

Metabolism, nutrient cycling and
denitrification in Boston Harbor
and Massachusetts Bay sediments
in 1993

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FINAL REPORT

**METABOLISM, NUTRIENT CYCLING, AND DENITRIFICATION IN
BOSTON HARBOR AND MASSACHUSETTS BAY SEDIMENTS IN 1993**

for

**Massachusetts Water Resources Authority
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EXECUTIVE SUMMARY

This study was undertaken to examine seasonal changes in benthic processes in Boston Harbor and Massachusetts Bay, and to better characterize their spatial variability. The study was designed to 1) provide data on benthic processes to support the modeling effort in Massachusetts Bay, 2) monitor the recovery of the sludge disposal area in Boston Harbor and 3) better characterize the baseline conditions in Boston Harbor and Massachusetts Bay prior to wastewater diversion.

Throughout a seasonal cycle in 1993, sediment stations in Boston Harbor and western Massachusetts Bay were sampled. During summer and fall, additional stations in Cape Cod Bay and Stellwagen Basin were sampled. Laboratory incubations of sediment cores were performed to determine rates of benthic respiration, nutrient flux, and denitrification. Porewater profiles and sediment carbon and nitrogen also were measured at all benthic flux stations. Results are compared to those from previous studies in 1991-1992. These data constitute a portion of the baseline monitoring results for MWRA's Harbor and Outfall Monitoring Program. The expanded geographic coverage in 1993, examination of seasonal and interannual patterns, and the inclusion of silicate fluxes all significantly improve quantitative understanding of benthic processes and their role in Harbor and the Bay nutrient cycles. Brief comments are provided relative to the utility of these measurements to document changes in the Harbor during recovery and to detect responses in the Bay after diversion of MWRA wastewater to the Bay.

The Bay and Harbor environments are quite different and, not surprisingly, the sediment stations in the Harbor and the Bay differed dramatically in almost every parameter measured. However, seasonal variations in water temperature and organic matter supply, including changes in wastewater discharges, play important roles in influencing benthic fluxes and, in part, create differences between benthic processes in the Harbor and the Bay.

Specific major results include the following:

- (1) Over the seasonal cycle, sediment oxygen uptake in the Harbor ranged from 7 mmol m⁻² d⁻¹ at a sandy site in the winter to 220 mmol m⁻² d⁻¹ at an organic-rich site in the summer. Oxygen uptake at station BH03, the former sludge discharge site near Long Island, was consistently higher than at any of the other Harbor stations.

- (2) Sediment oxygen uptake in the Bay ranged from 7 to 27 mmol m⁻² d⁻¹. Annual average respiration at the three nearfield sites (MB01, MB02, and MB03) only differed from each other by 5%, which was not significant. Respiration rates at the other shallow stations in Massachusetts Bay (MB04 and MB06) were similar to the nearfield stations. There was a significant relationship between temperature and the oxygen uptake rates at all the shallow Massachusetts Bay stations. Oxygen uptake rates at station MB05 in Stellwagen Basin were lower than at the other Massachusetts Bay stations. Some of the difference between the shallow and deep stations could be attributed to temperature differences.
- (3) Denitrification rates observed in Boston Harbor (<0.24 to 9.9 mmol m⁻² d⁻¹; mean=2.9) were significantly higher than those observed in Massachusetts Bay (<0.24 to 2.6 mmol m⁻² d⁻¹; mean=1.1). Highest rates were observed in Boston Harbor at stations with high sediment organic content, at summer temperatures, when exceptionally high numbers of macrofauna (amphipods) were present. Denitrification relative to Harbor nitrogen loading increased at station BH03 in 1993, but at other stations rates were comparable to 1992.
- (4) Nutrient fluxes at the Bay nearfield stations were not as similar to each other as oxygen fluxes. Like oxygen, Si fluxes increase with increasing temperature. Dissolved inorganic nitrogen (DIN) and PO₄ did not show clear seasonal patterns related to temperature.
- (5) Although there was some spatial variability among sites in the Bay, in the future a major change in organic matter delivery to the sediments should be reflected in a measurable change in benthic fluxes. We need to know more about interannual variation before we can confidently calculate a minimum detectable change, but the close correspondence between the shallow Massachusetts Bay stations is encouraging. The HydroQual water-quality model predicts that benthic fluxes will change by four-fold at the diffuser to nondetectable several kilometers away. If the depositional nearfield areas experience an increase in O₂ uptake in the range of 50%, and if interannual variation is low, it should be detectable.
- (6) Controls on denitrification appear to be different in different environments. The annual cycle of denitrification in the highly organic depositional areas of Boston Harbor appears to be driven by temperature. In contrast, the Massachusetts Bay stations and the sandy Harbor station did not show a consistent temperature response or seasonal trend.
- (7) Measurements of total carbon dioxide (DIC) release gave a higher estimate of carbon mineralized in the benthos than measurements of oxygen uptake for nearly all stations and times. The one exception was at station BH03 where oxygen uptake exceeded DIC release. At the other two Harbor stations, DIC release exceeded oxygen uptake by 41%. Over an annual cycle in the Bay, DIC release exceeded oxygen uptake by about 20% at stations MB02 and MB03. Station MB01 was characterized by a much higher respiratory quotient (RQ); at this station, respiration exceeded oxygen uptake by 75%. We need to investigate whether the high RQ at station MB01 was due to metabolism or whether carbonate dissolution was contributing to the DIC fluxes.
- (8) Harbor Station BH03, near the former MWRA sludge discharge site, has shown "recovery" in the large population of amphipods and other benthic animals colonizing the sediment for most of 1993. These animals have apparently greatly increased sediment metabolism, nitrogen release, and denitrification. In spite of the high metabolic activity at this site,

porewater sulfide concentrations over the top 10-12 cm have decreased, perhaps due to intense bio-irrigation. We expect that this increased metabolism is a transient response. The amphipod population was greatly reduced in October 1993 and metabolism appears to have slowed in response. The 1993 data from station BH03 shows that there is the potential for some transient responses that may be beyond the predictive capacity of the HydroQual water-quality model. Further monitoring in 1994 will help determine how long those transient responses will last.

- (9) During summer, when benthic fluxes are maximal, the depositional sediments in western Massachusetts Bay consume less than 30% of the carbon produced in primary production and replenish less than 15% of the nitrogen and phosphorous. The nature of the coupling of the productive surface layer with the benthos during stratification is uncertain. Also unknown is the extent to which variation in organic matter supply interacts with bottom water temperature to regulate benthic processes in the Bay. It is clear, however, that factors other than benthic nutrient flux are influential in determining trends in bottom-water quality.
- (10) Porewater constituents are important indicators of sediment processes. Porewater sulfide and redox potential (Eh) are dramatically different between the Harbor and the Bay, and may provide sensitive indicators of changes in organic matter loading. Because high concentrations of sulfides are toxic to infaunal animals, measurements of sulfides also provide a measure of habitat quality.

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1.0 INTRODUCTION

This study was undertaken to examine seasonal changes in benthic processes in Boston Harbor and Massachusetts Bay, and to better characterize their spatial variability. We measured sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen, silicate, and phosphorus at stations in Boston Harbor and Massachusetts Bay. The amount of nitrogen lost from the sediments as nitrogen gas by the microbial processes of denitrification was also measured. The study is a continuation and expansion of previous work carried out in the Harbor and in the Bay (Giblin *et al.*, 1991; Giblin *et al.*, 1992; Giblin *et al.*, 1993; Kelly and Nowicki, 1992; Kelly and Nowicki, 1993). This study was designed to (1) provide data to support the modeling effort in Massachusetts Bay, (2) monitor the recovery of the sludge disposal site in Boston Harbor, and (3) better characterize the baseline conditions in Massachusetts Bay and Boston Harbor prior to wastewater diversion. Silicate and urea were also included in the suite of benthic flux measurements for the first time.

We have discussed the importance of measuring benthic fluxes from an ecological perspective at length in several of our previous reports. Briefly, sediments of coastal environments play an important role in nutrient recycling and organic matter decomposition. The breakdown of organic material on the bottom releases nutrients to the overlying water; this process consumes oxygen. Released nutrients can be reused by the phytoplankton to support primary production.

In addition to serving as a source of inorganic N to the water column through nutrient regeneration, sediments may also act as an N sink via denitrification. During denitrification, nitrate is converted to N_2 and thus lost from the ecosystem. Denitrification may be considered a cleansing process that can retard eutrophication of heavily nutrient-loaded coastal systems. The amount of nitrogen which is lost by denitrification in coastal systems varies greatly, ranging from 15 to 70% of the inorganic nitrogen released by mineralization (Seitzinger, 1988). Previous studies for the MWRA have focused principally on the role of denitrification in the Harbor. Special emphasis in this report is placed on time trends, both seasonal and interannual, in the Harbor as well as in the Bay. Additionally, the factors that may influence denitrification are examined.

Predicting the response of Massachusetts Bay to nutrient inputs from wastewater or other sources requires that nutrient recycling in sediment and the water column, and nutrient loss via denitrification

and advection all be taken into account. These complex relationships have been synthesized into a linked hydrodynamic—water quality model which will be used to make management decisions about Massachusetts Bay. This study provides information on the rates of benthic processes including oxygen consumption, nutrient regeneration, and denitrification, which can be used in testing the model.

2.0 SAMPLING DESIGN

The sampling sites are shown in Figure 1. All of the Harbor sites sampled in 1993 had been sampled in 1992. Several of the Bay sites sampled in 1992 could not be resampled and a number of new sites were established. Stations in Cape Cod Bay were sampled for the first time.

The station names used in 1992 have been changed to help eliminate confusion and to make the names more consistent with designations being used in the MWRA database. The former station names are given in the description of the station locations.

Surveys were carried out during late February, mid-May, mid-July, late August, and late October. Sampling was delayed by bad weather and boat problems during February, and the sampling which began on February 24 was not completed until March 4. All other surveys were completed in two or three days. The station locations, sampling dates, water depths, water temperatures, and dissolved oxygen at the sites are shown in Table 1.

2.1 STATION LOCATIONS AND RATIONALE

Harbor. During 1992, we made annual measurements of benthic processes at two stations: a sandy station in Hingham Bay (BH08, formerly called T8) and a muddy station off Long Island (BH03, formerly called T3) which received sludge until December 1991 (Giblin *et al.*, 1993; Kelly and Nowicki, 1993). A number of other Harbor sites have been sampled one to three times since 1990 (Giblin *et al.*, 1991; 1992; Kelly and Nowicki, 1992). The results of the previous studies showed that stations BH03 and BH08 differed greatly in the rates of all the benthic processes that were

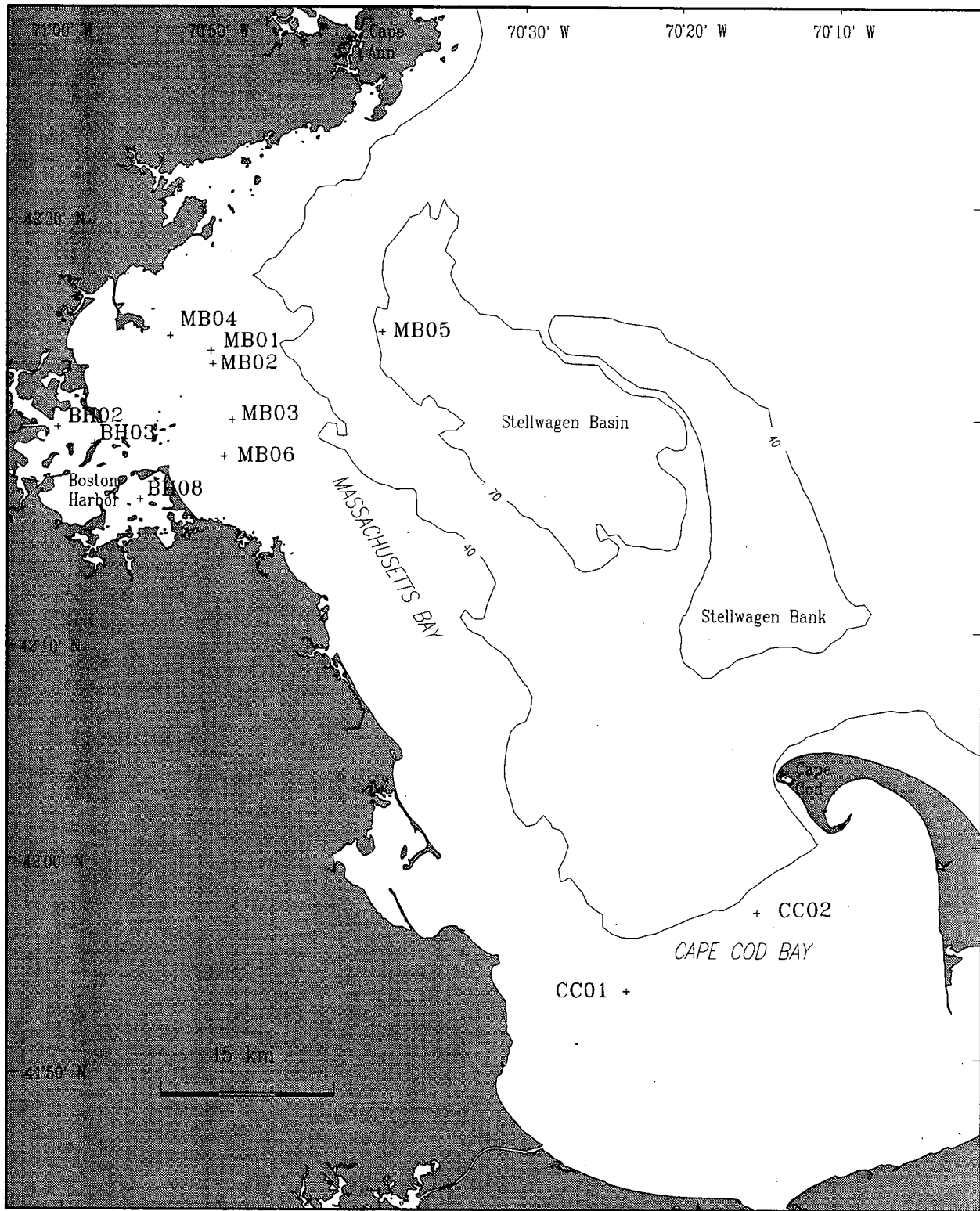


Figure 1. Benthic flux stations sampled in Boston Harbor, Massachusetts Bay, and Cape Cod Bay in 1993.

Table 1. 1993 Benthic flux station locations and associated bottom water quality information.

Event	Station	Date	Field Latitude			Field Longitude			Depth (m)	Temperature (°C)	Dissolved Oxygen (mg/L)
			deg	min	sec	deg	min	sec			
B9301	BH02	04-MAR-93	42	20	36.9	-71	0	2.2	12.2	1.6	11.0
B9301	BH03	24-FEB-93	42	19	47.4	-70	57	40.2	7.5	1.0	11.0
B9301	BH08	24-FEB-93	42	17	10.8	-70	54	41.4	11.6	1.0	10.7
B9301	MB01	02-MAR-93	42	24	9.6	-70	50	10.8	35.4	1.6	10.7
B9301	MB02	02-MAR-93	42	23	32.4	-70	50	1.8	38.6	1.7	10.8
B9301	MB03	02-MAR-93	42	20	52.2	-70	48	49.8	35.7	1.6	10.9
B9302	BH02	17-MAY-93	42	20	36.6	-71	0	1.8	9.8	12.3	9.2
B9302	BH03	17-MAY-93	42	19	48.0	-70	57	41.4	5.5	13.9	10.0
B9302	MB01	17-MAY-93	42	24	10.8	-70	50	9.6	33.7	4.5	10.1
B9302	MB02	17-MAY-93	42	23	32.0	-70	50	1.8	35.7	5.1	10.1
B9302	MB03	17-MAY-93	42	20	51.6	-70	48	54.6	36.3	5.4	10.3
B9302	MB06	17-MAY-93	42	19	9.0	-70	49	18.0	22.0	6.3	9.5
B9303	BH02	13-JUL-93	42	20	35.9	-70	59	59.3	11.6	17.0	8.9
B9303	BH03	13-JUL-93	42	19	48.0	-70	57	41.4	5.8	17.0	8.9
B9303	BH08	13-JUL-93	42	17	10.3	-70	54	45.7	13.0	15.7	8.8
B9303	MB01	12-JUL-93	42	24	10.1	-70	50	13.9	32.9	6.1	9.9
B9303	MB02	12-JUL-93	42	23	32.3	-70	50	4.9	33.5	5.5	9.6
B9303	MB03	12-JUL-93	42	20	53.5	-70	48	52.2	34.0	6.5	9.3
B9303	MB04	12-JUL-93	42	24	53.3	-70	52	52.7	29.6	6.6	10.1
B9303	MB06	12-JUL-93	42	19	12.0	-70	49	18.5	21.0	7.1	9.2
B9304	BH02	23-AUG-93	42	20	34.8	-71	0	3.6	9.8	18.3	8.1
B9304	BH03	23-AUG-93	42	19	48.0	-70	57	43.2	6.4	18.6	7.7
B9304	CC01	25-AUG-93	41	53	53.5	-70	24	15.1	34.1	8.7	9.2
B9304	CC02	25-AUG-93	41	57	29.9	-70	16	0.1	37.5	8.6	8.4
B9304	MB01	24-AUG-93	42	24	9.7	-70	50	12.5	32.3	10.2	8.9
B9304	MB02	23-AUG-93	42	23	33.0	-70	49	59.9	35.4	11.3	9.1
B9304	MB03	23-AUG-93	42	20	52.1	-70	48	53.3	36.6	9.6	9.2
B9304	MB05	24-AUG-93	42	25	0.5	-70	39	15.1	74.4	6.4	8.4
B9305	BH02	27-OCT-93	42	20	35.5	-71	0	0.0	11.0	12.5	7.9
B9305	BH03	27-OCT-93	42	19	49.1	-70	57	43.2	9.1	e	7.7
B9305	MB01	26-OCT-93	42	24	8.3	-70	50	6.7	32.3	10.5	7.1
B9305	MB02	26-OCT-93	42	23	33.0	-70	50	0.6	33.5	10.9	7.0
B9305	MB03	26-OCT-93	42	20	52.1	-70	48	57.6	33.5	e	e
B9305	MB05	26-OCT-93	42	25	3.0	-70	39	9.0	74.4	10.3	7.5

e: Data not reported

Stations BH02, BH03, and BH08 have been monitored for benthic macrofauna (as Stations T2, T3, and T8; see Kropp and Diaz, 1994).

Stations CC01, CC02, MB05, and MB06 have been monitored for benthic macrofauna (as Stations FF6, FF07, FF14, and FF13; see Coats *et al.*, 1995).

Other Massachusetts Bay Stations are in the vicinity of nearfield macrofauna sampling stations (see Coats *et al.*, 1995).

measured, and that these two stations represented extremes in the Harbor, with the highest rates nearly always being measured at station BH03 and the lowest rate measured at station BH08. However, with the cessation of sludge dumping in December 1991, conditions at station BH03 were changing rapidly and it was difficult to know how well this site represented the other muddy areas in the Harbor. The decision was made to continue to sample station BH03 to monitor recovery at this site but to also sample station BH02 (formerly called T2), another muddy station which had been sampled in August of 1991 and 1992, through an annual cycle. Station BH08 was sampled twice in 1993 to provide additional data to characterize sandy sites.

Bay. Prior to 1993, the Massachusetts Bay stations had only been sampled in autumn. Three stations from the nearfield area were chosen to be sampled over the annual cycle in 1993. Two sites, stations MB01 (formerly station W1) and MB02 (formerly station G8), are north and west of the future MWRA offshore diffuser and one station, MB03 (formerly station 11), is south and west of the Future Outfall. Two other stations were chosen just outside the nearfield area. Station MB04 is just outside the northeast corner of the nearfield, in the proximity of station G6 which was sampled in 1992. Station MB06 is south and west of station MB03. Both of these sites proved difficult to sample using a box corer and were only sampled once or twice. The deepest station (MB05) in Stellwagen Basin was sampled in August and October. We were unable to find suitable sampling locations between the diffuser and station MB05.

Two Cape Cod Bay stations, CC01 and CC02, were sampled in August. Data from these stations provide an initial comparison of flux rates relative to Massachusetts Bay and Cape Cod Bay sediments.

2.2 STATION DESCRIPTION

Harbor. The Harbor stations chosen for flux studies ranged from organic-rich, fine-grained sediments to hard sand and gravel. The stations have been previously described (Giblin *et al.*, 1993; Kelly and Nowicki 1993), but some differences at station BH03 in 1993 were noted.

Sediments at station BH03 were fine-grained and flocculent. A thick brown layer, which extended 6-10 cm below the surface of the sediment, was observed at this station during all sampling seasons. The depth of this brown layer was greater than what was observed in 1992. The tube-building ampeliscid amphipods, which appeared late in 1992, were present until October 1993. They were extremely numerous during the spring and summer. Benthic macrofauna sampling at this station in April 1993, recorded $> 27,000$ individuals m^{-2} of *Ampelisca* sp.; this and other amphipods were at a density $> 57,000 m^{-2}$ (Kropp and Diaz, 1994). In August 1994, this station had fewer individuals of the tube-mat taxon, *Ampelisca* sp., ($3,100 m^{-2}$), but the amphipods *Corophium bonelli*, *Unciola irronata*, *Phoxocephalus holbolli*, *Leptocheirus pinguis*, *Photis pollex*, and *Corophium crassicorne*—had a combined density $> 90,000 m^{-2}$ (Kropp and Diaz, 1994).

Station BH02 usually had a thin or absent oxidized surface layer with black sediments below. Benthic macrofauna were much less numerous at this station.

Sediments from station BH08 consisted of sand and gravel. There was a dense sand/shell/gravel layer at 8-10 cm depth at this site. Overall there was little color change with depth at this station.

Bay. Sediments from stations MB01, MB02 and MB03 were primarily fine-grained although on several occasions some sand was present. Animals were usually abundant. Qualitative observations suggest that station MB01 had greater numbers of animals than the other two Bay stations. Station MB04 and MB06 sediment contained some sand and gravel which frequently prevented us from obtaining a good sediment sample using the box corer. Sediments from station MB05 were very fine grained.

Cape Cod Bay stations were characterized by very soft sediments. Sipunculids were abundant at both stations. Station CC02 was covered with brittle stars, and large polychaetes were numerous.

3.0 METHODS

The methods used in this study have been previously described in Giblin *et al.* (1993) and in the CW/QAPP presented to MWRA (Kelly *et al.*, 1993a). They will be only briefly described here.

3.1 SAMPLING

All stations in Boston Harbor were sampled by SCUBA divers. The Massachusetts Bay samples were obtained with a box corer (40x40 cm or 50x50 cm). At each station, several sizes of sediment cores were taken. Two to three large 15-cm-diameter core tubes were used to obtain sediment for flux measurements. Replicate 6.5-cm-diameter core tubes were used to obtain sediment for porewater analysis. Three to four 2.5-cm-diameter cores were taken for porosity and solid phase analyses. Three to four additional cores, approximately 6.5-cm in diameter, were taken for direct measurements of N₂ flux. Bottom water temperature at all stations was determined by measuring the temperature of the near-bottom water collected in a Niskin sampler. Salinity was measured with a refractometer.

At each station 15 liters of water were collected with a diaphragm pump from just above the bottom and immediately filtered through a series of cartridge filters (nominally 20 and 1.0 μm). This water, which was held at *in-situ* temperatures, was used to replace the water in the cores collected for flux measurements.

3.2 BENTHIC RESPIRATION AND NUTRIENT FLUXES

Cores were transported to Woods Hole, MA, and placed in a dark incubator where they were held uncapped, overnight, at the *in-situ* temperature of the station. Flux measurements were begun within 12-48 h of sampling. Prior to initiating flux measurements, the overlying water of each core was replaced with the filtered seawater collected at each station. Two BOD bottles, filled with the filtered water from each station, were used to correct for respiration in the water overlying the sediments. Cores were sealed with core tops containing magnetic stirrers (Dornblaser *et al.*, 1989) and gently mixed. We monitored concentrations of oxygen in the overlying water throughout the incubation period. Incubation duration was determined by the time required for oxygen concentrations to fall by 2 to 5 ppm (generally 6 to 48 h). Water samples were taken periodically from each core throughout the incubation period. Benthic respiration was calculated as the slope of oxygen concentration versus time. The values were corrected for the oxygen (O₂) uptake in the water overlying the cores by using O₂ changes measured in BOD bottles. Taking measurements over time enabled us to determine whether oxygen consumption was linear over time.

Concurrent with O₂ measurements, samples of the overlying water were withdrawn for dissolved inorganic nitrogen and phosphorus, urea, and silicate analysis. Ammonium concentration was determined within 12 h from duplicate 3-mL subsamples by the technique of Solorzano (1969), modified for small sample size. A 3-mL sample for phosphate analysis was acidified to pH 2 with 10 μ l of 4.8N HCl and stored at 4°C until analysis. Samples were analyzed using the spectrophotometric method of Murphy and Riley (1962).

Additional water was frozen for later measurement of the nitrate + nitrite, silicate, and urea concentrations. Nitrate + nitrite was determined together using the cadmium reduction method on a rapid-flow analyzer (Alpkem RFA-300). Although the CW/QAPP reported a detection limit of $>0.5\mu\text{M}$, the detection limit in the 1993 analyses was considerably lower, $0.1\mu\text{M}$. DIN was calculated as the sum of ammonium, nitrate, and nitrite. Silicate was analyzed by reduction with stannous chloride using an autoanalyzer (Armstrong, 1951, as adapted by RFA, Alpkem Corp., 1986). Urea was analyzed by the method of Price and Harrison (1987).

At the beginning and end of the incubation period, 60-mL samples were also taken for total CO₂ analysis. These samples were stored at 4°C in glass BOD bottles with mercuric chloride as a preservative. Samples were analyzed with a high-precision coulometric CO₂ analyzer maintained by C. Goyet at the Woods Hole Oceanographic Institution. The instrument is capable of measuring total CO₂ with a precision of 0.05% ($1\mu\text{M}$).

3.3 POREWATER SAMPLING AND ANALYSIS

Sediment samples for extraction of porewater were sectioned into depth intervals in a glove bag under a nitrogen atmosphere. Sediments were sampled in 1-cm intervals down to 2 cm, 2-cm intervals to 10-cm and then in 4-cm intervals at greater depths. Nutrients, urea, silicate, sulfides (Cline, 1969), pH, and alkalinity (Edmond 1970) in porewaters were analyzed as previously described in Giblin *et al.* (1992). Sediment redox potential (Eh) was measured with a platinum electrode (Bohn, 1971). Eh measurements were made on a separate core. The values reported have been corrected for the potential of the reference electrode.

3.4 POROSITY AND SEDIMENT CARBON AND NITROGEN

Sediments were sectioned in 1-cm intervals to a depth of 10 cm and then in 2-cm intervals to the bottom of the core. Sediment wet weight was measured immediately and dry weight was measured after a minimum of 72 h in a 105°C oven. Porosity was measured on two sediment cores from each station and is defined as the (volume of water in the depth interval sampled)/(total volume of water + sediment).

Organic carbon and nitrogen analyses were performed on a Perkin Elmer 2400 CHN elemental analyzer following carbonate removal. The percent carbon and nitrogen measured in the sediment was corrected for the weight change due to the procedure.

3.5 DIRECT DENITRIFICATION

Sediment denitrification was measured as a direct flux of nitrogen (N_2) gas from sediment cores placed in gas-tight N_2 -free chambers. On each sampling date, two sediment cores were incubated from each site, one core was used for measurements of total sediment N_2 flux ("experimental core") and the other core was a control for background N_2 de-gassing ("control core"; Nowicki, 1994). To assess core-to-core variability, duplicate experimental cores were taken from stations BH03 and BH08 in April, May, June, and November of 1992.

A detailed description of sampling and measurement methods is given in Kelly and Nowicki (1993) and Nowicki (1994). Briefly, the surface 5 cm of each sediment core (0.005 m² x 20 cm deep) was placed, intact, into a gas-tight incubation chamber. Ambient seawater was placed over the sediments in the incubation chambers, and the chambers were maintained in the dark, at ambient temperatures, with constant stirring (Nowicki, 1994). The overlying seawater and a gas-filled head space in each chamber were sparged with a mixture of helium and oxygen (80 He:20 O₂) to remove nitrogen but to maintain dissolved oxygen concentrations at levels similar to those observed in bottom waters in the field. Control cores, taken at the time of sediment sampling, were treated in the same manner as the experimental cores, but were maintained without oxygen so that denitrification was effectively blocked. These anoxic control cores were used to monitor and correct for background fluxes of N_2

(due primarily to porewater de-gassing into the N₂-free head space) which were not caused by denitrification (Nowicki, 1994).

Measurements of the nitrogen and oxygen concentrations in the gas-filled head space of each chamber were determined from samples (50 μ L) withdrawn from the chamber sampling port with a gas-tight syringe. Concentrations of nitrogen and oxygen in the gas samples were measured with a Hewlett Packard Model 5890A gas chromatograph equipped with a thermal conductivity detector. Calibration curves, using a certified standard gas mixture, were run with each set of samples.

A detailed description of the method used for calculating sediment denitrification rates is given in the CW/QAPP plan (Kelly *et al.*, 1993a). Briefly, rates of N₂ gas production and O₂ uptake for sediments in the denitrification chambers were calculated from the slopes of four-point linear regressions of N₂ or O₂ concentration in the gas phase of each chamber over time. Statistical confidence limits were determined by calculating 95%-confidence intervals around the slopes of these regressions. Confidence intervals were calculated for fluxes from both the experimental cores and the anoxic control cores, and errors in the final calculated flux were propagated according to Ramette (1981). A Student's T-test was used to compare mean denitrification rates from different sampling stations or times.

3.6 DENITRIFICATION USING THE STOICHIOMETRIC METHOD

The stoichiometric method of measuring denitrification is an indirect method that relies on two assumptions. The first is that the amount of organic matter being decomposed within the sediments can be estimated from fluxes of decomposition end products across the sediment-water interface. The second assumption is that the elemental (C:N:P:O) ratio of the material being decomposed is known. The rate of decomposition and the elemental ratio of the material being decomposed are used to calculate an expected N flux from the sediments. The expected N flux is compared to the sum of the measured flux of ammonium and nitrate (DIN) from the sediments. Missing nitrogen is assumed to have been denitrified.

In Giblin *et al.* (1993) we thoroughly discuss the assumptions and problems with this method. We also compared three different ways to measure total sediment decomposition: oxygen uptake, oxygen uptake + alkalinity flux, and total DIC fluxes. Based upon that study we concluded that DIC fluxes were probably the best measure of total sediment metabolism for the calculation of denitrification. In this study we use DIC fluxes to calculate denitrification using the stoichiometric method. While DIC fluxes should be an accurate measure of total carbon decomposition, there is still the possibility of an artifact from carbonate dissolution or precipitation. Using the deviation of the DIC/DIN ratio from the Redfield ratio to estimate denitrification when substantial quantities of carbonate are being dissolved or precipitated will lead to an overestimation or underestimation of denitrification. For this study we assumed that the organic matter being decomposed had a C/N ratio of fresh phytoplankton and expected to see a DIC/DIN ratio of 6.625 in the absence of denitrification.

4.0 RESULTS AND DISCUSSION

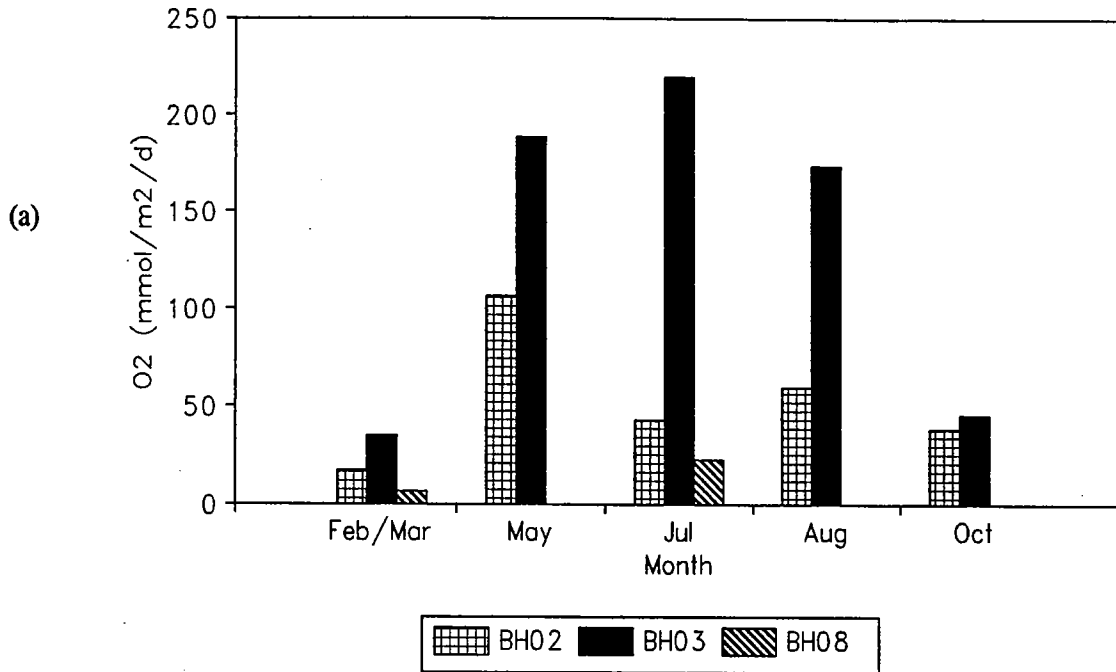
4.1 BENTHIC RESPIRATION AND NUTRIENT FLUXES

4.1.1 Oxygen Uptake*

Harbor. Sediment oxygen uptake ranged from approximately 7 to 220 mmol O₂ m⁻² d⁻¹ between February and October 1993 (Figure 2a). Respiration was always higher at station BH03 than at any of the other Harbor sites sampled in 1993, and rates were lowest at station BH08, consistent with the results from 1992 (Giblin *et al.*, 1992). Oxygen uptake rates at station BH03 increased throughout the spring and summer, reached maximal values in July, and then decreased. Stations BH02 and BH08 were not always sampled in 1992, and the sample collections that were made in 1993 did not correspond exactly to the times that these stations were sampled in 1992. However, comparing the August 1992 and 1993 data at station BH02, it appears that respiration rates were similar in both years. The rates observed at station BH08 in February and July 1993 are consistent with the pattern observed at this station in April and August of 1992. In contrast, for most of the year, we observed

*O₂ uptake was measured in large cores used for nutrient flux measurements by the Marine Biological Laboratory (MBL). It was also measured in denitrification cores by the University of Rhode Island (URI) as an ancillary measurement. Both rates are reported in the MWRA database, but MBL measurements are used in this report.

O₂ UPTAKE
Boston Harbor Stations 1993



Harbor Station BH03, 1992 and 1993

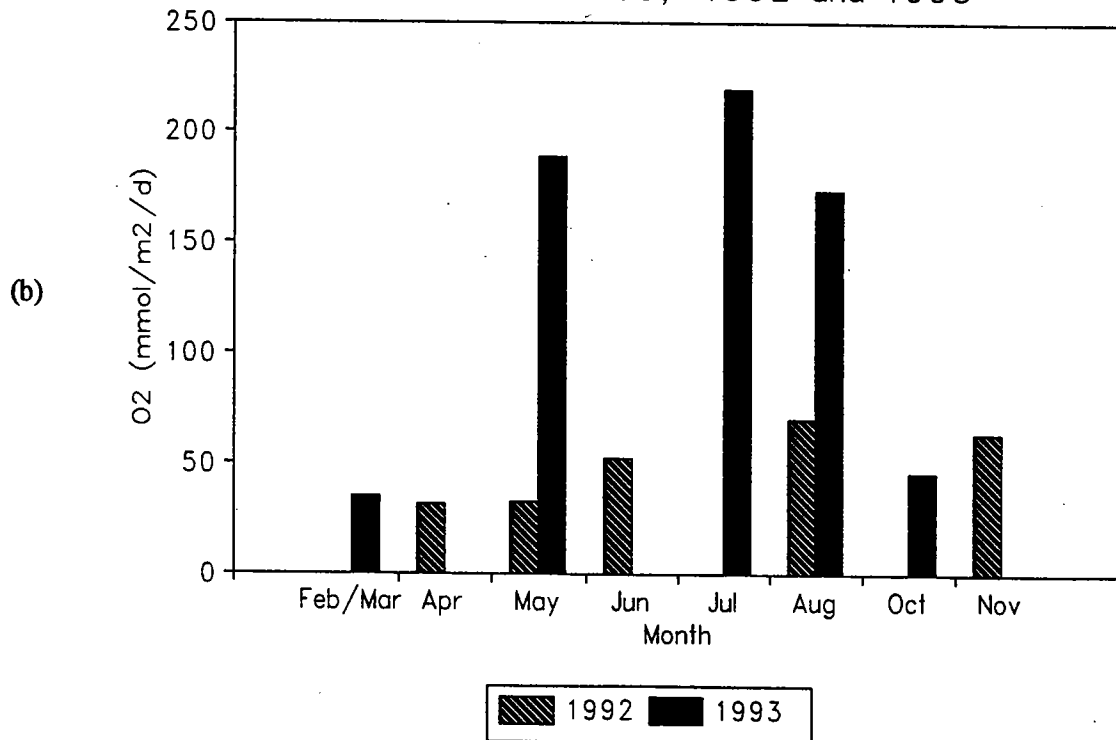


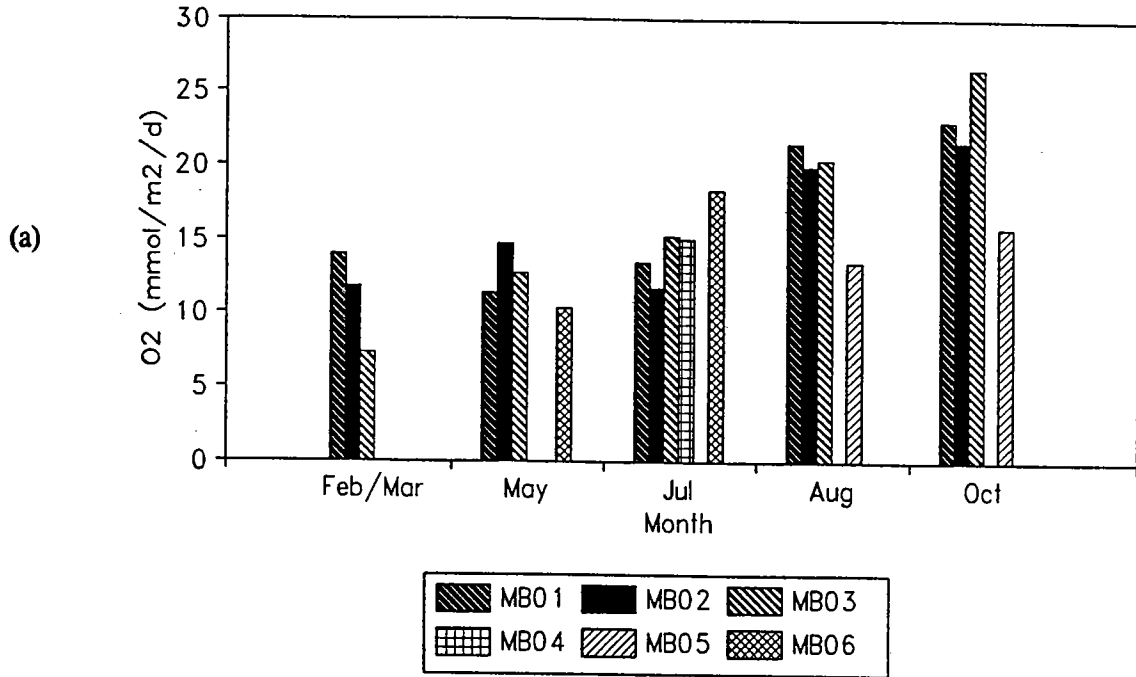
Figure 2. (a) Sediment oxygen uptake at the Boston Harbor stations in 1993. (b) Comparison of sediment oxygen uptake in 1992 and 1993 at Boston Harbor station BH03. Values are means of measurements from duplicate sediment cores.

much higher rates of oxygen uptake at station BH03 in 1993 than in 1992 (Figure 2b). The seasonal cycle of oxygen uptake at this station was also different between the two years. We believe that the difference between the two years is related to the large numbers of amphipods that colonized station BH03 in the late summer of 1992. These amphipods were observed in very high numbers late in 1992 and were present during the first four sampling periods in 1993. In October 1993, when the amphipods had largely disappeared, oxygen uptake was lower than in November 1992.

Bay. Average oxygen uptake rates at the Bay stations ranged from about 7 to 27 mmol O₂ m⁻² d⁻¹ (Figure 3a) and exhibited much less seasonal change than at the Harbor stations. There was no consistent difference in the respiration rates between any of the shallow Massachusetts Bay stations (MB01, MB02, MB03, MB04, and MB06). The 1993 rates are also similar to rates measured in these stations and at a nearby station in October and November of 1992 (Giblin *et al.*, 1992). Respiration rates at station MB05, which is in deeper and generally cooler water, were lower than at any of the other Massachusetts Bay stations in both months that samples were collected. Respiration rates of the two Cape Cod Bay stations were also lower in August than the shallow Massachusetts Bay stations.

The average respiration rates at all the shallow Massachusetts Bay stations were lowest in February and increased over the sampling period, peaking in October. Temperature, in part, appears to account for this seasonal pattern and perhaps also for some differences in the respiration rates among areas of the Bay. When respiration rate is plotted against temperature (Figure 3b), a relationship is evident. The correlation, however, was low using all the Bays stations ($R^2=0.15$ for linear fit, $R^2=0.21$ for exponential fit; $n=22$ for both). Station MB05 and the two Cape Cod Bay stations were colder *in situ* than the other stations during the August sampling period (Table 1). Although the August samples from all Bays stations were incubated at the same temperature (~ 9 °C), respiration rates at stations MB05, CC01, CC02 were lower. If the data are restricted to the five remaining (nearfield) stations, the correlation with temperature is high. A significant linear regression ($R^2=0.74$, $n=17$, $p<0.001$) was obtained as O_2 uptake = 1.38 (Temperature) + 6.76 . The fit was not improved by an exponential model. Station depth may also be a factor influencing the respiration rate. Station MB05 had lower respiration rates than the shallower stations in October when all the stations were sampled and incubated at the same temperature. Other researchers have noted that sediment respiration decreases with increasing water depth because more decomposition takes place in

O₂ UPTAKE
Massachusetts Bay Stations 1993



O₂ UPTAKE vs TEMPERATURE
Massachusetts Bay Stations 1993

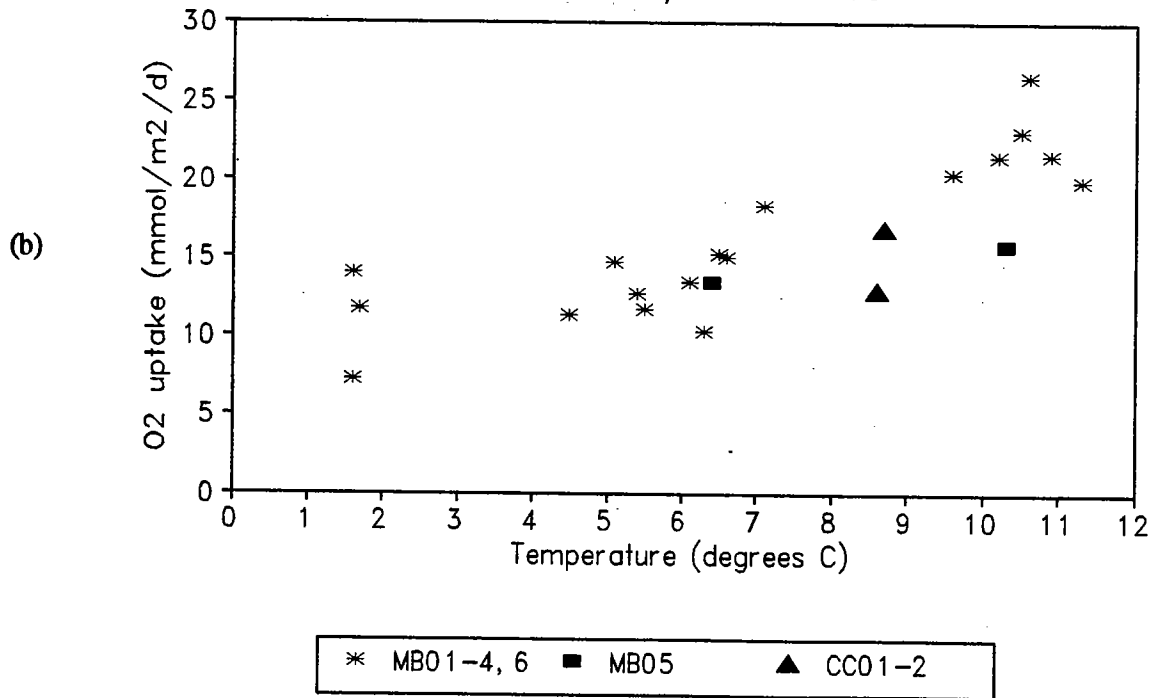


Figure 3. (a) Sediment oxygen uptake at the Massachusetts Bay stations in 1993. Values are means of measurements from duplicate sediment cores. (b) Relationship of oxygen uptake rates to bottom water temperatures at the Massachusetts and Cape Cod Bays stations in 1993. Note the change in scale for the y-axis compared to Figure 2.

the water column (Hargrave, 1975). However, samples from a more complete seasonal cycle would be needed to verify this.

Differences between the respiration rates at the Bay stations were not related to carbon concentrations in the sediments. Sediments in Massachusetts Bay exhibit considerable resuspension during storms (M. Bothner, USGS, personal communication). The carbon content of the sediment probably does not reflect the inputs of fresh organic matter to the bottom.

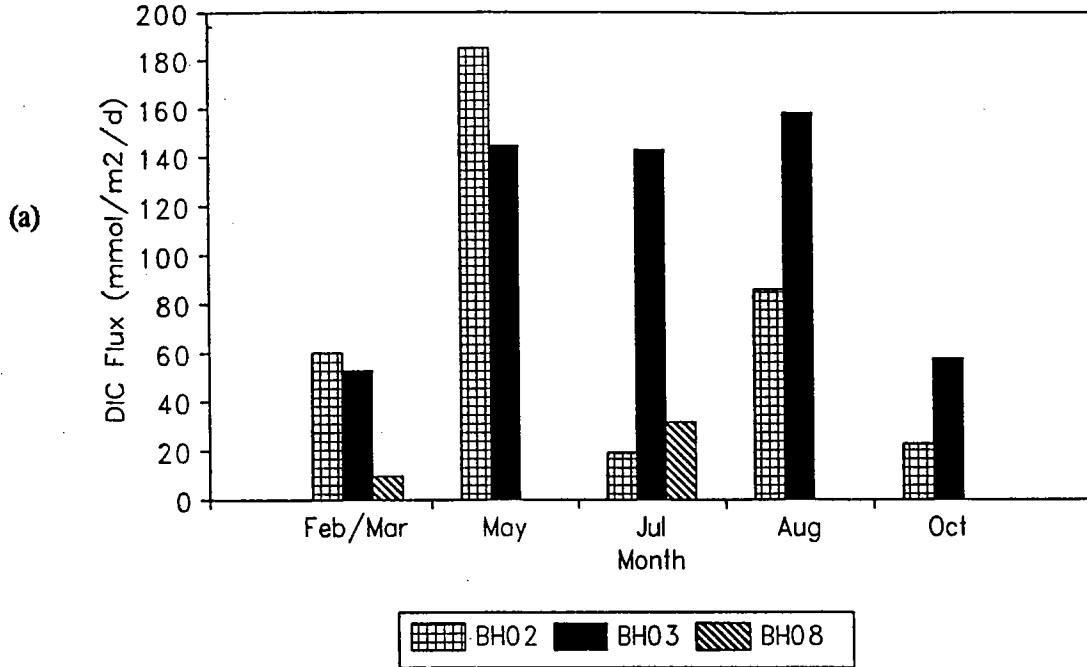
4.1.2 Total CO₂ Measurements

Harbor. Total CO₂ fluxes at Harbor stations ranged from approximately 10 to 185 mmol CO₂ m⁻² d⁻¹ between February and October 1993 (Figure 4a). The seasonal pattern of DIC fluxes differed somewhat from oxygen uptake. Fluxes were higher at station BH02 than at station BH03 during the beginning of the year but higher at station BH03 during the summer and autumn. Integrated over an annual cycle, however, the DIC fluxes and the oxygen uptake rates among the Harbor stations showed the same pattern of the highest respiration at station BH03 and the lowest at station BH08.

The ratio of DIC release to oxygen uptake (RQ or respiratory quotient) showed the widest range at station BH02, where the RQ varied from 0.44 to 3.48. Integrated over the annual cycle, DIC release accounted for 141% of the oxygen uptake (i.e., an RQ of 1.41). At station BH08 the RQ range was much narrower but the average at this station was the same as at station BH02. The RQ values at station BH03 were lower than at the other stations and had a seasonal average of 0.84. This was the only station where oxygen uptake exceeded DIC release.

The aerobic respiration of organic matter of a "Redfield" composition should have an RQ of about 1. Oxygen is a good indicator of total decomposition on an annual basis, even in systems where anaerobic processes, such as sulfate reduction, are important because most of the reduced end products of decomposition are ultimately reoxidized. On a seasonal basis, however, sulfur storage can change considerably, resulting in the oxygen measurement overestimating respiration at some times of the year and underestimating it at other times. However, over an annual cycle, the RQ should approach 1. Deviations from an RQ of 1 closely reflect the portion of sulfide that is permanently buried as pyrite or FeS. The annual RQ value of 1.41 measured at station BH02 would

DIC FLUX Boston Harbor Stations 1993



Massachusetts Bay Stations 1993

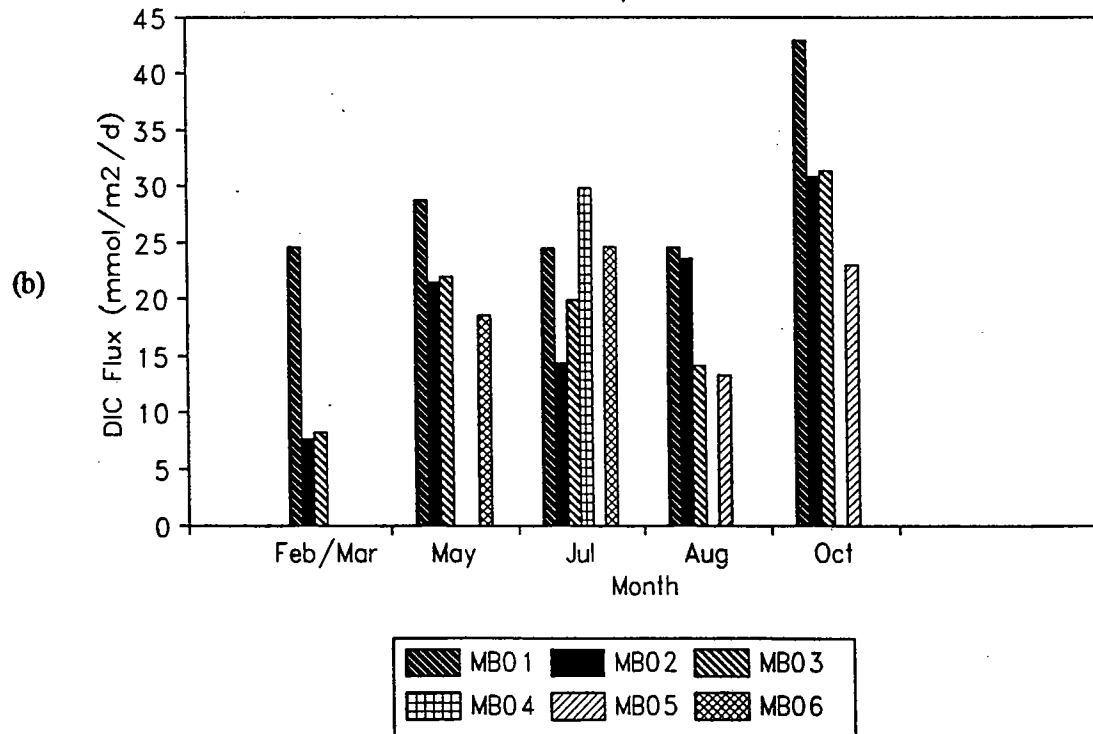


Figure 4. Flux of DIC (total CO₂ at (a) the Boston Harbor stations and (b) the Massachusetts Bay stations in 1993. Values are means of measurements from duplicate sediment cores.

reflect a high, but not unreasonable level of sulfur storage. The low RQ observed at station BH03 indicates that more sulfides were oxidized than were produced over the season. Although unusual, we believe that this is possible at this station. Both visual observations and porewater data indicate that in 1993 the sediments were less reducing at 4-8 cm than in 1992. This change in sediment oxidation could lead to a loss of sulfur which had been stored in previous years when the sediments were less reducing. In 1992, the RQ at station BH03 was greater than 1.

Bay. In Massachusetts Bay, total CO₂ fluxes ranged from about 7.8 to >40 mmol C m⁻² d⁻¹ (Figure 4b). On most occasions, DIC fluxes were higher than O₂ uptake and the average RQ at all Bay stations exceeded 1. A comparison of the three stations where annual data are available indicates that of all the Bay stations, the highest RQ (1.75) was at station MB01. Similar RQ values of 1.23 and 1.17 were determined for stations MB01 and MB03, respectively.

The annual RQ values observed at stations MB02 and MB03 are smaller than those observed at station BH02 and consistent with values reported in other studies. The value determined for station MB01 appears quite high and may indicate that considerable sulfur is being stored at this site or that some other process is affecting the RQ. One possibility is that the DIC flux is being enhanced by carbonate dissolution at this site. Few studies have evaluated changes in the carbonate inventory in temperate sediments. McNichol *et al.* (1988) found that carbonate dissolution enhanced DIC fluxes in Buzzards Bay 2% in the spring, but that carbonate dissolution was unimportant for the rest of the year. Examination of calcium profiles in the porewater did not reveal strong evidence for carbonate dissolution but the possibility deserves further investigation.

4.1.3 DIN Release from Sediments

Harbor. The combined flux of ammonium, nitrate, and nitrite from sediments to the overlying water ranged over two orders of magnitude, from about 0.2 mmol N m⁻² d⁻¹ at station BH08 in February to 20 mmol N m⁻² d⁻¹ at station BH03 in July (Figure 5a). The general seasonal pattern of DIN release matched that of oxygen uptake fairly well. Differences between the stations were also similar to that of oxygen uptake (i.e., the highest fluxes were usually observed at station BH03 and the lowest at station BH08).

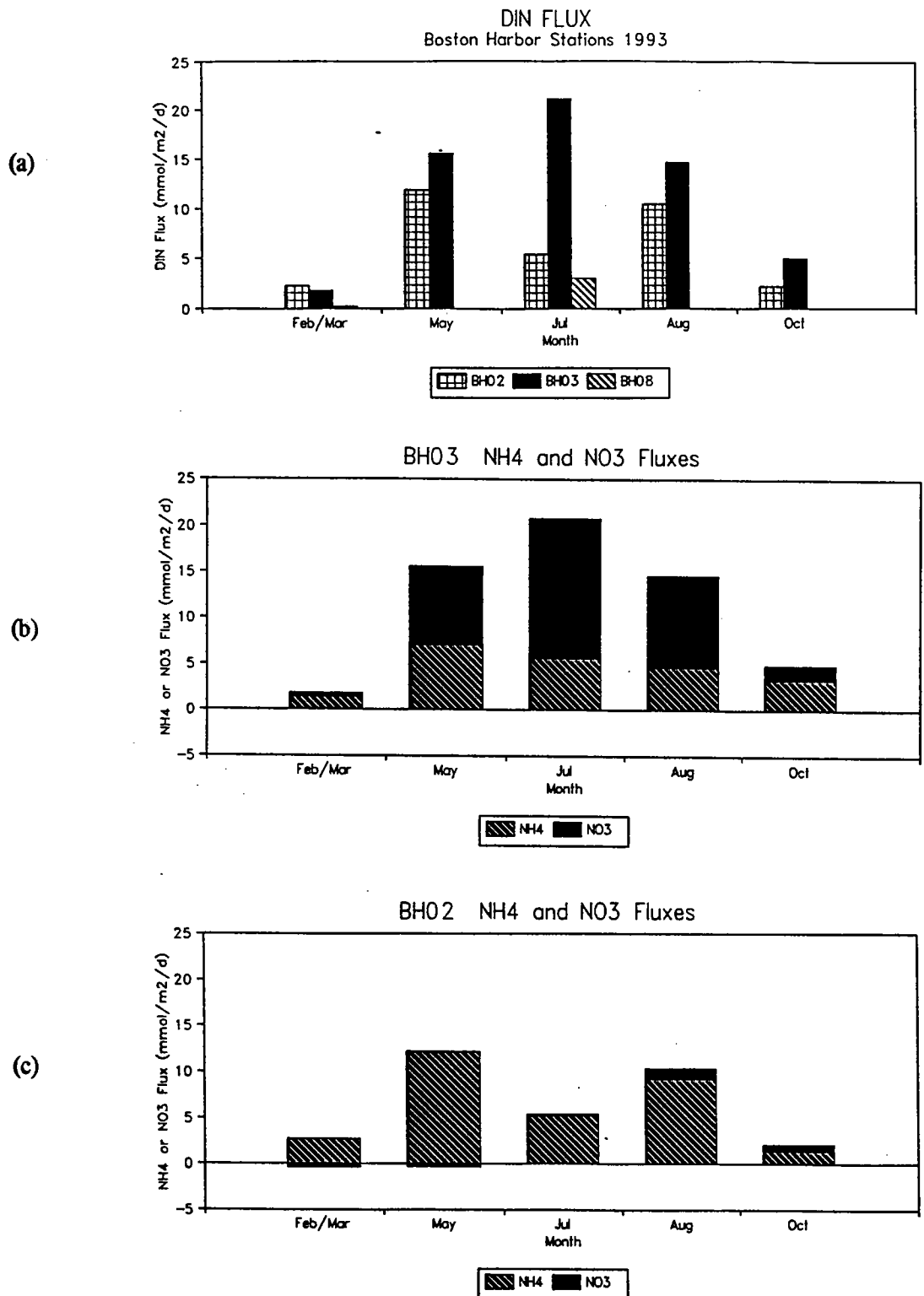


Figure 5. Nitrogen fluxes at the Boston Harbor stations in 1993. (a) Total DIN (NH₄ + NO₃ + NO₂) flux. (b) Total DIN flux at station BH03 separated into components of NH₄ and NO₃ (includes NO₂). (c) Total DIN flux at station BH02 separated into components of NH₄ and NO₃ (includes NO₂). Values are means of measurements from duplicate sediment cores.

The proportion of the DIN flux which was made up of nitrate + nitrite (hence referenced simply as nitrate) was consistently higher at station BH03 than at station BH02 (Figure 5b,c). During the first two sampling periods uptake of nitrate by the sediment at station BH02 was observed. The percentage of the sediment DIN flux that consisted of nitrate increased over the season at station BH02 and reached a maximum of 38% in October. In contrast, an efflux of nitrate from the sediments was observed at station BH03 at all times of the year and, during the spring and summer measurements, nitrate fluxes were greater than ammonium fluxes. Nitrate fluxes ranged from 28-80% of the DIN flux at station BH08.

There were large interannual differences in the nitrogen dynamics at station BH03. The DIN flux in May, July, and August of 1993 greatly exceeded that observed during a similar period in 1992, and the percentage of nitrate was much greater. The high percentage of nitrate is further evidence that these sediments were more oxidized in 1993 than in 1992.

Bay. Release of DIN from Bay sediments ranged from a low of $0.14 \text{ mmol N m}^{-2} \text{ d}^{-1}$ to a high of $2.2 \text{ N mmol N m}^{-2} \text{ d}^{-1}$ (Figure 6a). In contrast to what we observed in the Harbor, there was little seasonal pattern and a poor correlation with temperature. Also, the pattern of DIN release did not match the oxygen uptake pattern. There was no consistent pattern among the shallow Bay stations, but DIN release rates from the deep station (MB05) were lower than that of the shallow stations. Cape Cod Bay stations fell in the same range as the Massachusetts Bay stations.

Nitrate fluxes changed direction over the season at all of the shallow Massachusetts Bay stations. We observed a small amount of nitrate uptake during February and October at stations MB01, MB02, and MB03, while sediments characteristically produced nitrate during the spring and summer. Nitrate comprised 5-25% of the DIN flux from the sediments at stations MB01, MB02, MB03, MB04, and MB06 (i.e., illustrated with station MB01, Figure 6b). During the spring and summer nitrate, was a more important component of the DIN flux at station MB03 than at the other shallow stations, averaging 42% for this period (Figure 6c). Nitrate fluxes at the two Cape Cod Bay stations during August ranged from 20-35% of the total DIN flux. Nitrate fluxes at the deeper station MB05 ranged from 38% in August to 100% in October.

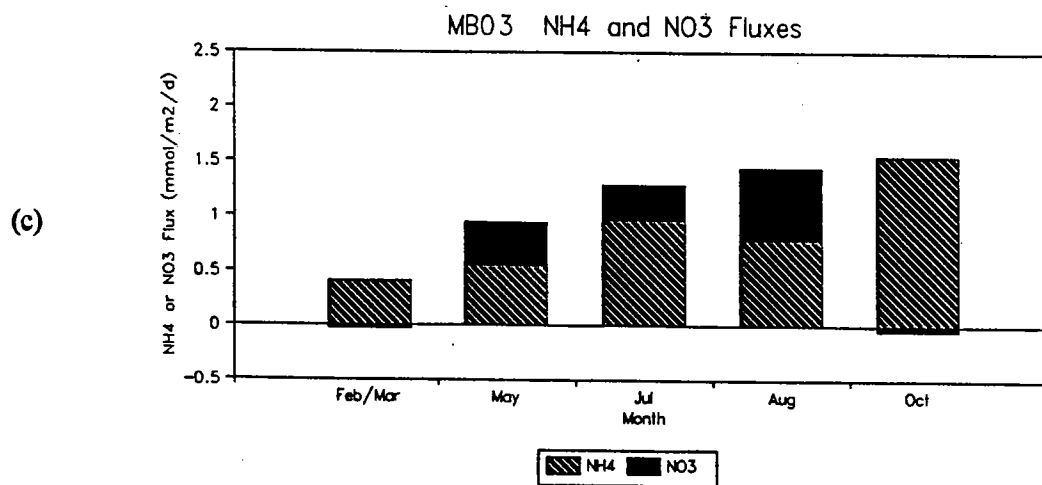
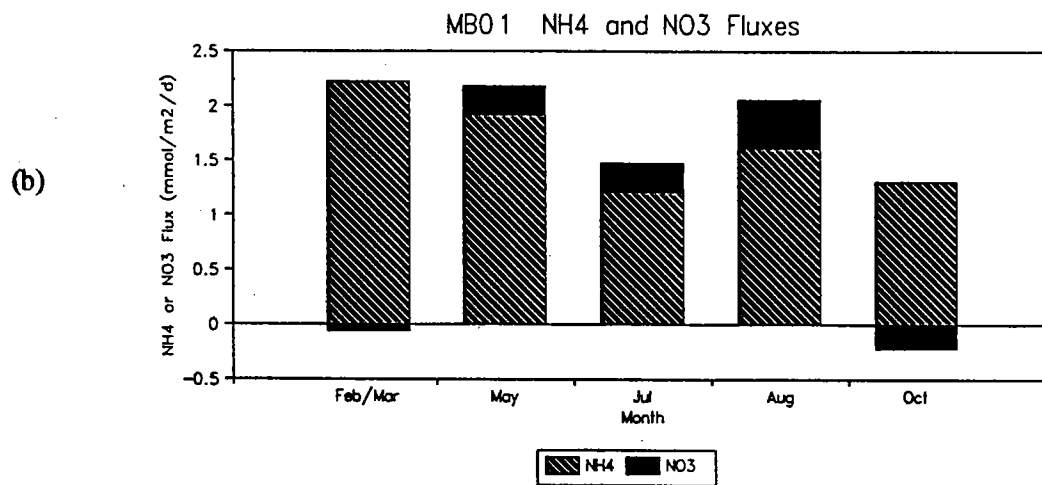
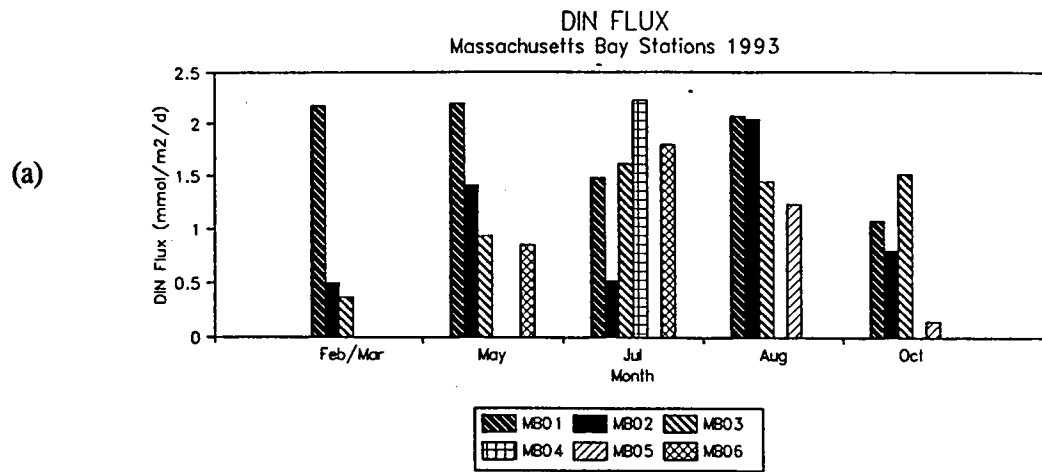


Figure 6. Nitrogen fluxes at the Massachusetts Bay stations in 1993. (a) Total DIN (NH₄ + NO₃ + NO₂) flux. (b) Total DIN flux at station MB01 separated into components of NH₄ and NO₃ (includes NO₂). (c) Total DIN flux at station MB03 separated into components of NH₄ and NO₃ (includes NO₂). Values are means of measurements from duplicate sediment cores.

4.1.4 Urea Fluxes

Urea is a nitrogenous compound excreted by some types of macrofauna. There have been a few reports of areas where urea makes a substantial contribution to the N flux from sediments. Unfortunately, a number of our samples had significant urea contamination. The source of contamination has been traced to the polyurea caps on the sample vials. Acid washing apparently caused the caps to break down and contaminate the samples. Because the data have been compromised, they are not reported in the database; however, the limited set of data suggests that urea is usually not an important contributor to N flux at these stations. We usually did not see any trend in the urea concentrations over time. If the samples in which urea concentrations exceeded 5 μM (which we feel were contaminated) are eliminated, trends in urea fluxes are still not apparent except at station MB02 where the fluxes averaged 0.53 $\text{mmol m}^{-2} \text{d}^{-1}$ in August. The regression at this station was significant and the replicate cores agreed reasonably well. Non-contaminating sample vials are now being used to collect samples for the urea analyses, which will be continued in 1994.

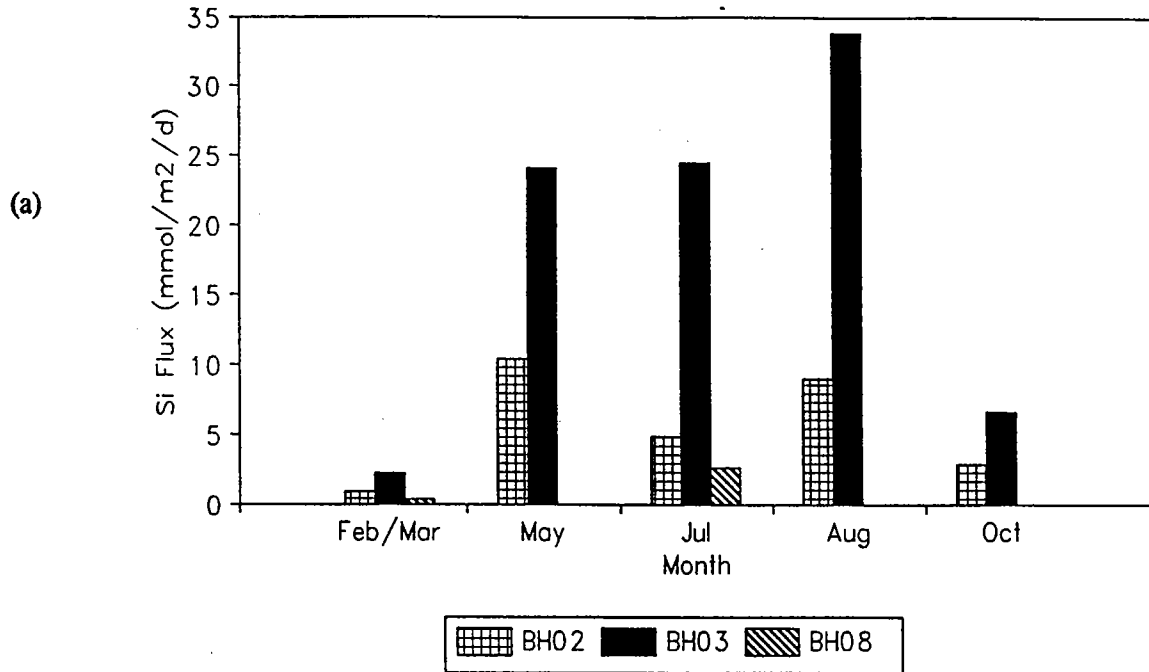
4.1.5 Silica Fluxes

Harbor. Silica fluxes ranged from 0.34 at station BH08 in February to $> 34 \text{ mmol m}^{-2} \text{d}^{-1}$ at station BH03 in August (Figure 7a). The station-to-station differences are the same as we observed for nearly all of the other parameters; fluxes were highest at station BH03 and lowest at station BH08. Silica release rates were highest in the spring and summer.

Bay. Silica fluxes ranged from 1.8 $\text{mmol m}^{-2} \text{d}^{-1}$ to 9.4 $\text{mmol m}^{-2} \text{d}^{-1}$ and followed a pattern similar to the oxygen uptake. There were no consistent differences between stations over the course of the season, even at station MB05 (Figure 7b). The pattern of silica release was correlated to temperature but there was more scatter than in the relationship between temperature and oxygen. A linear regression of flux as a function of temperature for the five Massachusetts Bay nearfield stations was significant ($R^2=0.47$, $n=18$, $p<0.002$), but an exponential fit was slightly better ($R^2=0.54$, $n=18$, $p<0.0001$).

Although Si fluxes on an absolute basis were higher in the Harbor than in the Bay, relative to DIC release, Si fluxes were higher in the Bay. The annual atomic Si/DIC flux ratio at station BH02 was

Si FLUX Boston Harbor Stations 1993



Massachusetts Bay Stations 1993

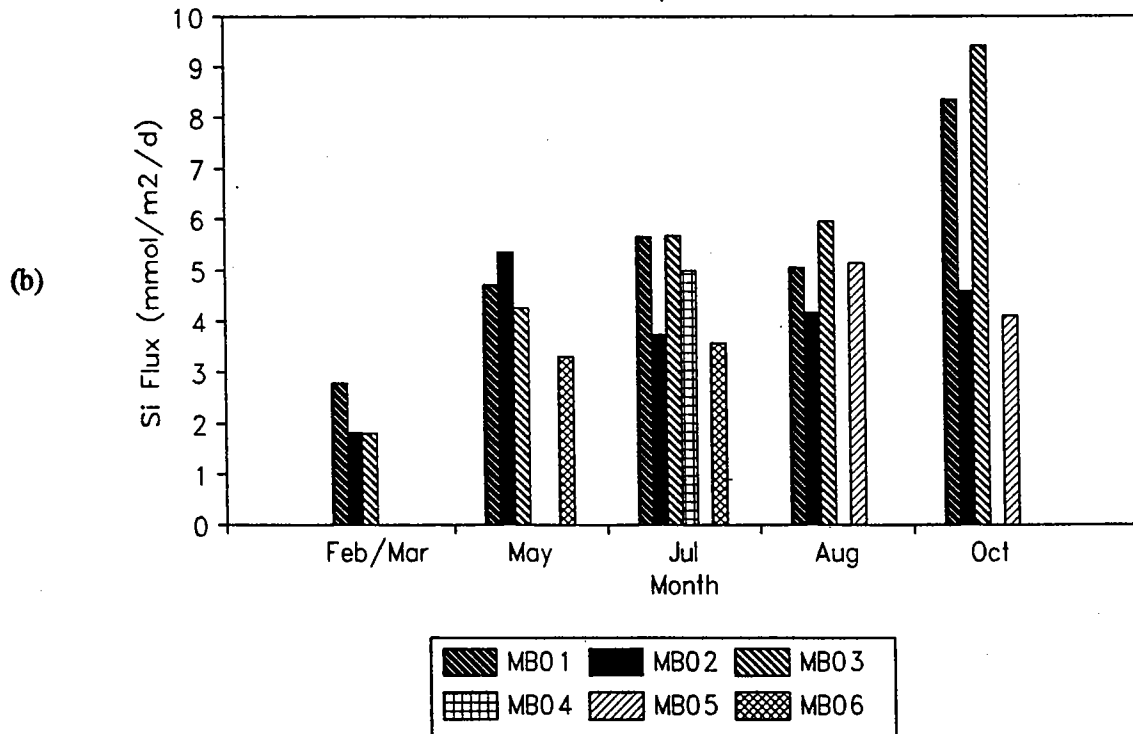


Figure 7. Silica fluxes at (a) the Boston Harbor stations and (b) the Massachusetts Bay stations in 1993. Values are means of measurements from duplicate sediment cores.

0.08 and 0.16 at station BH03. Annual Si/DIC flux ratios at the nearfield stations ranged from 0.18 to 0.28. It is difficult to establish the expected Si/DIC ratio. Richards (1958) calculated an average atomic ratio of 0.14 for the western North Atlantic. Using dissolved Si and O₂ data, Strickland (1965) found that a ratio of 0.34 was typical of marine phytoplankton. The flux ratio in sediments is influenced by the proportion of the organic matter derived from phytoplankton with Si frustules as opposed to other organic matter sources. Therefore, it is not surprising that the Harbor stations have a lower ratio than the Bay.

4.1.6 Phosphate Flux

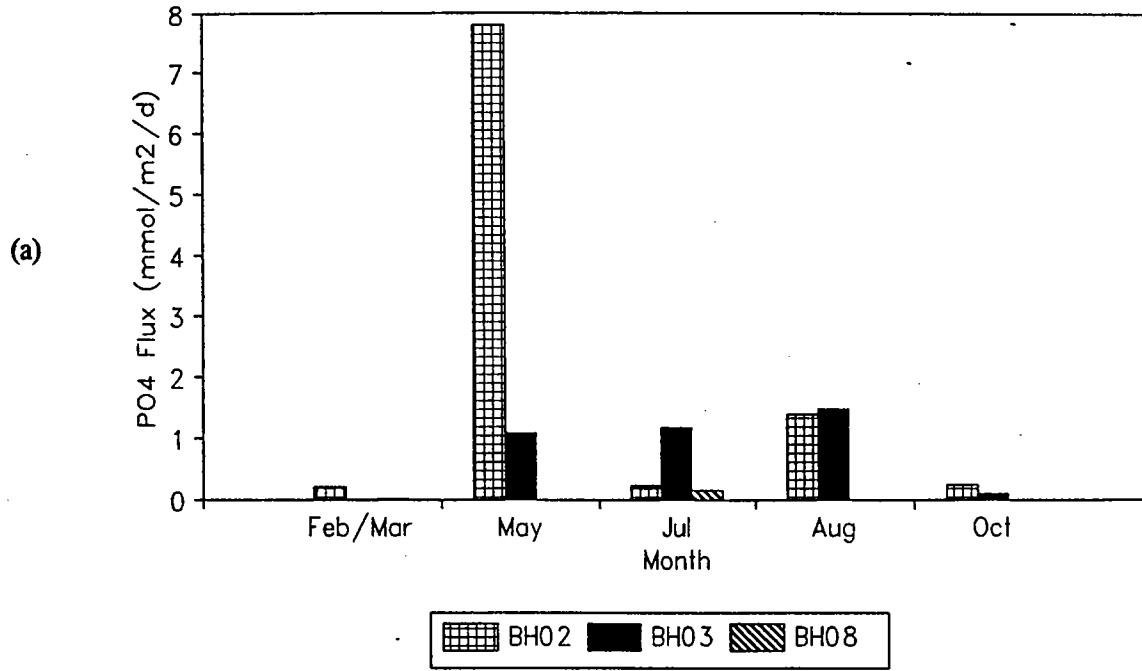
Harbor. Phosphate fluxes ranged from 0 to nearly 8 mmol P m⁻² d⁻¹ (Figure 8a). Although fluxes were higher in the spring and summer there was no relationship between phosphate flux and temperature. In contrast to the fluxes of C, O₂, Si or DIN at Harbor stations, DIP fluxes were often higher at station BH02 than at BH03. This is consistent with other monitoring data that indicate that these sediments are more highly reducing than sediments from other sample locations. The release of phosphate at any of the stations sampled in 1993 was not markedly different from fluxes observed in 1992.

Bay. In February, phosphate was either taken up by Bay sediments or there was no measurable flux (Figure 8b). During the rest of the year, phosphate was released from the sediments at all but two of the Bay stations. At station MB05 and one of the Cape Cod Bay stations, uptake of phosphate from the overlying water column was measured. Phosphate fluxes at the Bay stations resembled fluxes measured at the Harbor stations and did not show a strong linear regression with temperature ($R^2=0.20$, $n=18$, $p<0.06$ for nearfield stations). The fluxes observed in 1993 were consistent with the phosphate fluxes observed in the autumn of 1992.

4.2 SEDIMENT CARBON AND NITROGEN

Harbor. The three Harbor stations differed greatly in their carbon content (Table 2). Station BH08 had the lowest carbon concentration of 0.27%. Station BH03 had the highest carbon concentrations varying from 3.1% to 3.7%. The carbon concentrations at station BH02 fell between the other two

PO₄ FLUX
Boston Harbor Stations 1993



Massachusetts Bay Stations 1993

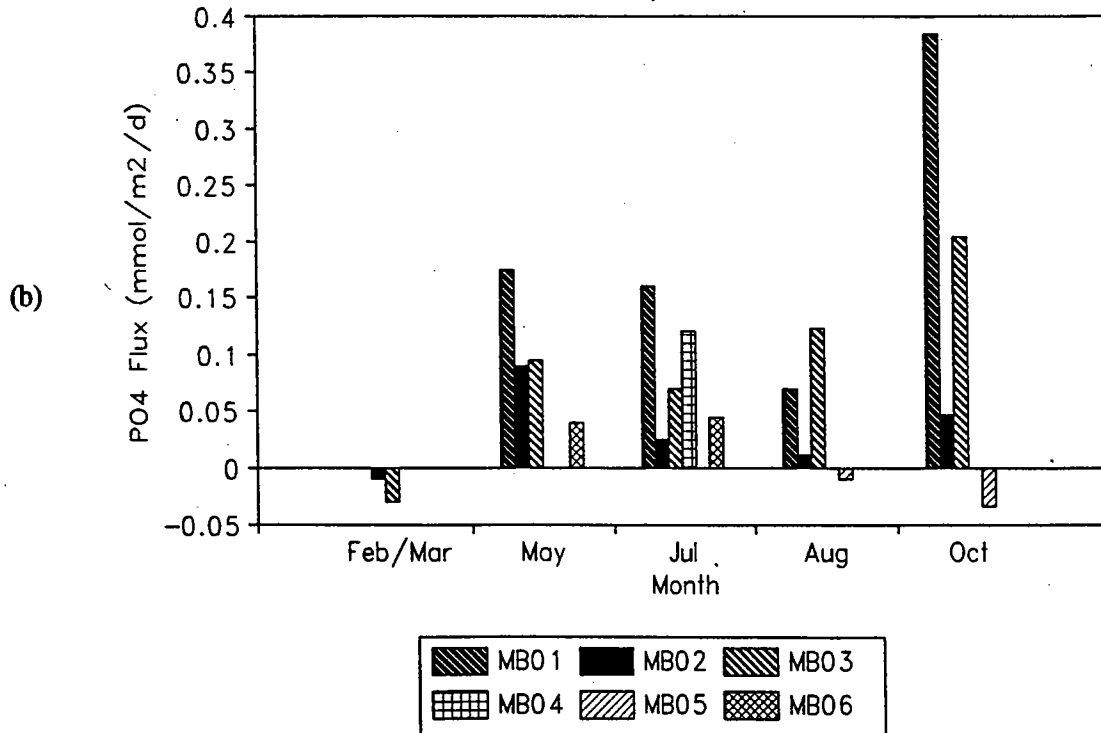


Figure 8. Phosphate fluxes at (a) the Boston Harbor stations and (b) the Massachusetts Bay stations in 1993. Values are means of measurements from duplicate sediment cores.

**Table 2. The %carbon and %nitrogen values for the surface 0-2 cm of the sediments collected during the 1993 survey.
The atomic/atomic C/N ratio is also shown.**

Month	Station	%C	%N	C/N	Month	Station	%C	%N	C/N
Feb/Mar	BH02	1.88	0.24	9.3	Aug	BH02	2.14	0.26	9.5
	BH03	3.65	0.42	10.1		BH03	3.52	0.44	9.3
	BH08	0.27	0.05	6.2		MB01	1.75	0.18	11.6
	MB01	4.29	0.52	9.5	MB02	0.36	0.03	13.6	
	MB02	0.86	0.09	10.8	MB03	1.67	0.19	10.5	
	MB03	3.37	0.45	8.8	MB05	1.32	0.15	10.1	
May	BH02	2.54	0.32	9.2	CC01	1.32	0.15	10.0	
	BH03	3.60	0.45	9.2	CC02	2.13	0.29	8.4	
	MB01	1.05	0.13	9.8					
	MB02	1.40	0.17	9.4	Oct	BH02	1.41	0.16	10.0
	MB03	0.60	0.07	10.4		BH03	3.13	0.36	10.1
	MB06	0.76	0.08	11.3		MB01	3.58	0.41	10.3
July	BH02	0.90	0.10	10.6	MB02	1.24	0.10	14.6	
	BH03				MB03	1.70	0.21	9.4	
	BH08				MB05	1.33	0.18	8.4	
	MB01	2.75	0.38	8.4					
	MB02	1.25	0.10	13.9					
	MB03	1.87	0.24	9.2					
	MB04	0.36	0.04	10.2					
	MB06	1.92	0.21	10.5					

stations and exhibited the greatest variation, ranging from 0.9% to 2.54% over the year. Some of this variation may be due to the very patchy nature of the station which is located at the edge of a steep slope.

Bay. There was a great deal of temporal variability in the sediment carbon values in the Bay stations (Table 2). Carbon concentrations at MB01 ranged from 4.3% in February to a low of 1.05% in May. The average carbon content at stations MB02 and MB03 was lower than at MB01 but still spanned a wide range, varying from 0.36% to 1.40% at MB02 and from 0.60% to 3.37% at station MB03. Temporal trends differed among each of the three stations. Because the soft sediments in this area of Massachusetts Bay are quite patchy, we suspect that the temporal changes do not reflect a biologically driven seasonal pattern, but rather slight differences in sample location or sediment movement due to storms.

Station MB04 had a fairly low carbon content, 0.36%, and was quite sandy. Station MB06 ranged from 0.76% to 1.92% on the two dates it was sampled. Station MB05 had a value of 1.3% on both sampling dates. At the two Cape Cod Bay stations, carbon content was 1.32% to 2.13% on the one date sampled.

4.3 SEDIMENT DENITRIFICATION RATES FOR BOSTON HARBOR AND MASSACHUSETTS BAY

In this section, rates of N_2 flux (denitrification) from all MWRA studies (1991-1993) are discussed. Several additional stations in Boston Harbor (BH07, T4, R4) were sampled prior to 1993; the results at these stations were reported by Kelly and Nowicki (1992, 1993).

4.3.1 Comparison of Denitrification in Boston Harbor and Massachusetts Bay

Measured rates of sediment denitrification were significantly ($p < 0.001$) higher in Boston Harbor than in Massachusetts Bay. Denitrification rates in Boston Harbor ranged from $< 0.24 \text{ mmol N m}^{-2} \text{ d}^{-1}$ at station BH02 in February to $9.9 (\pm 1) \text{ mmol N m}^{-2} \text{ d}^{-1}$ at station BH03 in August, with an arithmetic mean rate ($n=33$) for all stations for all dates (1992 and 1993) of $2.9 \text{ mmol N m}^{-2} \text{ d}^{-1}$. In Massachusetts Bay, rates ranged from $< 0.24 \text{ mmol N m}^{-2} \text{ d}^{-1}$ at station MB01 to $2.6 (\pm 0.6) \text{ mmol}$

$\text{N m}^{-2} \text{d}^{-1}$ at station MB03, with a mean of $1.1 \text{ mmol N m}^{-2} \text{d}^{-1}$ ($n=29$). Denitrification rates measured for the two stations in Cape Cod Bay in August 1993 were 1.6 and $1.7 \text{ mmol N m}^{-2} \text{d}^{-1}$ and could not be distinguished from the rates observed in Massachusetts Bay.

On three occasions the presence of unusual numbers of macrofauna in the cores from Boston Harbor significantly stimulated denitrification rates. In May 1992, a large clam worm (*Nereis virens*, 10 cm.) created numerous burrows in one of the replicate cores from station BH03. Rates in the core containing the clam worm were five times higher than rates observed in the replicate core. In November 1992 and August 1993, station BH03 cores were literally packed with active amphipods, and denitrification rates on those dates were significantly higher. However, even given the occasional increase in rates due to macrofauna at station BH03, denitrification rates were not statistically different for the two highly organic ($> 2 \text{ wt. \%}$ organic C) silt-clay sediments at stations BH02 and BH03. In contrast, denitrification rates for the sandy, low-organic (0.3 wt. \% organic C) sediments at station BH08 were significantly lower (mean = $1.5 \text{ mmol N m}^{-2} \text{d}^{-1}$, $p < 0.025$) than those observed at stations BH02 and BH03 (mean = $3.6 \text{ mmol N m}^{-2} \text{d}^{-1}$). Although denitrification rates at stations in Boston Harbor were statistically different depending on their sediment organic content, rates at stations in Massachusetts Bay were, in general, not distinguishable. The mean rate for the highest Bay station (MB03) was twice as high as the lowest station (MB01). These stations differed only at the 80% level of confidence.

To study the variability at a site, duplicate cores were incubated from Harbor stations BH03 and BH08 on four dates in 1992. At station BH08, 95% confidence intervals for fluxes from duplicate cores overlapped and denitrification rates for duplicate cores taken on the same date were not distinguishable. The coefficient of variation for replicate cores was 28% in April and 3-4% in May and June. At station BH03, large numbers of macrofauna clearly influenced measured denitrification rates. On three of the four sampling dates, duplicate cores from station BH03 were statistically ($p < 0.05$) different; the coefficient of variation for replicate cores was 24-26%. Because replicate cores have not been collected in Massachusetts Bay, it has not been possible to assess the variability in measurements from a station. However, for cores taken from five different stations in the Bay in July 1993, the coefficient of variation was 19%. This result, and the fact that replicate cores taken at station BH08 were not different, suggests that the practice of taking single experimental cores (rather than replicates) at each Bay station is adequate. It appears that we are likely to learn more by

continuing to do without replicates in order to sample more stations with greater geographic coverage. Rates measured in October 1992 and again in October 1993 at four stations in Massachusetts Bay differed by as much as a factor of five or six, suggesting that there is considerable year-to-year variability in denitrification rates.

4.3.2 The Effect of Temperature and Sediment Type

Boston Harbor stations, where denitrification rates were measured, could be separated into two groups, depending on sediment organic content and influence of temperature. At stations where organic content was relatively high ($\geq 2\%$ by weight), denitrification rates increased exponentially with temperature. At these stations where sediment organic matter was low ($< 2\%$ by weight), denitrification rates remained low and were generally not influenced by temperature. For example, at station BH02, seasonal increases in temperature explained 93% of the observed increase in denitrification rates (Figure 9). When rates for all of the “high organic” stations (BH02, BH03, BH07, T4) were combined (and the 3 macrofauna—stimulated data points for station BH03 were omitted), temperature accounted for 64% of the variability in the observed rates for Boston Harbor (Figure 10). In contrast, denitrification rates for the sandy, low-organic sediments at stations BH08 and R4 showed little apparent response to temperature (Figure 10).

In Massachusetts Bay, denitrification rates were uniformly low in February, but otherwise showed little consistent response to temperature (Figure 11). A comparison of Figures 10 and 11 shows that the magnitude and range of denitrification rates observed in the Bay was considerably smaller than that observed in the Harbor. The annual temperature range for the Bay is smaller as well (cf. Figures 9 and 10).

Denitrification rates were significantly higher at Boston Harbor stations characterized by higher sediment organic carbon content. However, in Massachusetts Bay, both denitrification rates and sediment carbon content were generally lower than in the Harbor. There was no consistent trend between denitrification rates and carbon (or nitrogen) content in Massachusetts Bay sediments. If denitrification rates and sediment carbon content are averaged for each station in the Harbor and Bay, mean sediment carbon content accounts for approximately 50% of the variation in the denitrification rates (Figure 12). However, most of the strength in this regression comes from the Harbor data.

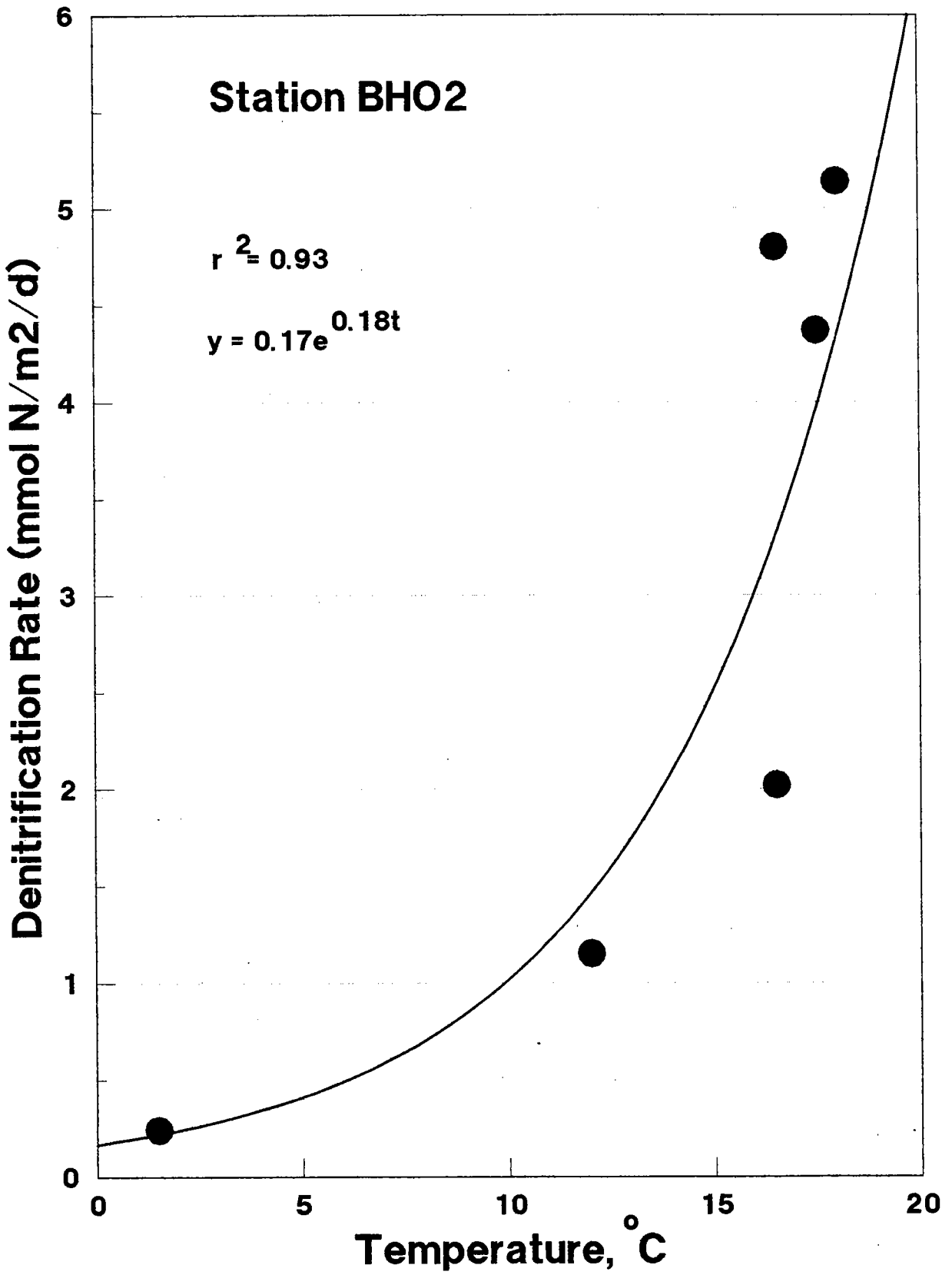


Figure 9. Observed sediment denitrification rates at station BH02 versus temperature (1991-1993).

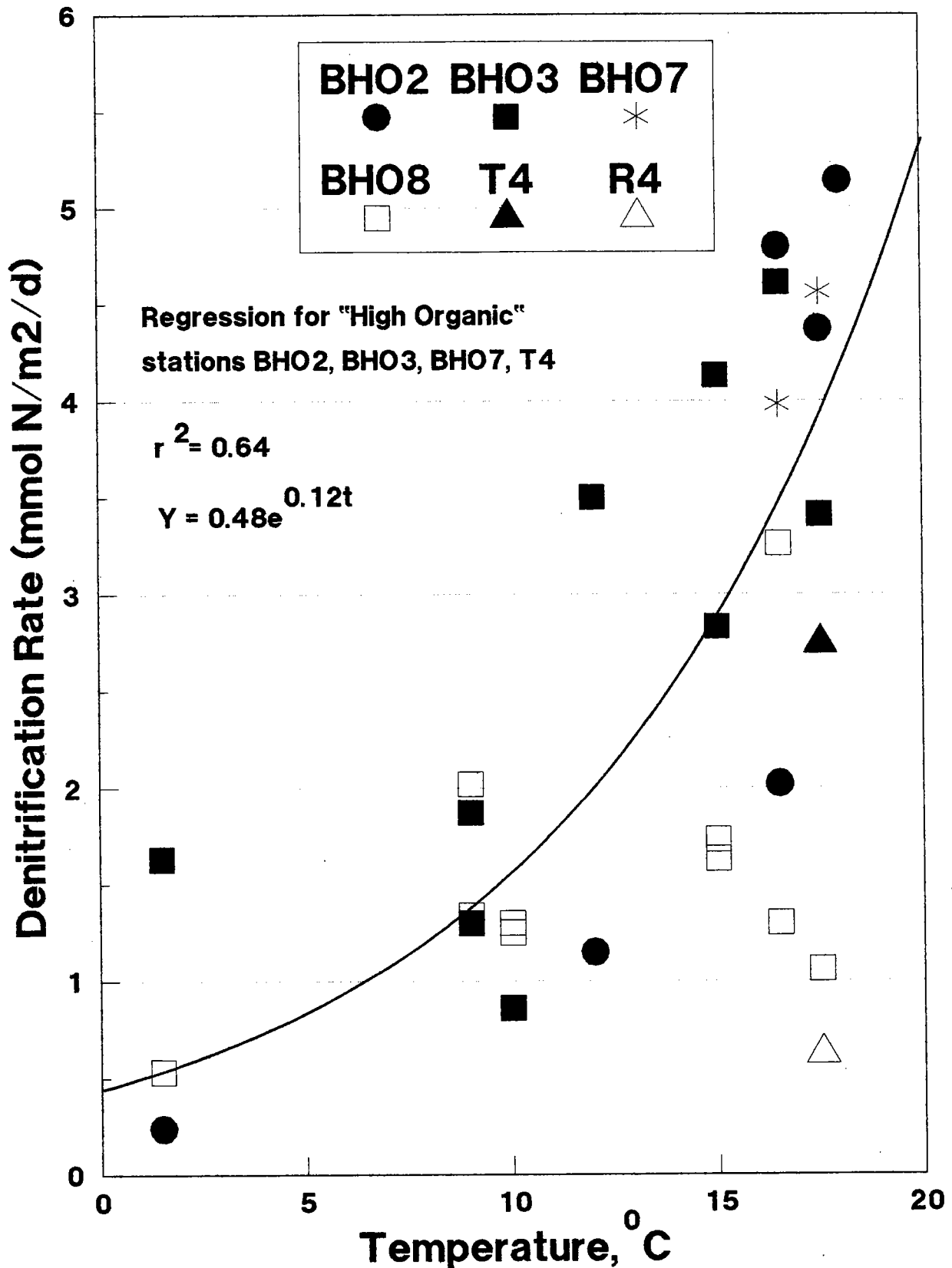


Figure 10. Sediment denitrification rates versus temperature for all stations in Boston Harbor (1991-1993). The regression includes only the stations with high sediment organic content (solid points) and excludes the three dates when exceptionally high numbers of macrofauna stimulated observed rates at BH03. Results for stations BH07, T4, and R4 are based on samples taken prior to 1993 and reported in Kelly and Nowicki (1992, 1993).

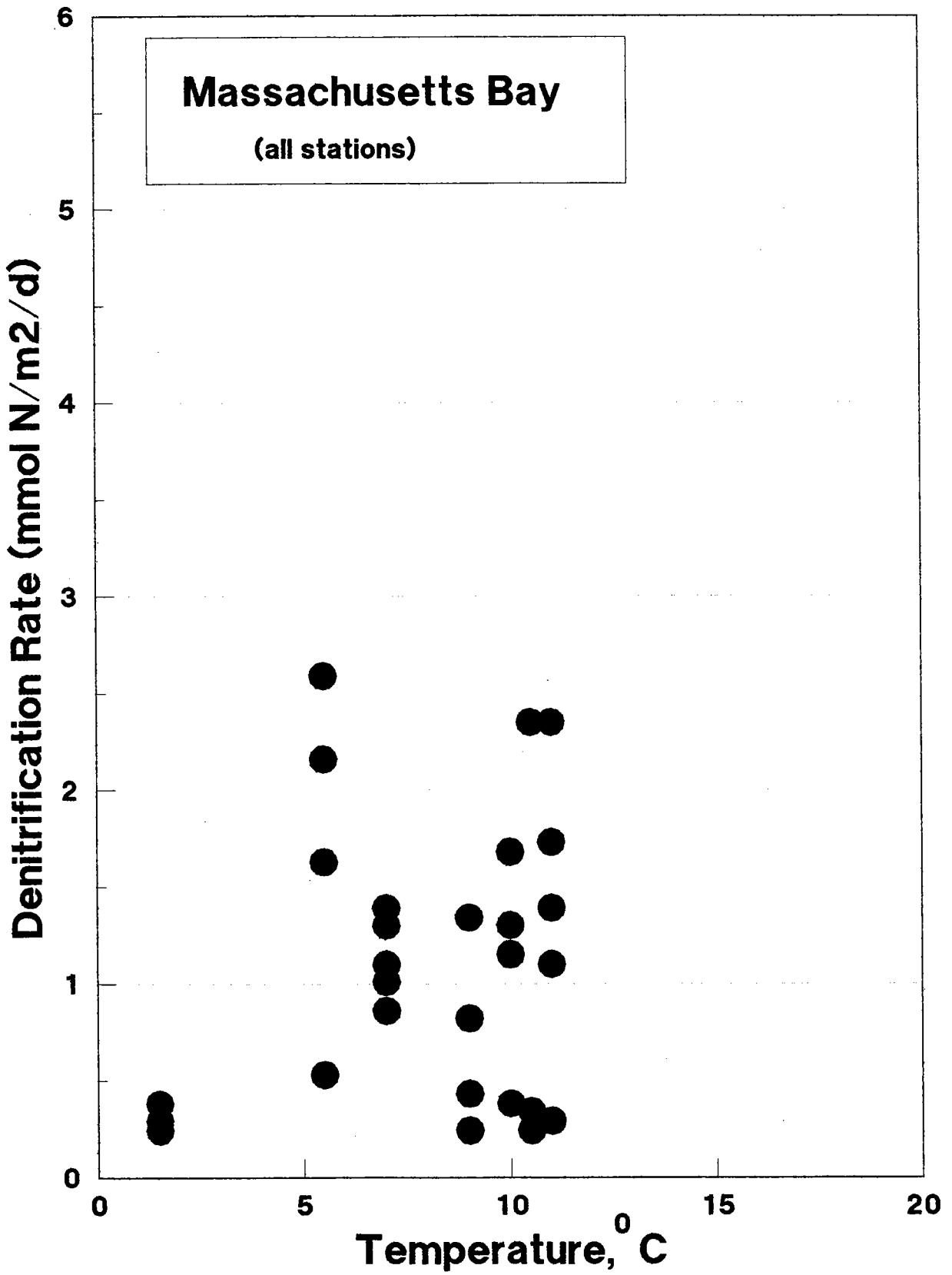


Figure 11. Observed rates of denitrification versus temperature for Massachusetts Bay sediments (1992-1993).

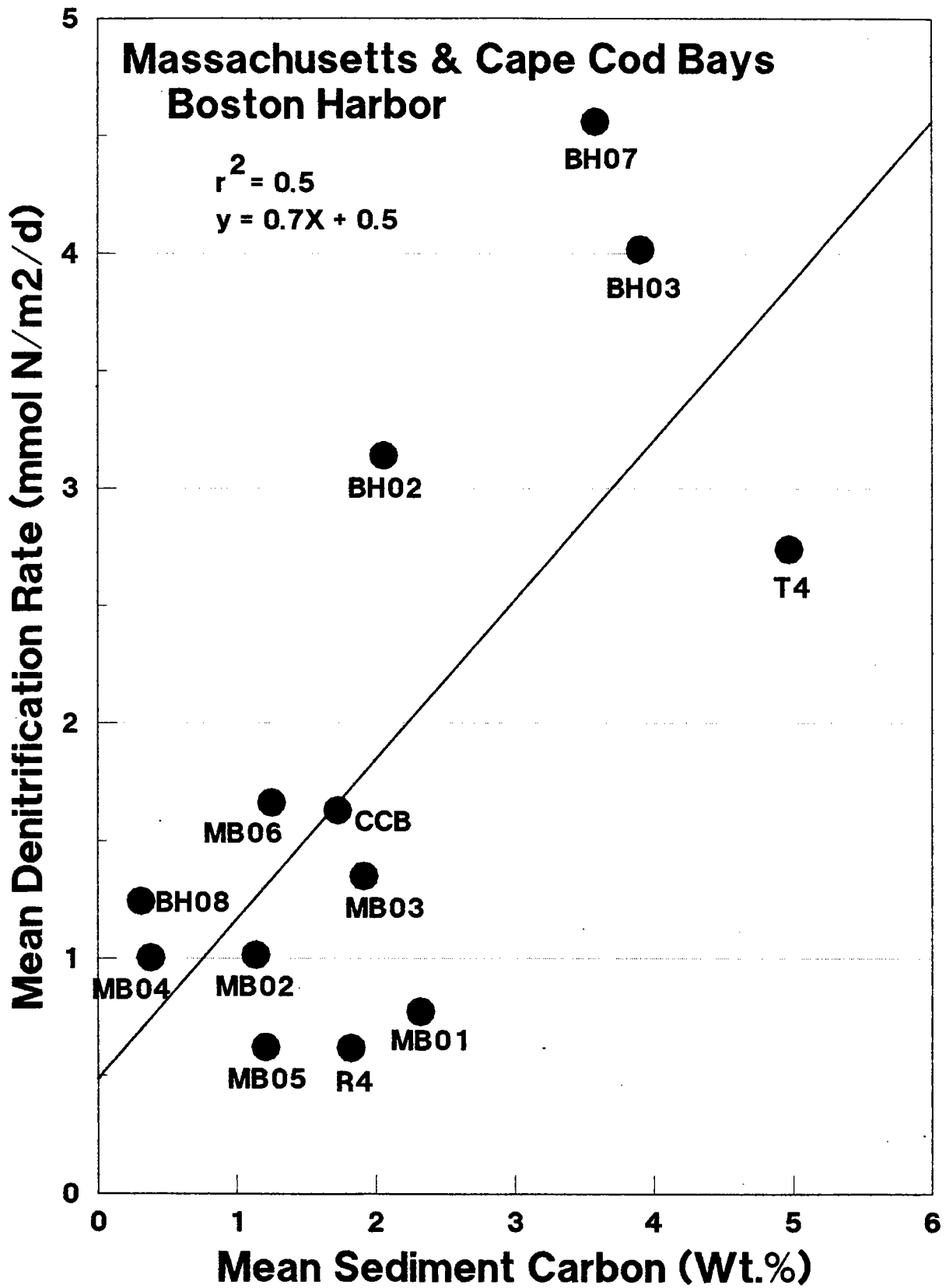


Figure 12. Mean denitrification rates as a function of mean sediment organic carbon content for Massachusetts Bay (MB), Cape Cod Bay (CCB), and Boston Harbor (BH and T4) stations. Results for Harbor stations BH07, T4, and R4 are based on samples taken prior to 1993 and reported in Kelly and Nowicki (1992, 1993).

4.3.3 Seasonal Cycles and the Importance of Temperature, Sediment Organic Content, and Benthic Fauna in Controlling Rates of Denitrification

Despite the apparent importance of denitrification in estuarine N cycling, few studies have successfully described the environmental factors involved in regulating the process. Clearly defining environmental regulators has been difficult because denitrification appears to be controlled by a number of interrelated factors that may have both positive and negative effects on the rate. Temperature, nitrate availability, organic carbon supply, and porewater oxygen concentrations have all been implicated as environmental controls for denitrification (e.g., Andersen *et al.*, 1984; Jenkins & Kemp, 1984; Smith *et al.*, 1985; Jorgensen & Sorensen, 1988; Seitzinger, 1988; Helmer & Labroue, 1993). Koike & Sorensen (1988) have suggested that, in estuaries where the supply of NO_3 is adequate, temperature may become the regulating factor. Binnerup *et al.* 1992 attribute the extremely high denitrification rates in Norsminde Fjord, Denmark to the favorable conditions created by a high riverine NO_3 input, ample organic substrate in the sediments, and abundant infauna periodically ventilating their burrows.

In Boston Harbor, increases in temperature clearly increased denitrification rates at “high organic” stations (>2 wt. % C) where carbon supply (and its resulting mineralized NO_3) was apparently not limiting. Highest rates of denitrification were observed at the station (BH03) with highest sediment organic content and active benthic macro-infauna (Figure 13). When organic carbon was not limited, active macrofauna increased denitrification rates, apparently by enhancing the penetration of oxygen to depth in the sediments. These results suggest that the annual cycle of denitrification in depositional, high organic sediments in Boston Harbor is driven by temperature. Superimposed on this seasonal temperature response is a macrofaunal effect. In contrast, there was no consistent seasonal cycle to denitrification rates at the sandy station BH08 sediments (Figure 13). Thus, at “low organic” stations (<2 wt. % C), insufficient carbon supply apparently depresses denitrification rates, even in the presence of increasing temperatures. The fact that apparently carbon-limited sediment sites can exist in an estuary with such a large nitrogen load probably reflects the fact that the bottom of Boston Harbor encompasses a patchwork of both “depositional” and “nondepositional” sediment sites (Knebel *et al.*, 1991). Jensen *et al.* (1988) have previously reported that regional differences in denitrification rates correlated with differences in the organic content of surface sediments in Aarhus Bight, Denmark.

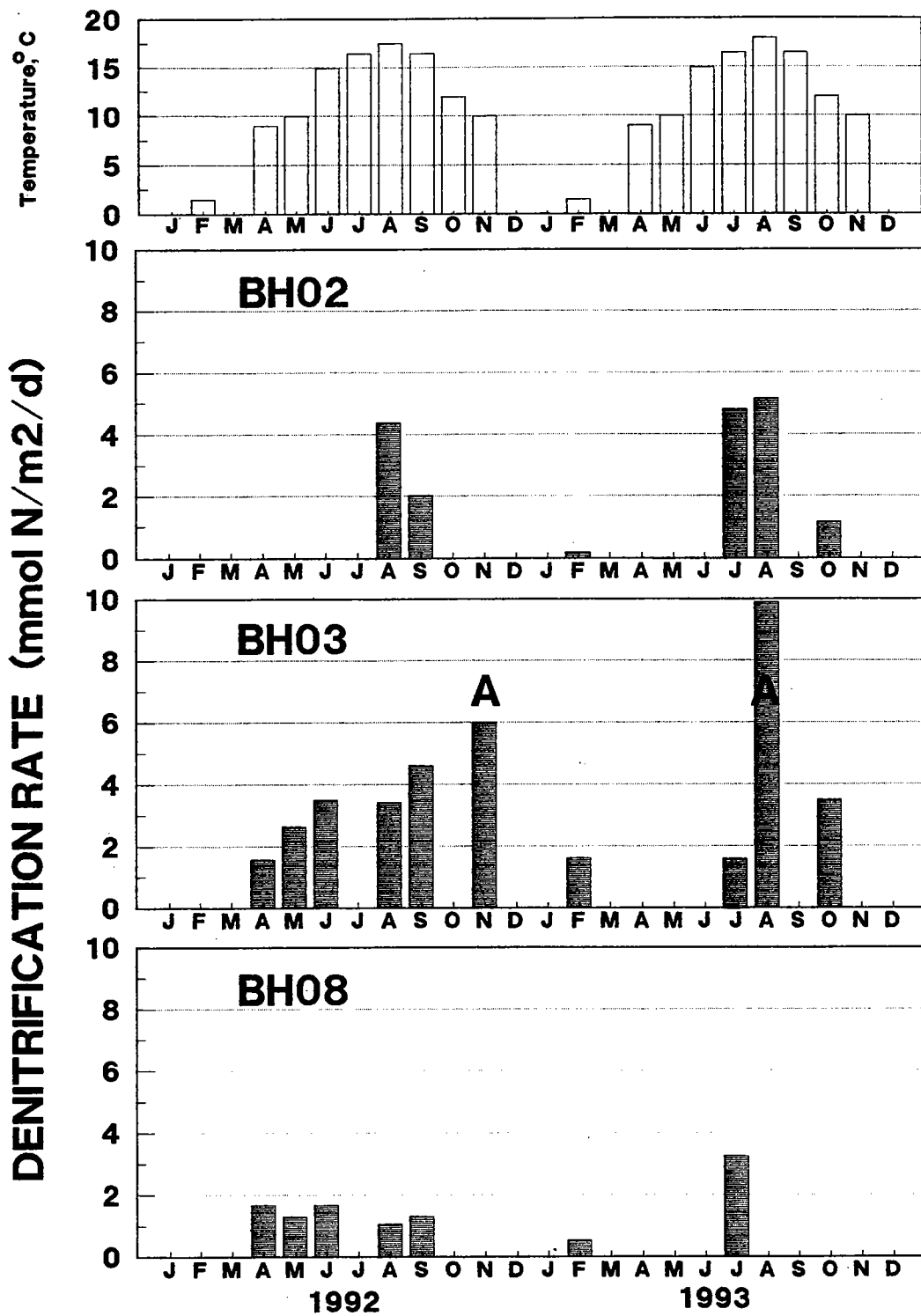


Figure 13. Annual cycles of sediment denitrification at three stations in Boston Harbor. Bottom water temperatures are also shown.

The same generalized cycle is shown for both years; this is based on *in situ* measurements at core sampling 1991-1993. The single September 1991 measurement has been plotted with the 1992 data. Cores taken from station BH03 in November 1992 and August 1993 (marked "A") contained high numbers of amphipods and had correspondingly high denitrification rates. Fluxes at station BH02 were non-detectable in February 1993 and have been plotted at the detection limit (0.24 mmol Nm⁻²d⁻¹).

The data for Massachusetts Bay sediments showed no distinct seasonal cycle, and considerable station-to-station and year-to-year variability (Figure 14). In general, denitrification rates were high in October and low in February when water temperatures reached their respective high and low points, but this was not always the case (e.g., October 1993, stations MB01, MB02). Highest denitrification rates were observed in May at two stations (MB02, MB03), perhaps in response to seasonal inputs of organic carbon from the water column (see discussion below).

In Massachusetts Bay a smaller annual temperature range and lower denitrification rates make it difficult to detect a temperature effect. It is likely that some estimate of the seasonal flux of organic matter from the overlying water column will prove to be a better predictor of denitrification rates for the Bay stations.

4.3.4 Comparison of Stoichiometric and Direct Method of Measuring Denitrification

Direct measurements of denitrification were compared to calculations using the stoichiometric method. There is considerable scatter in the relationship (Figure 15), and more scatter than observed in the 1992 data set (Giblin *et al.*, 1993). Although the relationship between the two methods shows a large variance among the Harbor stations, the average annual rates determined by the two methods are very similar. At all Harbor stations where data are available from both methods, the overall annual average loss of N using the direct method is $3.15 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and using the stoichiometric method it is $3.06 \text{ mmol N m}^{-2} \text{ d}^{-1}$. The agreement between the two methods is not as good in Massachusetts Bay, where the stoichiometric estimate is $2.06 \text{ mmol N m}^{-2} \text{ d}^{-1}$, or twice the rate of $1.03 \text{ mmol N m}^{-2} \text{ d}^{-1}$ measured using the direct method. Stations in Cape Cod Bay showed fairly good agreement with an average of $1.62 \text{ mmol N m}^{-2} \text{ d}^{-1}$ using the direct method and $1.14 \text{ mmol N m}^{-2} \text{ d}^{-1}$ using the stoichiometric method.

The large discrepancy between the two calculations of denitrification is partly because the stoichiometric method consistently calculates higher fluxes at station MB01 than were determined by the direct method. At station MB01 the difference between the annual average of the two methods was more than a factor of three. Station MB01 is also the station where we observed the highest RQ values (1.75). If carbonate dissolution is contributing to the DIC fluxes we observed at this station,

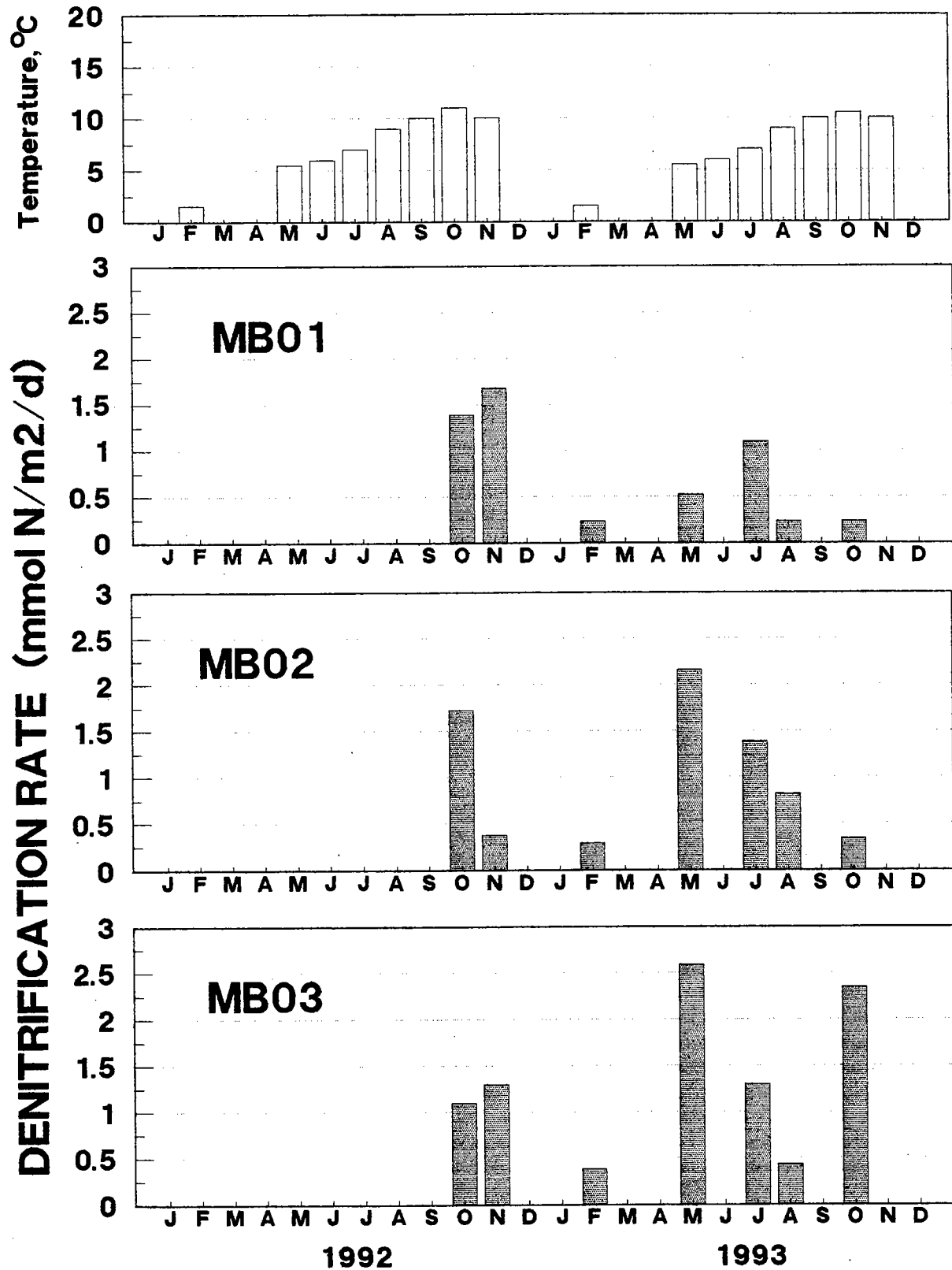


Figure 14. Annual cycles of sediment denitrification at three stations in Massachusetts Bay. Bottom water temperatures are also shown. The same generalized cycle is shown for both years; this is based on *in situ* measurements at core sampling in 1992 and 1993.

Denitrification Measurements 1993

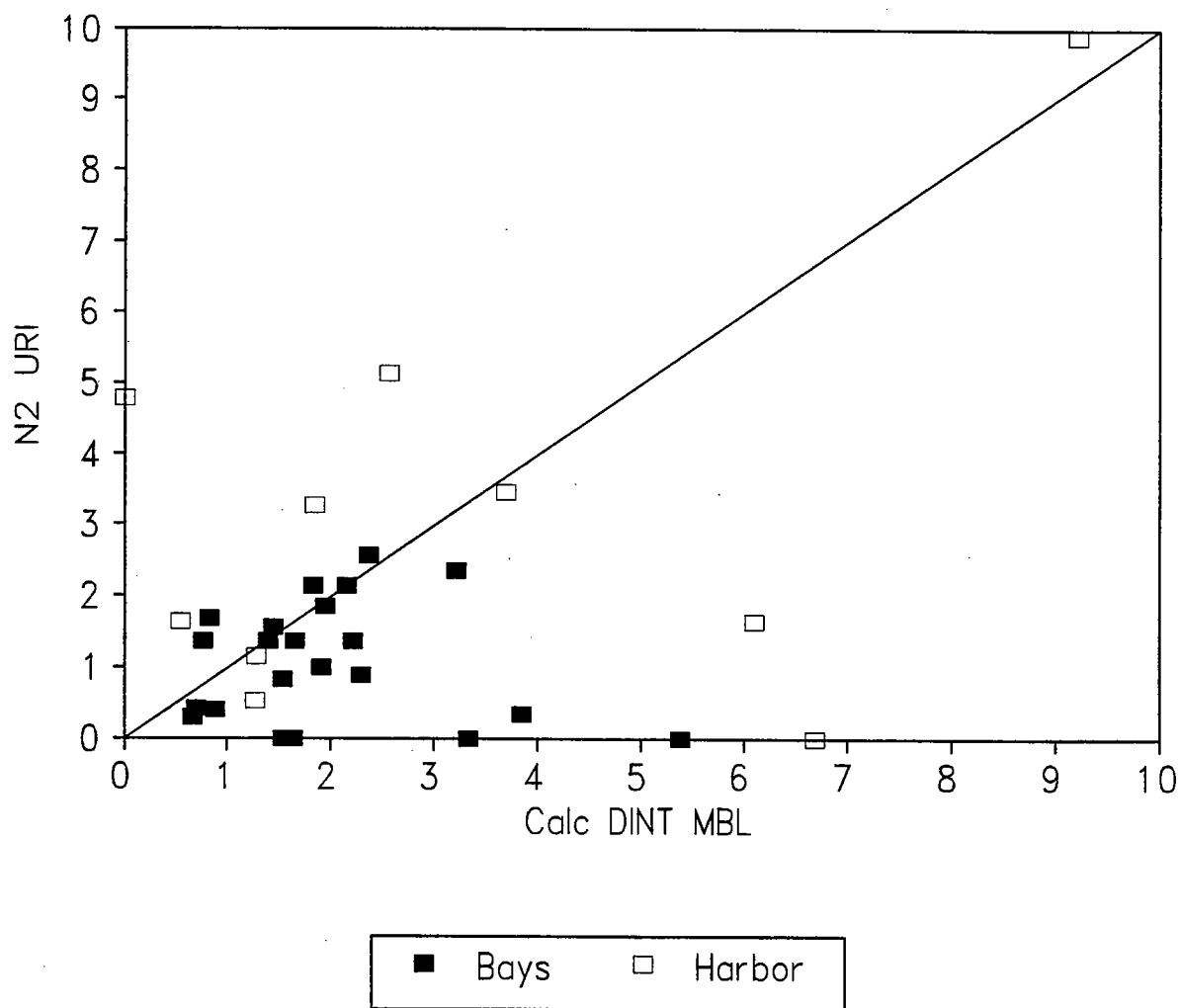


Figure 15. Comparison of denitrification rates derived two ways, by direct measurements made by URI (N_2 URI) and by the stoichiometric method as calculated by MBL (Calc DINT MBL). The solid line represents a 1:1 relationship. Units are $\text{mmols N m}^{-2} \text{d}^{-1}$.

our estimate of organic matter decomposition using DIC will be too high and the stoichiometric method will overestimate denitrification.

4.4 BENTHIC RESPIRATION, NUTRIENT FLUXES, AND DENITRIFICATION RATES IN AN ECOSYSTEM CONTEXT

4.4.1 BOSTON HARBOR

One way to gain perspective on the role of benthic processes on nutrient cycling in the Harbor is to express rates of sediment nutrient recycling relative to nitrogen input to the Harbor. Denitrification averaged 37% (\pm s.d. = 19.6, n = 10) of the total N flux (N_2 + DIN) measured at Harbor stations in 1993. The N_2 flux represented on average about 14.5% of the 21.7 mmol $m^{-2} d^{-1}$ input to the Harbor (Kelly and Nowicki, 1993; Alber and Chan, 1994). The percentage for individual measurements was lower at colder temperatures and low organic stations, as previously described in our studies. The 14.5% value is not an annual estimate, but it is higher than that calculated for an annual Harbor N budget (*circa* 1992—Kelly and Nowicki, 1993). The difference occurs for two principal reasons: (1) the measurements made in 1993, although spread across the annual temperature range, were biased to high organic sediments and (2) because metabolism and flux rates were generally higher at the high organic station (BH03). We do not know how widespread the phenomenon at station BH03 was; denitrification rates measured at other stations in 1993 were comparable to previous years. One should expect some transitional features in nutrient cycling as Harbor discharge practices change. Higher fluxes at station BH03 in 1993 may be a response to sludge abatement (ceased December 1991) and represent one transient aspect of the Harbor recovery process.

One can also compare DIN or total N (N_2 + DIN) fluxes to N loading. In July and August, benthic rates at station BH03 equaled or exceeded loading rates (> 21.7 mmol $m^{-2} d^{-1}$). In contrast, at station BH02, sediment N recycling was about 50% of loading during summer. MWRA effluent is currently about 80-90% of the Harbor N load. After the effluent is diverted offshore, during the summer the major N flux into the Harbor will probably arise from the sediments rather than come from external loading. Kelly *et al.* (1985) described experimentally how the nutrition of coastal systems changes from internally regulated to externally driven as a function of increased nutrient loading and

eutrophication. During recovery from nutrient enrichment, the opposite change is expected. In short, the Harbor's nitrogen cycling will change in a fundamental way. Studies suggest that the recovery of sediments and establishment of new nutrient dynamics between the water column and sediments takes years rather than decades (e.g., Oviatt *et al.*, 1984). With the rapid flushing rate of the Harbor, recovery should be quick, but this may make the transition from a system regulated by external loads to one dominated by internal recycling all the more dramatic and ecologically unpredictable.

4.4.2 BAY

In Massachusetts Bay, comparison of benthic fluxes with nutrient loading is not warranted because of differences in the spatial scale of flux and loading estimates. However, the fraction of total N flux in the Bay that was due to denitrification was similar to that in the Harbor, in spite of generally lower fluxes in the Bay. N₂ flux was 36% (± 23.6) of the total N flux for 20 measurements made in Massachusetts Bay in 1993. Because the N₂ flux as a percentage of total N flux is generally similar in the Harbor and Bay, it is arguable that the role of denitrification in sediment N recycling will not change much as the sediments in the Bay become enriched in organic matter. Future data collections will allow a test of this theory.

Only two measurements were made in Cape Cod Bay (August) and they indicated that, relative to the Harbor and Bay, perhaps a higher percentage of total N flux was due to N₂ (58% ± 3 for n=2). As suggested previously, the N₂ fluxes in Cape Cod Bay were similar to rates in Massachusetts Bay, but the DIN flux in Cape Cod Bay was relatively low for the season and temperature. Additional measurements in Cape Cod Bay are required to draw any conclusions regarding a similarity or difference between the two Bays.

Nutrient Fluxes and Annual Water-Column Trends in Western Massachusetts. Fluxes in Massachusetts Bay can be examined in relation to events occurring in the water column. Five benthic flux stations sampled in western Massachusetts Bay (MB01, MB02, MB03, MB04, MB06) form an arc about 10 km out from Boston Harbor. These flux stations are bracketed by a group of water column stations being monitored on the western side of the nearfield (Figure 16). The 1993 seasonal patterns in bottom water quality and surface layer chlorophyll for the western nearfield are shown in Figures 17 and 18.

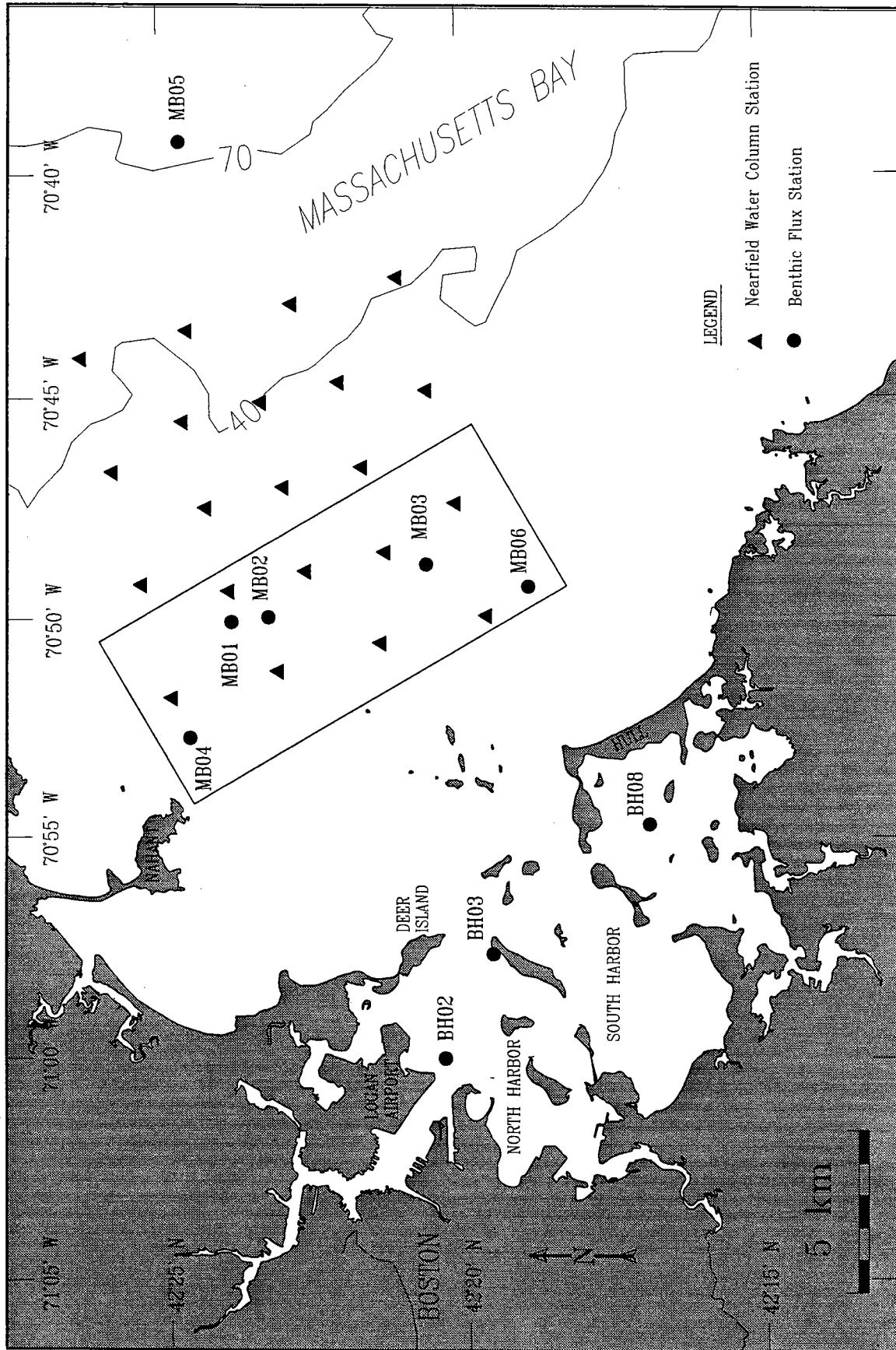


Figure 16. Nearfield water column sampling stations in relation to benthic flux stations. Data from eight water column stations within the box in the western nearfield were used to illustrate seasonal patterns in the water column in Figures 17-19.

In 1993 in Massachusetts Bay a late winter-spring bloom was observed, with a small seasonal peak in chlorophyll detected in April as thermal stratification of the water column ensued (Figure 17a). During the summer, chlorophyll concentrations were variable, but generally increased to high concentrations in mid-October, when water column destratification occurred. Near-bottom temperature rose sharply from late March to May and continued to rise into the fall (Figure 17b). Dissolved oxygen (DO) in bottom waters increased in February and March, decreased from April to June, remained stable in July, and then decreased between August and October (Figure 17c). Bottom-water nutrients (Figure 18) generally decreased to a minimum in late spring/early summer and then rose sharply (DIN), slightly (PO_4), or were fairly stable (SiO_4) until mixing of the water column occurred in October.

The spring bloom in 1993 was weak, and as presented earlier, flux patterns for nitrogen forms did not show strong seasonal trends when accounting for the variability of all cores. A response of the benthos to deposition of a winter-spring bloom can occur (e.g., Nixon *et al.*, 1980). Interestingly, however, the pattern for N_2 flux (Figure 14) suggested a peak in May after the spring bloom, when temperature had risen but was still cold (5-6 °C). Mean denitrification rates in May and July were significantly higher than in February ($p < 0.05$); whereas, rates in August and October were not different from rates in February. Monthly mean flux rates for DIC, PO_4 , SiO_4 , and NO_3 suggest a slight increase in May, especially relative to the low temperature, and there were significant differences between February and May fluxes for PO_4 ($p < 0.02$), SiO_4 ($p < 0.01$), and for NO_3 ($p < 0.03$). The preliminary interpretation of these data is that some fluxes, denitrification included, may be particularly responsive to winter-spring production events and the initiation of seasonal warming.

The principal pelagic event in the 1993 annual cycle was not the winter-spring bloom but the increase in chlorophyll to the concentrations of an intense fall bloom (Figure 17a). From late August to mid-October, the western nearfield area experienced a succession of diatoms, culminating in dominance by the diatom.

Asterionellopsis glacialis. Interestingly, the fall bloom abruptly terminated about 1-2 weeks prior to the October benthic flux measurements and water column chlorophyll was depleted in November, the week after the flux measurements were made (cf. Figure 17 and Figure 19).

1993, Western Nearfield Stations

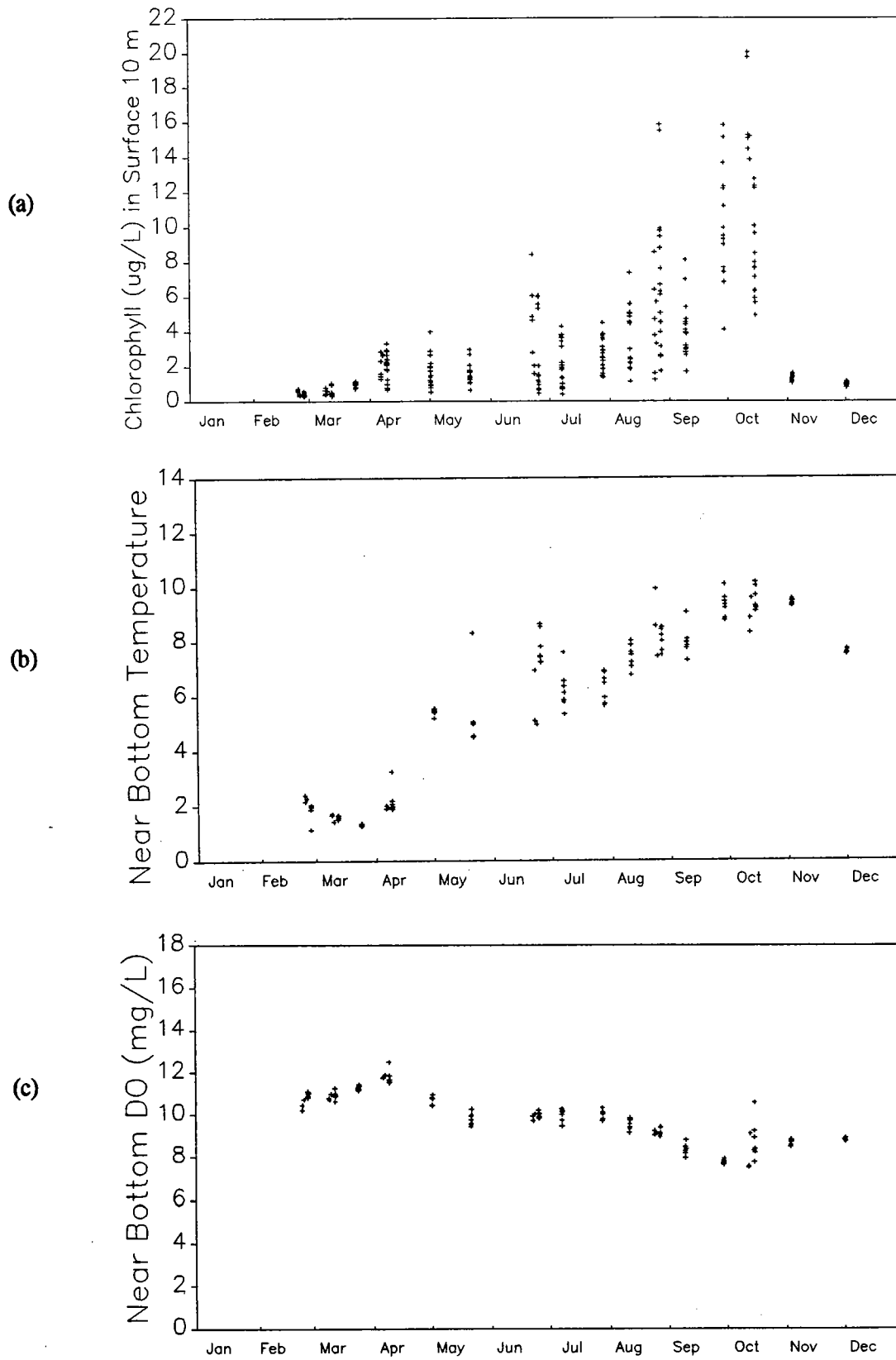


Figure 17. Seasonal patterns in the water column in the western nearfield during 1993: surface chlorophyll, near-bottom temperature ($^{\circ}\text{C}$), and near-bottom dissolved oxygen (DO).

1993, Western Nearfield Stations

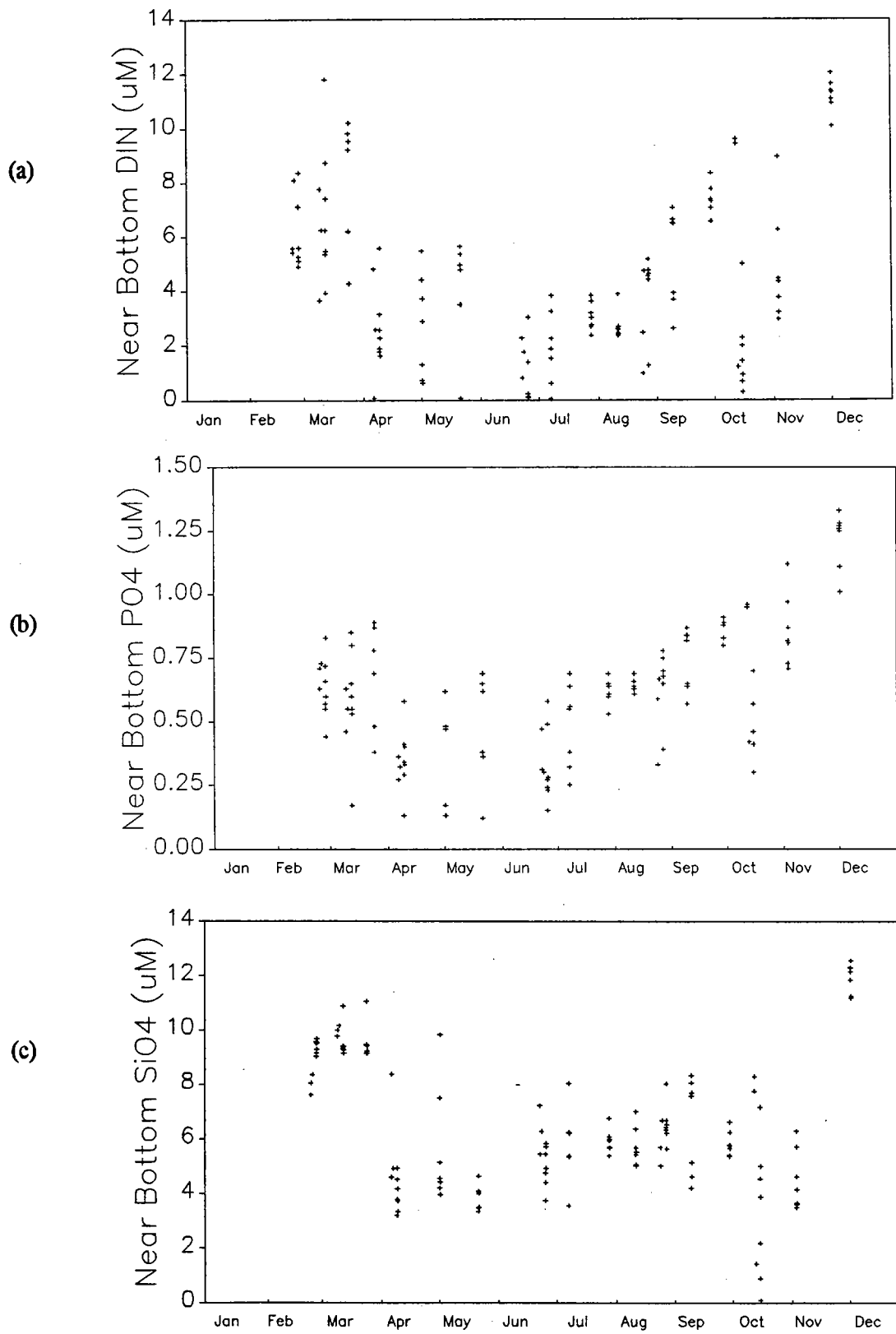


Figure 18. Seasonal patterns in the water column in the western nearfield during 1993: near-bottom nutrients.

In spite of station-to-station variability, DO uptake, SiO₄ release, DIC release, and PO₄ flux were correlated to bottom temperature although the correlation was weaker for the latter two parameters. Rates for all parameters mentioned above were clearly highest in October. However, given the concomitant increase in chlorophyll over the summer-fall period (Figure 19), the input of organic matter may also have increased. The settling rate of organic matter from the surface layer to the bottom layer during the strong stratification is unknown; organic deposition can be less under summer stratification than during well-mixed conditions (Hargrave and Phillips, 1986). However, some diatom-based organic matter must have deposited in October and, in part, contributed to the high fluxes observed soon thereafter. In view of the concomitant trends, we cannot fully discriminate the effects of temperature relative to organic matter supply on fluxes in the Bay. On the other hand, the fall bloom may give a sense for the short-term increase in benthic fluxes that can occur after a major diatom bloom because the difference in both bottom water and incubation temperatures for all cores between the August and October measurements was small, only about 1° C. Average fluxes in October were about 15% higher (O₂), 47% higher (Si), 68% higher (DIC), 212% higher (N₂), and 315% higher (PO₄) than in August. Both NH₄ and NO₃, and thus DIN, were lower in October. Note, however, that the fluxes for August and October were only significantly different, for DIC ($p < 0.056$) and NO₃ ($p < 0.02$) when considering stations as replicates.

Nutrient Fluxes and Primary Production in Western Massachusetts Bay. One way to put benthic fluxes in perspective is to relate rates of metabolism and nutrient recycling to primary production in the overlying water column. This is of greatest interest during summer and early fall when many benthic fluxes reached annual maxima. Water column primary production is variable, but recent MWRA monitoring data, as well as historical data, suggest that net daytime primary production (NPP) in the summer is about

1 g C m⁻²d⁻¹ in the western nearfield area (Kelly *et al.*, 1993; Kelly, 1994). During summer-fall, the depositional sediments of the western nearfield appear to consume, at most, an amount of carbon equal to 31% of the production in overlying water [i.e., depositional sediment flux divided by NPP (same units) x 100 (Table 3)]. The RQ was very high at one station and the DIC may include nonrespiratory losses; using O₂ and an RQ=1, the implied percentage of production is 23% rather than 31% (Table 3). Benthic DIN flux could supply about 12% of the N required for primary production, while benthic phosphate flux could supply about 14% of P requirements for production.

Western Nearfield 1993
Means by survey

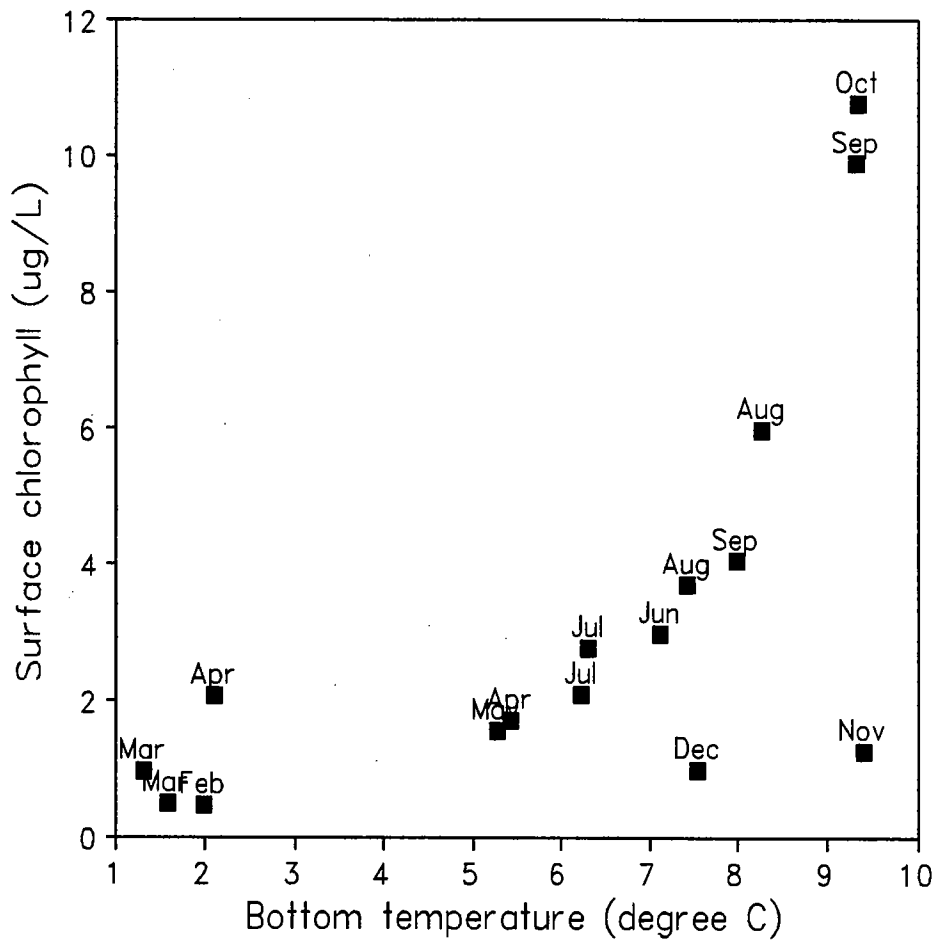


Figure 19. Surface (0 to 10 m) chlorophyll concentration relative to bottom temperature in the western nearfield during 1993.

Table 3. Benthic flux and water column changes in the western nearfield during summer 1993.

	Fluxes from Depositional Sediments ^a (mmols m ⁻² d ⁻¹)	% of NPP ^b	Extrapolated Area-Weighted Flux ^c (mmols m ⁻² d ⁻¹)	% of NPP ^b	Potential Influence on Bottom Water Layer ^d		Approximate Change Observed in Bottom Water over 100-Day Period
					Δ Conc/Day (μM d ⁻¹)	Δ Conc for 100-Day Period (μM)	
O ₂	-18.8	23	-8.1	10	0.54	54	-70 ^e
DIN	1.5	12	0.6	5	+0.04	+4	+6
PO ₄	0.11	14	0.048	6	+0.003	+0.33	+0.5
SiO ₄	5.6	—	2.4	—	+0.16	+16	No Trend
DIC	25.5	31	11	13	—	—	—

^a Average for July, August, and October for nearfield flux stations.

^b Assumes 1 g C m⁻²d⁻¹ net primary production (NPP), or 83.3 mmol C m⁻² d⁻¹. C/N ratio of 6.625 and C/P ratio of 106 were used for DIN and PO₄ calculations and an RQ of 1 assumed to compare O₂ with NPP.

^c Based on assumption of 29% area represented by depositional sediments; remaining area has flux at 20% of depositional area rates. Extrapolated area - weighted flux = 0.29 (depositional sediment flux) + 0.71 (0.2 depositional sediment flux).

^d Uses extrapolated area-weighted flux and assumes 15 m bottom layer for western Massachusetts Bay.

^e 70 μM = 2.25 mg O₂ L⁻¹

N₂ flux loss from the sediments could remove <7% of the N necessary for primary production. Therefore, DIN and N₂ together amount to 19% of NPP, which is similar to that calculated from O₂.

The sediments sampled at benthic flux stations are relatively small pockets of silt-clay depositional environments and it is difficult to extrapolate depositional sediment flux rates to the entire area covered by the water column stations. As an initial guide, we assumed that about 29% of the area is depositional (Knebel, 1993). Fluxes in sandy and hard-bottom areas were assumed to be 20% of these depositional areas (cf. Kelly, 1994). Because depositional sediments cover only a fraction of the bottom in the nearfield area, the role of sediments in supplying nutrients for primary production must be less, as the calculation suggests (Table 3).

Fluxes in Western Massachusetts Bay Relative to Bottom-Water Trends during Stratification. Another way to gain perspective on the role of benthic fluxes in water column nutrient dynamics is to compare fluxes to trends in water column nutrients. An area-weighted calculation again involves the period of

strong stratification from June through late September when near-bottom DO decreased and DIN increased. Results of calculations on the potential contribution of benthic fluxes to a stagnant, closed bottom layer during stratification are compared to observed bottom-water trends (Table 3).

The calculated influence of benthic fluxes on the bottom water was smaller than the actual DO, DIN, and PO_4 changes observed during the period. Generally, benthic fluxes (as extrapolated) amount to about 66-77% of the observed change in bottom water. This is a reasonable result, possible because other processes (e.g., water column uptake and recycling, advection, and vertical diffusion to surface layers) influence bottom waters. The behavior of SiO_4 appears anomalous. No strong summer trend in bottom-water SiO_4 concentration was apparent, although benthic fluxes could have produced an increase of 16 μM (Table 3). The discrepancy between the potential flux contribution and the observed bottom-water change for SiO_4 cannot be further reconciled with these data, especially because the bottom layer is neither fully stagnant nor closed. However, during the summer-fall, the ratio of Si/N in benthic fluxes was stable or increasing as the ratio in bottom water was decreasing, which absolutely implicates additional processes being significant in determining Si/N ratios and thus bottom water quality in general.

A conclusion from these observations is that factors other than fluxes from depositional areas are influential in controlling bottom water column concentrations. Benthic fluxes alone should not be used to infer trends in bottom water nutrients; conversely, water column concentrations of dissolved nutrients and their ratios should be used cautiously to infer rates and stoichiometry of benthic fluxes (cf. Becker, 1992). We know that physical/ecological processes may differentially influence nutrients in the water column. Previous observations in Massachusetts and Cape Cod Bays suggest that silicate/nitrogen ratios can influence plankton community composition. But plankton also directly influence Si/N ratios (cf. Kelly, 1994) probably occurred during the large 1993 summer-fall diatom bloom. Finally, the observations and calculations simply reinforce the notion that many water-column and benthic processes must be integrated if attempts are made to model, predict, or understand the ecological response to an outfall in western Massachusetts Bay.

4.5 POREWATER CONSTITUENTS

Some of the routinely measured porewater constituents, such as alkalinity and dissolved sulfide, are indicators of anaerobic processes. These constituents were highest at the two Harbor stations (BH02 and BH03) where the greatest amount of metabolic activity was observed. At stations BH02 and BH03, sulfide concentrations routinely exceeded 1 mM below 14 cm depths (Figure 20a) and alkalinity values almost always exceeded 5 mM at depth. In contrast, sulfide was seldom detected in the porewater from Bay cores (Figure 20a) and alkalinity values rarely exceeded 5 mM in those cores. The differences in porewater chemistry of the Bay cores and the two Harbor cores was also reflected in the redox potential (Eh) at these locations (Figure 20b). Eh values in the Massachusetts Bay cores tended to asymptote at about -50 to -150 mV while values less than -200mV were often reached in cores from stations BH02 and BH03. The more negative values corresponded to the depths where dissolved sulfide was detected.

The porewater composition at station BH03 appeared to have changed between 1992 and 1993. During 1992 we frequently observed dissolved sulfide at 4-6 cm in the sediment (Figure 21a). In 1993 we usually did not detect sulfide until 8-10 cm (Figure 21a). The Eh values in the 4-10 cm of sediment were also consistently higher in 1993 than in 1992 (Figure 21b).

The presence of sulfide gives some insight into benthic habitat quality. Animals are seldom found in high numbers in the zone of the sediment where substantial quantities of dissolved sulfide are present. Our qualitative observation that the benthic animals greatly increased in numbers late in 1992 at station BH03 and stayed high for most of 1993 is consistent with the observed increase in sediment oxidation and the decrease in sulfides.

Porewater constituents appear to be a useful indicator organic matter loading in environment of interest and monitored for the MWRA. Porewater sulfides and Eh are distinctly different between the Harbor and the Bay. Porewater constituents also provide insight into changes in habitat quality; the change in benthic animal abundance at station BH03 was accompanied by large changes in the porewater chemistry.

Porewater Profiles for February, 1993
H₂S

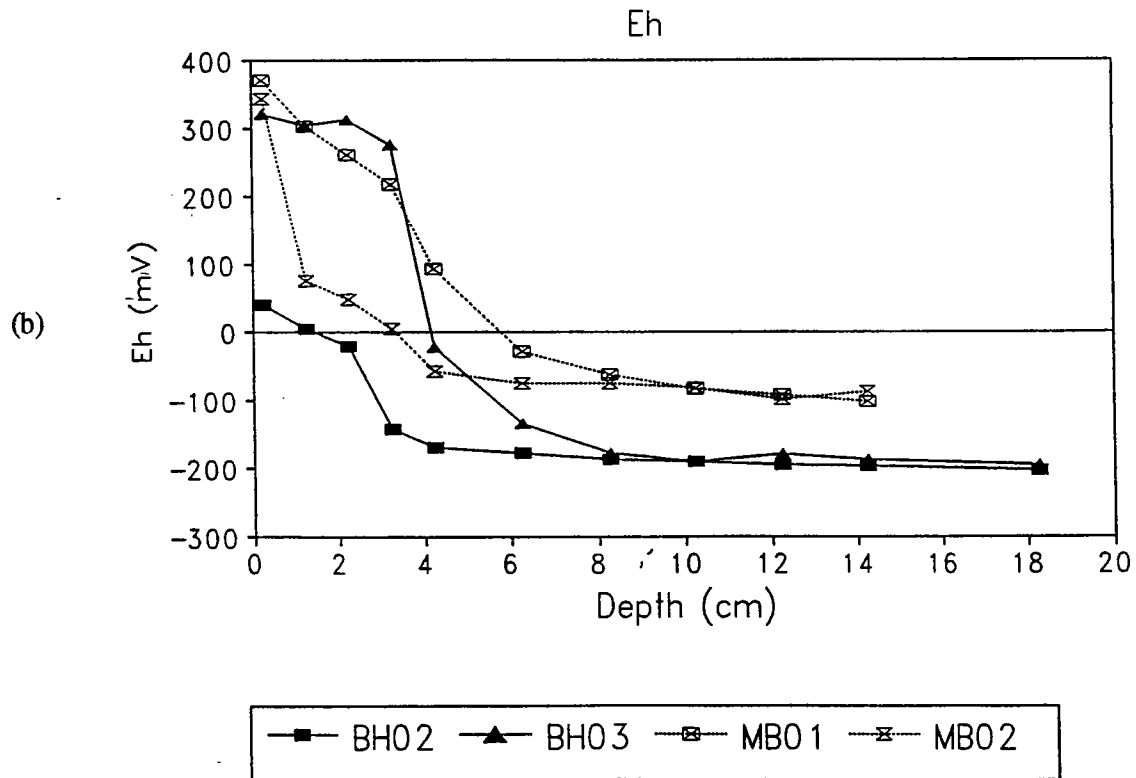
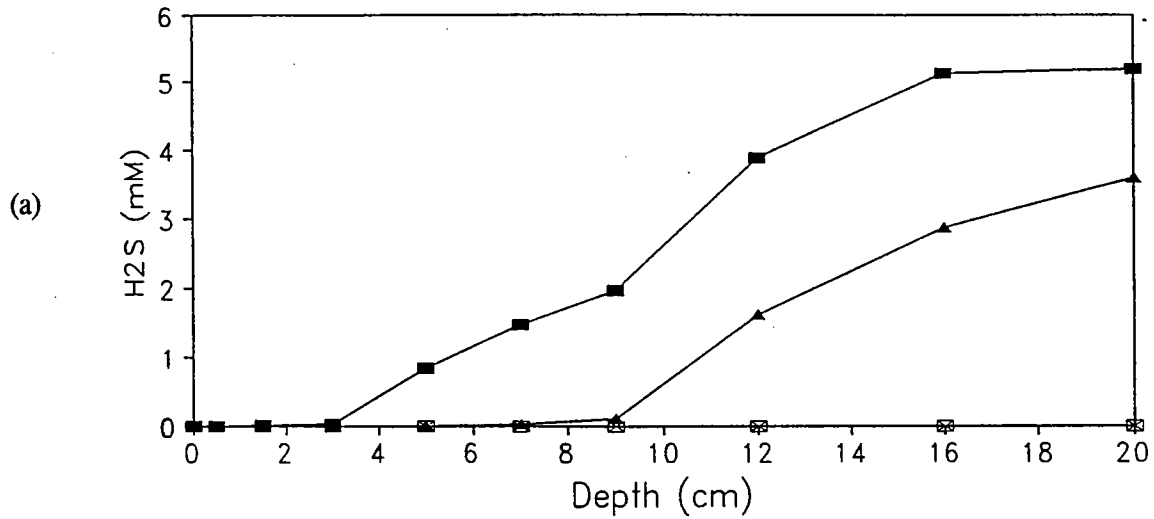
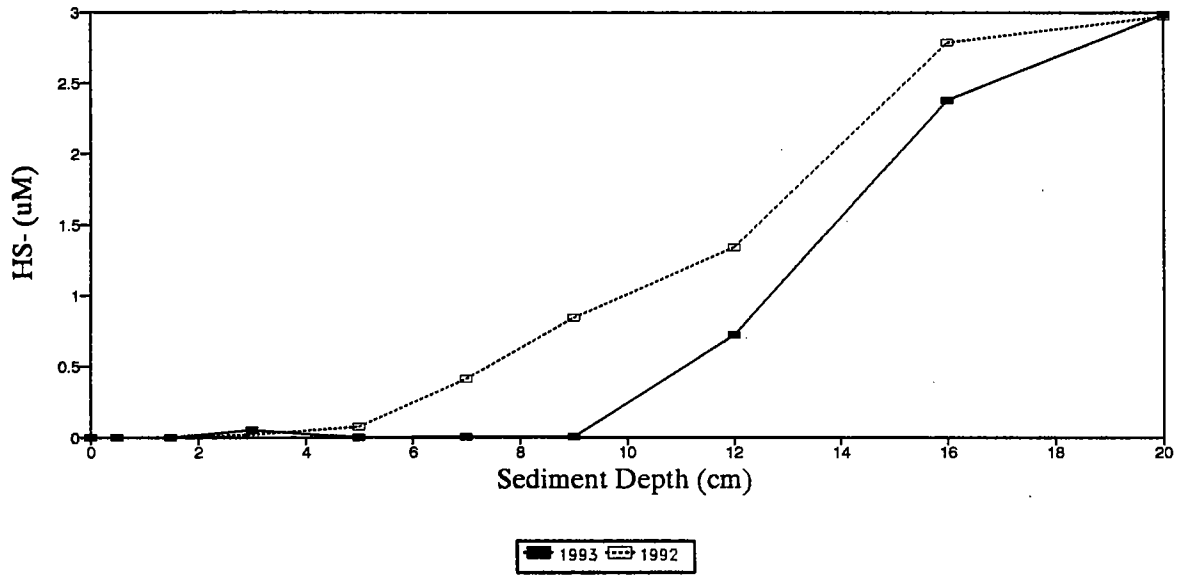


Figure 20. Porewater profiles of (a) H₂S and (b) Eh at two Boston Harbor (BH02, BH03) and two Massachusetts Bay (MB01, MB02) stations in February 1993. Values are taken from single sediment cores.

Porewater HS- at Station BH03
1993 compared to 1992



Porewater Eh at Station BH03
1993 compared to 1992

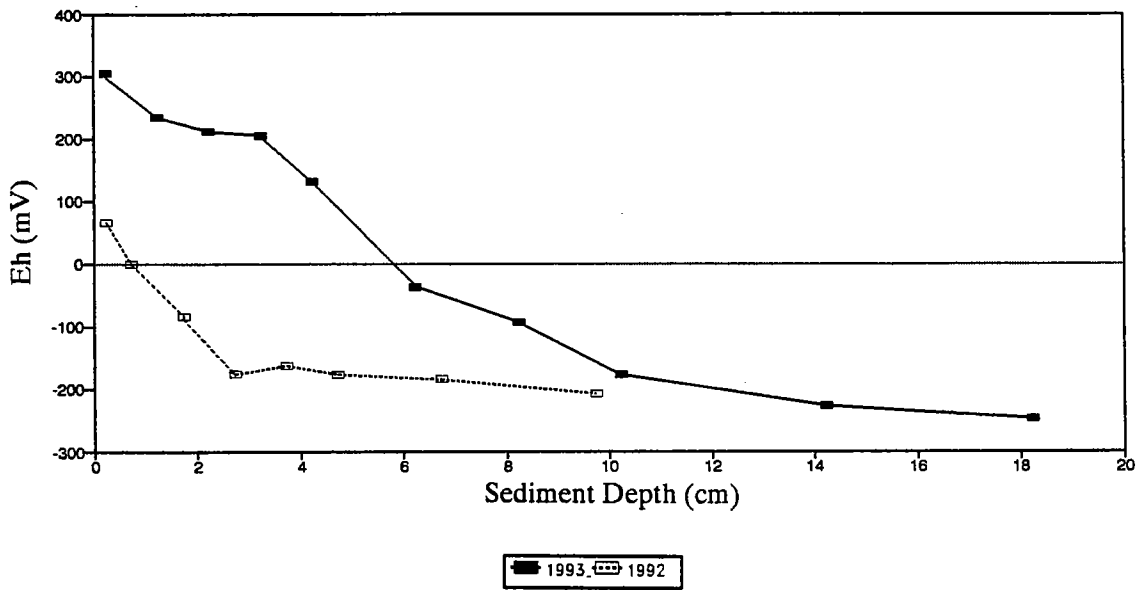


Figure 21. Comparison of porewater profiles measured at Boston Harbor station BH03 in 1992 and 1993; (a) H₂S and (b) Eh. Values are taken from single sediment cores.

5.0 SUMMARY AND MONITORING DESIGN ISSUES

- (1) Over the seasonal cycle, sediment oxygen uptake in the Harbor ranged from 7 mmol m⁻² d⁻¹ at a sandy site in the winter to 220 mmol m⁻² d⁻¹ at an organic-rich site in the summer. Oxygen uptake at station BH03, the former sludge discharge site near Long Island, was consistently higher than at any of the other Harbor stations.
- (2) Sediment oxygen uptake in the Bay ranged from 7 to 27 mmol m⁻² d⁻¹. Annual average respiration at the three nearfield sites (MB01, MB02, and MB03) only differed from each other by 5%, which was not significant. Respiration rates at the other shallow stations in Massachusetts Bay (MB04 and MB06) were similar to the nearfield stations. There was a significant relationship between temperature and the oxygen-uptake rates at all the shallow Massachusetts Bay stations. Oxygen uptake rates at station MB05 in Stellwagen Basin were lower than at the other Massachusetts Bay stations. Some of the difference between the shallow and deep stations could be attributed to temperature differences.
- (3) Denitrification rates observed in Boston Harbor (<0.24 to 9.9 mmol m⁻² d⁻¹; mean=2.9) were significantly higher than those observed in Massachusetts Bay (<0.24 to 2.6 mmol m⁻² d⁻¹; mean=1.1). Highest rates were observed in Boston Harbor at stations with high sediment organic content, at summer temperatures, when exceptionally high numbers of macrofauna (amphipods) were present. Denitrification relative to Harbor nitrogen loading increased at station BH03 in 1993, but at other stations rates were comparable to 1992.
- (4) Nutrient fluxes at the Bay nearfield stations were not as similar to each other as oxygen fluxes. Like oxygen, Si fluxes increase with increasing temperature. Dissolved inorganic nitrogen (DIN) and PO₄ did not show clear seasonal patterns related to temperature.
- (5) Although there was some spatial variability among sites in the Bay, in the future a major change in organic matter delivery to the sediments should be reflected in a measurable change in benthic fluxes. We need to know more about interannual variation before we can confidently calculate a minimum detectable change, but the close correspondence between the shallow Massachusetts Bay stations is encouraging. The HydroQual water-quality model predicts that benthic fluxes will change by four-fold at the diffuser to nondetectable several kilometers away. If the depositional nearfield areas experience an increase in O₂ uptake in the range of 50%, and if interannual variation is low, it should be detectable.
- (6) Controls on denitrification appear to be different in different environments. The annual cycle of denitrification in the highly organic depositional areas of Boston Harbor appears to be driven by temperature. In contrast, the Massachusetts Bay stations and the sandy Harbor station did not show a consistent temperature response or seasonal trend.
- (7) Measurements of total carbon dioxide (DIC) release gave a higher estimate of carbon mineralized in the benthos than measurements of oxygen uptake for nearly all stations and times. The one exception was at station BH03 where oxygen uptake exceeded DIC release. At the other two Harbor stations, DIC release exceeded oxygen uptake by 41%. Over an annual cycle in the Bay, DIC release exceeded oxygen uptake by about 20% at stations MB02 and MB03. Station MB01 was characterized by a much higher respiratory quotient (RQ); at this

station, respiration exceeded oxygen uptake by 75%. We need to investigate whether the high RQ at station MB01 was due to metabolism or whether carbonate dissolution was contributing to the DIC fluxes.

- (8) Harbor Station BH03, near the former MWRA sludge discharge site, has shown "recovery" in the large population of amphipods and other benthic animals colonizing the sediment for most of 1993. These animals have apparently greatly increased sediment metabolism, nitrogen release and denitrification. In spite of the high metabolic activity at this site, porewater sulfide concentrations over the top 10-12 cm have decreased, perhaps due to intense bio-irrigation. We expect that this increased metabolism is a transient response. The amphipod population was greatly reduced in October 1993 and metabolism appears to have slowed in response. The 1993 data from BH03 shows that there is the potential for some transient responses that may be beyond the predictive capacity of the HydroQual water-quality model. Further monitoring in 1994 will help determine how long those transients will last.
- (9) During summer, when benthic fluxes are maximal, the depositional sediments in western Massachusetts Bay consume less than 30% of the carbon produced in primary production and replenish less than 15% of the nitrogen and phosphorous. The nature of the coupling of the productive surface layer with the benthos during stratification is uncertain. Also unknown is the extent to which variation in organic matter supply interacts with bottom water temperature to regulate benthic processes in the Bay. It is clear, however, that factors other than benthic nutrient flux are influential in determining trends in bottom-water quality.
- (10) Porewater constituents are important indicators of sediment processes. Porewater sulfide and redox potential (Eh) are dramatically different between the Harbor and the Bay and may provide sensitive indicators of changes in organic matter loading. Because high concentrations of sulfides are toxic to infaunal animals, measurements of sulfides also provide a measure of habitat quality.

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