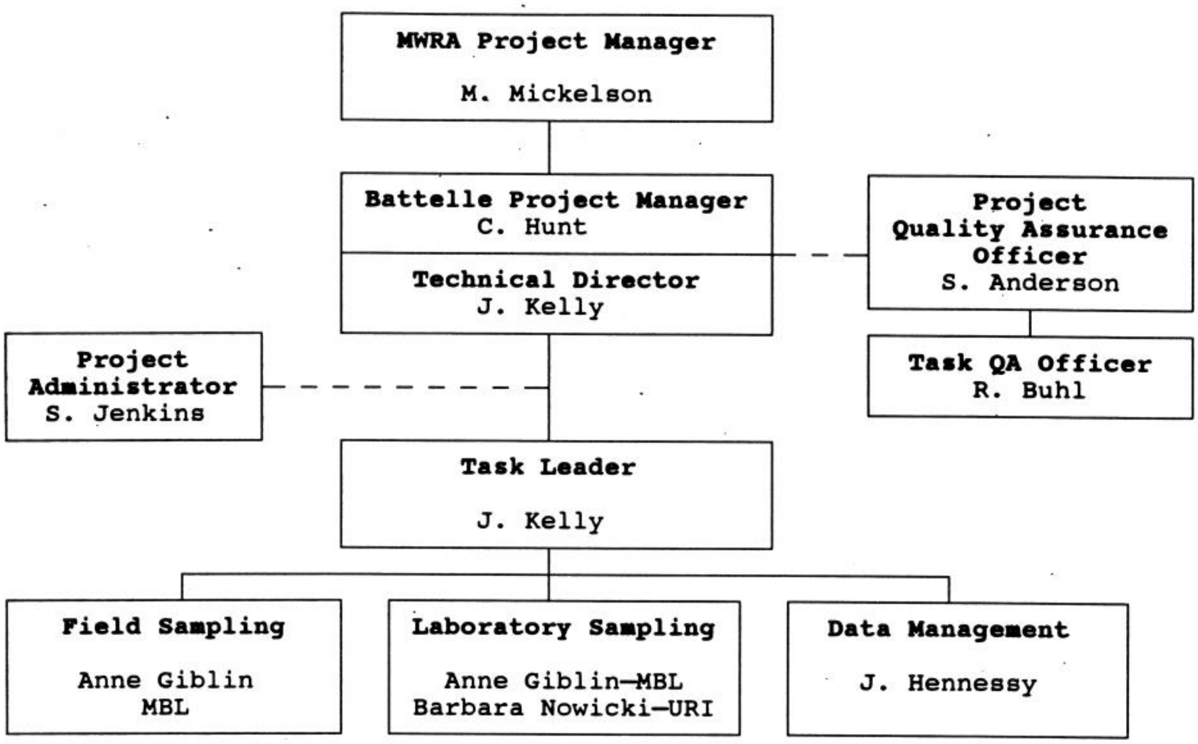

Figure 1. Project Organization

Although there are no plans for URI to provide field personnel, Dr. Nowicki will provide the URI cores and transport coolers, BOD bottles, seawater carboys, and arrange for transport of samples to URI. Other responsibilities of field survey personnel will be defined as necessary in each survey plan.

10.3 Laboratory Analysis Program

Benthic respiration/nutrient flux, and pore water/sediment measurements and sample archival will be conducted by MBL. Denitrification studies and BOD bottom-water sample titrations will be performed by URI.

10.4 Data Management and Reporting

Battelle will prepare survey plans and reports, and will be responsible for overall project data management, including linking station sampling data with laboratory data submitted by subcontractors.

In the field, the BOSS operator will be responsible for recording all position data and measurements (e.g., bottom depth, water temperature) in Battelle electronic files and on COC forms. Samples will be released from his/her custody to MBL and URI personnel at the dock. Battelle log forms will be returned to the Task Leader.

URI and MBL will be responsible for data management of their respective laboratory studies data. The subcontractor laboratories will report data in electronic format to Mr. John Hennessy, Battelle's Project Area Leader for Data Management. Ms. Rosanna Buhl, Battelle's Task QA Officer will be responsible for QA review of the data reported under Task 19.

11. DATA QUALITY REQUIREMENTS AND ASSESSMENTS

11.1 Field Program

11.1.1 Precision and Accuracy

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

Table 5. Objectives for Field Measurements				
Variable (Lab)	***Qualifier***	***Lower Detection Limits***	***Accuracy***	***Precision (better than)***
Navigation (BOS)	—	NA	15-100 m	30 m
Temperature (MBL)	Seawater	NA	NA	0.5°C
Salinity (MBL)	Seawater	NA	NA	1‰
Dissolved Oxygen (URI)	Seawater	NA	NA	0.05 mg L^{-1}

NA: Not Applicable

11.1.2 Completeness

BOSS navigation outputs positions at an interval of 2 s. The BOSS software system will display all position fixes and save these fixes in an electronic file during sampling. Even with a few bad data streams from the Northstar to the computer, the software will provide enough fixes within the sampling period for 100% location data collection.

For each box core brought on deck, the BOSS operator will mark the event in the BOSS 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 BOSS 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, 7.7-cm-dia cores, and 6.5-cm-dia cores) is obtained. If only six cores are obtained, then subsamples archived for sediment solids will be taken from the 15-cm-dia cores after flux measurements. The survey will be considered 100% complete only if six cores are obtained at the required number of stations (6 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.

11.1.3 Comparability

Corrected latitude/longitude positions will be recorded, and these positions will be comparable to those obtained by other Tasks in the MWRA monitoring project as well as by other researchers that have used or are using undifferentiated GPS or corrected LORAN. The station locations are targets and sampling will be attempted within about 100 m of the targets, according to the BOSS navigation display; objectives will not be compromised if suitable sediments are obtained slightly outside this radius. SCUBA and box coring techniques are standard practice for sediment collection of samples for flux and pore water measurements and the surveys follow established procedures for previous MWRA surveys in the Harbor and the Bay.

Dissolved oxygen concentrations will be measured by the same laboratory and by the same methods that will be used for the water column monitoring tasks. Temperature and salinity data will be less precise than data obtained by concurrent MWRA water quality monitoring in the region.

11.1.4 Representativeness

The LORAN TDs 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. The Chief Scientist will instruct the BOSS operator to note in the BOSS log any visual observations of the core samples. Water retrieved by Niskin bottle or pumped to the ship will be highly representative of the near-bottom waters at each station.

11.2 Laboratory Program

11.2.1 Precision and Accuracy

For the benthic nutrient flux studies, MBL will generate data for ammonia, nitrate/nitrite, phosphate, carbon dioxide, dissolved oxygen, nitrogen gas, sulfides, alkalinity, and pH. 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 far more important than accuracy. For porewaters, nutrient concentrations are relatively high and usually will be well above detection limits.

More than the precision of individual chemical analyses, the precision of flux estimates is of interest. Precision for flux estimates may be 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 URI 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 $\sim$5 μMol N_2 $m^{-2}h^{-1}$.

11.2.2 Completeness

It is expected that flux measurements will be completed for all parameters in two 15-cm-dia cores and two 7.7-cm-dia cores (one oxic, one anoxic) intended for flux incubations. However, 100% completion can not 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 (7.7-cm-dia-cores), the relevant objectives will be met fully.

Oversampling will help ensure that the minimum requirements for completion are met. Additionally, for the MBL measurements, oxygen will be continuously monitored to ensure estimates of oxygen flux. For MBL studies, a time series of samples for nutrients will also be taken; except for total carbon dioxide data, which will be collected only at the start and finish of incubations, fluxes could be estimated (with less confidence) using fewer data points than planned . Measurements of carbon dioxide in two cores should ensure that the minimum requirements are met.

Table 6. Objectives for Laboratory Measurements

Variable (Lab)	*Matrix*	*Units*	*Lower Detection Limits*	*Accuracy*	*Precision (Better than)*
O_2 (MBL)	SW	μM	NA	NA	5%
Total CO_2 (MBL)	SW	μM	NA	NA	1 μmole
NH_4 (MBL)	SW, PW	μM	0.5 (PW)	NA	5%
$NO_2 + NO_3$ (MBL)	SW, PW	μM	0.5 (PW)	NA	5%
PO_4 (MBL)	SW, PW	μM	0.5 (PW)	NA	5%
Sulfide (MBL)	PW	μM	2 (PW)	NA	5%
pH (MBL)	PW	mV	NA	NA	5%
Eh (MBL)	PW	mV	NA	NA	5%
Alkalinity (MBL)	PW	mEq	NA	NA	5%
N_2 (URI)	GAS	μmoles	NA	NA	4%
O_2 (URI)	GAS	μmoles	NA	NA	1%

NA: Not Applicable

For URI 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 less 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 19 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.

11.2.3 Comparability

Data will be directly comparable to results obtained previously at the same or similar sites in Boston Harbor and Massachusetts Bay, and to those of similar studies conducted in Buzzards Bay and Narragansett Bay. Direct measurements of sediment denitrification based on nitrogen gas flux (URI) can be compared to calculated indirect estimates of denitrification activity from stoichiometric analyses of sediment dissolved nitrogen and carbon flux (MBL).

11.2.4 Representativeness

Evaluation of previous studies has helped ensure that the sampling sites selected for the Harbor and Outfall Monitoring Project will be representative of the Boston Harbor/Massachusetts Bay system. Flux measurements that will be made during the conduct of Task 19 have already been used in many systems to characterize sediment processes and are, therefore, considered to yield rates representative of the Boston Harbor/Massachusetts Bay system.

12. SAMPLING AND ANALYTICAL PROCEDURES

12.1 Navigation and Field Sampling

Vessel positioning during sampling operations will be accomplished with the BOSS navigation system. This system consists of a Northstar model-800 integrated global positioning system (GPS)/LORAN interfaced to the BOSS computer. The GPS receiver has six dedicated channels and is capable of locking onto six different satellites at one time. This capability ensures strong signal reception, and accurate and reliable positioning with 2-s updates. The GPS/LORAN system will automatically choose between GPS and LORAN, based on best accuracy.

The BOSS software acquires data from all onboard electronic sampling systems and navigation systems. Once the data are acquired, they are automatically written to a data file and logged concurrently with position data from the navigation system. The navigation portion of the display will show the coastlines digitized from standard NOAA charts, navigation aids, sampling stations, and vessel track. During operations, position fixes will be electronically recorded at 2-s intervals.

Undisturbed sediment cores will be collected from Harbor stations by SCUBA divers. Coring methods described by Dornblaser *et al.* (1989) will be followed. From stations in Massachusetts Bay, undisturbed sediment cores will be collected with a 40x40-cm box corer as described in Section 7.3. Two 15-cm-dia cores will be mounted in the box corer. After the box corer is brought on deck and it is determined that the sample is acceptable, three 7.7-cm-dia cores, three 6.5-cm-dia cores, and three 2.5-cm-dia cores will be obtained at each station by gently pushing the tubes into the box corer sample to a depth of approximately 15 cm. The ends of each tube will be capped and a sample identification label will be attached. The core samples will be stored and transported to the laboratory in the dark. 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. The field thermometer will be calibrated using standard practices (e.g., 0 and 100°C distilled water reference points for calibration). The field refractometer will be calibrated with distilled water prior to readings.

12.2. Laboratory Sample Processing and Analysis

12.2.1 Measurement of Benthic Respiration and Nutrient Flux (MBL)

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 the *in situ* temperature (± 2°C) of the station from which they were collected. The overlying water of each core will be replaced with the filtered seawater collected from each station. Benthic flux measurements, initiated within 12-24 h of sample collection, will be made in accordance with the procedures presented in Giblin *et al.* (1993). These methods are summarized below.

Two 300-mL BOD bottles of filtered water from each station will be used for analyses to correct for water column respiration and regeneration. Just prior to initiating the flux measurements, the water overlying each core will be replaced with additional filtered seawater collected at each station. 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 a sufficient amount. At warm temperatures, this oxygen concentration will be just below 5 ppm, but no lower than 2-4 ppm, the concentrations at which benthic animal respiration may be impaired. An Orbisphere 2112 dissolved oxygen meter probe, inserted into an opening in the core top, will provide approximately five measurements of oxygen concentration for each core.

Concurrent with the oxygen measurements, a syringe will be used to withdraw 20- to 30-mL samples of the overlying water for analysis of dissolved inorganic nitrogen and phosphate. Replacement water will be added with a second syringe. Samples for nutrient analyses will be processed within 1 h. Ammonium concentrations will be determined for duplicate 3-mL samples according to the method described by Solorzano (1969), modified for small 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 by the spectrophotometric method of Murphy and Riley (1962). The water remaining in the syringe ($\sim$12 mL) will be transferred to clean vials and frozen for future analyses for nitrate and nitrite. These nutrients will be determined together using the cadmium reduction method on a rapid-flow Alpkem RFA-300 analyzer. 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.

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 removed with a syringe and transferred to a 60-mL glass BOD bottle. The samples will be stored in the dark at 4°C until the analyses are conducted by K. Goyet at the Woods Hole Oceanographic Institution (WHOI). Carbon dioxide concentrations will be determined with a high-precision coulometric carbon dioxide analyzer.

Samples for ammonia, nitrate/nitrite, and phosphate will be analyzed against reference standards having nutrient concentrations bracketing those of the samples. 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. The high-precision coulometric carbon dioxide analyzer will be calibrated with bicarbonate and seawater solutions of a known carbon dioxide content (supplied by K. Goyet of WHOI). 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.

12.2.2 Measurement of Sediment Denitrification and Oxygen Flux (URI)

Two of the 7.7-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 estimated. The methods that will be used to measure sediment denitrification and oxygen flux are fully described in Kelly and Nowicki (1993).

Upon arrival at URI's Marine Ecosystems Research Laboratory (MERL) facility, the surface 5 cm of both cores from each station will be transferred to a 7.8-cm-dia gastight chamber (slightly modified from Seitzinger *et al.*, 1980). This chamber is designed to hold an intact sediment core with its overlying water and the air space above. The chamber is fitted with ports for exchanging the overlying water phase and for sampling a gas phase overlying the water phase.

Once sediments and overlying water have been transferred into the chamber, the overlying water will be replaced with approximately 800 mL of filtered seawater collected at the same station as the core sample. For one replicate core from a station (the "experimental" core), the filtered water will first be sparged with a helium/oxygen gas mixture to remove 95-99% of the ambient nitrogen gas dissolved in the seawater. After the water is exchanged, the air space of the core will be replaced with a helium/oxygen gas mixture to remove excess nitrogen gas and to maintain the overlying water's ambient oxygen concentration. Before incubation, nitrogen will be flushed from the cores two to three times daily. 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). Gas samples, which will periodically be withdrawn from the incubation chamber ports, will be analyzed for nitrogen gas and oxygen by gas chromatography methods.

After the water/gas phases have been flushed of nitrogen gas several times, they will be sealed and incubated in the dark at ambient collection temperatures ($\pm$ 2°C). Each core chamber will be equilibrated by continuous stirring with a magnetic stir bar, located at the water-gas interface, and rotated by an air-driven magnet mounted on top of the chamber. The mixing rate will be adjusted to maintain a constant flow of water and particles across the sediments, and to slightly resuspend the sediments.

Gas samples, periodically (once per day) withdrawn through the chamber's sampling ports, will be analyzed for nitrogen and oxygen. Replicate 50-μL samples will be collected with a helium-flushed gastight syringe inserted through a rubber serum stopper in the chamber's 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 Hewlett-Packard Model-5890A gas chromatograph (GC) equipped with a thermal conductivity detector. The GC uses a ⅛-in x 2-m stainless steel column packed with 5-Å 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 (20% oxygen:3% nitrogen:77% helium). The gas mixture is certified to meet the specified concentrations with a tolerance of ±5% for nitrogen and ±4% for oxygen. Standards are routinely run with each daily set of samples from the sealed incubation chambers.

12.2.3 Analysis of Sediment Porewaters and Archival of Solids (MBL)

The methods that will be used for porewater sampling and analysis are detailed in Giblin *et al.* (1993). Briefly, two 6.5-cm-dia cores 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 10 cm, and at 4-cm intervals beyond 10-cm core depths. 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 table-top 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.

The third 6.5-cm-dia core from each station is collected for Eh measurements. Eh will be measured with a platinum electrode progressively pushed into the sediment core; readings will be made at each depth after stabilization of the mV readings.

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 using a standard pH meter and probe 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 second 2.5-cm-dia core may also be used to estimate porosity. For another 2.5-cm-dia core, the top 0-2 cm may be sectioned and frozen wet.

If 2.5-cm-dia cores are not collected, one 2.5-cm-dia core 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.

13. SAMPLE CUSTODY PROCEDURES

Field samples will be identified by a unique sample ID which is a concatenation of *event_id* (5-character ID unique to each survey); see Table 4 for the list of *event_ids* for planned benthic surveys and *marker_no* which is a non-repeating number for each survey generated by the BOSS software).

Sediment and seawater samples will be collected. Table 7 shows these two protocols and the samples to be collected under each protocol. When either sediment or seawater sampling is complete at a station, this action will be electronically flagged in the BOSS data file using a unique *marker_no* so that pertinent information can be recorded. When this *marker_no* is created by BOSS, the software electronically saves the following information in a log file:

- Station ID
- Marker_no
- Sample ID
- Date and time of event
- Position of vessel at time of event
- Bottom depth (if system is connected to BOSS echo sounder)
- Protocol code
- Lab code

This same information will be printed on barcoded labels generated by the BOSS. The barcode contains the sample ID. The BOSS operator will attach one label to the BOSS Station Log (Figure 2), one label will be attached to samples described in Table 7, and another label will be attached to the samples' accompanying COC forms (Figures 3 and 4). Temperature and salinity readings in the field will be entered manually on each of three forms (Figures 2, 3, and 4).

Table 7. Protocol Codes and Related Samples/Measurements.

Protocol	*Lab*	*Description (Code)*
SED	URI	(3) Cores for denitrification flux (DNF)
	MBL	(2) Cores for metabolism and nutrient flux/possible sediment archival (FLUX) (3) Cores for pore water analyses (PW) (3) Cores for archival/porosity (ARCH)
SW	URI	(2) BOD bottles drawn from Niskin for O_2 analyses (BOD)
	MBL	Temperature and salinity measured from Niskin (T,S)
	URI/MBL	Seawater pumped/filtered and carboy filled for each laboratory (FSW)

All sample labeling and station recording will be completed for one station prior to collection of samples at another station. If less than the intended set of samples for either protocol is collected, but the minimum to complete the station is collected and further sampling will not be done, the samples that *are* obtained will be noted on the BOSS Station Log in comments adjacent to the protocol label. If a label is not attached to a sample container (i.e., a BOD bottle), the laboratory id (e.g., the BOD bottle number) will be written on the COC in a comments section next to the protocol label (see Figure 4). If the system is not connected to the BOSS echo sounder, then bottom depth read from the vessel's instruments will be entered manually in a comments section of the electronic file. In the event that barcoded labels can not be printed, the COC forms and labels will filled out in indelible ink. Each completed COC form will be signed and dated by the staff member entering the information.

The sample COC forms (Figures 3 and 4) will accompany samples to their final destination and the BOSS Station Log form will be returned directly to the Task Leader. Each BOSS Station Log form (Figure 2) is designed for one station; each sample COC form is designed to contain information for each protocol (SED, SW) from two stations.

STATION LOG

For BOSS Sediment Coring and Bottom Water Niskin Sampling

Project Name: Harbor and Outfall Monitoring MWRA Contract No. S138

Station:	Battelle Ocean Sciences
Record by:	397 Washington St
Date:	Duxbury, MA 02332

Station		Comments:
Time		
Latitude		
Longitude		
Bottom Depth		
Event		
Lab URI/MBL	Matrix SED	
Protocol CORE	Sampled by	

Station		Temperature:
Time		Salinity:
Latitude		BOD Bottle Nos.:
Longitude		Comments:
Bottom Depth		
Event		
Lab URI/MBL	Matrix SW	
Protocol SW	Sampled by	

Sample Type	Gear	Samples
SED-Bay	Box Corer	3 DNF, 2 FLUX, 3 PW, and 3 ARCH
SED-Harbor	Scuba	3 DNF, 2 FLUX, 3 PW, and 3 ARCH
Seawater	Niskin/Carboy	2 BOD and 2 FSW

Weather Observations
General:
Seas:
Wind:

PLEASE RETURN THE ORIGINAL OF THIS COMPLETED FORM TO JACK KELLY -BATTELLE

Figure 2. BOSS Station Log Form.

CHAIN OF CUSTODY RECORD		
For Sediment Cores and Seawater		
Project Name: Harbor and Outfall Monitoring MWRA Contract No. S138		
		Marine Biological Laboratory
Record by:		Ecosystems Center
Date:		Woods Hole, MA 02543
Station		Comments:
Time		
Latitude		
Longitude		
Bottom Depth		
Event		
Lab URI/MBL	Matrix SED	
Protocol CORE	Sampled by	
Station		Temperature:
Time		Salinity:
Latitude		Comments:
Longitude		
Bottom Depth		
Event		
Lab URI/MBL	Matrix SW	
Protocol SW	Sampled by	
Station		Comments:
Time		
Latitude		
Longitude		
Bottom Depth		
Event		
Lab URI/MBL	Matrix SED	
Protocol CORE	Sampled by	
Station		Temperature:
Time		Salinity:
Latitude		Comments:
Longitude		
Bottom Depth		
Event		
Lab URI/MBL	Matrix SW	
Protocol SW	Sampled by	
Relinquished By/Date/Time/Company	Transporter/Airbill #	Recieved By/Date/Time/Company
PLEASE RETURN THE ORIGINAL OF THIS COMPLETED CHAIN OF CUSTODY FORM TO JACK KELLY -BATTELLE		

Figure 3. Chain-of-Custody Form for Sediment Cores and Seawater Samples (MBL)

CHAIN OF CUSTODY RECORD	
For Sediment Cores, Seawater, and BOD Bottles	
Project Name: Harbor and Outfall Monitoring MWRA Contract No. S138	
	University of Rhode Island
Record by:	MERL-GSO
Date:	Narragansett, RI 02882-1197
Station	Comments:
Time	
Latitude	
Longitude	
Bottom Depth	
Event	
Lab URI/MBL Matrix SED	
Protocol CORE Sampled by	
Station	Temperature:
Time	Salinity:
Latitude	BOD Bottle Nos:
Longitude	Comments:
Bottom Depth	
Event	
Lab URI/MBL Matrix SW	
Protocol SW Sampled by	
Station	Comments:
Time	
Latitude	
Longitude	
Bottom Depth	
Event	
Lab URI/MBL Matrix SED	
Protocol CORE Sampled by	
Station	Temperature:
Time	Salinity:
Latitude	BOD Bottle Nos:
Longitude	Comments:
Bottom Depth	
Event	
Lab URI/MBL Matrix SW	
Protocol SW Sampled by	

Relinquished By/Date/Time/Company	Transporter/Airbill #	Recieved By/Date/Time/Company

PLEASE RETURN THE ORIGINAL OF THIS COMPLETED CHAIN OF CUSTODY FORM TO JACK KELLY -BATTELLE

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

13.1 Custody of Electronic Data

For each survey, field custody of electronic data will be the responsibility of the Battelle BOSS software operator, who will be identified in each survey plan. Field custody of the electronic data consists of creating floppy disk backups of all electronic data generated each day. Each floppy label will include a survey ID, date, name of person creating the backup files, and a disk number, and will be kept with the Sample Log Notebook. When the equipment is returned to Battelle's laboratory, a second complete backup, labeled as "Set 2", will be generated on floppy disks. "Set 2" will be in the custody of Mr. Carl Albro of Battelle.

13.2 Custody of Samples

Field documentation will consist of a laboratory record book (LRB) for the Task and COC forms. All original BOSS Station Log forms and returned sample COC forms will be kept in a labeled project Sample Log Notebook.

The Battelle BOSS operator will be in custody of all samples on board the vessel. Custody of samples will be transferred to subcontractors when the vessel arrives at the dock. Upon transfer, the COC form will be signed by both the BOSS operator that relinquished custody and the subcontractor's representative assuming custody of the samples.

Upon receipt of samples at the subcontractor's laboratory, the subcontractor will examine the samples received, verify that the information recorded on the COC forms is accurate, and log the samples into the laboratory by signing the COC form on the *Received By* line and by entering the date and time of sample receipt. Any inconsistencies between samples listed as having been released and samples that were actually received, or any damage to containers, labels, etc. will be noted on the COC form and immediately communicated to the Project Area Leader. Sample numbers that include the complete field sample ID will be used to track the samples through the laboratory. It is the responsibility of the subcontractor to ensure that all samples are stored under the conditions outlined in this CW/QAPP and that appropriate documentation is complete. All archived samples will remain in the custody of the subcontracting laboratory for a period of 1 year after sample collection, at which time the MWRA will be contacted about their disposition.

14. 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 by the subcontractors. Maintenance of and repairs to instruments will performed in accordance with manufacturers' manuals. Any deviations to this policy will be noted.

The GPS receiver (integrated in the Northstar 800 GPS/LORAN system) will provide a corrected latitude/longitude position that will be used to automatically calibrate the LORAN latitude/longitude when GPS data are not being received. Positions will also be checked at certain fixed calibration points; the absolute positions of these calibration points will be obtained from published charts and light lists. The time and position of the calibration sites will be printed out by the BOSS software and entered in the BOSS Survey Notebook. Following the survey, all navigation calibration information will be assessed to determine whether it is necessary to apply a calibration adjustment to the LORAN positions.

The Northstar 800 GPS/LORAN system automatically undergoes a thorough self-test when turned on. Cable connections, antenna mounts, and brackets will be inspected and secured at regular intervals.

Because samples for the flux studies are analyzed in real time, it is critical that the primary analytical instruments — URI's gas chromatograph (GC) and MBL's DO sensor — are maintained and calibrated regularly. Maintenance of the GC is particularly critical because there is no backup instrument. In the event of problems with this instrument, the survey and sampling schedules would be adjusted.

A log book detailing GC performance on all standards is maintained by URI 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 (20% oxygen:3% nitrogen:77% helium). The gas mixture is certified to meet the specific concentrations with a tolerance of $\pm 5\%$ for nitrogen and $\pm 4\%$ for oxygen. 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.

The MBL 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.

15. DOCUMENTATION, DATA REDUCTION, AND REPORTING

15.1 Documentation

The specific types of documentation that will be maintained for Task 19 include the following:

- 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 Task QA Officer; summarizes QA activities associated with the project.

All data and notes will be initially recorded either (1) electronically onto computer storage media from BOSS 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

After each survey, BOSS navigation and sampling data will be processed. Any navigation adjustments will be applied based on calibration points (Section 14) and station positions will be plotted relative to the shoreline. Samples for the survey, based on completed station protocols (or modifications thereof on the COC forms) will be summarized by station. The station maps and sample tables will be included in survey reports (see Section 19). Field data that will be incorporated into the Harbor Studies Database are sample ID, station ID, date, time, latitude, longitude, bottom depth, measured temperature, measured salinity, and protocol code. Data submitted by URI and MBL will be concatenated with the station information, linked by the sample ID, and will form the basis for Task 19 Data Reports (see Section 19). Upon receipt of the subcontractors' data, each floppy disk will be logged in and assigned a unique login identifier. Any changes or additions to data, necessary for loading into the Harbor Studies Database, will be made using SQL scripts. The original diskette, SQL scripts, and data-loading documentation will be filed at Battelle according to login identifier. The Data Sources Notebook will contain copies of the COC forms and data entry information.

15.2.2 Subcontractors

For each survey, researchers from MBL will provide PC-based spreadsheets that will contain the following data for entry into the MWRA Harbor Studies Database and for use in Task 19 reports:

- Flux rates of oxygen, total carbon dioxide, ammonium, nitrate + nitrite, dissolved inorganic nitrogen, and phosphate for each "flux-rate core" collected at each station. The correlation coefficient for the regression of oxygen concentration over time will also be reported. The incubation temperature, and the initial and final concentrations of each analyte will be reported.

- Concentrations of parameters (see Table 3), by depth interval, for each core analyzed for porewater constituents.

Fluxes of oxygen, dissolved inorganic nitrogen, and phosphate will be calculated from five data points using a linear regression (Giblin *et al.*, 1993). 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 the subcontractor for the duration of the project.

Subcontractors will provide, along with the data submissions for each survey, a list of samples, by station, that have been archived. Additionally, MBL researchers will provide a detailed description of field and laboratory methods, and note any discrepancies from this CW/QAPP.

URI researchers will provide, for each survey, PC-based spreadsheets containing the following data for entry into the MWRA Harbor Studies Database and for use in Task 19 reports:

- 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 correlation coefficient for the regression of gas concentration over time will be reported. The temperature of the incubation, as well as the initial and final concentrations of each analyte in each core, will also be reported.

- The concentration of dissolved oxygen (mg L^{-1}) as calculated for each 300-mL BOD bottle titrated for each station.

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 $m^{-2}day^{-1}$.

Statistical confidence limits will be provided for each individual nitrogen flux measurement by calculating 95% confidence intervals around the slopes of four-point linear regressions of concentration versus time. Confidence intervals will be calculated for fluxes from both the experimental cores (F_t) and the anoxic control cores (F_d), and errors in the final calculated flux (F_t - F_d) will be propagated according to Ramette (1981).

The subcontractor will maintain, for the duration of the project, (1) all records of calculations, (2) raw data collected during incubations, and (3) BOD-bottle oxygen data. Additionally, URI researchers will provide a detailed description of laboratory methods and note any discrepancies from this CW/QAPP.

16. DATA VALIDATION

A primary component of data validation is compliance with the quality control (QC) criteria specified in (1) the QA Project Plan developed specifically for the

Harbor and Outfall Monitoring Project and (2) Section 11 (Data Quality Requirements and Assessments) of this CW/QAPP.

All data collected and analyzed as part of Task 19 will be subject 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 Project Managers or Battelle Task Leader.

- Analytical results and supporting data will be reviewed to ensure that the data are complete, accurate, and technically sound.

- Battelle database staff will check the submitted data and associated documentation for completeness, freedom from errors, and technical reasonableness. Database staff will also check their data entry process for errors.

- Battelle database staff will ensure that all new software developed for this Task is validated prior to the entry of data.

The Battelle Task Leader will be responsible for validation of all data generated by Battelle. Subcontractor Project Managers 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 Task Leader will review all subcontractor data for completeness, internal consistency, and technical reasonableness.

17. PERFORMANCE AND SYSTEMS AUDITS

The Battelle QA Officer for the Harbor and Outfall Monitoring Project is Ms. Sandra Anderson. She will direct the conduct at least one systems audit to ensure that Task 19 is carried out in accordance with this CW/QAPP.

As coordinated by Ms. Anderson, Battelle's Task QA Officer, Rosanna Buhl, will oversee the implementation of this CW/QAPP for the work conducted under Task 19. Tabular and graphical data reported in deliverables, and associated raw data generated by Battelle will be audited by Ms. Buhl. Raw data will be reviewed for completeness and proper documentation. For electronically acquired data (e.g., navigational data), Ms. Buhl will verify that computer software used to process the data have been validated.

Audits of the data collection procedures at subcontractor laboratories will be the responsibility of the Subcontractor Project Managers, Dr. Anne Giblin and Dr. Barbara Nowicki. All data and deliverables will be audited by an individual who is not directly associated with the technical conduct of the work. Each deliverable must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality. The implementation of performance audits is the responsibility of the Task Leader; performance audits to verify data accuracy will be conducted at the discretion of Dr. Kelly. Performance reviews may include assessment of QC samples such as blanks, spikes, standard reference materials, and replicates.

18. CORRECTIVE ACTION

All technical personnel share responsibility for identifying and resolving problems encountered in the routine performance of their duties. Dr. Carlton Hunt, Battelle's Project Manager, will be accountable to MWRA and to Battelle management for overall conduct of the Harbor and Outfall Monitoring Project, including the schedule, costs, and technical performance. He is responsible for identifying and resolving problems that (1) have not been addressed timely or successfully at a lower level, (2) influence multiple components of the project, (3) necessitate changes in this CW/QAPP, or (4) require consultation with Battelle management or with MWRA.

Identification of problems and corrective action at the laboratory level (such as meeting data quality requirements) will be resolved by laboratory staff or by Subcontractor Project Managers. Issues that affect schedule, cost, or performance of Task 19 will be reported to the Task Leader or to the Battelle Project Manager. They will be responsible for evaluating the overall impact of the problem to the project and for discussing corrective actions with the MWRA Project Manager.

Problems identified by the QA Officer will be reported and corrected as described in the QA Program Plan for the Harbor and Outfall Monitoring Project.

19. REPORTS

Deliverables due to MWRA under Task 19 include the following:

- 10 Survey Plans (one for each of the 10 benthic flux surveys)
- 10 Survey Reports (one for each of the 10 benthic flux surveys)
- 10 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 (i.e., no draft survey plans will be prepared) 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 also 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 Draft Benthic Flux Data Report will be prepared and submitted to MWRA for each of the first four surveys in a calendar year (see Table 4). No final of these individual survey data reports will be delivered. The fifth Flux Data Report will be submitted in January (1994, 1995) and will include the data from *all* five surveys of the previous calendar year. This will be submitted as a Draft and a Final Report. A 1993 Benthic Flux Data Report is due in January 1994 and a 1994 Flux Data Report is due in January of 1995. Each Flux Data Report will describe deviations from the CW/QAPP. Each report will include a map of sampling locations and tabular listings of results including (1) a summary of the stations for which sampling was completed; (2) station locations and field measurement results for each survey; (3) flux rates by station, core, and parameter; (4) sediment pore water analyte concentrations by depth interval of each core; and (5) a listing of any remaining archived samples. The data collated and summarized in the fifth Benthic Flux Data Report of each year will be used to develop an Annual Benthic Flux Report, which will synthesize the results of the five surveys of each calendar year and which will be prepared under Task 25 of the Harbor and Outfall Monitoring Project.

One copy of the Draft Benthic Flux Data Reports will be submitted to MWRA within three months of sample collection. Three copies of the final reports will be submitted to MWRA within two weeks of the receipt of MWRA's comments. The final submission will include one unbound, one-sided copy suitable for reproduction, a WordPerfect 5.1 text file, and original quality black-and-white graphics on 8½ x 11 paper.

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