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

for

BENTHIC NUTRIENT FLUX STUDY: 1995-1997

Task 16
MWRA Harbor and Outfall Monitoring Project

submitted to

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

prepared by

Stephen J. Cibik
ENSR Consulting and Engineering

Brian L. Howes
Woods Hole Oceanographic Institution

submitted by

ENSR CONSULTING AND ENGINEERING
35 Nagog Park
Acton, Massachusetts 01720
(508) 635-9500

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MWRA Harbor and Outfall Monitoring Project
Benthic Nutrient Flux Task 16

2.0 PROJECT REQUESTED BY

Massachusetts Water Resources Authority

3.0 DATE OF REQUEST

November 2, 1994

4.0 DATE OF PROJECT INITIATION

November 9, 1994

5.0 PROJECT MANAGEMENT

Dr. Michael Connor, MWRA Director of Environmental Quality Department
Dr. Michael Mickelson, MWRA Harbor and Outfall Monitoring Project Manager
Mr. Kenneth Keay, MWRA Benthic Nutrient Flux Area Manager

Dr. James Blake, ENSR Project Manager for Harbor and Outfall Monitoring
Dr. James Bowen, ENSR Technical Director for Harbor and Outfall Monitoring
Mr. Stephen J. Cibik, ENSR Benthic Nutrient Flux Area Manager
Dr. Brian Howes, Woods Hole Oceanographic Institution Principal Investigator

6.0 QUALITY ASSURANCE (QA) MANAGEMENT

Ms. Debra McGrath, ENSR Project QA Director

7.0 PROJECT DESCRIPTION

7.1 Objective and Scope

The overall objective of the Benthic Nutrient Flux Study (Task 16) is to quantify the seasonal flux of selected nutrients and oxygen between the sediments and their overlying waters at selected stations in Boston Harbor and Massachusetts Bay in the vicinity of the Massachusetts Water Resources Authority (MWRA) effluent outfall. These fluxes relate directly to total annual carbon, nutrient and oxygen dynamics in shallow marine ecosystems. The magnitude of flux can be influenced by many environmental factors including temperature and availability of labile organic carbon. While the partitioning of organic matter degradation between aerobic and anoxic pathways can dampen the magnitude of the seasonal excursion in surface oxygen consumption rates, integration of seasonal measures provides an evaluation of annual organic matter deposition. The goal of this task is to monitor the interactions between the sediments and the overlying water column as part of the overall Harbor and Outfall Monitoring Program, providing information necessary for evaluation of potential changes to Boston Harbor and Massachusetts Bay ecosystems resulting from the MWRA outfall relocation.

The scope of this task includes collection of sediment cores by diver and box core sampler throughout the year, focusing on the periods of greatest microbial activity, with an additional low temperature sampling to provide seasonal data. Cores will be collected for oxygen and nutrient flux, with separate parallel cores collected for N_2-denitrification; redox potential and chlorophyll-a; total organic carbon, grain size, and porosity; and for porewater electrode measurements. Porewater extraction for chemical analysis will be performed on flux cores after incubation.

Incubations will be performed very near the ship's landing to prevent disturbance to the cores resulting from overland transport, and will be begun within hours of arrival at the remote laboratory site. N_2-denitrification measurements will be conducted in Woods Hole on sediment cores from selected sites during 1995 and 1996, and at all stations in 1997.

Specific objectives of Task 16 are the following:

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

- Measure N_2-denitrification in upper sediments, with attention to separation of N_2 flux from the sediment pool versus N_2 flux due to denitrification.

- Measure porewater profiles of key constituents to support modeling of nutrient afflux from surficial sediments and give insight into changing levels of nutrient loading not detectable by bulk sediment properties.

- Analyze surficial sediments for total organic carbon (TOC), total nitrogen (TN), chlorophyll-a, grain size and porosity to correlate with surface oxygen uptake measurements.

- Integrate results of flux and porewater measurements with water quality data collected under other tasks of the project to characterize and evaluate variability of sediment flux characteristics in relation to potential impact of discharging effluent into Massachusetts Bay.

This Combined Work/Quality Assurance Project Plan (CW/QAPP) presents the organization, objectives functional activities, and specific quality assurance (QA) and quality control (QC) activities associated with the benthic nutrient flux task. This document also describes the specific protocols that will be followed for sampling, sample handling and storage, chain of custody, and laboratory and field analyses. The CW/QAPP was prepared in accordance with EPA guidance documents on CW/QAPP preparation (EPA, 1984, 1988) and is based, in large part, on the CW/QAPP produced previously under an earlier contract between MWRA and Battelle Ocean Sciences (Kelly et al., 1993).

7.2 Data Usage

The Benthic Nutrient Flux Task provides information with which to evaluate and monitor the ecological and biogeochemical processes occurring at the sediment/water interface. Assessment of natural variability in flux measurements represents an important component with which to identify what is natural versus what may be the result of loading to the overlying water column. Integration of results of this task with benthic community and water quality data collected under other tasks of the project will allow characterization and evaluation of sediment processes in relation to the relocation of the MWRA effluent discharge into Massachusetts Bay.

7.3 Technical Approach

7.3.1 Field Program

Five surveys per year will be conducted between 1995 and 1997 in Boston Harbor and Massachusetts Bay. Each survey will be preceded by the submittal of a Survey Plan, which will detail sampling dates, locations, vessel, personnel, any deviations in methodology from the CW/QAPP, and general survey operations. In addition, a brief description of approach and requirements will be included. At the conclusion of each survey, activities will be summarized in a Survey Report, which will detail stations, cores collected and incubations conducted, as well as assays and current status and disposition of samples. The report will detail any problems encountered or departures from stated protocols and their potential impacts on the program.

The five surveys performed each year will focus on the periods of greatest microbial activity (four samplings) with a single low temperature sampling (February/March). The high activity periods in systems like Massachusetts Bay are set by a combination of environmental temperature and availability of labile organic carbon. In sediment systems, microbial activity as measured by surface oxygen uptake will generally increase between two and three times for each 10°C increase in temperature. The response of sediment nutrient flux to changes in temperature is more complex. For example, biogeochemical processes like denitrification, which reduces flux of fixed nitrogen to the water column, increase with temperature as does ammonification which increases sediment nutrient losses. However, at any given temperature, microbial activity is generally set by the availability of labile organic matter. Therefore, the four sampling events during periods of higher activity focus on determining rates: (1) after the deposition of the spring bloom (and after onset of stratification), (2 and 3) during the warmest months of peak activity (July and August), and (4) in the fall after the breakdown of stratification and at about the mean annual temperature (October).

Cores will be collected at all eight stations in each of the three years (1995-1997) for the oxygen and nutrient flux (Task 16.3), and sediment solid assays (16.6). It should be noted that the station located in Qunicy Bay was added to the program in July of 1995. Porewater analyses (Task 16.5) will be performed using the flux cores after incubation. N_2-denitrification measures (Task 16.4) will be conducted at stations BH02 and BH03 during all three years, and at all stations in 1997 to yield a direct measure of denitrification and for comparison to estimates derived from the flux cores. Denitrification measurements will also be performed at the Quincy Bay station in 1996. Station locations for each survey are depicted in Figure 1; coordinates for each station are included in Table 1.

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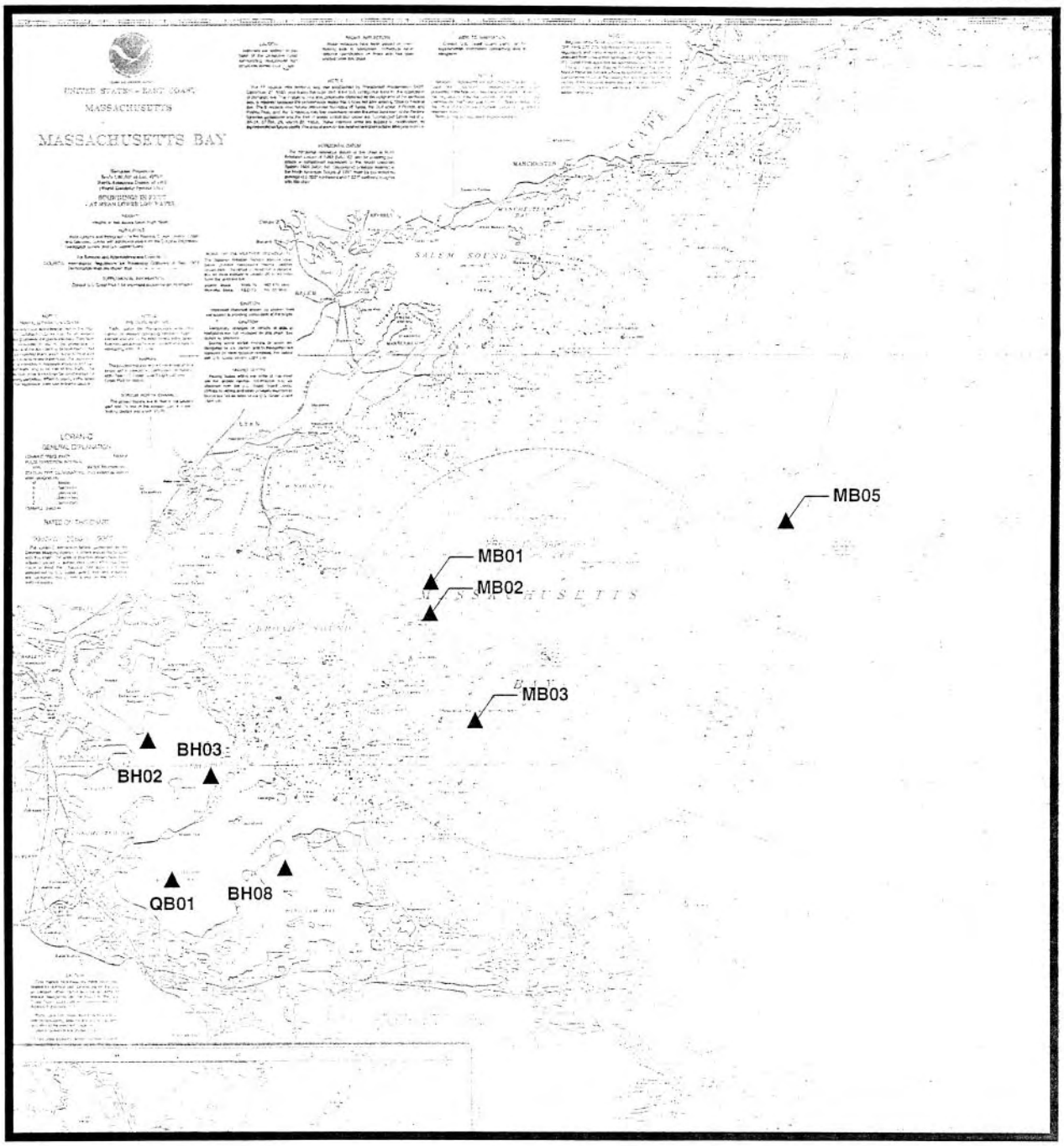

FIGURE 1
Station Locations for Benthic Flux Surveys

TABLE 1

Locations for Long-Term Monitoring of Benthic Flux

Station I.D.	Depth (m)	Latitude	Longitude
BH08A	9.5	42°17.46'N	70°55.33'W
BH03A	6.7	42°19.70'N	70°58.05'W
BH02	6.1	42°20.62'N	71°00.13'W
MB05	75.6	42°25.01'N	70°39.26'W
MB01	34.7	42°24.16'N	70°50.20'W
MB02	35.4	42°23.54'N	70°50.02'W
MB03	34.1	42°20.87'N	70°48.90'W
QB01	3.05	42°17.614'N	70°59.274'W

Note: Stations followed by "A" are near historic stations with the same numerical prefix.

Cores will be collected by diver or by box core sampler (40 x 40 x 50 cm) depending on sediment type and station depth. Cores will be maintained at *in situ* temperatures on board ship until return to a shore laboratory. Incubations will be performed at a field laboratory very near the ship landing in order to prevent disturbance to the cores due to transport. It is anticipated that the incubations for the study period will be performed at Hewett Cove Marina/Hingham Shipyard. Baffles placed in the core headspace and proper handling procedures will be used during the transport of cores to further minimize core disturbance. To assess core disturbance, a fine brick dust or clay will be lightly applied to the surface of two extra cores to be collected each day to identify any vibrational mixing (as opposed to bioturbation). All of the sediment incubations (flux cores and N_2-denitrification) will be incubated immediately upon return to the remote field laboratory. The use of a remote laboratory (as opposed to the facilities in Woods Hole) is to prevent disturbance to the oxygen/nutrient flux cores as a result of overland transport. Vehicle transport of cores can result in vibrational compaction of the surficial sediments thus altering subsequent flux rates (in addition to obvious disturbances from larger jostling and vehicle motion, particularly during starts and stops). The fewer smaller denitrification (N_2) cores will be transported to Woods Hole using a temperature controlled bath upon a shock absorption system. This transport is required by the instrumentation used in this assay and is acceptable due to the better ability to transport these cores and the details of the assay itself.

Water samples will be collected from near the bottom at each station by Niskin bottle for field measurement of dissolved oxygen (DO), temperature, and salinity. Additional volume will be collected and filtered for subsequent use in the flux incubations.

7.3.2 Laboratory Program

The flux and porewater measurements will follow the methods of Jorgenson (1977), Klump and Martens (1983), and Giblin et al. (1993) for nutrients and metabolism, and the methods of Kelly and Nowicki (1993) for denitrification measurements. Table 2 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

Five surveys per year will be conducted between 1995-1997. For each survey, seven stations will be sampled for oxygen and nutrient flux determination (four 15.5-cm flux cores/station). For N_2-denitrification, two stations will be sampled (four 10-cm denitrification cores/station) in 1995, three in 1996 (four 10-cm denitrification cores/station), and seven stations will be sampled during 1997 (two

TABLE 2

Monitoring Parameters

Parameter	Volume	Container	Processing & Storage
Nitrate + Nitrite	60 ml	polyethylene (acid washed)	0.22 µm membrane stored on ice (dark; 24 hr) or frozen to -20°, <30 d
Ammonium	60 ml	polyethylene (acid washed)	0.22 µm membrane stored on ice (dark) run within 24 hrs
Ortho-Phosphate	60 ml	polyethylene (acid washed)	0.22 µm membrane stored on ice (dark) run within 24 hrs
Silicate	60 ml	polyethylene (acid washed)	stored on ice (dark; 24 hr) or frozen to -20°, <30 d
Urea	60 ml	polyethylene	frozen to -20°, <30 d
Total Organic Carbon/Nitrogen	Solids	polyethylene	combusted GFF, dried or glass (acid washed), <7 d
Alkalinity, pH	5 ml	glass	run immediately
Dissolved Sulfide (porewater only)	1-10ml	syringes	collected directly into reagent, <24 hr
Chlorophyll-a	15 cm^3	polyethylene	extracted immediately at -20° (dark), analyze w/i 7 d
Flux (O2 uptake)		15 cm core	immediately by probe
Flux (O2, N2; oxic)	1 ml	syringe	immediate injection in GC
Flux (N2; anoxic)	1 ml	syringe	immediate injection in GC
N2, Ar (end flux)	1 ml	syringe	immediate injection in GC
Redox (Eh)/Apparent RPD*	6.5 cm core	polethylene	Redox measured immediately by electrode; RPD visually
CO_2	10 ml	glass serum bottle	acidification, analysis w/i 24 hr

TABLE 2 (Cont'd)

Monitoring Parameters

Parameter	Volume	Container	Processing & Storage
Grain size	0-2 cm section	polyethylene	wet sieve/pipette analysis
Porosity	0-2 cm section	polyethylene	dry 60°C
Temperature (ambient)	8-1	Niskin bottle	probe (field)
Salinity (ambient)	8-1	Niskin bottle	conductivity probe/refractometer (field)
Oxygen (ambient)	300 ml	Winkler	potentiometric titration dark, cold, analyze w/i 48 hr
***Redox Potential Discontinuity [Depth]**			

10-cm denitrification cores/station). Porewater will be extracted from each of the flux cores immediately upon completion of the incubation. The porewater from equal depths will be pooled to improve the spatial validity of the data and to reduce the impact of small scale effects (e.g., worm burrows) which may occur when fewer and/or smaller cores are used. Additional cores will be collected and transported with the flux cores for profiling of Eh and pH (one 6.5-cm redox core) and extraction of chlorophyll-a, TOC, TN and grain-size (one 6.5-cm pigment core). Table 2 describes the parameters to be measured in headspace waters of the flux cores, the porewater samples and the sediments. Two additional flux cores will be collected per day for application of brick dust or clay (bentonite) to evaluate any potential core disturbance during transport. Twenty liters of seawater will be collected from near the bottom at each station for the incubations.

8.0 PROJECT FISCAL INFORMATION

Task 16 is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S186) between MWRA and ENSR Consulting and Engineering.

9.0 SCHEDULE OF ACTIVITIES AND DELIVERABLES

Sampling activities associated with Task 16 are scheduled in 1995, 1996, and 1997 for February/March, May/early June, July, August, and October. Exact dates will be determined as the study progresses in order to adjust to temperature conditions, variations in advent of the spring phytoplankton bloom and to ensure temporal separation of at least 16 days between samplings in consecutive months. The actual dates for sampling activities will be dependent upon weather conditions and sea state.

Deliverables associated with each sampling round include survey plans, which will be submitted to the MWRA two weeks prior to initiation of the survey. Survey reports will be submitted one month after each survey. Flux data reports and electronic data for each survey will be submitted three months after each survey.

10.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

10.1 Project Management

Project organization is shown in Figure 2. Dr. Michael Mickelson is the MWRA Project Manager and Dr. Ken Keay is the MWRA Project Area Manager for Task 16. They will be informed of all matters pertaining to work described in this CW/QAPP. Dr. James Blake is the ENSR Project Manager responsible for the overall performance of this project. Dr. James Bowen is the ENSR Technical Director responsible for the technical performance of this project. The Quality Assurance Director for the project is Ms. Debra McGrath. Mr. Stephen Cibik is the Project Area Manager and will have overall responsibility for the task.

Dr. Brian Howes will lead the Woods Hole Oceanographic Institution (WHOI) technical team and will have overall responsibility for WHOI operations. Analytical support will be coordinated by Ms. Dale Goehringer, and field operations by Mr. George Hampson. Mr. Raveendra Ika of Envitec will be responsible for grain size analyses performed on core subsamples.

10.2 Field Program

ENSR will arrange for vessel and crew, schedule cruise logistics and provide chain-of-custody forms. WHOI will provide the box core sampler and any additional sampling gear specific to the required sampling. The WHOI Principal Investigator will designate a Chief Scientist for each survey, who will communicate with the ENSR and MWRA Project Area Managers as needed and will be responsible for recording all required station sampling data on survey forms and for ensuring the technical quality of the field sampling program.

10.3 Laboratory Analysis Program

Benthic respiration, benthic nutrient flux, porewater and sediment measurements, denitrification studies and associated sample archival will be conducted by WHOI. Grain size analysis will be performed by Envitec.

10.4 Data Management and Reporting

WHOI will prepare survey plans, survey reports, and flux reports. WHOI will be responsible for data management of their laboratory studies data and will report data in electronic format to the ENSR Area

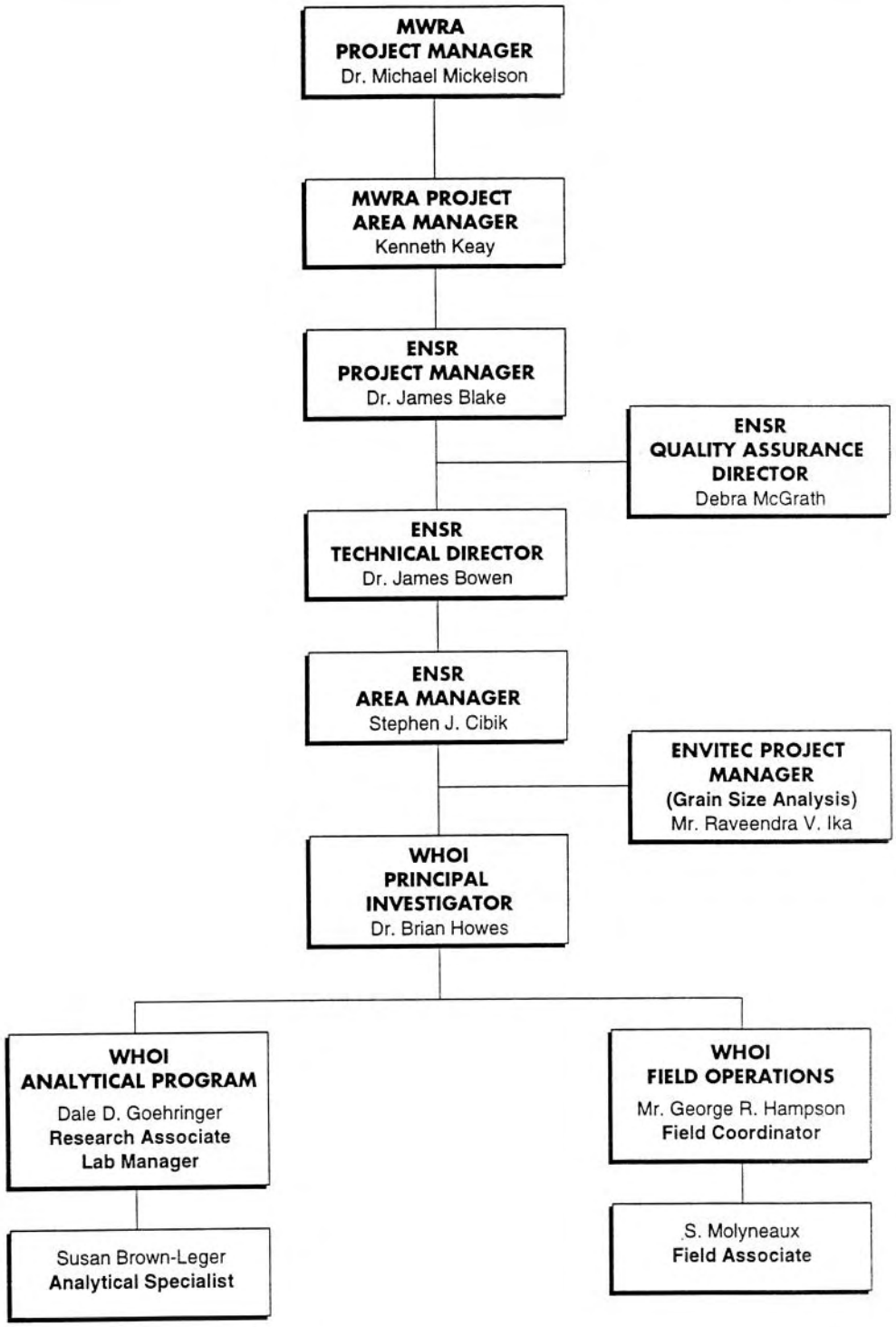

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FIGURE 2
Benthic Nutrient Flux Team

Manager, Mr. Stephen Cibik. Mr. Raveendra Ika will be responsible for transmittal of data for grain size analysis to the ENSR Area Manager. ENSR will be responsible for overall project data management. Ms. Debra McGrath, ENSR's Project QA Director, will be responsible for QA review of the data reported under this task.

11.0 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

Program design and sampling procedures can affect the utility of collected data. The purpose of this CW/QAPP is to ensure that all data generated under this task will be of sufficient quality to accomplish the task's objectives. The quality of the data can be defined in terms of quantitative and qualitative parameters. Quantitative objectives are completeness, accuracy, and precision. Qualitative parameters include comparability, representativeness, and traceability.

11.1 Field Program

Elements of the field program include navigation, field measurements of seawater overlying the bottom (DO, temperature and salinity), core sample collection, and core incubations. Data quality objectives for the field component of Task 16 are discussed in the following sections.

11.1.1 Accuracy and Precision

Accuracy is the agreement between a measurement and a true value. Precision is the degree of variability among individual measurements of the same parameter under similar conditions. Field parameters include navigational data and measurements of DO, temperature, and salinity. Data quality objectives for navigation will be achieved by the use of highly accurate differential Global Positioning System (GPS), consisting of a Northstar 941XD GPS. This system will provide navigational readout with an accuracy of 10 meters 95 percent of the time, and accuracy of 2 to 5 meters 65 percent of the time.

DO measurements of water overlying the sediments will be performed by the Winkler method using potentiometric titration, which will also be used to calibrate the oxygen electrode used in the O_2 flux measurements. In addition, the electrode calibration will be periodically checked during incubations by air-calibration. Temperature will be taken using an Omega Temperature probe calibrated to an NIST-traceable thermometer. Salinity measurements will be determined from specific conductance using a laboratory conductivity meter or refractometer calibrated before each use with a three-point calibration against a sodium chloride standard (20, 30, and 40 parts per thousand). Eh and pH profiles will be

assayed directly in a 6.5 cm core and on extracted porewater, respectively. A three-point standardization is conducted before each pH profile (and for alkalinity as well) determination with a single point post-assay check standard. Eh electrodes require only single point calibration before and after each profile.

A high degree of replication will be employed for the benthic flux incubations, with O_2 flux measurements being taken in each of four replicate cores. Duplicate assays for time-series nutrient flux measurements will be taken, with end-point analyses to be performed on the other two cores for nutrients and CO_2. Two pairs of denitrification cores (four cores total per station) will be used at the two sites in 1995 and the three sites in 1996, and one pair will be used at all of the sites sampled in 1997. The greater replication in the initial two years will allow a good estimate of the within station variability which will facilitate the interpretation of the greater areal sampling data in 1997. Pooling the extracted porewater from the large flux cores increases the area integrated by this sampling and should increase both the accuracy and precision of the porewater data.

11.1.2 Completeness

For each core brought on deck (either by box core sampler or SCUBA), the event will be logged with time, date and location. A station will be considered completed only if the required number of cores are obtained. The goal for sample collection under this task will be the collection of 100% of the cores outlined in section 7.4. However, under unusual circumstances the objectives of the study can be met by the collection of a subset of these cores. Under such circumstances the objectives will be considered to have been met if a minimum of two undisturbed flux cores, two denitrification cores, and one core each for chlorophyll/solids analysis and redox profiling have been collected.

Completeness of field data will be ensured by comparing the total number of data points planned with the valid data obtained. The data quality objective is over 90% completion. Completeness will be calculated as:

Percent Completeness = ([Valid data obtained]/[Total data planned]) x 100

11.1.3 Comparability

The sampling and analytical techniques to be used are methods generally used by researchers in the field as well as those used and reviewed by EPA, NOAA and the National Science Foundation. Conformance with accepted norms for these procedures will result in data comparable in quality and utility to those generated in other research endeavors.

Study locations are comparable to those sampled in previous MWRA monitoring projects (Giblin et al., 1994). SCUBA and box coring techniques to be employed for collection of sediment samples, as well as analytical methods for flux and porewater measurements, will yield data directly comparable to procedures employed in previous MWRA surveys in the Harbor and the Bay (Kelly et al, 1993). The only notable deviations from the previous studies relate to the use of larger diameter cores for the denitrification assays and porewater extractions, and the additional effort made to reduce handling disturbances.

The use of larger denitrification cores (10-cm dia.) compared to earlier studies by Battelle (7.5-cm dia.) will have no effect upon the measured rates. However, the larger core diameter provides for collection of a core with almost twice (1.8) times the surface area of the smaller cores. The effect of the larger denitrification cores is to decrease the variance between cores since each core has greater spatial coverage, and to possibly improve the data quality since the larger cores have a smaller area of core wall disturbance per unit of sediment volume. However, the data from both core sizes remain directly comparable since the assays use similar methodologies, with only an added benefit that the larger cores may allow for the detection of smaller changes through time as a result of potentially reduced variability due to core collection and handling. Similarly, our use of all of the flux cores (15.5-cm dia) at a station rather than previously used 6.5-cm cores for extracting porewater yields a greater areal coverage and should reduce the impact of individual small-scale features (eg. burrows) on measured chemical species. The result should be porewater profiles which more accurately represent each monitoring station.

A major goal of this project is to determine the *in situ* rates of key benthic fluxes within Boston Harbor and Massachusetts Bay. A significant amount of effort is undertaken to minimize potential artifacts due to core handling and transport, specifically the use of baffles in the core headspaces, gimballed temperature baths and incubation of flux cores at a remote shore laboratory. By minimizing experimental errors and maintaining a high degree of replication, the ability to perceive changes in oxygen and nutrient fluxes and denitrification over time will be enhanced.

11.1.4 Representativeness

Representativeness of collected data will be ensured through high-accuracy navigation and the methodologies to be employed for sample collection, transportation, and analysis. The Chief Scientist is responsible for evaluating the condition of the sediment cores at the time of collection and prior to incubation. Reasonable effort will be made to obtain representative cores from the designated stations. In the event that cores cannot be obtained from designated stations, the situation will be discussed with the Authority Project Manager and alternative sampling locations will be considered.

The condition of cores will be evaluated (through examination of cores to which brick dust or clay was added) prior to incubation. The degree to which cores may have been disturbed during transport to the field laboratory will be noted. These observations will be used in the interpretation of results and, if necessary, support potential modifications to sampling/handling practices in future surveys.

11.1.5 Traceability

Each core sample will be logged in a field notebook upon collection to indicate the time, date, location, and sample characteristics. All field measurements will be recorded in the notebook, as will observations of sampling conditions. Any deviations from the CW/QAPP will be recorded for documentation in the survey report. Information specific to cores or subsamples will be transferred to chain-of-custody forms for all samples which are to be transported to analytical laboratories.

11.2 Laboratory Program

11.2.1 Accuracy and Precision

Accuracy and precision for the analytical methods used in this study appear in Table 3. Section 12 provides additional details on the analytical procedures that will ensure data quality and Section 14 describes instrument calibration methods. Microbial rate measurements (respiration, nutrient flux, etc.) do not have microbiological rate standards that can be run to calibrate the assays.

11.2.2 Completeness

The completeness of analyses will be ensured by comparing the total data planned with the valid data obtained. The data quality objective is over 90% completion. Completeness will be calculated as:

Percent Completeness = ([Valid data obtained]/[Total data planned]) x 100

11.2.3 Comparability

All data developed for this project must be demonstrated to be comparable to similar data generated by other laboratories or by other studies at the same or similar sites in Boston Harbor and Massachusetts Bay. This is to be accomplished by the employment of standardized sampling methods and analyses that have been previously approved by EPA and/or MWRA. The methodologies employed by the WHOI laboratory

TABLE 3

Objectives for Field and Laboratory Measurements

Variable (Lab)	Matrix	Units	Lower Detection Limits	Accuracy and Precision* (Better than)
O_2	SW	µM	BEL	5%
Total CO_2	SW	µM	BEL	5 µmole
NH_4	SW, PW	µM	0.1, 0.5	5%
$NO_2 + NO_3$	SW, PW	µM	0.1, 0.5	5%
PO_4	SW, PW	µM	0.1, 0.5	5%
Silicate	SW, PW	µM	0.5	5%
Urea	SW, PW	µM	0.5	5%
Sulfide	PW	µM	2	5%
pH	PW	unitless	NA	5%
Eh	PW	mV	NA	5%
Alkalinity	PW	mEq	BEL	5%
N_2	GAS	µmoles	0.001	4%
O_2	GAS	µmoles	0.001	1%
Argon	Gas	µmoles	0.001	4%
TOC	Sed	µmoles/cm^3	BEL	10%
TN	Sed	µmoles/cm^3	BEL	10%
Grain-size	SED	%	0.1%	20%
Porosity	SED	unitless	0.0005	5%
Temperature	SW	°C	BEL	1%
Salinity	SW	ppt	BEL	0.01
Chlorophyll-a	SED	µg/cm^3	0.1	10%

*Accuracy based on results of laboratory control standard; precision based on relative percent difference of duplicate samples

SW: Seawater
PW: Porewater
NA: Not Applicable
BEL: Detection Limit far Below Environmental Levels

are identical or comparable to those used by previous researchers at these sites, as well as methodologies being used in other project tasks for analyses of these parameters in the water column.

11.2.4 Representativeness

Representativeness of laboratory procedures will be ensured by proper handling, storage and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

11.2.5 Traceability

Complete documentation of sample identification will be maintained from field sampling through laboratory analysis and sample archival. Subsamples analyzed within the WHOI laboratory as well as those forwarded to Envitec will be traceable to the original core and to its sample collection. All documentation will be maintained on chain-of-custody forms (Section 13).

12.0 SAMPLING AND ANALYTICAL PROCEDURES

12.1 Navigation and Field Sampling

Vessel positioning during sampling operations will be accomplished through the use of a Northstar 941XD differential Global Positioning System (GPS). This system will routinely provide navigational readout with an accuracy of 10 meters. Upon achieving a scheduled station, undisturbed sediment cores will be collected by SCUBA divers or by box core sampler (see also Sections 7.3.1 and 7.4). Except under extraordinary circumstances, all of the Boston Harbor stations will be sampled by SCUBA diver and the Massachusetts Bay stations by box corer. One of the "shallow" Massachusetts Bay stations (MB01, MB02) may be attempted by diver on each of the warmer weather cruises. These stations are at the depth limit of routine diving capability. The dive program is under the supervision of the WHOI research diving program. All of the diving protocols and safety guidelines are reviewed and must be found acceptable by the Director of the WHOI dive program before each sampling cruise. Details of the certification and safety procedures required by WHOI are available through the WHOI dive program.

A box core will only be sub-sampled if the corer is "holding water" and the sub-sampling is conducted with more than 10-cm of water overlying the sediment surface and if the sediment surface appears undisturbed, without significant resuspension of surficial sediment or visible "cracks". Determinations of acceptability will be made by the Chief Scientist and core quality noted. The cores required for flux and

other analyses will be collected by hand insertion of each of the core tubes into the sediment surface of the sediments contained within the box. The core tubes will have their bottom stoppers inserted before core removal. In the case where only a portion of the box core is usable, a second box will be collected and the sub-cores apportioned equally between the two. The origin of each sub-sample will be noted in order to evaluate the variation between boxes. Diver collected cores will be collected within a 1 m^2 area by first inserting all of the core tubes. As with the sub-cores within the box corer, the bottom stoppers are inserted before removal of the cores. Cores are capped during transport to the surface to prevent disturbance. Upon collection of all cores their surface is again inspected for disturbance and if none is visible they are placed in the gimballed temperature controlled shipboard bath to maintain *in situ* temperatures.

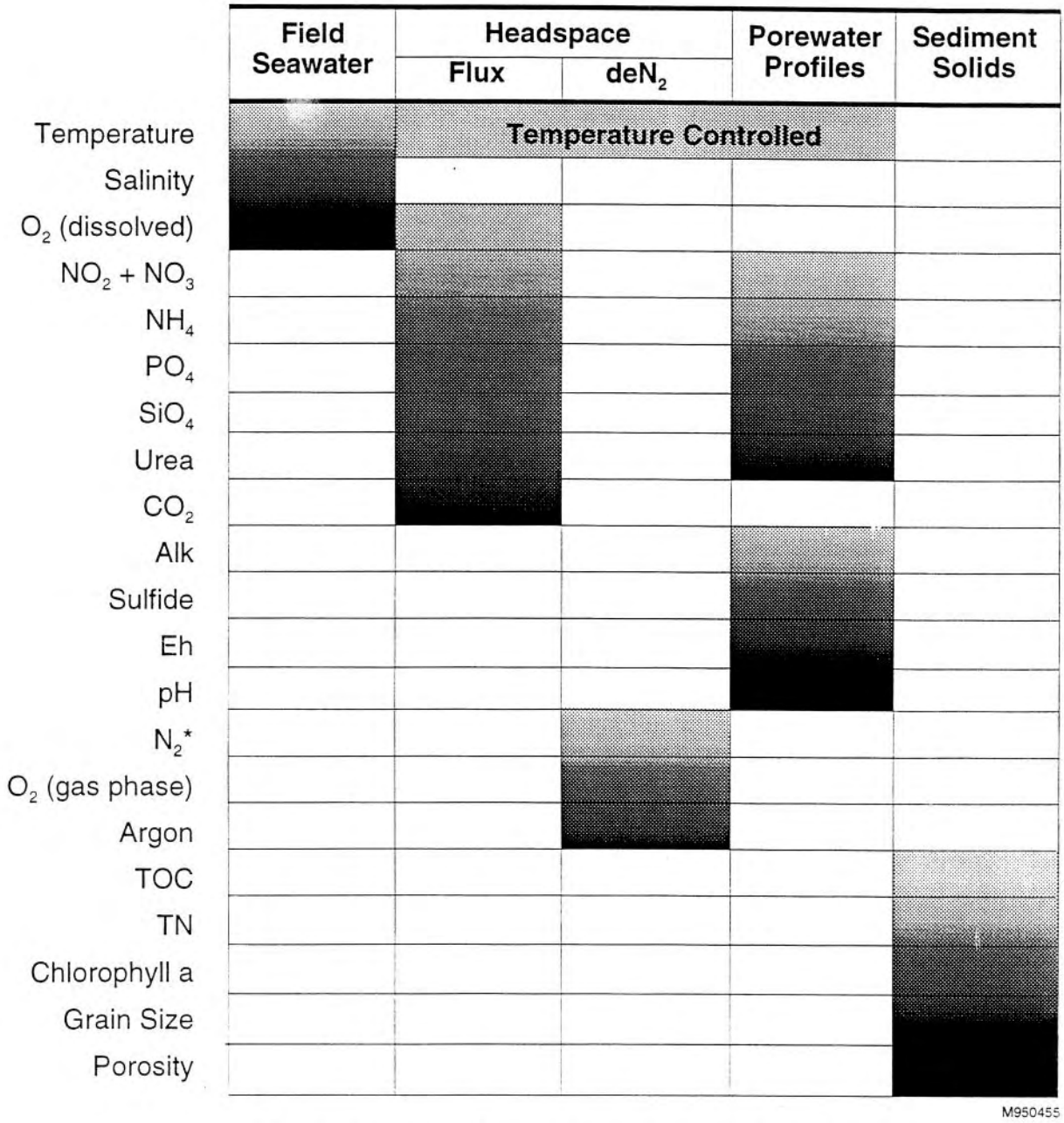
At each benthic flux station water bottom water will be collected by Niskin bottle and filtered for use as the headspace water in the incubating cores. Within Boston Harbor water will be collected at ca. 1 m above the bottom while within Massachusetts Bay at the "shallow" (30-40 m) stations and the deep station, water will be collected from 2-3 m and 5 m above the bottom, respectively. Water temperature and salinity will be determined by inserting a temperature compensated specific conductivity probe with thermistor into a 1 liter sub-sample from the Niskin collected immediately upon retrieval. Oxygen within the bottom water will be determined by Winkler method and potentiometric titration of 300-ml sub-samples (in BOD bottles) from the Niskin bottle following the procedure of the ongoing Baseline Water Quality Monitoring Program.

The sampling procedures employed are standard methods comparable to those used in existing MWRA data collections. All of the field and laboratory measurements and the samples from which they originate are summarized in Figure 3.

12.2 Laboratory Sample Processing and Analysis

12.2.1 Measurement of Benthic Respiration and Nutrient Flux

Upon arrival at the field laboratory flux cores are once again inspected for disturbance and the cores with brick dust or clay are inspected for the loss of the dusting of tracer from the core surface. Any surface disturbance or natural features are noted. Cores with large cracks in the sediment surface or with very turbid overlying water (indicative of surface resuspension) will not be assayed. However, cores with minor disturbances will be incubated and evaluated relative to the noted level of disturbance.



* N_2 is also measured in sediments at end of deN_2 incubation.

FIGURE 3
Summary of Field and Laboratory Measurements

Cores will be sealed from the atmosphere with gas-tight core tops fitted with magnetic stirrers that gently mix the overlying water without disturbing the sediment surface. In the flux cores oxygen will be determined using an Orbisphere meter and electrode equipped with a stirrer (the probe fitted through an opening in the core top) calibrated at 100% and 50% of atmospheric equilibration at the temperature and salinity of the headspace water of the cores. A single probe is used for all of the oxygen assays so that it can be calibrated before and after each measurement in the cores from each station. Given the slow rate of oxygen consumption at some sampling locations and times, the ability to constantly check electrode calibration to counter potential problems with electrode drift resulted in the "movable electrode approach". The electrode is inserted through a tight-fitting port in the cap of each chamber. Introduction of air is prevented by the port configuration.

The headspace of the flux cores from each of the seven stations will be replaced with 0.22 micron filtered water (collected from each core site). Subsamples of the filtered water will be incubated in parallel in 300-ml BOD bottles to provide control data for oxygen in the headspace not associated with sediment flux. Since the rate of change of each of the analytes is dependent upon temperature, the incubation time will vary with season. In all cases the incubation will continue until a significant flux is detected or to 48 hours. The headspace will be set so as to maximize the signal and minimize the incubation time (ideally 18 hours).

Since the ability to detect changes in sediment fluxes between years is central to the flux monitoring program, four flux cores will be collected if achievable under sampling conditions. Sediment oxygen uptake will be measured in time course in all flux cores, with nutrient samples collected at each time point in two of the flux cores and only end-point measurements of nutrients in the additional two flux cores.

Four to five time points (plus time zero) will be conducted per flux core incubation. Dissolved oxygen will not be allowed to decline to less than 50 percent of air equilibration. Since oxygen disappearance rates may exceed those of other solutes, incubations will be continued after completion of the oxygen uptake assay by aerating the headspace until the solute flux assays are completed (18 to 48 hours). At each time point, headspace water will be removed through a port in the gas tight headspace with equal replacement with the setup water; samples are immediately filtered (Millipore 0.22 micron in-line filtration) into acid leached 60cc polyethylene bottles upon removal. The water sample is removed by simultaneously drawing water into a 60cc syringe from a depth of about 2 cm below the top cap of the chamber while injecting an equal amount of filtered water into the "well" in the top cap. This approach allows water removal without even brief pressure changes to the headspace, which can potentially affect flux rates. All fluxes will be adjusted for water removals and measured activities within the headspace water.

Ammonium, nitrate + nitrite, urea, ortho-phosphate and silicate will be analyzed for each of the time point sample volumes from two cores, with endpoint measurements on the remaining two cores. Analytical techniques are listed in Table 4. Total carbon dioxide concentrations will be measured in the headspace at time zero and at the end of the incubation interval in two of the flux cores per site. Samples will be analyzed using a nitrogen gas stream and infrared detection (Beckman IR Analyzer). Accumulations in the headspaces will be used to calculate flux rates. The time-course measurements will be used to ensure calculations from linear increases.

12.2.2 Measurement of Sediment Denitrification

In 1995 N_2-denitrification measurements will be performed at two sites, BH02 and BH03; in 1996 denitrification will be performed at BH02, BH03, and QB01; in 1997 measurements will be made at all eight benthic flux stations. Incubations at each station occupied in the various years will consist of two pairs of denitrification cores per station (4 per station) in 1995 and 1996 and one pair per station in 1997. One of each pair will be incubated with a helium/oxygen headspace and one control with an anoxic headspace. Headspace water will be from the station where the cores originated. Measurements will follow the procedures of Seitzinger et al. (1980) with the modifications noted by Kelly and Nowicki (1993). However, rather than performing 2 back-to-back incubations on a single pair of cores we will conduct analyses on replicate pairs of cores. The latter approach is supported by the generally small analytical error associated with multiple incubation of the same core material (Kelly and Nowicki 1993) as opposed to spatial variation assessed by replicate cores.

Correction for the nitrate uptake from the overlying water in the cores (as opposed to nitrification/denitrification in the sediments) will be made from the nitrate measurements of headspace waters at the beginning and end of the incubation. The anoxic headspace in the denitrification cores will prevent nitrification of porewater ammonium, which provides almost all of the nitrate for sediment denitrification in these types of sediments in nature. At the end of the incubation the total mass of N_2 and argon within the sediments and headspace will be determined. The difference in total mass of N_2 between the paired cores yields an additional estimate of denitrification not dependant upon the assumption of equal diffusion rates within the cores (after correcting for any differences in sediment volume). The ratio of N_2 to argon will be used to assess the total mass of denitrified nitrogen associated with the core. This calculation uses argon as a tracer for N_2 whose source was the atmosphere versus denitrification. N_2, O_2 and argon will be measured by gas chromatography using a thermal conductivity detector. Injections will use sample loops to increases precision. Argon determinations require a second analysis where the sample first flows through a copper furnace to remove O_2.

TABLE 4

Laboratory Analyses

Parameter	Matrix	Units	Method	Reference
Nitrate + Nitrite	water	µM	Autoanalyzer	a
Ammonium	water	µM	Indophenol	b
Orthophosphate	water	µM	Molybdenum blue	c
Total Organic Carbon/Nitrogen	sediment	µmoles/cm^3	Acid treatment, drying Elemental Analysis	d
Alkalinity	water	mEq	Titration	e
pH	water	unitless	Meter and Probe	f
Salinity	water	°/oo	Specific Conductance/ refractometer	g
Silicate	water	µM	Autoanalyzer	h
Urea	water	µM	Autoanalyzer	i
Sulfide	water	µM	Colorometric	j
Oxygen uptake	sediment	µmol/m^2/hr	Time-course D.O.	k
N_2, O_2, Ar	gas	µmol/m^2/hr	Time-course	k
Nutrient flux	sediment	µmol/m^2/hr	Time-course [conc]	l
Grain Size	sediment	phi classification (sand fraction)	Wet sieve	m
		percent clay or silt	pipette analysis	m
Porosity	sediment	unitless	Oven-dry at 60°C	m
Redox	sediment	mV	Platinum electrode	n
CO_2	water	µmol/m^2/hr	Infrared analysis	o
Chlorophyll/ Pigments	sediment	µg/cm^3	Cold 90% acetone extract, acid corr.	h

TABLE 4 (Cont'd)

Laboratory Analyses

Parameter	Matrix	Units	Method	Reference

a Lachat Autoanalysis procedures based upon the following techniques:
--Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.
--Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in sea water. J. Mar. Res. 11: 87-96.

b Scheiner, D. 1976. Determination of ammonia and Kjeldahl nitrogen by indophenol method. Water Resources 10: 31-36.

c Murphy, J. and J.P. Reilly. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytical Chemica Acta 27:31-36.

d Perkin-Elmer Model 2400 CHN Elemental Analyzer Technical Manual.

e Alkalinity, Standard Methods 16th Ed. 403; Hach Alkalinity Titration Kit

f pH Value, Standard Methods 16th Ed. 423; Corning 130 pH Meter

g Salinity: temperature compensated American Optical Refractometer; Specific Conductance: Fisher Scientific Digital Conductivity Resistivity Meter

h Parsons, T.R., Y. Maita and C. Lalli. 1989. Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, 173 pp.

i RFA Alpchem Autoanalyzer Technical Manual.

j Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr. 14: 454-458.

k Incubation: Jorgensen, B. 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. 22:814-832.; Winkler Titration: reference h.

l Klump, J. & C. Martens. 1983. Benthic nitrogen regeneration In: Nitrogen in the Marine Environment, (Carpenter & Capone, eds.). Academic Press.

m NOAA. 1993. Comprehensive descriptions of complementary measurements. Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects, 1984 - 1992 (Volume II). NOAA Technical Memorandum NOS/ORCA/CMBAD 71. Envitec SOPs (Attachments A and B).

n Bagander, L.E. and L. Niemisto. 1978. An evaluation of the use of redox measurements for characterizing recent sediments. Est. Coast. Mar. Sci. 6: 127-134.

o Howes, B.L., J.W. Dacey and J.M. Teal. 1985. Annual carbon mineralization and belowground production of *Spartina alterniflora* in a New England salt marsh. Ecology 66:595-605.

12.2.3 Analysis of Sediment Porewaters

Porewater concentrations of key constituents can be used both to model nutrient afflux from surficial sediments and give insight into changing levels of nutrient loading not detectable by bulk sediment properties (e.g., TOC). Porewater will be obtained from sectioning flux cores into 10 1-cm sections to a core depth of 10 cm by anaerobic-refrigerated centrifugation. The porewater from similar depths will be pooled (equal porewater volumes) and assayed for ammonium, nitrate + nitrite, urea, ortho-phosphate, silicate, alkalinity and dissolved sulfides. Direct and indirect sulfide interferences to nutrient assays will be controlled by removing the sulfide by oxidation and refiltration. The close interval sampling of the surficial sediments should better quantify the structure of the profile of porewater constituents in the surface 10-cm where most of the biogeochemical activity is occurring. Measures by Giblin et al. 1993 indicated that the variation in porewater profiles almost always was found within the 0-10 cm interval. The greater detail in this surface layer is sought to improve the calculations of flux for which the data are (and has been) primarily sought.

Nutrient assays will use the methods for the nutrient flux samples scaled to the smaller volumes and generally higher concentrations of most constituents in porewater. Alkalinity will be measured by titration and sulfide by the colorimetric technique. Profiles of pH and Eh will be determined by standard glass electrodes, respectively, on extracted porewater and a separate 6.5 cm redox core by direct insertion. Measurements of pH will be at 10-mm intervals; for Eh measurements will be at 2-mm intervals to a depth of 20 mm and then 10-mm intervals to 100 mm depth. The redox discontinuity depth (RPD) is determined as the layer of maximum rate of change in measured Eh. Dissolved sulfides will be measured within 24 hours using a modification of Cline's (1969) method to accommodate the smaller porewater volumes.

12.2.4 TOC, TN and Grain-size Analysis of Surficial Sediments

TOC and TN

Subsamples (0-2-cm depth) will be collected from each of the four flux cores per location after each incubation. In this manner, the correlation between TOC and surface oxygen uptake will be directly determined. TOC will be assayed after sulfuric acid treatment to remove carbonates. Samples will be collected to permit determination of TOC and TN by CHN elemental analysis on both a cubic centimeter and dry weight basis.

Sediment Grain Size

Grain size analyses will be performed utilizing a combined sieve analysis and pipette analysis (NOAA, 1993). Additional detail is provided in the Envitec SOPs for Sediment Grain size by Sieve Analysis and by Pipette Analysis (Attachments A and B). The sieve analysis will be used to separate and calculate the proportion of sediment particles greater than 62.5 μm (i.e. the sand fraction) up to 2 mm; material over 2 mm will be reported as gravel. Sediment samples will be dry sieved through a sieve series based on the Wentworth grade scale that includes a 2.0 mm, 1.0 mm, 0.5 mm, 0.250 mm, 0.125 mm, and 0.063 mm sieve. Sediment retained in each sieve will be weighed on an analytical balance accurate to 0.001 g to produce the proportion of sediment in each sediment category. This analysis will yield a result for gravel (greater than 2 mm) and results for each phi class between 2 mm and 0.063 mm.

The pipette portion of the analysis is based on Stokes' Law for determining the settling rate of particles through a column of distilled water. The procedure requires placing the sediment passed through the 0.063 mm sieve into a sedimentation cylinder and withdrawing a sample with a 20 ml pipette at three time intervals. The sample is placed into a tared crucible, dried at 105°C, and weighed on an analytical balance accurate to 0.001 g. The pipette analysis will provide two additional data points: total silt (0.063 m to 0.004 mm) and total clay (<0.004 mm).

12.2.5 Chlorophyll-a and Phaeopigment Analysis of Sediments

Sub-samples (15 cm^3) of sediments from 1-cm intervals from the surface to 5-cm depth will be extracted in cold acetone (-20°C) in the dark. The sediments will be treated with a magnesium carbonate suspension to prevent degradation of chlorophyll-a during extraction. Pigments will be analyzed using either a spectrophotometer or a fluorometer depending upon the concentrations encountered. Chlorophyll-a will be separated from phaeopigments by analyzing the extract before and after acidification with HCl. These data will be used to gauge seasonal changes in deposition of phytoplankton relative to the rates of organic matter turnover measured as oxygen uptake in the flux cores.

13.0 SAMPLE CUSTODY PROCEDURES

13.1 Custody of Samples

Sample custody will be maintained through the field log book, laboratory record book, and chain-of-custody forms. All original station log forms (Figure 4) and any chain-of-custody forms (Figure 5) will

STATION LOG

MWRA Benthic Nutrient Flux Monitoring	Event ID:
Chief Scientist: Date:	Station ID:
Signature:	Visit # : Core Collection Mode* (A or B):
Weather Observations:	Bottom Depth:
Seas:	Time on Station: EST/DST (circle)
Wind:	LAT: LONG:
Tide:	Time off Station: EST/DST (circle)
General:	Recorded by:
	Notes:

* CORE COLLECTION MODE:		Core #	Time	Latitude	Longitude
A) Divers (Initials):		A			
B) Box Corer (#) :		B1			
		B2			
		B3			

SAMPLE (CORE) ID/diam.		1	2	3	4
Flux / 15.5 cm	F				
Denitrification / 15.5 cm	D				
TOC/Grain Size / 6.5 cm	T				
Redox/Chl a / 6.5 cm	R				
Spare / 6.5 cm					

NISKIN CAST

Cast #	Depth (m)	Time	Temp (°C)	Salinity	Bottle #	********BOTTOM WATER RESPIRATION****** Depth	Time Fixed	Bottle Code
					1			
					2			
					3			
					4		XX	
					5		XX	
					6		XX	

CTD CAST (if performed)

CAST #1 TIME : CAST #2 TIME :

R:\PUBS\PROJECTS\4501005\033.TXT

FIGURE 4
Station Log

ENSR	CHAIN OF CUSTODY RECORD		
MWRA Harbor and Outfall Monitoring		Event ID:	
Chief Scientist:		Field Logbook No:	
Signature:		Chain of Custody Tape No:	
Send Results To	Steve Cibik ENSR 35 Nagog Pk. Acton, MA 01720	Analytical Laboratory (Destination)	
Relinquished by: (print name) Signature	Date: Time:	Received by: (print name) Signature	Date: Time:
Relinquished by: (print name) Signature	Date: Time:	Received by: (print name) Signature	Date: Time:
Relinquished by: (print name) Signature	Date: Time:	Received by: (print name) Signature	Date: Time:

Sample ID	Subsample ID	Date	Time (circle one) EST/EDT	Analysis	Container	Media	Preservative

FIGURE 5
Chain of Custody Record

be kept in a project Sample Log notebook. The Chief Scientist will maintain custody of all samples on board the vessel. The Chief Scientist will record in the log book event information such as station, location, sampling time, water depth, and *in-situ* measurement data.

Samples will be collected by trained field and laboratory personnel with complete sample identification filled in on pre-printed labels on each bottle. Sample log information and chain-of-custody forms will include the event and sample IDs. Event codes will utilize a five-character code including the task, year, and event number (e.g., F9501 = Flux sample taken in 1995 during the first sample round). Sample IDs will indicate station location ("BH" for Boston Harbor; "MB" for Massachusetts Bay; "QB" for Quincy Bay), two-character station number, one character visit number, and two-character sample code (A1 = dive number one; B1 = box core number one). For example, a sample ID might begin with BH081B1 = Station BH08, visit one, box core sample one. The visit number will only change if a station must be re-occupied on a subsequent occasion to complete sampling.

Subsequent coding would then indicate sample type and number, as follows: F2, D2 = flux core, denitrification core number two, respectively; R1 = redox core number one; W1 = water column measurement number one). This sequence will also indicate sequential samples taken on a particular dive (e.g. BH081A2F4 = station BH08, visit one, dive two, flux core number four), or subsamples of individual box cores brought on deck (e.g. BH081B2F4 = Boston Harbor station 08, visit one, box core number two, flux core number four).

Subsamples taken from each flux, denitrification, or redox core will be coded by subsample type and number, parameter, and sample number. Subsample type codes are consistent with the sample IDs, with F1 = flux core number one, D1 = denitrification core #1, W1 = water column sample #1, and R1 = redox core #1. Two-character parameter codes will be used, as follows:

- TM = temperature;
- SA = salinity;
- O2 = oxygen;
- AM = ammonium;
- NO = nitrate + nitrite;
- UR = urea;
- OP = orthophosphate;
- SI = silicate;
- AL = alkalinity;
- SU = sulfide (dissolved);

- N2 = nitrogen;
- AR = argon
- CO = carbon dioxide;
- EH = redox potential;
- PH = pH;
- TC = total organic carbon;
- TN = total nitrogen; and
- GS = grain size.
- PO = porosity
- CH = chlorophyll-a

Finally, the sequential number of the subsample will be indicated by a two-digit number. As an example, the subsample code for the time zero ammonium sample from flux core 1 would be F1AM00, the ambient temperature measurement from the overlying water column would be W1TM01, and R1EH10 would be the code for redox potential at the 10-cm core depth. All supporting measurements and observations noted during incubations and laboratory analyses should be noted in the field log book or laboratory notebook.

Samples generated in the field laboratory will be transported to Dr. Howes's laboratory at the Woods Hole Oceanographic Institution and received by the analytical specialists who are solely responsible for their custody from analysis through storage, minimizing the number of individuals involved in sample transfer. After processing, the remaining sample will be archived frozen (-20°C) or dried (depending on analysis) until the end of the study. Subsamples for grain size analysis will be collected by the WHOI flux technician and forwarded to Envitec for analysis.

Transfer of samples will be documented on the chain-of-custody forms, which will be signed and dated by both the person relinquishing the samples as well as the recipient. One sheet of the multiple-page form will be retained by the Chief Scientist, who will forward the document to the Project Area Manager. The remaining sheets will accompany the samples to the laboratory for subsequent sample transfer.

14.0 CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

All analytical equipment (Bausch and Lomb Spectrophotometer, Lachat Autoanalyzer, Perkin-Elmer Elemental Analyzer, etc.) is calibrated through the processing of standards in the normal analytical procedure.

Meters and electrodes are multi-point calibrated with certified ion standards. Laboratory analytical balances are under annual manufacturer service and calibration, although certified calibration weights are maintained on site as well. Infrared analyzers, gas chromatographs and oxygen probes are multi-point calibrated with certified gas standards under controlled temperature and salinity. Maintenance of and repairs to instruments are performed in accordance with manufacturers' requirements. Maintenance logs will be maintained for all equipment.

Samples for ammonium, nitrate+nitrite, and orthophosphate 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 will be run in duplicate. The carbon dioxide analyzer will be calibrated with bicarbonate and seawater solutions of a known carbon dioxide content. The dissolved oxygen meter will be calibrated by Winkler titration, and further checked against air-saturated water 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.

15.0 DOCUMENTATION, DATA REDUCTION, AND REPORTING

15.1 Documentation

Documentation will include this CW/QAPP, survey plans, survey reports, sample collection logs (Figure 4), chain-of-custody forms (Figure 5), and laboratory records. Sample collection information will be recorded on standard forms which document the sample information discussed in Section 13.2. The Chief Scientist will be responsible for ensuring the completeness and accuracy of all documentation prior to sample arrival at the analytical laboratory.

The laboratory manager will assume responsibility for sample and data documentation in the laboratory. Initially, all laboratory data will be recorded either (1) electronically onto computer storage media from laboratory data systems or (2) manually into laboratory notebooks or on established data forms. All 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 manager to ensure that all data entries and hand calculations are verified. Laboratory records of sample preparation will be maintained.

15.2 Data Reduction

Data reduction involves the process of converting raw numbers into data that have direct chemical meaning or can be compared statistically. Raw data will be maintained in duplicate notebooks. Calculation to concentration will be done in an adjacent column for easy comparison. The calculation is based upon the regression equation calculated from the chemical standards. The results will be reported in terms of concentration, as means and standard errors and rate measurements in terms of rate per cm^3 or m^2 of bottom per day. Flux (µmol/area/day) of a constituent will be determined from the linear rate of change in the concentration of that chemical species in the water overlying the sediment core (by regression) expressed as µM/day (r) times the volume of overlying water (V) divided by the surface area of the core (A) or Flux = (r*V)/A.

In the denitrification core incubations the flux of N_2 in the oxic and anoxic rates will be calculated as in the flux cores and the rate of denitrification determined as "excess" of oxic over anoxic rates. Calculations of rates in both the flux and denitrification cores will follow the procedures of the previous studies (Kelly and Nowicki 1993, Kelly et al. 1993) to ensure direct comparison of results. Additional modeling approaches will be examined based upon the actual results of the field studies. Any additional models or calculations will be detailed and referenced in the appropriate reports to MWRA. Students t-test for paired samples and analysis of variance will be used for interpretation. Data will be transcribed only for the statistical analysis and each point will be checked for accuracy. It is the responsibility of the laboratory manager 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 will be entered into PC-based spreadsheets, verified, and submitted to ENSR. Data validation procedures are discussed in Section 16.

15.3 Reporting

Three formats will be used to report the results of Task 16 to MWRA:

(1) Data submitted for inclusion in the Harbor Studies Database
(2) Data presented in Flux Data Reports
(3) Data summarized and interpreted in annual synthesis reports.

15.3.1 Harbor Studies Database

Only data that have designated as final by the Project Area Manager will be loaded into ENSR's copy of the Harbor Studies Database. All data will be loaded into the database by ENSR data management staff following the formats described below. Upon receipt, each diskette will be logged in and assigned a unique log in identifier. Any changes or additions to data, necessary for loading into the database, will be made using well-documented scripts that indicate the original values. The original diskette, scripts, and data-loading documentation will be filed at ENSR according to the log in identifier. The data sources notebook will contain the chain-of-custody forms and data entry information.

15.3.2 Flux Data Reports

Flux data reports will be submitted to MWRA in both hard-copy and electronic forms. Included will be all sample collection information summarized from the Survey Reports from each sampling event. Data will be presented in tables containing the results of all individual sample analyses plus QC data. Included will be the appropriate flux rate calculations for nutrients and gases assayed during the flux incubations.

15.3.3 Annual Synthesis Reports

An annual report presenting results, statistical analysis, and interpretation of the benthic flux task will be submitted to the Authority under Task 33.4. Results will be presented in both tabular and graphical formats. Spatial and temporal trends in nutrient fluxes, denitrification, porewater profiles, and bulk sediment parameters will be examined and interpreted. Results from both the water column surveys and benthic community analyses will be considered in this interpretation.

16.0 DATA VALIDATION

All data reported for this project will be reviewed to check for errors in transcription, calculation, or computer input by the technical staff of the appropriate laboratory. The validation procedures that will be performed are:

- 100% of data that are hand-entered into a database or spreadsheet will be verified for accuracy either by (1) printing the spreadsheet and proofreading against the original hand entry or by (2) duplicate entry into the database and comparison of the entries to detect

any differences. These tasks will be carried out by two people and documented for each data set.

- All manual calculations will be checked for accuracy by a second staff member.

- Calculations performed by software 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 prior to final data submission.

- Subsets of the analytical data will be reviewed by in-house or subcontractor data validators. The data will be reviewed for adherence to analytical protocols and to pre-established criteria (e.g., for holding times, surrogate recoveries, initial and continuing calibration, matrix spikes, laboratory duplicates, blank contamination, SRM recoveries).

- Database staff will check the received data and associated documentation for completeness, freedom from errors, and technical reasonableness.

- All new software developed for this task will be validated before entry of data.

The ENSR Project Area Manager will be responsible for validation of all data generated by ENSR to ensure that the data are accurate, complete, and scientifically reasonable. Subcontractors will be responsible for conducting similar data validations. As an additional data validation step, ENSR Project Area Manager will review all subcontractor data for technical reasonableness.

17.0 PERFORMANCE AND SYSTEM AUDITS

This project will be monitored by the Project QA Director. Tabular and graphic data reported in deliverables and associated raw data generated by ENSR will be reviewed by the Project QA Director or his/her designee. Raw data will be reviewed for traceability, accuracy, completeness, and proper documentation.

All deliverables generated during the course of this project will be submitted to an internal review prior to delivery of drafts to MWRA.

Audits of the subcontractor laboratory data-collection programs will be the responsibility of the subcontractor. During the time 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 ENSR Project Area Manager and 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.

Performance audits, procedures used to determine quantitatively the accuracy of the total measurement system or its components, will be the responsibility of subcontractor laboratories and may include 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 ENSR 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 ENSR 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 Task Manager, the ENSR Project Area Manager, and the WHOI Principal Investigator. Problems relating to the overall successful completion of the project will be reported to the MWRA Task Manager in a timely manner for discussion and resolution between the ENSR 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 ENSR Project Area Manager or the ENSR Project Manager. They will be responsible for evaluating the overall impact to the project and for discussing corrective actions with the MWRA Task Manager.

A QA/QC Corrective Action Log will be maintained by the Project QA Director and submitted to MWRA at quarterly intervals. The log will include documentation of QA/QC activities as they occur, 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

Reporting under this task will be through submittal of survey plans, survey reports, and flux data reports. The content of the survey plans and reports are discussed in Section 7.3.1. Flux data reports will provide the data from each survey in tabular form, including calculated flux rates for nutrients and gases. Annual Benthic Nutrient Flux Reports will present overviews of the survey results for each year. In these reports, the overall objectives of this task will be realized through integration of these results with other tasks. Spatial and temporal trends in nutrient fluxes will be examined and interpreted with respect to these other data sets.

20.0 REFERENCES

American Public Health Association. 1985. Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition. (A.E. Greenberg, R.R. Trussell and S. Clesceri, eds.). Published by American Public Health Association. 1268 pp.

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APPENDIX A

STANDARD OPERATING PROCEDURES
FOR
SEDIMENT GRAIN SIZE BY SIEVE ANALYSIS

SEDIMENT GRAIN SIZE BY SIEVE ANALYSIS

1.0 INTRODUCTION

Grain size analysis of dried sediment samples is performed using a series of standard sieves to separate the sample into fractions. This procedure is essentially the same as the Battelle procedure decribed in section 3.2.3.1 of the method by Padell and Hillaman (NOAA, 1993). Each fraction is characterized based on the weight of sample that passed through a particular sieve size but does not pass through the next smallest sieve. Six (6) sieves are used, typically having the following sizes 2.0 mm, 1.00 mm, 0.500 mm, 0.250 mm, 0.125 mm and 0.063 mm. The fraction of the sample retained in each sieve is weighed on an analytical balance to ± 0.001 g. Results are reported as a table of the percentage of sample in each size class represented by the sieves from > 2.0 mm down to < 0.063 mm, seven (7) classes in all.

2.0 APPARATUS AND MATERIALS

A series of U.S.A. Standard Testing Sieves that meet the ASTM E-11 specification is utilized. Table 1 gives the size opening and sieve number for the sieves to be used.

Table 1. Sieve number and size opening

Sieve Number	Size Opening
No. 10	2.0 mm
No. 16	1.00 mm
No. 30	0.500 mm
No. 60	0.250 mm
No. 120	0.125 mm
No. 330	0.063 mm

A Sieve Shaker, model SS-8R (Gilson Screen Co., Malinta, OH) is employed to agitate the sample in the sieve set and cause fractionation. An analytical balance, model AE100 (Mettler Instrument Corp., Hightstown, NJ) is used for weighing individual fractions. The total weight of the dried sample prior to sieving is obtained on a Mettler model PM600 balance.

Additional equipment utilized for this procedure includes a drying oven, spatulas for transferring the sample and 250 mL or 500 mL wide mouth sampling containers.

SEDIMENT GRAIN SIZE BY SIEVE ANALYSIS

3.0 Procedure

An amount of wet sediment suitable to provide 60 to 100 g dry wt is weighed out into a clean plastic beaker. The sample is dried at 100 °C, cooled to room temperature and weighed. If the sample forms clumps or a solid cement-like clump, it must be carefully broken up.

Sieves are fitted tightly together in decreasing order with the sieve containing the largest size opening at the top. The dried sample is introduced into the top sieve and the sieve cover secured in place. The stack of sieves is placed on the mechanical shaker and shaken for a minimum of 10 min.

After shaking, the sieves are carefully taken apart and the contents of each sieve are transferred to a tared weighing dish and weighed to the nearest 0.001 g.

4.0 Calculations

The percentage of the total sample contained in each sediment fraction is computed using the following equation

$$\% \text{ sediment in fraction} = \frac{\text{weight of sediment retained on sieve}}{\text{total weight of sample}} \times 100$$

5.0 Reporting

Results are reported as a table containing each of the seven (7) size fractions from > 2 mm down to < 0.063 mm, and the percentage of sample contained in each.

6.0 References

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APPENDIX B

STANDARD OPERATING PROCEDURES
FOR
SEDIMENT GRAIN SIZE BY PIPETTE ANALYSIS

SEDIMENT GRAIN SIZE BY PIPETTE ANALYSIS

1.0 INTRODUCTION

Grain size analysis of previously dried and sieved sediment samples is performed using a procedure based on the Stokes Law settling rate of particles through a column of distilled water. The fraction of a sample that has passed through a 0.063 mm sieve is placed in a graduated cylinder, shaken and allowed to settle after temperature equilibration. Sample is withdrawn with a pipette at specified time intervals, placed in tared weighing bottles, dried and weighed. Results are reported as a table containing each of the two (2) size fractions including total silt (0.063 mm to 0.004 mm) and total clay (< 0.004 mm) and the percentage of sample contained in each (Head, 1992; NOAA, 1993).

2.0 APPARATUS AND MATERIALS

Two glass sedimentation cylinders graduated at 500 mL and each fitted with a rubber bung are required. A supply of distilled water, dispersant solution (Calgon), a 20-mL sampling pipette, constant temperature bath (25 ± 0.5 °C) deep enough to immerse the cylinders, a thermometer and a stop-clock are utilized in this procedure. Finally, glass weighing bottles, a drying oven, desiccator and analytical balance are used to dry and weigh the sample withdrawn from the cylinders.

3.0 Procedure

3.1 Preparation of Suspension

-Transfer the soil that passed through the 0.063mm sieve with the aid of a funnel into a 500 mL sedimentation cylinder (without loss of sample).
-Make up the water level in the cylinder to approximately 475 mL by adding distilled water and place the cylinder in the constant temperature bath, set at 25 °C.
-Place 25 mL of dispersant solution into the second sedimentation cylinder and make up to the 500 mL graduation mark. Place this tube in the same constant temperature bath.
-Insert a rubber bung into each cylinder to obtain a watertight fit
-Shake the cylinders and allow them to stand in the bath until they reached the bath temperature (about 1hr)
-Remove each cylinder in turn, shake thoroughly and vigorously by applying end-over-end cycles during a period of 2 min and replace upright in the bath. At the instant when the cylinder containing the soil suspension is placed in the bath, start the stop-clock (t=0).

SEDIMENT GRAIN SIZE BY PIPETTE ANALYSIS

3.2 Sampling with pipette

Samples are normally taken at two specified time intervals from t = 0.
-Gently lower the pipette into the suspension until the tip is 100 mm below the surface (this must cause no turbulence in the suspension).
-At the exact sampling times, draw a sample (volume V mL) up into the pipette and withdraw the pipette steadily from the suspension.
-Place the drawn samples into a weighed glass weighing bottles. Wash any suspension on the inside of the pipette into the bottle with distilled water.

3.3 Determination of dry solid matter

-Place the weighing bottles and contents in an oven at 105 °C until the samples are evaporated to dryness.
- Cool in a desiccator and weigh carefully to the nearest 0.001 g
(Accurate weighing is essential because the mass of sample recovered is very small)
-Determine the mass of soil in the sample, m, by difference.

4.0 Calibration sampling

-Between stipulated sampling times, take a pipette sample from the sedimentation tube containing dispersant only, exactly as described for the soil suspension.
-Transfer the pipette sample to a weighed glass weighing bottle, dry, cool and weigh accurately to determine the mass of solid material in the dispersant, W_c.

5.0 Calculations

Data obtained from the pipette test sample enable the percentages of total silt (coarse silt, medium silt and fine silt) and clay present in the sample to be calculated.
The mass of solid material in the whole 500 mL of suspension, W, at any sampling time can be calculated by proportion from the measured mass in the pipette volume, V mL

i.e.

$$W = m \times (500g/V\ mL)$$

SEDIMENT GRAIN SIZE BY PIPETTE ANALYSIS

The percentage by mass (%M) of particles smaller than the particle diameter corresponding to each sampling operation is calculated from

$$\%M = \frac{W - W_c}{m_t} \times 100$$

where m_t is the initial sample dry mass

6.0 Reporting

Results are reported as a table containing each of the two (2) size fractions including total silt, 4 phi (0.063 mm to 0.004 mm) and total clay, 8 phi (< 0.004 mm) and the percentage of sample contained in each (NOAA, 1993).

7.0 References

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