Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments in 1994

Massachusetts Water Resources Authority

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FINAL REPORT

METABOLISM, NUTRIENT CYCLING AND DENITRIFICATION IN BOSTON HARBOR AND MASSACHUSETTS BAY SEDIMENTS IN 1994

for

Massachusetts Water Resource 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. We measured sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen (ammonium, nitrate, urea), silicate, and phosphorus at stations in Boston Harbor and Massachusetts Bay. The amount of nitrogen being 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; 1992; 1993; 1994; Kelly and Nowicki, 1992; 1993). This study was designed to: (1) provide data to support the modelling effort in Massachusetts Bay, (2) monitor the recovery of the sludge disposal site in Boston Harbor, and (3) to better characterize the baseline conditions in Massachusetts Bay and Boston Harbor prior to wastewater diversion in 1996. Sediment chlorophyll *a* and phaeopigment concentrations are also provided for the first time.

This study provides information on the rates of benthic processes including oxygen consumption, nutrient regeneration and denitrification for stations in Boston Harbor and Massachusetts Bay. Special emphasis in this report is placed upon time, both seasonal and inter-annual, and on the comparison of the measured benthic fluxes versus those predicted using the water quality model developed by HydroQual.

The studies major conclusions are:

(1) Sediment oxygen uptake in the Harbor ranged over the seasonal cycle from approximately 20 mmol m^{-2} d^{-1} in the winter to 105 mmol m^{-2} d^{-1} at an organic rich site in autumn. For the first time since monitoring began, oxygen uptake at Station BH03, the former sludge disposal site near Long Island, was not consistently higher than any of the other Harbor Stations. Fluxes at this station still show considerable temporal variability which may be related to the sporadic presence of large numbers of benthic infauna.

(2) Sediment oxygen uptake in the Bay agreed extremely well with data from previous years ranging from 6 to 22 mmol m^{-2} d^{-1}. As was the case in 1993, the three nearfield sites, MB01, MB02, and MB03 had annual average respiration rates that were not significantly different from one another. Two other nearfield shallow stations sampled in August (NF8 and NF12) had similar respiration rates to the other nearfield stations. There was a significant relationship between the oxygen uptake rates of all the shallow Massachusetts Bay stations vs. temperature.

(3) Oxygen uptake rates at stations deeper in the Bay in Stellwagen Basin (MB05 and MB07) had lower respiration rates than other shallower Massachusetts Bay stations for most of the year. Some of the difference between the shallow and deep stations could be attributed to temperature.

(4) Denitrification rates in Boston Harbor ranged from non-detectable to 6.9 mmol N m^{-2} d^{-1}. The rates observed in 1994 were lower than in 1993, largely due to the large decrease in denitrification rates at BH03 in 1994. Highest rates were observed at BH03 in October when exceptional numbers of amphipods were present.

(5) Denitrification rates in Massachusetts Bay ranged from non-detectable to 2.7 mmol N m^{-2} d^{-1}. Rates at the nearfield stations averaged 1.2 mmol N m^{-2} d^{-1}, nearly identical to rates measured in 1993.

(6) Dissolved inorganic nitrogen and phosphate fluxes at the Bay nearfield stations were not as similar to each other as oxygen fluxes but the stations all exhibited similar seasonal trends. The 1994 DIN fluxes were within 20% of the 1993 values but the phosphate fluxes were nearly twice as high. Silica flux rates at all the nearfield stations were very similar. Silica release from the sediments in 1994 was 48% greater than in 1993 mostly due to higher fluxes in July.

(7) Although there is some spatial and temporal variability in the fluxes from Bay sites, a major change in organic matter delivery to the sediments should be reflected in a measurable change in benthic fluxes. The close correspondence between rates of oxygen uptake and DIC and nutrient fluxes from the shallow Massachusetts Bay stations, and the low inter-annual variability of the oxygen, DIC and DIN fluxes is encouraging. The HydroQual model predicts that benthic fluxes will change by four-fold at the diffuser to non-detectable several km away (Hunt and Steinhauer, 1994). If the depositional nearfield areas experience an increase in the range of 50%, it should be detectable.

(8) The release of total carbon dioxide over the season gave a higher estimate of carbon mineralized in the benthos than did oxygen uptake for all stations. At two Harbor stations (BH02 and BH03), DIC release exceeded oxygen uptake by about 40%. Over an annual cycle at the nearfield Bay stations (MB01, MB02, MB03) DIC release exceeded oxygen uptake by 54-60%. At the deeper Bay stations (MB05 and MB07), oxygen uptake and DIC release were nearly equal.

(9) At all stations urea was a very minor component of the nitrogen flux we measured (urea, nitrate, ammonium, N_2). Over the annual cycle ammonium was the most important component of the nitrogen flux in the Harbor, followed by N_2 with nitrate making up a smaller, but significant component of the flux. In the nearfield ammonium and N_2 had nearly identical contributions to the total nitrogen flux with nitrate making up an average of 6% of the N released from all nearfield stations. The most important component of the nitrogen flux at the farfield stations was N_2, which made up 66% of the total nitrogen flux with the remainder being almost equally composed of ammonium and nitrate.

(10) Depositional sediments in Massachusetts Bay could consume between 17% (based upon oxygen) to 28% (based upon DIC) of the production in the overlying water. Benthic nutrient release could supply 11% of the N and 25% of the P required for primary production.

(11) Porewater constituents are important indicators of sediment processes. Porewater sulfide and Eh are dramatically different between the Harbor and the Bay and may provide sensitive indicators of changes in organic matter loading.

(12) In general, there is good agreement between measured fluxes and fluxes predicted by the HydroQual model in the Bay. Overall, silica shows the largest consistent difference between measured and predicted fluxes. This may reflect the bias of the sampling toward depositional areas or suggest some problem with the model parameterization.

(13) Station BH03, the former sludge disposal area, continues to exhibit large inter-annual differences in benthic fluxes and porewater chemistry. Fluxes in 1994 were considerably lower than in 1993. High flux rates appear to be correlated with visual observations of large numbers of benthic invertebrates.

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1.0 INTRODUCTION

This study was undertaken to examine temporal and spatial patterns of benthic processing of organic matter in Boston Harbor and Massachusetts Bay. We measured sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen (ammonium, nitrate, urea), silicate, and phosphorus at stations in Boston Harbor and Massachusetts Bay. The amount of nitrogen lost from sediments as nitrogen gas by the microbial processes of denitrification was also measured. Sediment chlorophyll *a* and phaeopigment concentrations are also provided for the first time. The study is a continuation and expansion of previous work carried out in the Harbor and in the Bay (Giblin *et al.*, 1991; 1992; 1993; 1994; Kelly and Nowicki, 1992; 1993). This study was designed to: (1) provide data to support the modelling effort in Massachusetts Bay, (2) monitor the recovery of the sludge disposal site in Boston Harbor, and (3) to better characterize the baseline conditions in Massachusetts Bay and Boston Harbor prior to wastewater diversion in 1996.

We have discussed the importance of benthic fluxes from an ecological perspective at length in 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 and consumes oxygen. The nutrients which are released 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 effectively 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, generally ranging from 15 to 70% of the inorganic nitrogen mineralized during decomposition (Seitzinger, 1988).

This study provides information on the rates of benthic processes including oxygen consumption, nutrient regeneration and denitrification for stations in Boston Harbor and Massachusetts Bay. Special emphasis in this report is placed upon time, both seasonal and interannual, and on the comparison of the measured benthic fluxes versus those predicted using the water quality model developed by HydroQual.

2.0 SAMPLING DESIGN

The sampling sites are shown in Figure 1. All of the Harbor sites sampled in 1994 were sampled previously in 1992 and 1993. Several sites in Massachusetts Bay (MB07, NF8 and NF12) were sampled for the first time. Surveys were carried out during early March, early-May, mid-July, late August, and late October. All survey cruises were completed in two or three days. The sampling dates, times, water depths, water temperatures, and bottom water oxygen concentrations of the sites are shown in Table 1.

2.1 Location and Rationale for Stations

Harbor

During 1992 we made annual measurements of benthic processes at two stations; a sandy station in Hingham Bay (BH08), and a muddy station off Long Island (BH03) (Giblin *et al.*, 1993; Kelly and Nowicki, 1993). A number of other Harbor sites have been sampled one to four times since 1990 (Giblin *et al.*, 1991; 1992; Kelly and Nowicki, 1992). Station BH03 received sewage sludge until December of 1991 when discharge ceased. During 1992, conditions at BH03 were changing rapidly and it was difficult to know how well this site represented the other muddy areas in the Harbor. During 1993 both BH03 and BH02 were sampled five times over the season. Station BH08 was sampled twice to provide some further information on sandy sites.

Four Harbor stations were sampled during 1994. BH03 was chosen to follow the long term recovery at this site following the termination of sludge dumping. Station BH02 was monitored because it is considered more typical of the muddy sediments near the sewage outfall. Stations BH08 and BH07 were sampled once in July. These two stations are considered typical of the sandy (BH08) and muddy (BH07) areas in the Southern Outer Harbor.

Bay

Prior to 1993, the Massachusetts Bay stations had been sampled only in autumn. During 1993 we obtained an annual cycle at three stations located in the nearfield area of the proposed outfall - MB01, MB02, MB03. These stations were sampled again five times during 1994. In 1993 we sampled several other stations just outside the nearfield area (MB04 and MB06) but both sites were difficult to box core and were

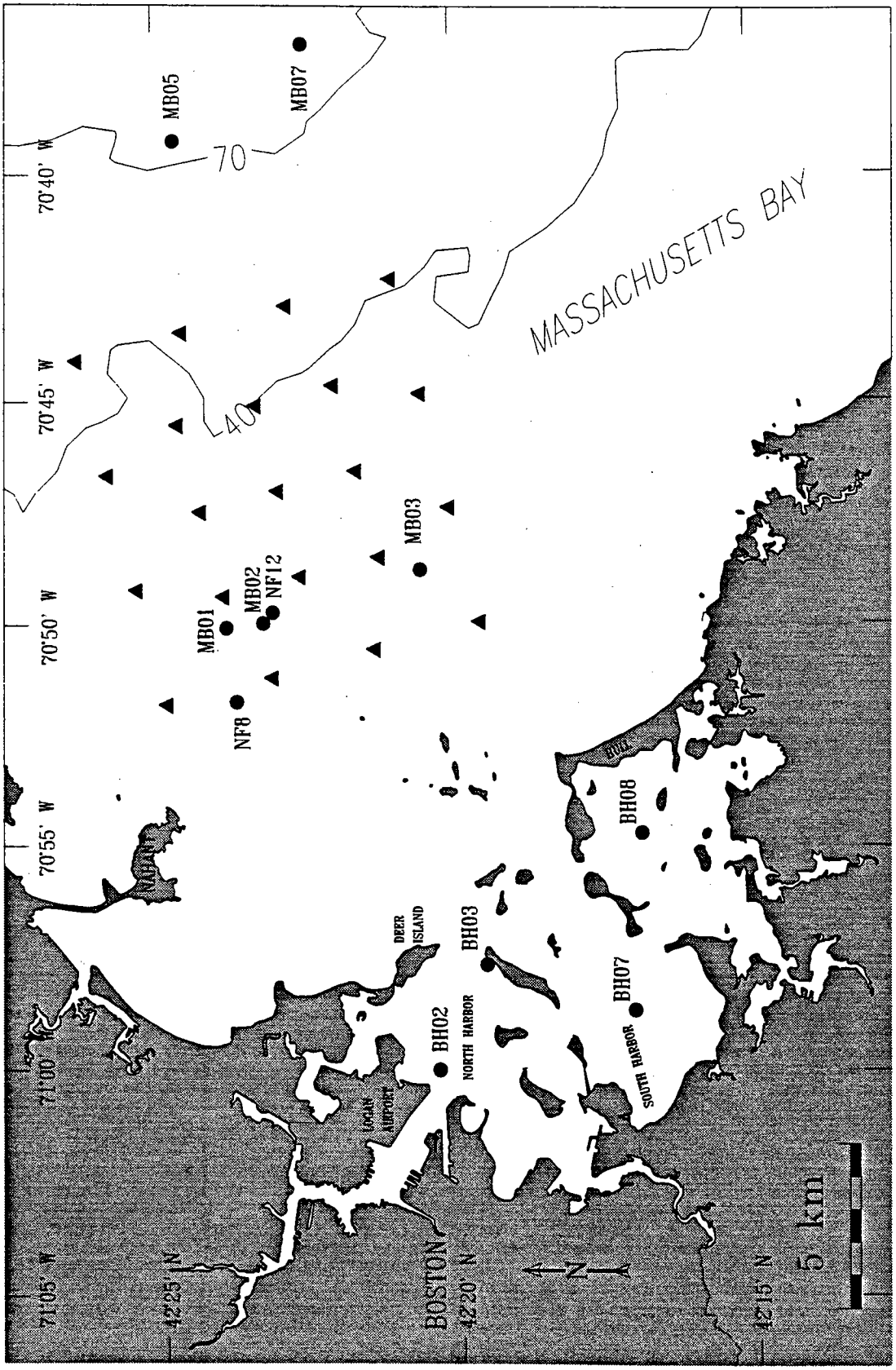


Figure 1. **Benthic flux stations sampled in Boston Harbor and Massachusetts Bay in 1994. Triangles show MWRA water column sampling nearfield stations in 1994.**

Table 1. 1994 benthic flux station locations and associated bottom water quality information.

Event	Station	Date	Field Latitude deg min sec	Field Longitude deg min sec	Depth (m)	Temp (°C)	Dissolved Oxygen (mg/L)
B9401	BH02	09-Mar-94	42 20 59	71 00 03	13.4	1.3	11
B9401	BH03	09-Mar-94	42 19 78	70 57 69	8.5	1.3	11.29
B9401	MB01	08-Mar-94	42 24 17	70 50 19	35.1	1.6	11.43
B9401	MB02	08-Mar-94	42 23 54	70 50 00	34.9	1.6	11.61
B9401	MB03	08-Mar-94	42 20 87	70 48 89	34.9	1.5	11.36
B9401	MB05	08-Mar-94	42 24 98	70 39 26	76.2	2.1	11.01
B9402	BH02	04-May-94	42 20 62	71 00 05	11	8.6	10.12
B9402	BH03	04-May-94	42 19 80	70 57 70	8.5	7.8	9.73
B9402	MB01	03-May-94	42 24 18	70 50 20	32.9	4.1	9.68
B9402	MB02	03-May-94	42 23 58	70 50 10	33.5	4.1	9.64
B9402	MB03	03-May-94	42 20 80	70 48 91	33.8	3.7	9.46
B9402	MB05	03-May-94	42 24 97	70 39 30	75.6	3.9	9.93
B9402	MB07	03-May-94	42 22 51	70 37 06	75.6	4.0	9.88
B9403	BH02	11-July-94	42 20 60	71 00 07	12.8	16.5	8.9
B9403	BH03	11-July-94	42 19 82	70 57 73	10.1	16.6	9.22
B9403	BH07	11-July-94	42 17 32	70 58 72	7	17.1	8.94
B9403	BH08	11-July-94	42 17 17	70 54 73	12.2	15.5	9.27
B9403	MB01	12-July-94	42 14 16	70 50 18	34.1	7.2	8.73
B9403	MB02	12-July-94	42 23 54	70 50 06	33.5	7.1	8.76
B9403	MB03	12-July-94	42 20 87	70 48 90	33.5	7.6	8.39
B9404	MB01	29-Aug-94	42 24 14	70 50 20	33.5	9.9	6.81
B9404	MB02	29-Aug-94	42 23 55	70 50 07	34.5	10.3	6.92
B9404	MB03	29-Aug-94	42 20 89	70 48 90	34.1	10.2	7.16
B9404	MB05	29-Aug-94	42 25 00	70 39 26	74.7	7.7	7.18
B9404	MB07	29-Aug-94	42 22 53	70 37 08	75.6	7.6	7.34
B9404	NF12	29-Aug-94	42 23 42	70 49 81	34.8	10.1	7
B9404	NF8	29-Aug-94	42 24 03	70 51 81	30.8	10.0	6.76
B9405	BH02	18-Oct-94	42 20 59	71 00 04	12.65	13.6	*
B9405	BH03	18-Oct-94	42 19 78	70 57 68	7.93	12.7	*
B9405	MB01	20-Oct-94	42 24 18	70 50 24	33.54	11.8	5.57
B9405	MB02	20-Oct-94	42 23 55	70 50 06	35.37	11.7	5.89
B9405	MB03	20-Oct-94	42 20 88	70 48 92	36.28	11.3	5.38
B9405	MB05	20-Oct-94	42 24 99	70 39 12	77.13	10.5	6.26

* No data reported

not re-sampled in 1994. Two other nearfield stations, NF8 and NF12 were sampled in August to provide more information on spatial variability in the nearfield area.

Two deep stations in Stellwagen basin were sampled (MB05 and MB07). Station MB05 had been previously sampled in August and October of 1993 and was sampled four times in 1994. Station MB07 was south of MB05 in similar water depth and sampled in May and July. MB07 had not been sampled in previous years.

3.0 METHODS

The methods used in this study have been previously described in Giblin *et al.* (1993) and in the Combined Work/Quality Assurance Project Plan (CW/QAPP) presented to MWRA (Kelly *et al.*, 1993). They will be only briefly described here. Because the monitoring of these stations in 1995 will be carried out by other investigators we have noted any deviations from the CW/QAPP and discuss specific aspects of the methods which may not be obvious from the previous reports.

3.1 Sampling

All stations in Boston Harbor were sampled by SCUBA divers. The Massachusetts Bay samples were obtained using a box corer (40×40 cm or 50×50 cm) with pre-mounted 15-cm core tubes. Two to three large pre-mounted core tubes were used to obtain sediment for flux measurements. Additional cores were collected from the filled box core after retrieval. Replicate 6.5-cm diameter core tubes were collected 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 N_2 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 using 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 overlying water in the cores just prior to flux measurements.

3.2 Benthic Respiration and Nutrient Fluxes

Cores were transported to Woods Hole, MA, submerged in water in large insulated containers and maintained at in-situ temperatures. Before transporting the cores, care was taken to be sure that the headspaces of the cores were completely filled with water. This prevents sediment disturbance during handling. Upon arrival cores were 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 hours 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 obtained 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 hrs). 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 uptake in the water overlying the cores by using O_2 changes measured in BOD bottles. Taking measurements over time enabled us to determine whether oxygen consumption was linear over time.

Concurrent with O_2 measurements, samples of the overlying water were withdrawn for dissolved inorganic nitrogen and phosphorus, urea, and silicate analysis. Ammonium concentration was determined within 12 hrs. from duplicate 3 ml subsamples by the technique of Solorzano (1969), modified for small sample size. A 3 ml sample was saved for phosphate analysis and acidified to pH 2 with 10 μl of 4.8N HCl and kept at 4 °C until analysis. Samples were analyzed using the spectrophotometric method of Murphy and Riley (1962).

Additional sub-samples were frozen for later measurement of the nitrate + nitrite, silicate, and urea concentrations. Nitrate + nitrite were determined together using the cadmium reduction method on a rapid flow analyzer (Alpkem RFA-300). Although the CW/QAPP reported a the limit of detection limit of

>0.5 μM, the detection limit in both 1993 and 1994 was considerably lower, 0.1 μM. DIN was calculated as the sum of ammonium, nitrate, and nitrite. Silicate was analyzed by reduction with stannous chloride using an autoanalyzer (method of Armstrong, 1951 as adapted by RFA, Alpkem Corp., 1986). Urea was analyzed using the method of Price and Harrison (1987). This method is reported superior to the enzymatic methods more commonly used but the reagents are extremely toxic and the entire procedure, including the absorbance measurements, should be carried out in a fume hood. In 1993 we did not report the urea data because of contamination problems. Although we did have contamination in 1993 serious enough to compromise the absolute urea values by more than 100% the values were still quite low and we believe that fluxes of urea in 1993 were nearly always low relative to the DIN fluxes. We discovered that the vials we were using for sample storage (standard scintillation vials) had caps made of polyurea. Evidently the caps were breaking down during the acid washing of the vials and contaminating the samples. We switched to new caps and did not experience any contamination problems in 1994.

Our 1993 silica fluxes were quite high compared to Si fluxes predicted by the HydroQual model and when compared to Si build up in the overlying water when Massachusetts Bay was stratified. We have rechecked all of our Si procedures and purchased a certified Si standard. We have found no problems with our methods. In this report we discuss reasons why the Si fluxes we measure may be higher than expected from either the model or the concentrations in bottom water.

At the beginning and end of the incubation period, 60 mL samples were also taken for total CO_2 analysis. These samples were stored at 4°C in glass BOD bottles with mercuric chloride (50 μL of a $HgCl_2$ saturated solution) as a preservative. Samples were analyzed with a high precision coulometric CO_2 analyzer capable of measuring total CO_2 with a precision of 0.05% (1 μM).

3.3 Porewater Sampling and Analysis

Sediment samples for porewater extraction 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 in a separate core using a platinum electrode (Bohn, 1971). The values reported here have been corrected for the potential of the reference electrode.

3.4 Porosity and Sediment C and N

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 after a minimum of 72 hrs at 105°C. 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).

The depth intervals were measured from the apparent top of the sediment surface. At some stations, especially BH03, a large number of biogenic tubes protruded above the sediment surface. These were included in the sediment sample so reported carbon and nitrogen values include all of the material in the core. Because these tubes had substantial quantities of water in them they may have increased the apparent porosity of the surface samples.

Organic carbon and nitrogen were measured on the top 2 cm of sediment. Analyses were performed on a Perkin Elmer 2400 CHN elemental analyzer following carbonate removal. The % carbon and nitrogen measured on the sediment was corrected for the weight change due to the procedure which was usually 3-7%.

3.5 Chlorophyll *a* and Phaeopigments

Chlorophyll pigments were measured in 1 cm increments down to 5 cm from a 2.5 cm diameter core. Each sediment section was placed in a separate centrifuge tube and frozen. Samples were later extracted with cold acetone in the dark. After extraction, samples were centrifuged and the absorbance of the supernatant was measured at 750 and 665 nm before and after acidification (Strickland and Parsons, 1972).

Some of the 1994 samples were stored in polystyrene centerfuges tubes which became brittle when frozen. Some samples were lost when these tubes were centrifuged. This problem was solved by switching to polyethylene tubes.

In reviewing the data we discovered that some of the absorbances at 750 nm were quite high. Evidently when transporting the tubes to another lab there was some resuspension of the sediment. These tubes should have been recentrifuged before analysis. In theory, the 750 nm wavelength corrects for turbity so this may not represent a serious problem. However, in a few cases the turbity was high enough that the data may be compromised. Data where the turbidity was high is flagged in the MWRA data base. In this report we have limited our discussion to the average chlorophyll and phaeopigment concentrations in the top 5 cm. When substantial numbers of samples from any core are missing or appear to have been compromised we have not included the data in this report.

3.6 Direct Measurements of Denitrification

Sediment denitrification was measured as the direct flux of N_2 gas from sediment cores in gas-tight N_2-free chambers. Two sediment cores were incubated from each site on each sampling date; one was used for measurements of total sediment N_2 flux ("experimental core") and the other as 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 m^2 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 O_2) to remove nitrogen but to maintain dissolved oxygen concentrations at levels similar to those observed in bottom waters in the field. Control cores were taken at the time of sediment sampling, and were treated in the same manner as the experimental cores, but were maintained without oxygen so that coupled denitrification was prevented. These anoxic control cores were used to monitor and correct for background fluxes of N_2 (due primarily to N_2 into porewater diffusing into the N_2-free head space) which were not caused by denitrification (Nowicki, 1994).

Measurements of the concentrations of nitrogen and oxygen in the gas-filled head space of each chamber were determined from samples (50 μL) withdrawn with a gas-tight syringe from the chamber sampling port. 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 were run with each set of samples using a certified standard gas mixture.

The URI oxygen data is taken as an ancillary measurement and is present in the MWRA data base but not reported here. In general there is good agreement between the two data sets at low rates of oxygen uptake but at the highest rates of oxygen uptake, the URI data tends to be lower than the MBL data.

A detailed description of the method used for calculating sediment denitrification rates is given in the CW/QAPP (Kelly *et al.*, 1993). Briefly, rates of N_2 gas production and O_2 uptake for sediments in the denitrification chambers were calculated from the slopes of 4-point linear regressions of N_2 or O_2 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.

3.7 Denitrification Using the Stoichiometric Method

The stoichiometric method of measuring denitrification is an indirect method which involves three 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. The third assumption is that denitrification is the major processes removing the missing nitrogen.

Giblin *et al.* (1993) thoroughly discusses the assumptions and problems with this method. We compared three ways to measure total sediment decomposition: oxygen uptake, oxygen uptake + alkalinity flux, and total DIC fluxes. We concluded that DIC fluxes were probably the best measure of total sediment metabolism. However, there is the possibility that DIC fluxes are being influenced by 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

Most of the 1994 data is summarized in graphical form to facilitate discussion. All of the raw data is available in electronic form from MWRA.

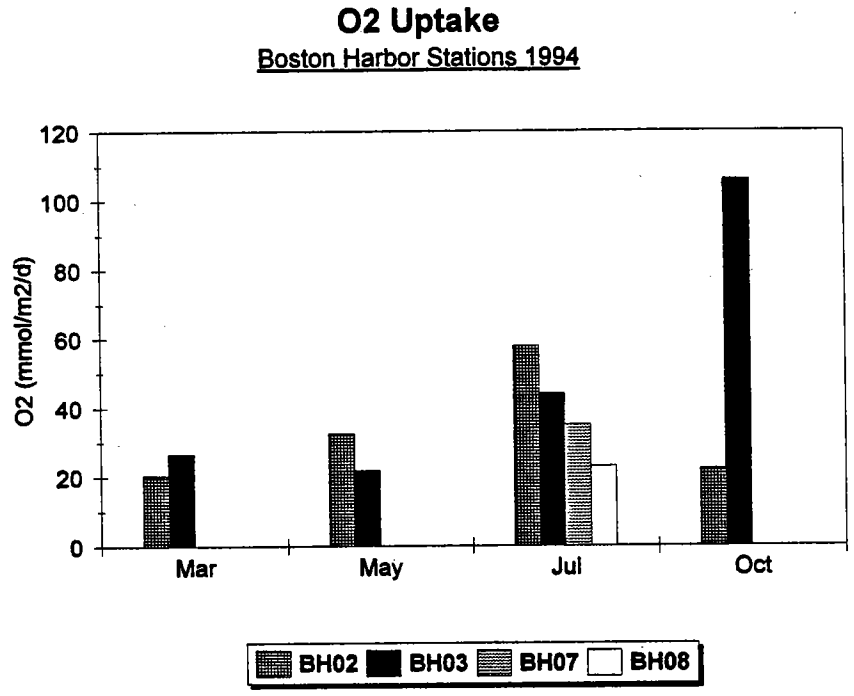
4.1 Benthic Respiration and Nutrient Fluxes

4.1.1 Oxygen Uptake

Harbor

Harbor sediment oxygen uptake ranged from approximately 20 to 105 mmol O_2 m^{-2} d^{-1} between March and October 1993 (Figure 2a). Respiration at BH02 followed the seasonal change in water temperature, peaking at 57 mmol O_2 m^{-2} d^{-1} in July. The rates at BH02 (off Logan Airport) were fairly similar to those observed in previous years except that the high respiration rate measured in May 1993 was not repeated in May of 1994 (Giblin *et al.*, 1992; 1993).

Respiration at BH03 (the old sludge discharge site) followed a different seasonal pattern than BH02, peaking at 105 mmol O_2 m^{-2} d^{-1} in October. Both rates and the seasonal pattern of respiration at this station were more similar to that observed in 1992 than in 1993 (Figure 2b). The year to year differences we have observed in respiration rates at this site continue to be correlated with qualitative observations by divers of animal abundances. In later summer 1992 high abundances of amphipods were noted at this



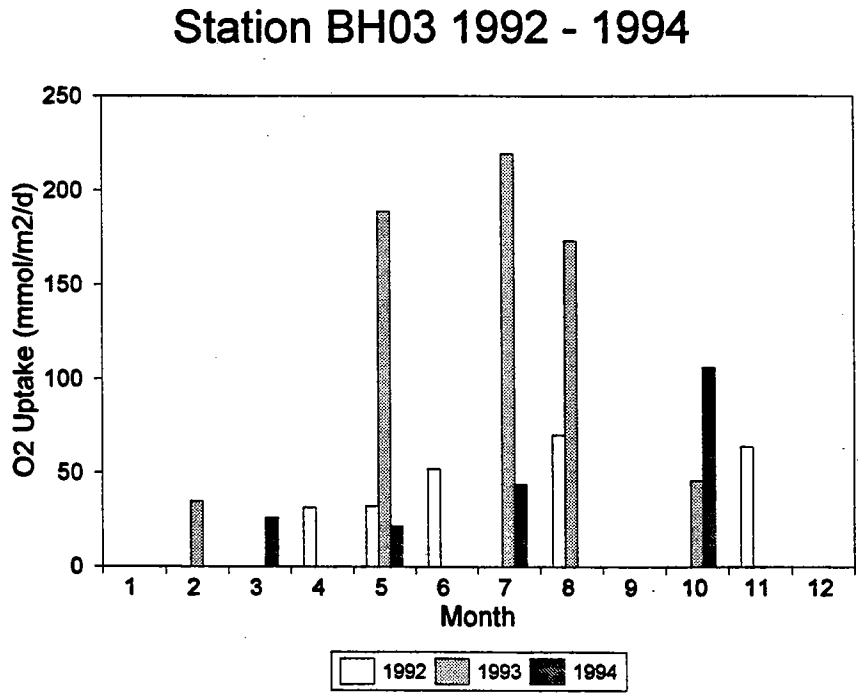


Figure 2. **(a) Sediment oxygen uptake at the Boston Harbor stations in 1994. (b) Comparison of sediment oxygen uptake in 1992, 1993, and 1994 at Boston Harbor Station BH03.**

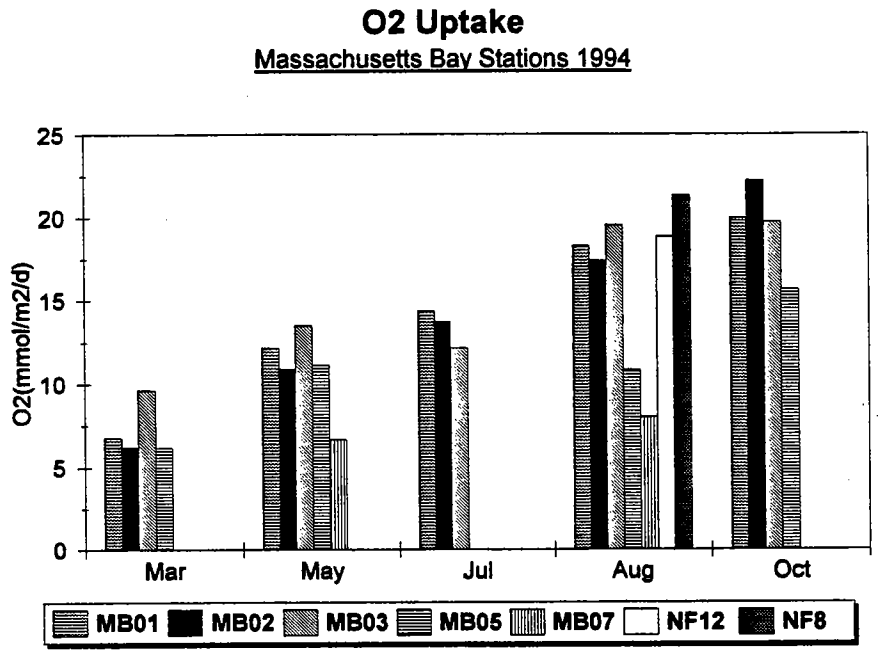
station when respiration rates were peaking. These amphipods were also observed in very high numbers during the first 4 sampling periods in 1993. In October of 1993, when the amphipods had largely disappeared, oxygen uptake had fallen to values lower than in November of 1992. Animal abundances remained at moderate levels until the last sampling of 1994, when densities and respiration increased again.

In contrast to 1992 and 1993, respiration rates at station BH03 were not consistently higher than at any of the other harbor sites; station BH02 had similar or higher respiration rates for three of the four sampling periods. However, when integrated over the annual cycle oxygen uptake at BH03 exceeded that of BH02. When sampled in July, station BH08 had the lowest respiration rate of all the stations sampled. This is consistent with our data from 1991-1993 (Giblin *et al.*, 1992; 1993).

Bay

The temporal pattern and magnitude of oxygen uptake of the Bay Stations were similar to that seen in previous years. Oxygen uptake rates ranged from about 6 to 22 mmol O_2 m^{-2} d^{-1} and reached their maximum values in October (Figure 3a). As was the case for 1993, there was no consistent difference in the respiration rates between any of the three shallow Massachusetts Bay stations routinely sampled (MB01, MB02, MB03). The two other nearfield stations sampled in August (stations NF8 and NF12) had respiration rates similar to the more frequently sampled shallow stations. Average seasonal respiration rates of the two deeper stations in Stellwagen basin (MB05 and MB07) were lower than shallow stations but the differences were not always significant during all months.

In our previous report (Giblin *et al.*, 1994) we suggested that temperature appears to account for the seasonal pattern of respiration as well as much of the difference in the respiration rates between all the Bay stations (Figure 3b). When respiration rate is plotted against temperature there is a fairly good relationship. However, it does appear that the deeper stations (MB05 and MB07) in Stellwagen Basin do have lower respiration rates than the shallower Bay stations even when correcting for the temperature differences. As noted in our last report, others have observed that in some locations sediment respiration decreases with increasing water depth because less organic matter reaches the bottom due to increased decomposition in the water column (Hargrave, 1975).



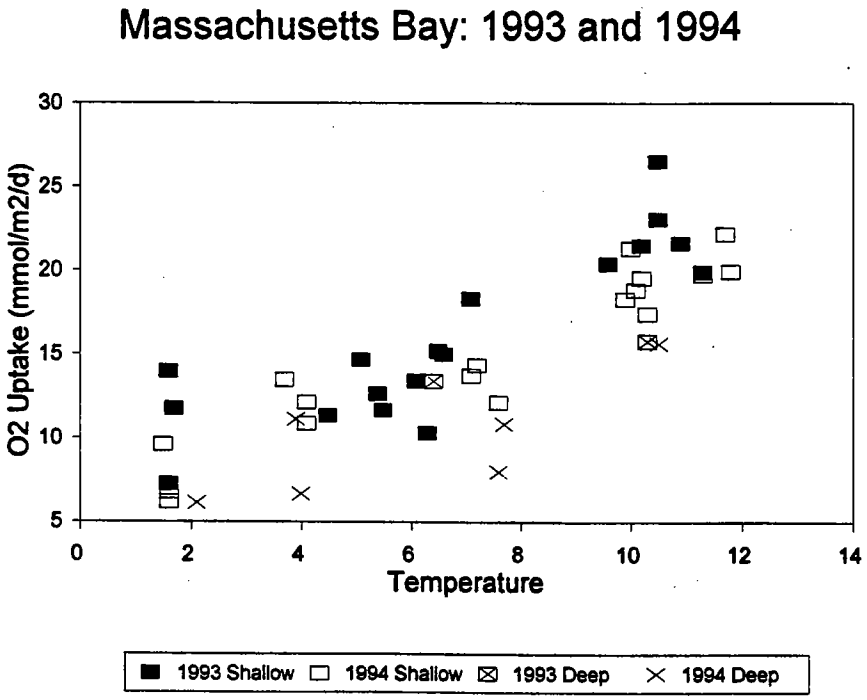


Figure 3. **(a) Sediment oxygen uptake at the Massachusetts Bay stations in 1994. (b) Relationship of oxygen uptake to bottom water temperature in 1993 and 1994 for shallow (~30 m) and deep (>70 m) stations.**

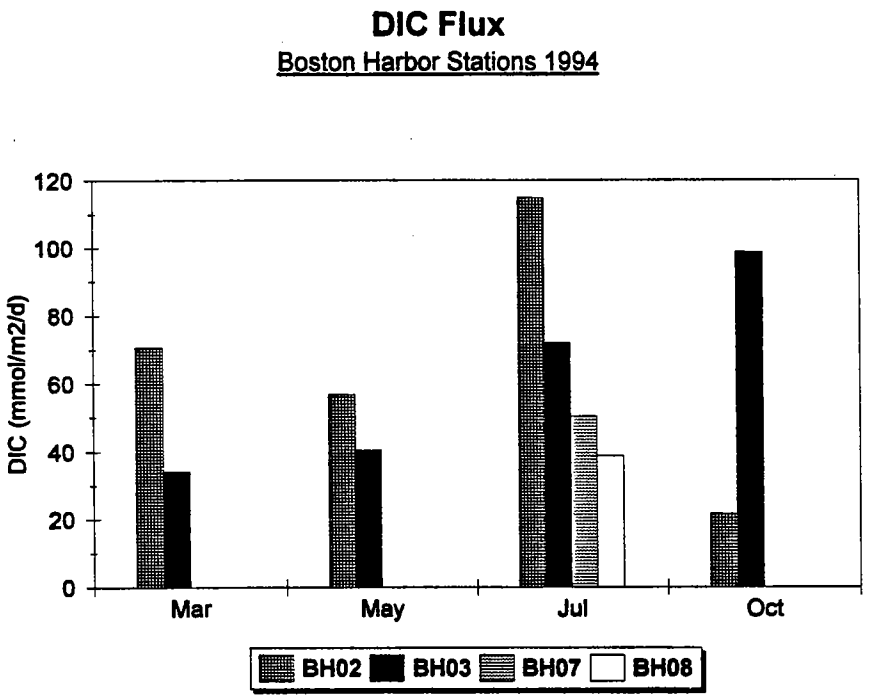
4.1.2 Total CO_2 Measurements

Harbor

Total CO_2 fluxes at Harbor stations ranged from approximately 21 to 115 mmol CO_2 m^{-2} d^{-1} between March and October 1993 (Figure 4a). The seasonal pattern of DIC fluxes was fairly similar to oxygen uptake. Fluxes were higher at station BH02 (off Logan Airport) than at BH03 (the former sludge discharge site) from March through July but higher at BH03 during October. Integrated over an annual cycle, the DIC fluxes at BH02 were slightly higher than at BH03. In July, DIC fluxes at BH07 and BH08 were lower than at BH02 and BH03. The same differences in the annual patterns of oxygen release between 1993 and 1994 were evident in the DIC release.

The ratio of DIC release to oxygen uptake (RQ or respiratory quotient) had a large range at station BH02; 0.97 to 3.47. Integrated over the annual cycle, DIC release at this station was 204% of the oxygen uptake, higher than the 141% we measured in 1993. Station BH03 also had a higher RQ in 1994 than in 1993. In 1993 oxygen uptake exceeded DIC release (RQ=0.84) while in 1994 DIC release was 143% of oxygen uptake.

As discussed in our previous report (Giblin *et al.*, 1993), the aerobic respiration of organic matter with an oxidation state close to carbohydrates (CH_2O) should have an RQ of 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, storage of reduced compounds such as sulfide can change considerably causing oxygen to overestimate respiration at some times of the year and underestimate it at other times. Over an annual cycle the RQ should be closer to 1. Deviations from an RQ of 1 closely reflect the portion of sulfide which is stored in the sediments as pyrite or FeS. The average annual RQ value of 1.74 we measured at Station BH02 in 1994 could reflect a high amount of sulfur storage and suggests that sulfur storage was greater in 1994 than in 1993. The change in the RQ we observed at station BH03 indicates that in 1993 more sulfides were oxidized over the season than were produced but that in 1994 the situation had reversed and sulfides were being stored. This change is consistent with the lower animal abundances at this station and the decreased sediment irrigation in 1994 when compared to 1993.



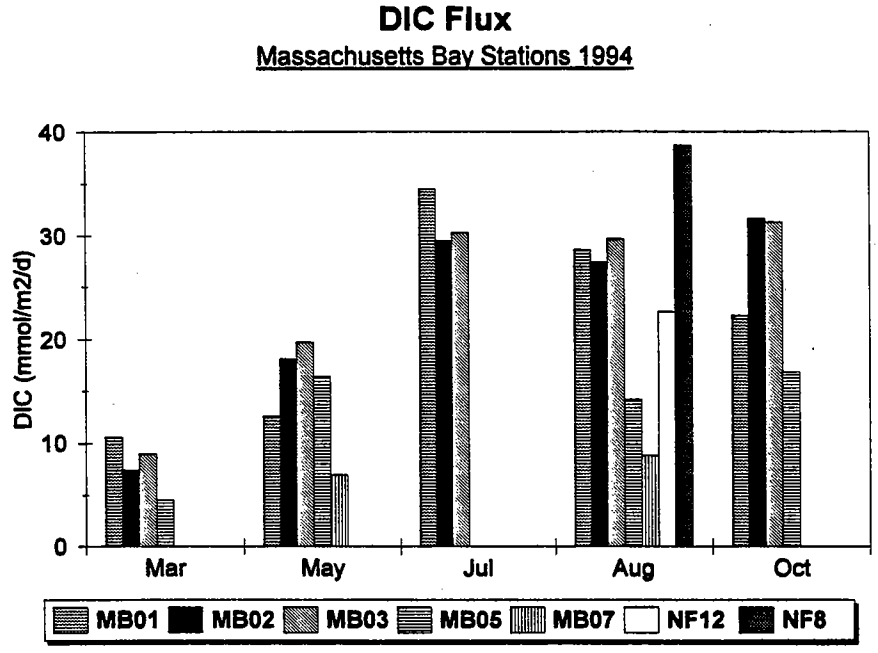


Figure 4. **Flux of DIC (total CO_2) at (a) the Boston Harbor stations and (b) the Massachusetts Bay stations in 1994.**

Bay

In Massachusetts Bay total CO_2 fluxes ranged from 4.5 to 38.7 mmol C m^{-2} d^{-1} (Figure 4b). On most occasions, DIC fluxes were higher than O_2 uptake and all Bay stations had an average RQ greater than 1. The average annual RQ we measured in 1993 at station MB01 was considerably higher than MB02 or MB03 but in 1994 all stations had similar values (1.54-1.60). The RQ's of the deeper stations (MB05 and MB07) were lower, averaging 1.07.

In our previous report we discussed the possibility that the DIC flux is being influenced by carbonate dissolution at these sites. To examine this possibility, we examined calcium fluxes from two cores. We were not able to detect a calcium flux suggesting that carbonate dissolution was not taking place but more samples would have to be analyzed before it could be ruled out.

4.1.3 DIN Release from Sediments

Harbor

The combined flux of DIN from sediments to the overlying water ranged from a slight DIN uptake of 0.03 mmol N m^{-2} d^{-1} at Station BH03 in March to a release of more than 11 mmol N m^{-2} d^{-1} at Station BH02 in July (Figure 5a). At station BH02, and to a lesser extent at BH03, the seasonal pattern of DIN release was similar to the pattern of oxygen uptake.

Sediments from stations BH03 and BH02 both took up nitrate from the overlying water in March and released it during the rest of the year (Figure 5b, 5c). During May through October the nitrate fluxes from station BH03 were somewhat higher than those of BH02, and nitrate made up a considerably greater proportion of the total DIN flux at BH03 during May and July.

We continue to observe large inter-annual differences in the nitrogen dynamics at station BH03. The DIN fluxes in May and July 1993 greatly exceeded what we observed during a similar period in 1992 or 1994. The percentage of the DIN flux which consisted of nitrate was much greater in 1993 than in either 1992 or 1994.

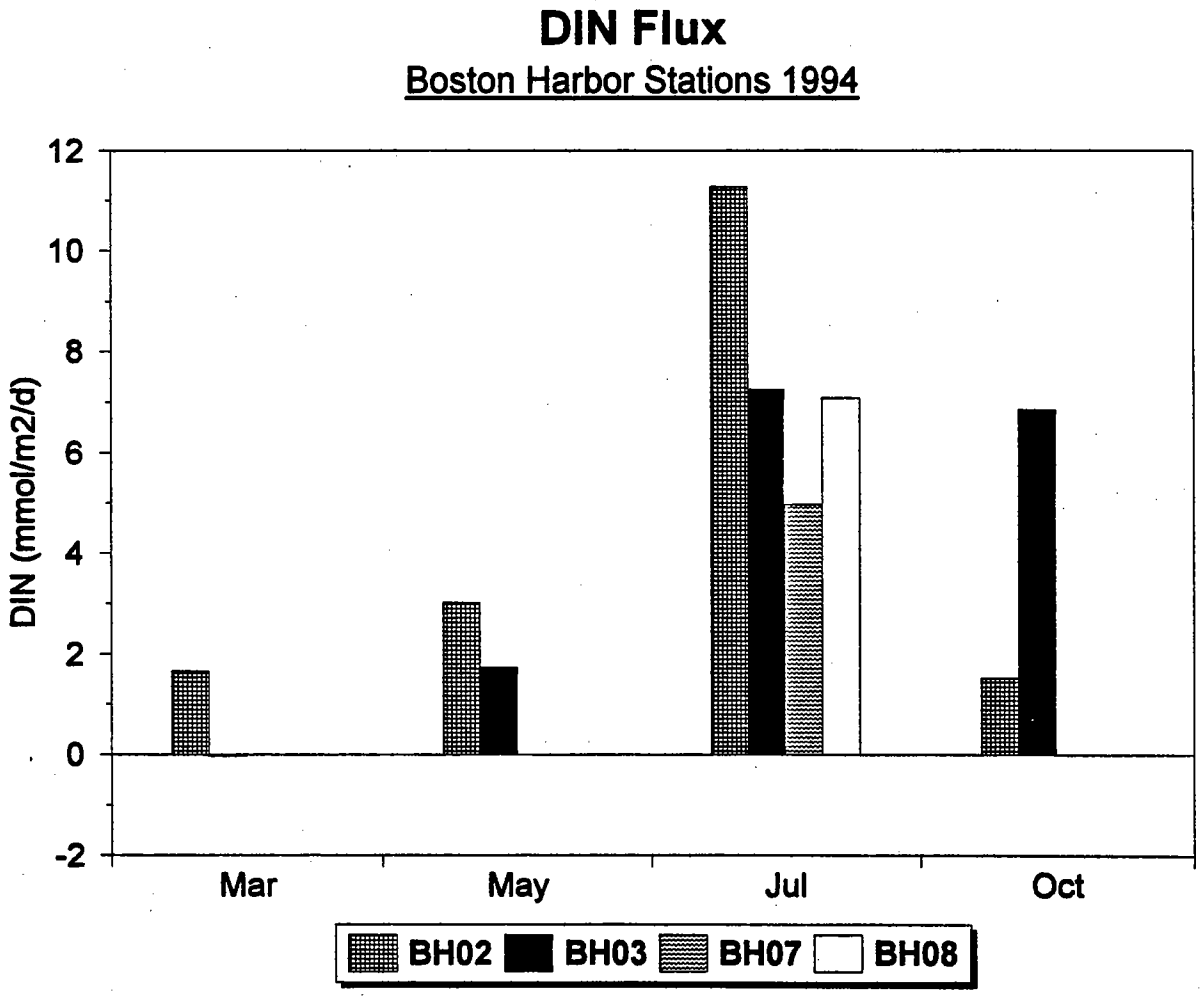
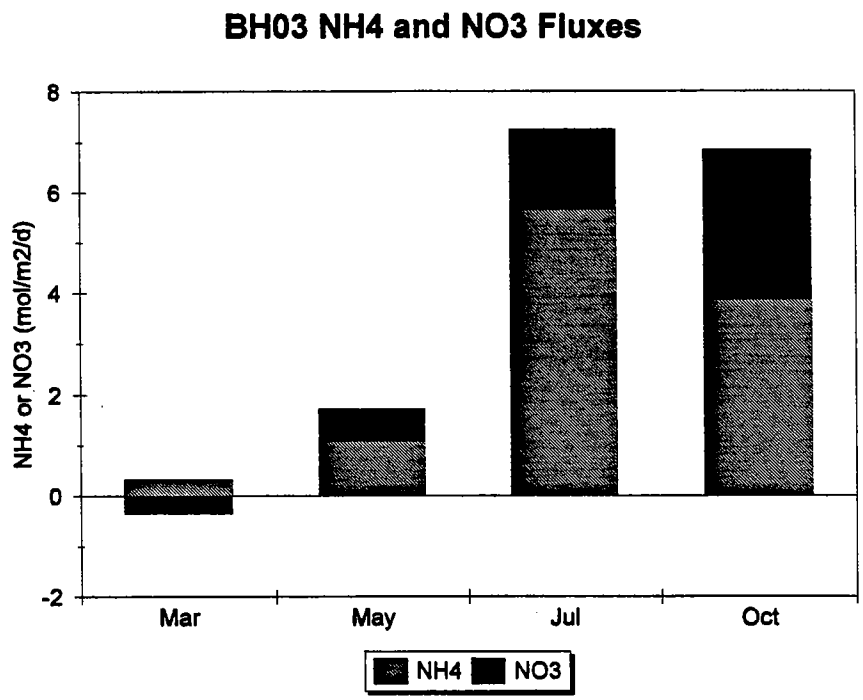


Figure 5. Nitrogen fluxes at the Boston Harbor stations in 1994. (a) Total DIN (NH_4 + NO_3 + NO_2) flux.



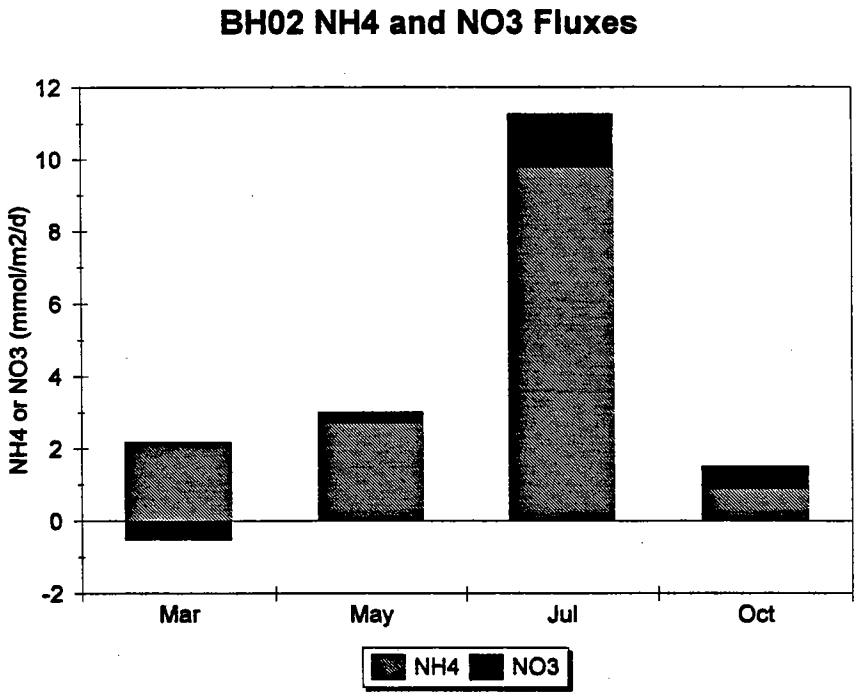


Figure 5. ***(Cont.)*** **Nitrogen fluxes at the Boston Harbor stations in 1994. (b) Total DIN flux at Station BH03 broken into components of NH_4 and NO_3 (includes NO_2). (c) Total DIN flux at Station BH02 broken into components of NH_4 and NO_3 (includes NO_2).**

Bay

Release of DIN from Bay sediments ranged from a low of 0.07 mmol N m^{-2} d^{-1} to a high of 3.9 mmol N m^{-2} d^{-1} from station NF8 in July (Figure 6a). In contrast to what we observed in 1993, there was a strong seasonal pattern and the pattern of DIN release matched the oxygen uptake pattern. The rate of DIN release was consistently higher at shallow Bay stations than at deeper Bay stations.

In 1994, we did not observe nitrate uptake during early spring and late autumn (February and October) unlike 1993. Nitrate made up 10-100% of the DIN flux at all Massachusetts Bay Stations at different times of the year (illustrated with MB01, Figure 6b). Nitrate was a more important component of the DIN flux at deeper stations than at the shallow stations, averaging 12% at the shallow stations and 52% at station MB05 (Figure 6c).

4.1.4 Urea Fluxes

Urea is a nitrogenous compound excreted by some macrofauna. In some areas urea makes a substantial contribution to the N flux from sediments. Because urea has an exceedingly low C/N ratio (0.5) large urea fluxes must be taken into account when making stoichiometric calculations of denitrification. In addition, urea is readily broken down by bacteria in the water column to inorganic nitrogen which provides nitrogen for phytoplankton growth.

Our urea data from 1993 was compromised by bottle top contamination. Never the less, it appeared that urea fluxes were quite low. The 1994 data confirms this conclusion; urea fluxes from Harbor and Bay sites were very low ranging from -0.03 to 0.14 mmol m^{-2} d^{-1}. The r^2 values for the majority of the regressions of concentration against time were low and in most cases not significantly different from zero. Urea does not appear to be an important part of the nitrogen fluxes in this region. In the Harbor, urea fluxes were less than 6% of the DIN flux, with one exception, during May. In May, the urea N flux was 0.28 mmol N m^{-2} d^{-1} (two moles of N per mole of urea) while the DIN flux was 3.0 mmol m^{-2} d^{-1}. The majority of the urea fluxes in the Bay were less than 0.04 mmol m^{-2} d^{-1} and only once did the flux exceed 0.06 mmol m^{-2} d^{-1}. Most of the regressions had slopes which were not significantly different from zero. Urea nitrogen fluxes in the Bay usually were less than 5% of the DIN flux and never exceeded 10% of the DIN flux.

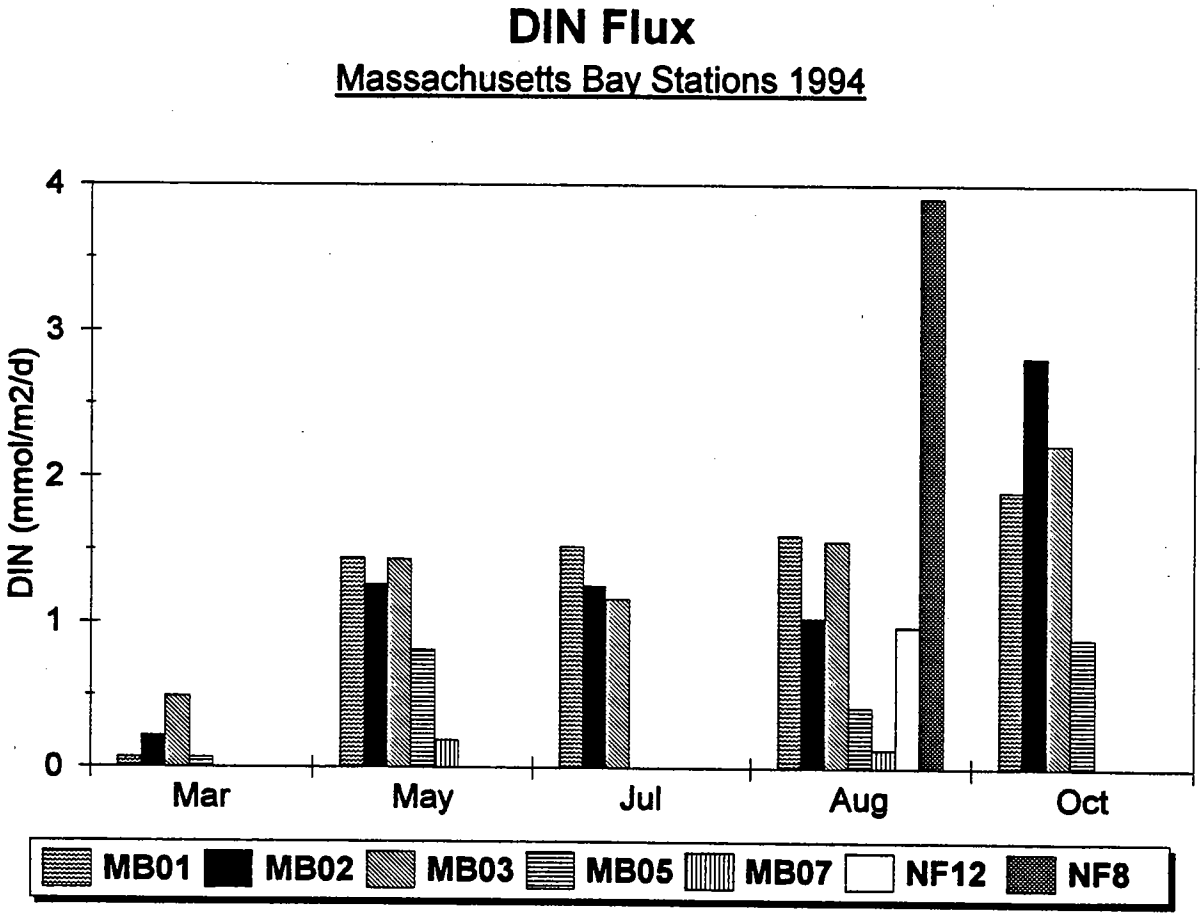
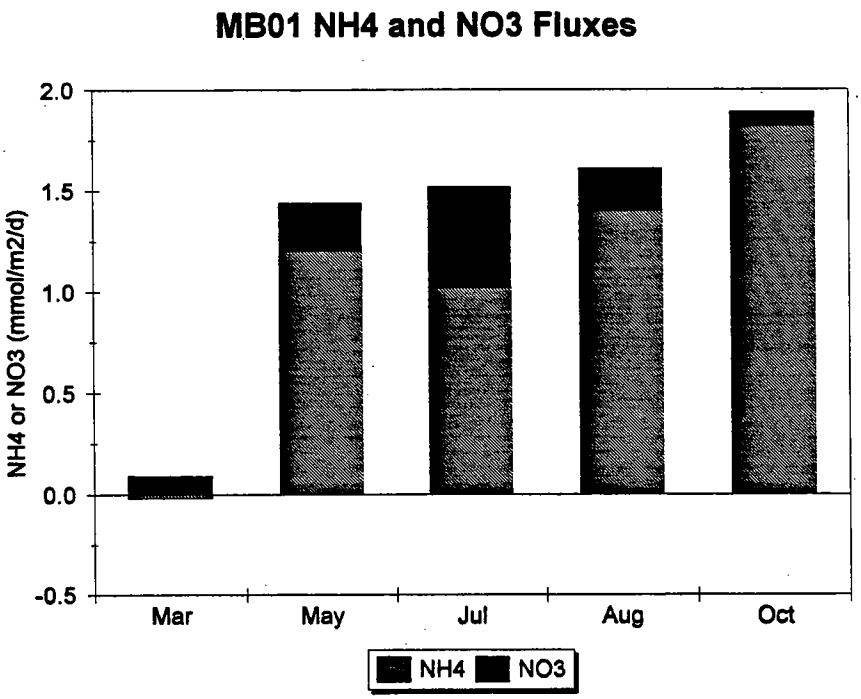


Figure 6. Nitrogen fluxes at the Massachusetts Bay stations in 1994. (a) Total DIN (NH_4 + NO_3 + NO_2) flux.



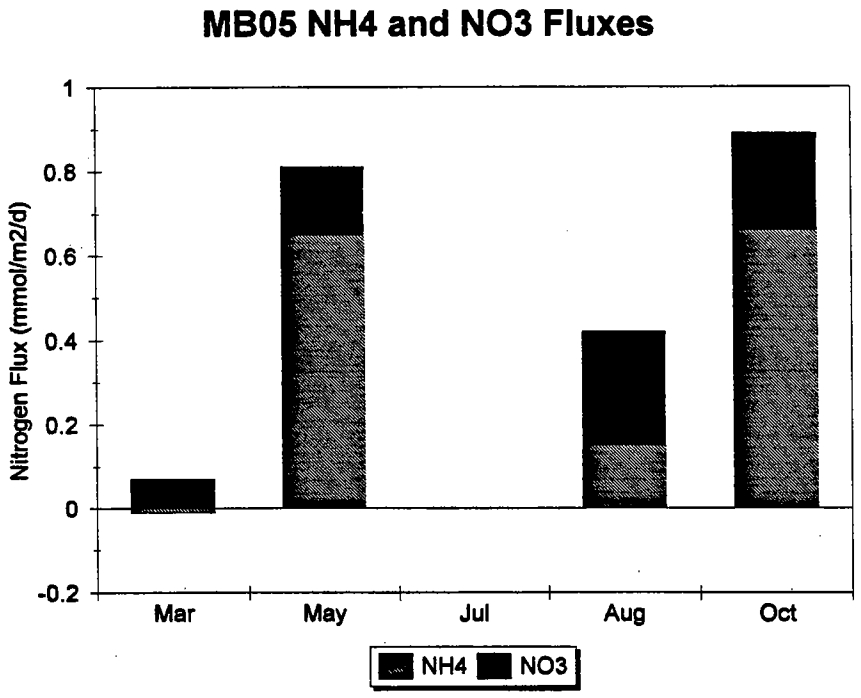


Figure 6. *(Cont.)* Nitrogen fluxes at the Massachusetts Bay stations in 1994. (b) Total DIN flux at Station MB01 broken into components of NH_4 and NO_3 (includes NO_2). (c) Total DIN flux at Station MB05 broken into components of NH_4 and NO_3 (includes NO_2).

4.1.5 Silica Fluxes

Harbor

Silica fluxes reached their maximum values at both BH02 and BH03 in July (Figure 7a). The annual silica flux at BH02 was higher than at BH03. Silica fluxes during 1994 were considerably lower at BH03 than they had been in 1993. During March and October, station BH03 had non-detectable or negative silica fluxes. During July when four stations were sampled, the lowest silica fluxes were at station BH08, as was the case in 1993.

Bay

Silica fluxes in 1994 were 48% greater than in 1993 ranging from 2.0 mmol m^{-2} d^{-1} to 14.7 mmol m^{-2} d^{-1} (Figure 7b). The rates in March, August and October were very similar in both years but rates in May and July were 20 - 30% higher than in 1993. As was the case in 1993, there were no consistent differences between stations over the course of the season, even when shallow and deep stations were compared. Silica flux rates from NF8 and NF12 were nearly identical to rates measured at the three permanent stations in the nearfield area.

In both 1993 and 1994 we found that relative to DIC release, Si fluxes were higher in the Bay. Over the annual cycle the atomic Si/DIC flux at Station BH02 was 0.14 and the ratio was 0.10 at Station BH03, similar to values measured in 1993. Annual Si/DIC flux ratios at the Bay nearfield stations (MB01, MB02 and MB03) were considerably higher than in the Harbor ranging from 0.28 to 0.32. Although we do not have as complete an annual cycle at the deeper stations in Stellwagen Basin the Si/DIC flux ratios at these sites were always higher than at shallower stations.

The flux ratio observed from sediments will be influenced by the proportion of the organic matter derived from siliceous phytoplankton (see discussion in Giblin *et al.*, 1994). Therefore it is not surprising that the Harbor Si/DIC ratios were lower in the Bay. Another factor which may account for the high fluxes we measure and the high ratio is the focusing of Si rich particles in depositional areas (discussed in the modeling section).

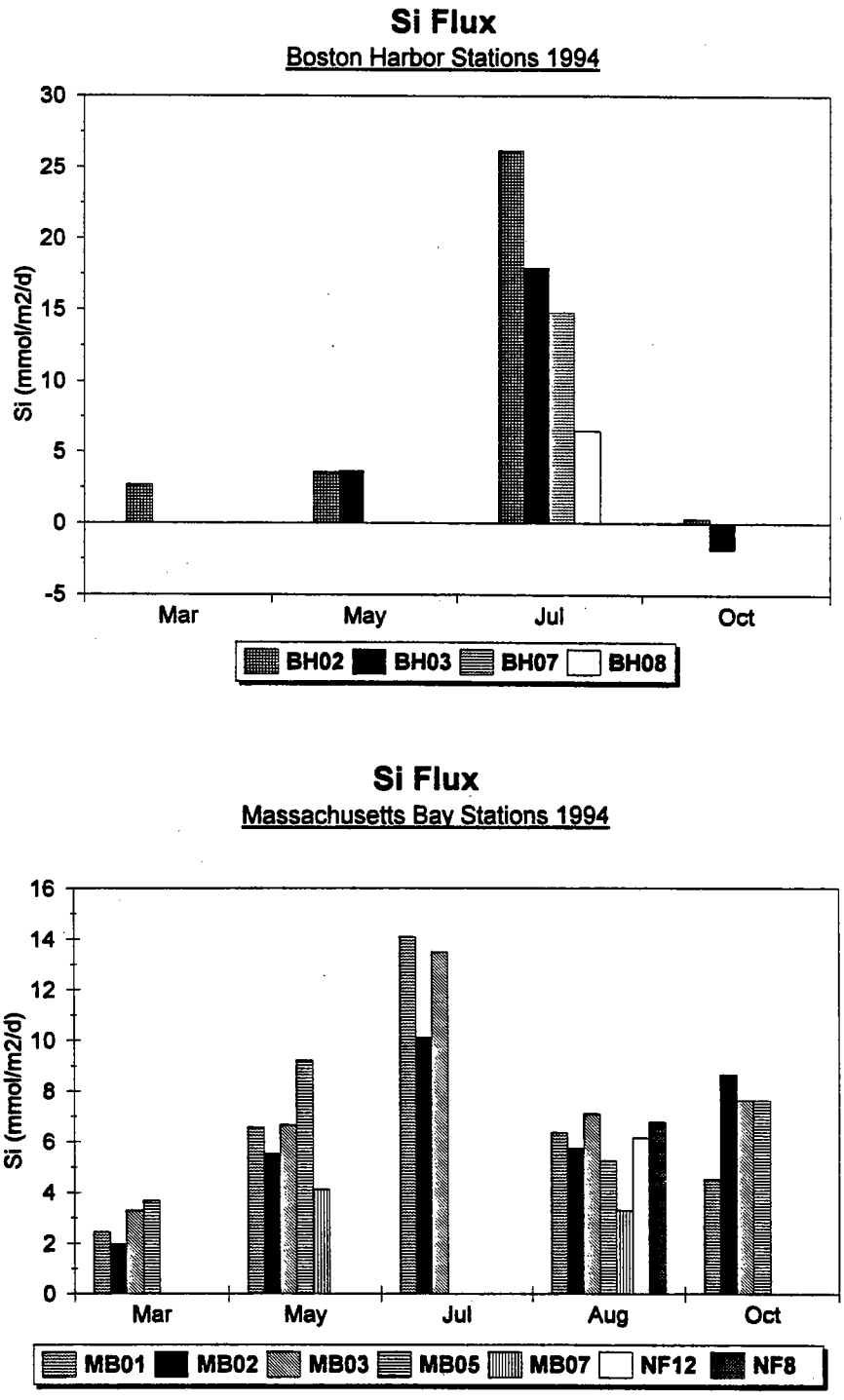


Figure 7. **Silica fluxes at (a) the Boston Harbor stations and (b) the Massachusetts Bay stations in 1994.**

4.1.6 Phosphate Flux

Harbor

Phosphate fluxes from the Harbor stations ranged from -0.4 to nearly 1 mmol P m^{-2} d^{-1} (Figure 8a). There was no relationship between phosphate flux and temperature or oxygen uptake. The maximum phosphate fluxes we observed at both BH02 and BH03 were lower than we observed in 1993 and the seasonal pattern was also different. In both years, DIP fluxes were higher at Station BH02 than at BH03.

Bay

Phosphate fluxes from Bay stations in 1994 were quite similar to those we observed in 1993 both with respect to seasonal pattern and the magnitude. 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 the shallow Bay stations reaching maximal values in August (MB01) or October (MMB02 and MB03). Stations NF8 and NF12 had fluxes in the same range as the other shallow Bay stations. One of the deeper Bay stations, station MB05, exhibited a pattern similar to the shallow stations. Station MB07 took up phosphate from the overlying water column both times it was sampled.

4.2 Sediment Carbon, Nitrogen and Pigments

Harbor

There was a great deal of spatial and temporal variation in surface carbon content (Table 2). Station BH08 had the lowest carbon concentration of 0.33%. Station BH03 had the highest carbon content varying from 2.7% to 3.5% over the four sampling periods, similar to carbon concentrations we observed in 1993. The carbon concentrations at BH02 exhibited a greater temporal variation than BH03, ranging from 0.52% to 1.98% over the year. As discussed in our previous report, 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. Station BH07 had a carbon content of 2.81% when measured in July.

Pigment concentrations at Harbor stations did not show a clear-cut seasonal pattern. Chlorophyll *a,* which is the active pigment present in living or recently dead plants, showed no seasonal pattern. There was a trend of increasing phaeopigment concentrations in the sediments as the season progressed.

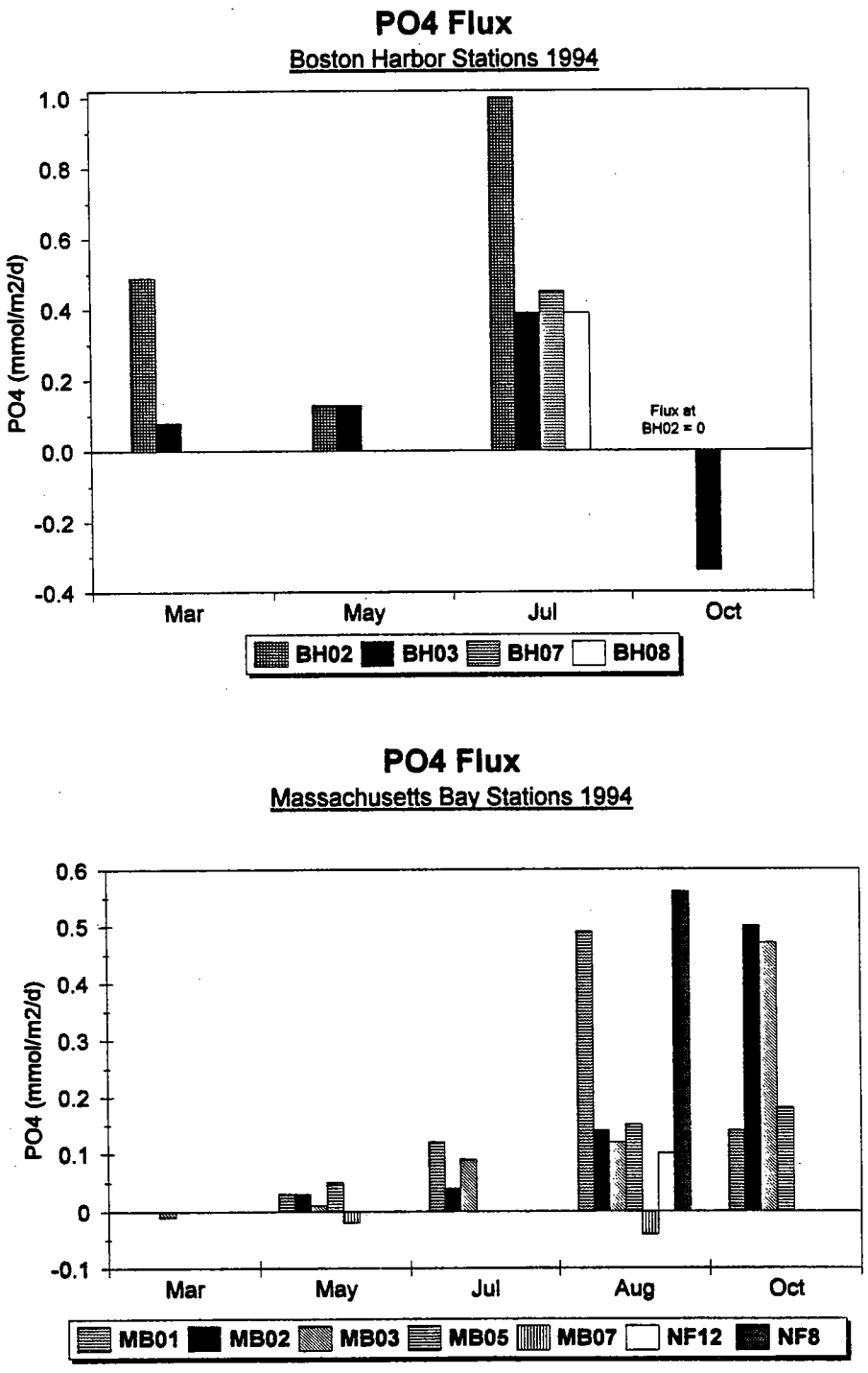


Figure 8. **Phosphate fluxes at (a) the Boston Harbor stations and (b) the Massachusetts Bay stations in 1994.**

Table 2. Sediment C†, N†, chlorophyll††, and phaeopigment†† concentrations.

Survey	Month	Station	%C	%N	Chla $\mu g\ cm^{-3}$	Phaeo $\mu g\ cm^{-3}$
B9401	Mar	BH02	1.8	0.22	2.9	9.13
		BH03	3.18	0.39	3.4	17.4
		MB01	0.68	0.07	0.74	4.14
		MB02	0.45	0.04	0.6	4.21
		MB03	0.73	0.08	0.67	4.67
		MB05	1.87	0.18	0.91	5.38
B9402	May	BH02	1.98	0.25	**	**
		BH03	2.7	0.32	**	**
		MB01	1.46	0.13	2.66	11.3
		MB02	0.75	0.07	1.44	10.62
		MB03	0.76	0.09	1.47	10.89
		MB05	1.18	0.14	1.77	10.03
		MB07	1.26	0.16	**	**
B9403	Jul	BH02	1.47	0.17	* 6.27	* 21.69
		BH03	3.33	0.37	4.8	22.8
		BH07	2.81	0.35	* 5.75	* 19.35
		BH08	0.33	0.03	* 3.98	* 7.31
		MB01	1.3	0.14	2.64	19.86
		MB02	1.02	0.11	1.61	14.15
		MB03	0.61	0.07	2.53	22.93
B9404	Aug	MB01	1.51	0.14	1.36	21.03
		MB02	1.65	0.15	4.99	12.19
		MB03	1.44	0.16	* 4.29	* 19.35
		MB05	1.26	0.15	1.5	12.64
		MB07	1.53	0.19	* 1.63	* 12.95
		NF12	0.93	0.11	* 4.13	* 14.95
		NF8	2.02	0.21	* 4.59	* 22.79
B9405	Oct	BH02	0.52	0.06	4.39	13.52
		BH03	3.54	0.4	2.72	24.95
		MB01	1.33	0.14	1.28	14.05
		MB02	1.98	0.2	5.11	16.47
		MB03	2.27	0.21	2.07	18.56
		MB05	1.05	0.12	1.72	11.39

† Sediment C and N were measured on the top 2 cm of sediment.

†† Chlorophyll a and phaeopigment concentrations were averaged over the 5 cm.

** Average not calculated because several depths are missing or data is highly suspect

* Data are suspect due to high blanks

Bay

Carbon content in surface Bay sediments ranged from 0.45% to 2.27% (Table 2). There was a great deal of temporal variability (Table 2). For example, carbon content at MB02 ranged from 0.45% in February to a high of 1.98% in October. 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 during storms.

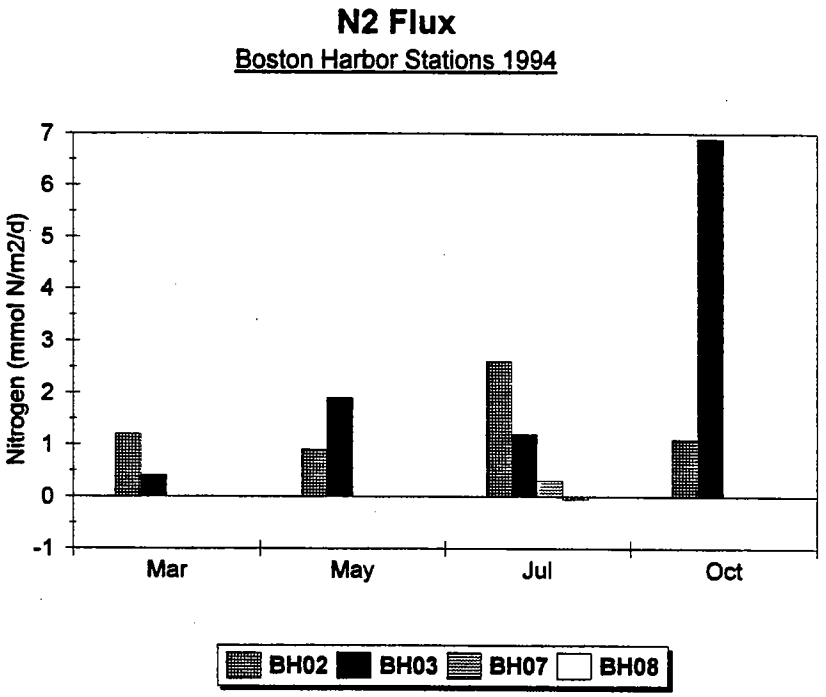
Pigment concentrations in Bay sediments were low in early March, suggesting that the spring bloom had not reached the sediments yet. Chlorophyll *a* concentrations generally peaked in spring or summer and declined in October.

4.3 Sediment Denitrification Rates for Boston Harbor and Massachusetts Bay

In the past we have found that denitrification rates for Boston Harbor tend to be correlated with water temperature and sediment organic content (Giblin *et al.*, 1994). This remains true for the 1994 data as well. In general, highest rates occurred in areas with highly organic sediments in the Harbor, with lower rates observed for low-organic sandy sediments in the Harbor (Station BH08), and in the near-field region of Massachusetts Bay. Lowest rates were found in the far-field region of the Bay in Stellwagen Basin (Stations MB05, MB07).

Harbor

In 1994 denitrification rates in Boston Harbor ranged from non-detectable (Station BH08, July) to 2.6 mmol N m-2 d-1 (BH02; July), with a single extremely high rate (6.9 mmol N m-2 d-1) observed in October at Station BH03 when exceptional numbers of amphipods were present (Figure 9a). In the past we found extremely high rates of denitrification at Station BH03 when there were large numbers of amphipods present (November 1992 and August 1993). Seasonally, at the silt-clay stations (BH02, BH03, BH07), lowest rates occurred in February/March with highest rates in mid to late summer. This pattern was repeated during all three years of measurements. In contrast, denitrification rates for the sandy low-organic (0.3 wt. % C) sediments at Station BH08 showed little response to seasonal temperature changes in 1992 and 1993, and rates at this station were not detectable in July of 1994. Denitrification



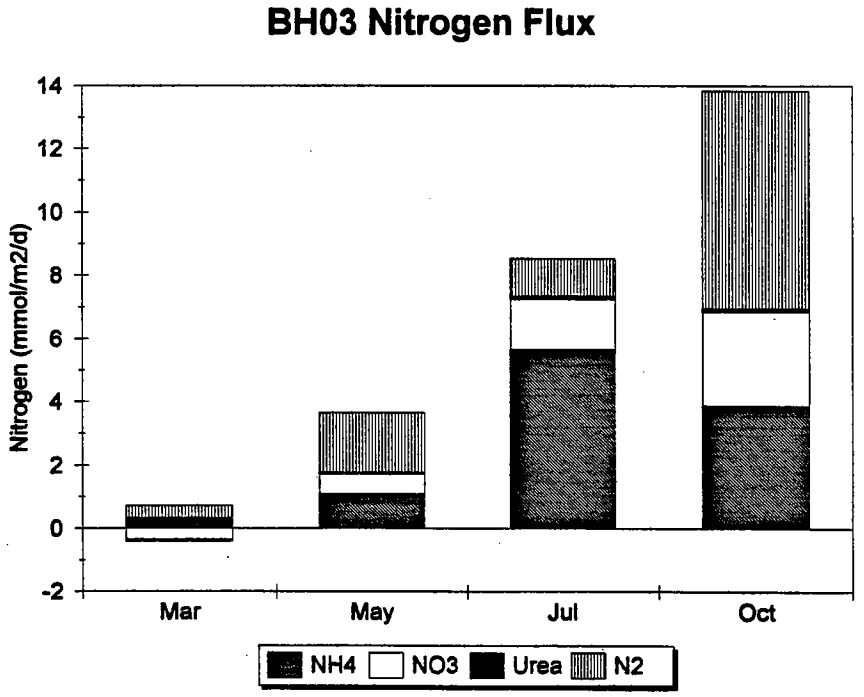


Figure 9. **Annual cycles of sediment denitrification for stations in Boston Harbor during 1994. (a) N_2 flux. The negative flux for Station BH08 in July is below detection limits and within the error for the techniques. (b) Total nitrogen flux at Station BH03 broken into four component forms.**

rates were lower in the Harbor in 1994 than in the previous two years. In fact, the mean denitrification rate for the Harbor (all stations, all dates excluding BH03 in October) was the same as the mean for Massachusetts Bay. This is a striking contrast to results for 1992 and 1993 when Harbor rates were significantly higher than Bay rates. The reason for this inter-annual variability is unknown.

Over the annual cycle the N_2 flux from the sediments makes up a significant proportion of the total benthic N flux, averaging 27% of the total flux at BH03 (Figure 9b), and 37% at BH02. Ammonium is the most important component of the flux at both stations, making up just over half of the total N flux. Urea, as discussed above, is of minor importance.

Bay

In Massachusetts Bay, denitrification rates ranged from non-detectable (Station MB01, October) to 2.7 mmol N m^{-2} d^{-1} at Station NF8 in August (Figure 10a), and were similar in magnitude to 1993 rates. There was no consistent seasonal pattern to denitrification rates in Massachusetts Bay, and considerable year to year and station to station variability. The mean rate of denitrification for Massachusetts Bay sediments in 1994 (1.1 mmol N m^{-2} d^{-1}, n = 22) was the same as the mean for the previous two years.

N_2 flux from Bay sediments makes up a greater percentage of the total benthic N flux than in the Harbor. In nearfield sediments, ammonium and N_2 had nearly identical contributions to the total benthic nitrogen flux with nitrate making up an average of 6% of the N released (illustrated with station MB01, Figure 10b). Denitrification was relatively more important in the offshore stations. The most important component of the nitrogen flux at the farfield stations was N_2, making up 66% of the total nitrogen flux with the remainder being almost equally composed of ammonium and nitrate (illustrated with station MB05, Figure 10c).

4.3.1 Comparison of Stoichiometric and Direct Method of Measuring Denitrification

We compared the annual average of the direct measurements of denitrification to the annual average of measurements calculated using the stoichiometric method for stations where we had several measurements. In the past we have observed that there is considerable scatter in the relationship between the two methods when individual dates are compared but that annual averages show good agreement (Giblin *et al.*, 1993;

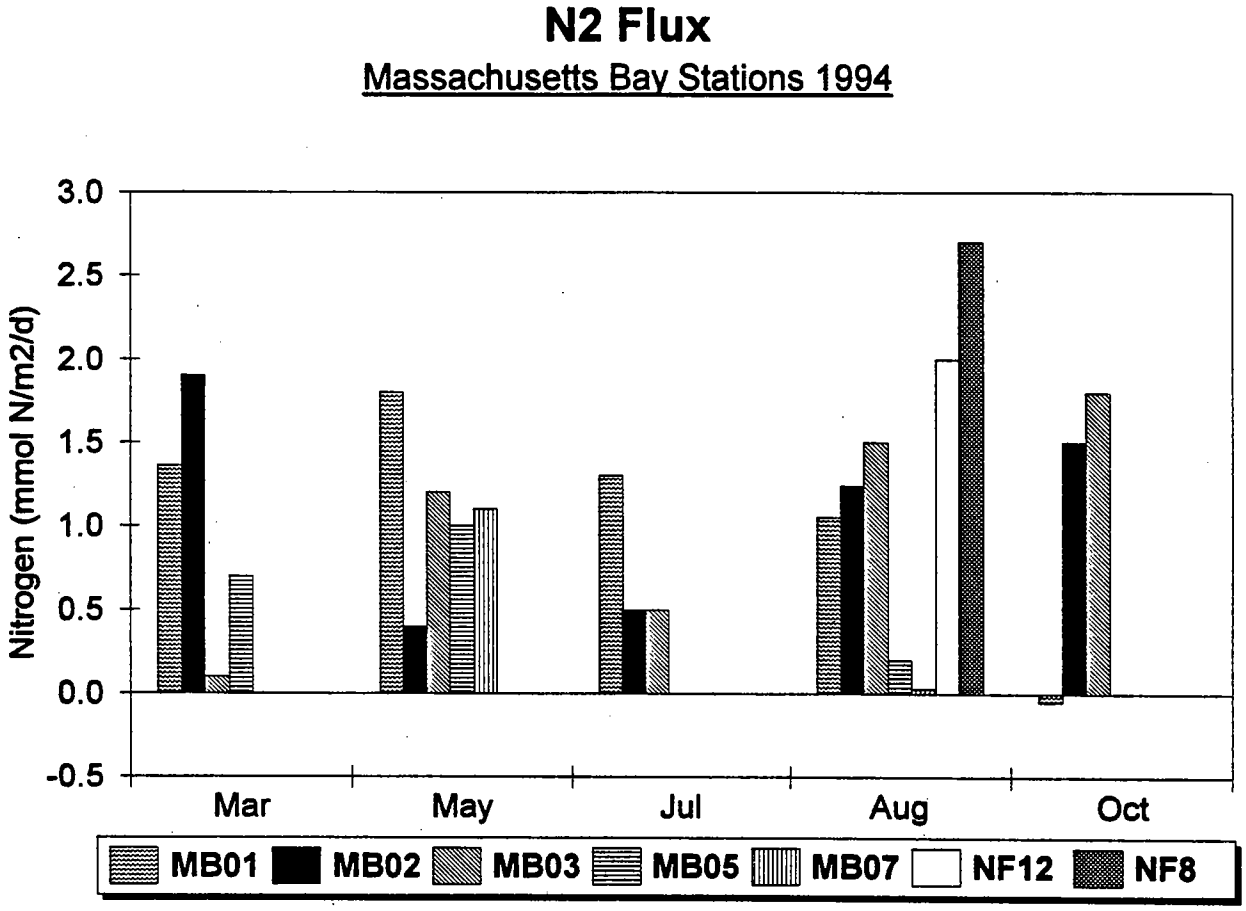
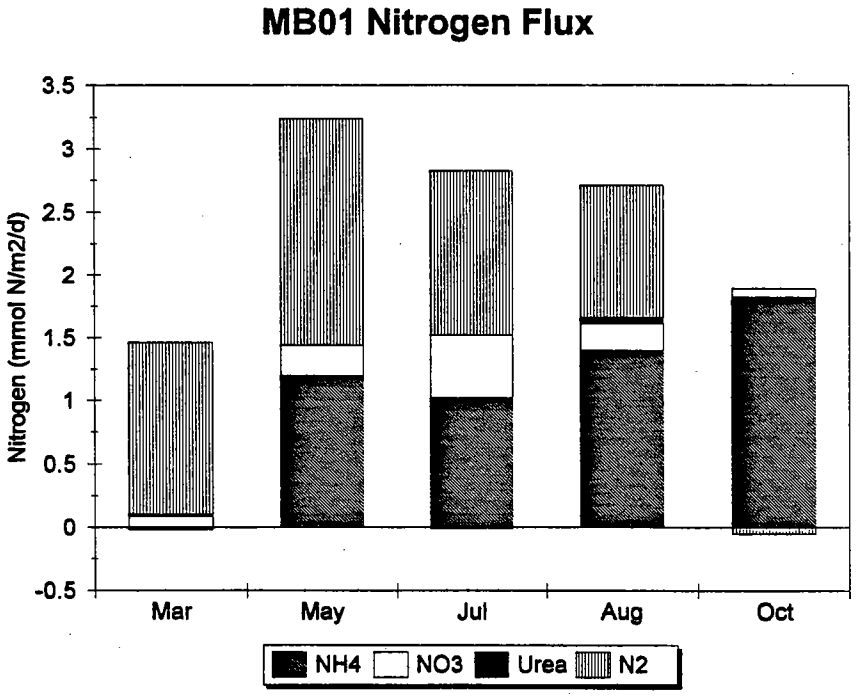


Figure 10. **Annual cycles of sediment denitrification for stations in Massachusetts Bay during 1994. (a) N_2 flux. The negative flux for Station MB01 in October is below detection limits and within the error for the techniques.**



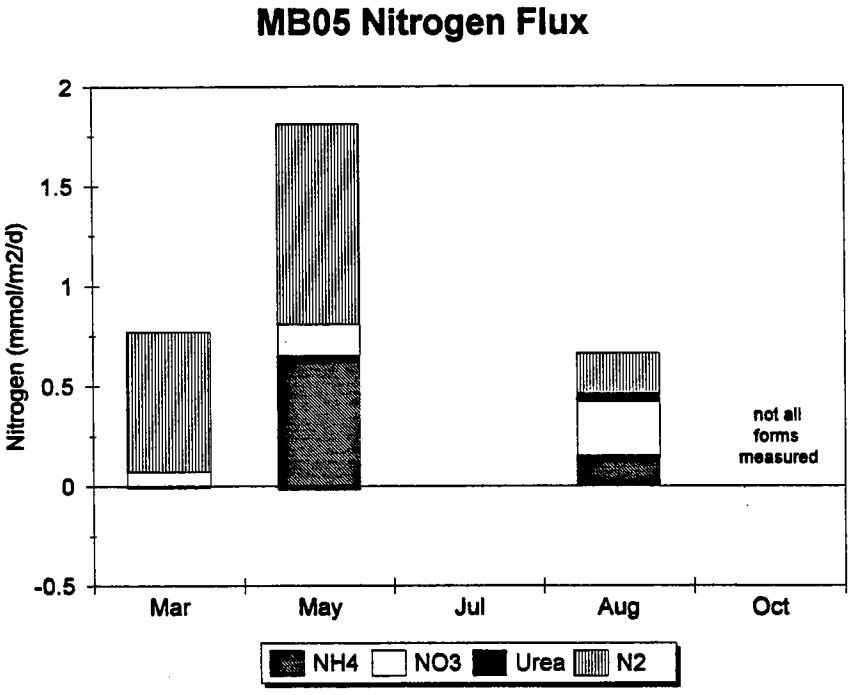


Figure 10. ***(Cont.)*** **Annual cycles of sediment denitrification for stations in Massachusetts Bay during 1994. (b) Total nitrogen flux at Station MB01 broken into four component forms. (c) Total nitrogen flux at Station MB05 broken into four component forms.**

1994). The average loss we calculated for Harbor stations in 1994 using stoichiometry was higher than the directly measured values. At BH03 approximately 2.6 mmol N m^{-2} d^{-1} was estimated using the direct method and 5.2 mmol N m^{-2} d^{-1} from stoichiometry. The difference at BH02 was greater, with the stoichiometric estimate of 5.6 mmol N m^{-2} d^{-1} being more than three times higher than the directly measured value of 1.5 mmol N m^{-2} d^{-1}.

The directly measured values of denitrification were also lower than the calculated N loss in Bay sediments. Here the average rates calculated using the stoichiometric for shallow stations averaged 2.1 mmol N m^{-2} d^{-1}, while the rates measured using the direct method averaged of 1.2 mmol N m^{-2} d^{-1}. We did not have a complete seasonal cycle for the Stellwagen Basin stations but averages for the dates where data were available show about a two fold difference between the two methods. The average of the direct measurements at MB05 and MB07 was 0.61 mmol N m^{-2} d^{-1} while the rates calculated using the stoichiometric method averaged 1.25 mmol N m^{-2} d^{-1}.

4.4 Coupling Sediment Fluxes with the Water Column of Western Massachusetts Bay

4.4.1 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 particular interest during summer and early fall when benthic fluxes characteristically reach 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 at least 1 g C m^{-2} d^{-1} in the western nearfield area (Kelly, 1994; Kelly and Turner, 1995a). Data summarized for measurements in 1994 provide an average summer-fall NPP rate of 1.3 g m^{-2} d^{-1} (Kelly and Turner, 1995b). Following assumptions and calculations as presented in Giblin *et al.* (1994) for the 1993 sampling year, Table 3 repeats the exercise for 1994 flux data.

Table 3. Benthic flux and water column changes in the western nearfield during summer 1994.

	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	-17.9	17	-7.7	7	-0.52	-52	-89[e]
DIN	1.8	11	0.8	5	+0.05	+5	+4.4
PO_4	0.25	25	0.1	10	+0.007	+0.7	+0.3
SiO_4	8.3	—	3.6	—	+0.24	+24	+9
DIC	29.7	28	12.8	12	—	—	—

a Average for July, August, and October for nearfield flux stations (MB01, MB02, MB03, NF8, NF12).
b Assumes 1.3 g C m^{-2} d^{-1} net primary production (NPP), or 108 mmol C m^{-2} d^{-1}. C/N ratio of 6.625 and C/P ratio of 106 were used for DIN and PO_4 calculations and an RQ of 1 assumed to compare O_2 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 89 μM = 2.86 mg O_2 L^{-1}

Mean summer-fall 1994 fluxes were, for the most part, similar to those measured in 1993 (cf. Table 3 of Giblin *et al.*, 1994). Of the five flux parameters listed in Table 3, average rates for O_2, DIN, and DIC were within 20% of each other across the two years. SiO_4 in 1994 was 148% higher in 1994, in part elevated by generally high fluxes in July 1994. The average PO_4 flux was in 1994, however, was more than double that measured in 1993.

Simple calculations suggest that during summer-fall the depositional sediments of the western nearfield could consume, at most, an amount of carbon equal to 28% of the production in overlying water [i.e., depositional sediment flux divided by NPP (same units) x 100 (Table 3). The RQ [CO_2/O_2] was high on average, 1.66, and this may suggest DIC flux due to nonrespiratory processes; using O_2 and an RQ=1, the implied percentage of production is 17% rather than 28% (Table 3). Benthic DIN flux could supply about 11% of the N required for primary production, while benthic phosphate flux could supply about 25% of P requirements for production. Measured N_2 flux loss from the nearfield sediments over the summer/fall period averaged 1.3 mmols N m^{-2} d^{-1}, and thus could remove about 10% of the N assimilated by primary

producers. DIN and N_2 together amount to 24% of NPP, which is intermediate to that calculated by O_2 and DIC, and almost exactly that calculated by PO_4.

These simple calculations provide an upper bound estimate of the percentage. Depositional areas, such as we sampled, only make up a small percentage of Massachusetts Bay. It is not appropriate to assume depositional sediment flux rates apply to the entire area. There is uncertainty in apportioning soft-depositional sediment fluxes across the heterogeneous sedimentary regime within the entire area. As a guide (like Giblin *et al.*, 1994), we assumed that about 29% of the area is depositional (Knebel, 1993) and that fluxes in sandy and hard-bottom areas are 20% of those in 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 of an extrapolated area-weighted flux in Table 3 suggests. Results of this calculation, with fluxes representing about 5-12% of NPP, are similar to those obtained for 1993 (Giblin *et al.*, 1994).

4.4.2 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. In 1994, five benthic flux stations in shallow western Massachusetts Bay (MB01, MB02, MB03, NF8, NF12) were bracketed by a group of eight water column stations that were monitored on the western side of the nearfield (cf. Figure 1 and Giblin *et al.*, 1994). Patterns in bottom water quality and surface layer chlorophyll for the water column stations during the summer/early fall stratified period in 1994 are displayed in Figures 11 and 12.

There was a notable, progressive decline in bottom-water DO concentrations from June to late September-October (see also Kelly and Turner, 1995b). There was a fall bloom expressed as elevated chlorophyll concentrations in late September-October, but it was small compared to fall of 1993 (cf. Kelly and Turner, 1995a and Giblin *et al.*, 1994). Benthic metabolism in 1993 and 1994 showed a similar pattern in relation to temperature (Figure 3b), but appeared to be slightly higher in 1993. Inter-annual variability in fluxes may reflect the inter-annual differences in water column events the sedimentations of organic matter which fuels benthic metabolism.

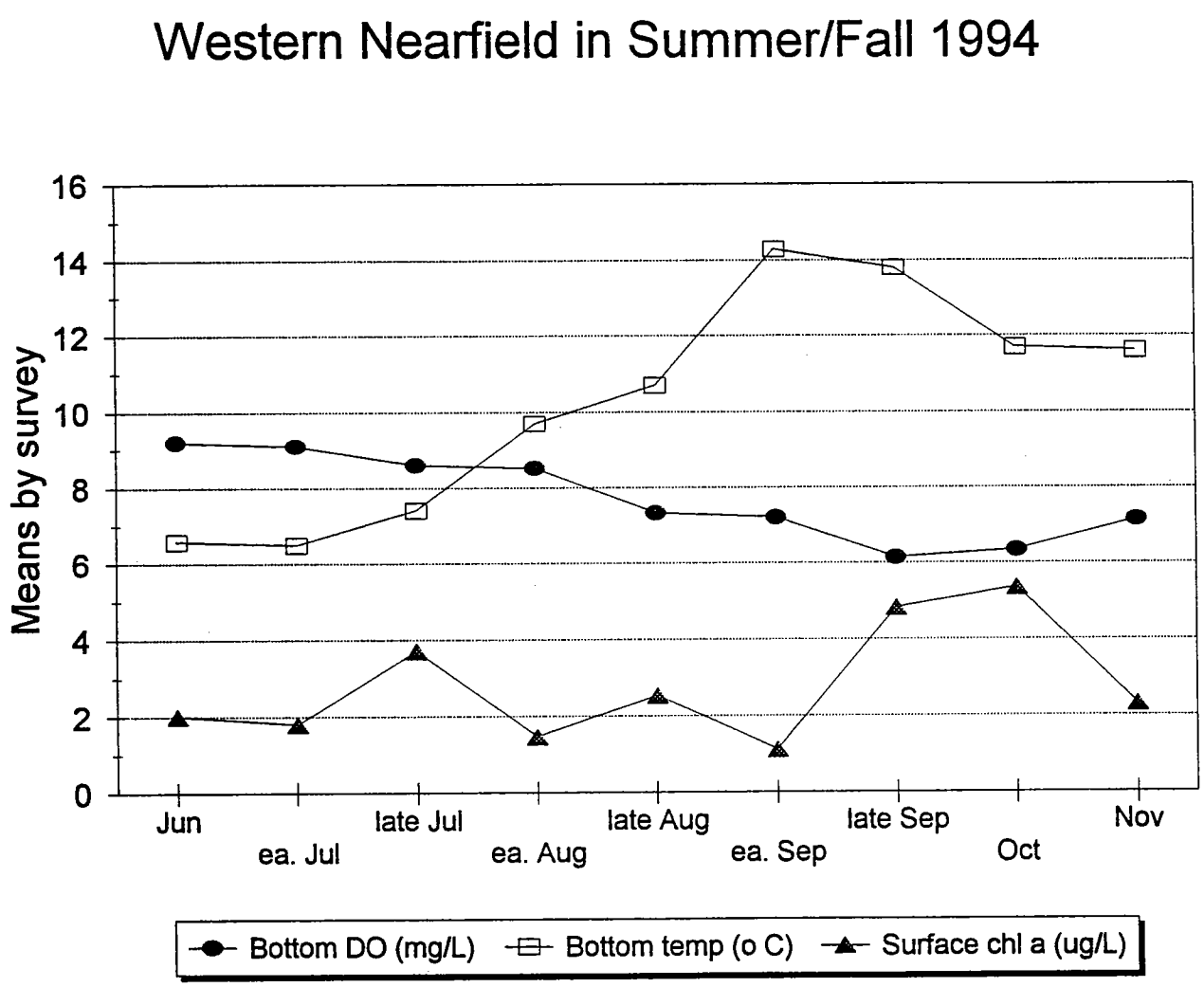


Figure 11. **Seasonal patterns in the water column in the western nearfield during 1994: surface chlorophyll, near-bottom temperature, and near-bottom dissolved oxygen (DO).**

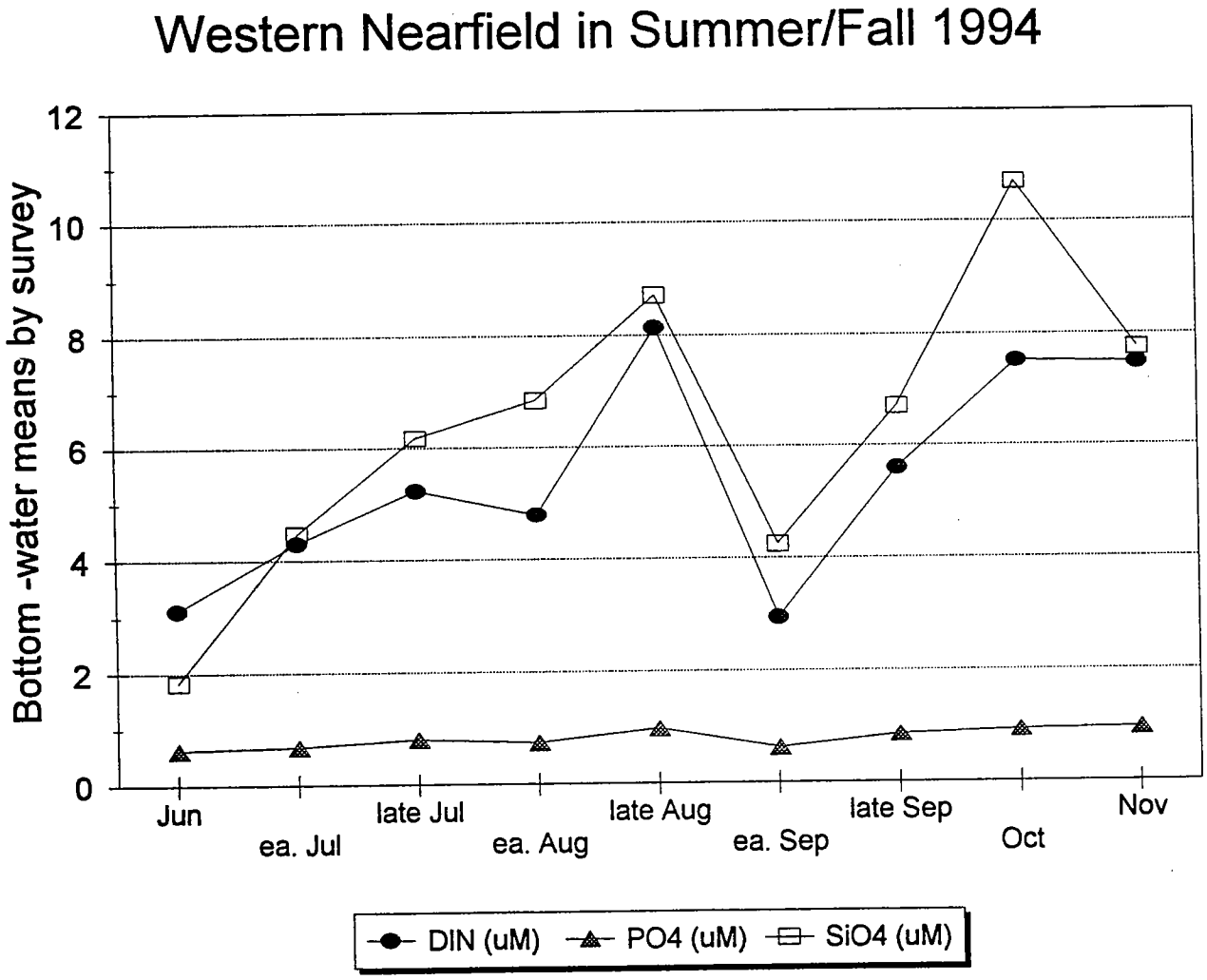


Figure 12. **Seasonal patterns in the water column in the western nearfield during 1994: near-bottom nutrients.**

The concomitant (to the DO decrease) increase in bottom-water nutrient concentrations was less progressive (Figure 12). DIN, PO_4, and SiO_4 concentrations simultaneously increased from June to late August, but dipped in early September, before increasing again in October. The reason for the early September dip in concentrations is not fully known, but one can consult Kelly *et al.* (1995a,b) and Libby *et al.* (1995) for more details of water column dynamics in these months in 1994.

A calculation using benthic fluxes in Table 3 involves the entire period when near-bottom DO progressively decreased and nutrients generally increased. Following Giblin *et al.* (1994), projections of the potential contribution of benthic fluxes to a stagnant, closed bottom layer during stratification were made for a 100-d period similar to that covered by the flux measurements (Table 3). The projected influence of benthic fluxes on the bottom water was similar to the actual DIN change observed during the period encompassing about 100 d. In contrast, projections from PO_4 and SiO_4 fluxes were high compared to observed bottom-water change. Projections from DO flux were low compared to observed bottom-water change.

Because of the variability in nutrients over the entire period, we also made the comparison for a 60 d period which thus covers the initial rise in nutrient concentrations (Figure 12). Results, shown in Figure 13, again illustrate that the observed change in DO was larger than projected and that the observed SiO_4 change was much less than projected. These results for 1994 are similar to 1993.

The projections should not be expected to fully match the observations because there is uncertainty in the area extrapolation, but also because other processes (e.g., water column uptake and recycling, advection, and vertical diffusion to surface layers) significantly influence bottom waters. Nevertheless, the exercise confirms the previous conclusion that the behavior of SiO_4 appears highly anomalous compared to other nutrients and DO (Giblin *et al.*, 1994). It has been noted that SiO_4/DIN ratios for fluxes in the Bay are regularly high compared to fluxes in Boston Harbor, but the observed anomaly in SiO_4 interaction with the overlying water (Figure 13) cannot be further reconciled with these data, especially because the bottom layer is neither fully stagnant nor closed as the projections must assume.

Our earlier conclusion (Giblin *et al.*, 1994) is confirmed with these observations: factors other than benthic fluxes from depositional areas are influential in controlling Bay bottom water column concentrations.

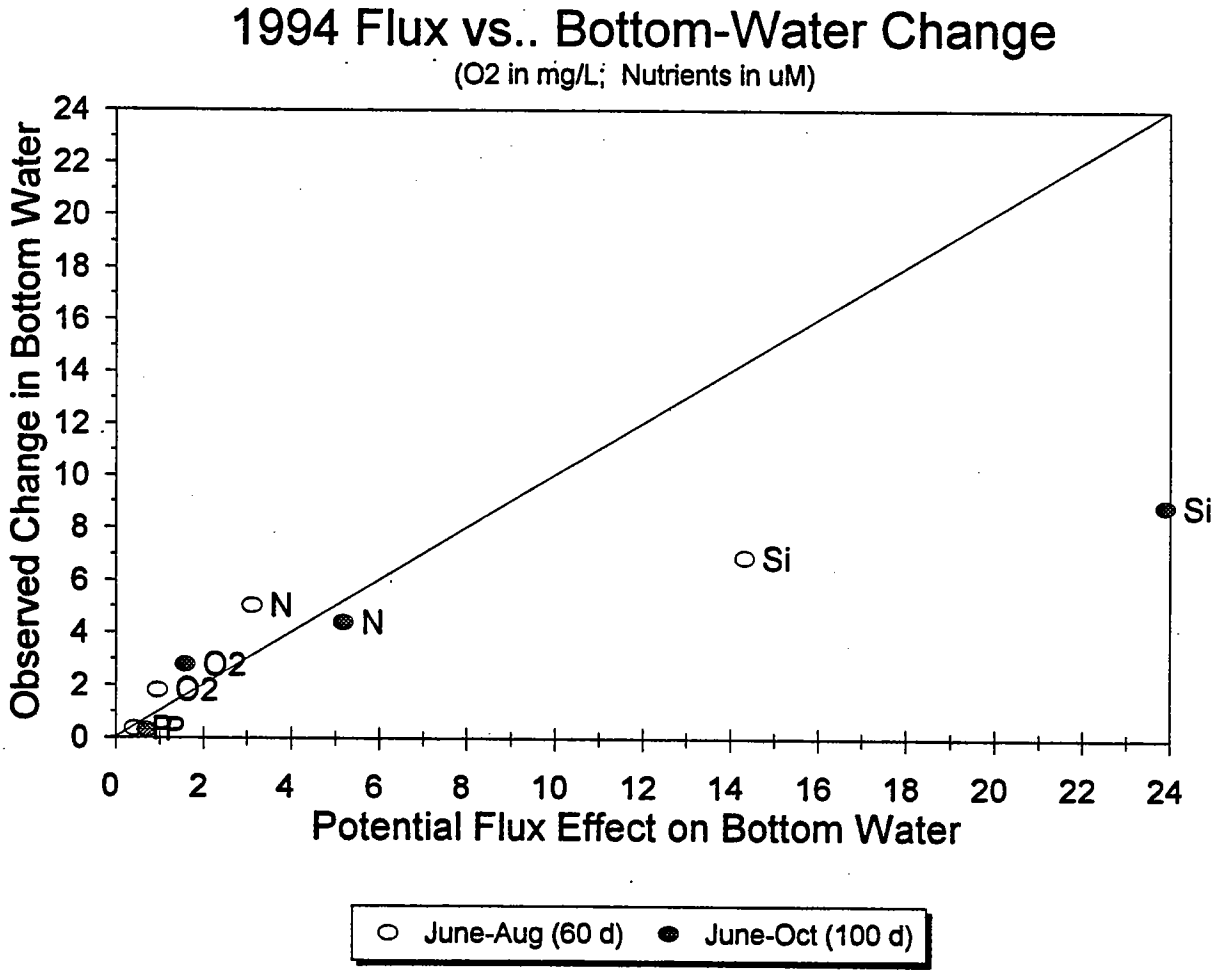


Figure 13. **Comparison of observed change in the western nearfield bottom water during summer/fall 1994 with projected change due to measured sediment metabolism and nutrient exchange.**

Stoichiometry of fluxes from sandy non-depositional areas, not included in flux measurements, may differ from the sampled soft-sediments; in principle this could alter the area-extrapolated projections, but only if sandy areas had very low Si/N flux ratios and/or unexpectedly high flux rates. It is clear that, at present, benthic fluxes alone should not be used to project trends in bottom water nutrients; conversely, water column concentrations of dissolved nutrients and their ratios should not be used to infer rates and stoichiometry of benthic fluxes (cf. Becker, 1992) and direct flux measurements must be made instead. These observations reinforce the notion that water-column and benthic processes must be integrated if attempts are made to model, predict, or understand ecological response to an outfall in western Massachusetts Bay.

4.5 Porewater Constituents

Porewater profiles in the Harbor were fairly typical of values we have observed in previous years. Station BH02 had a shallow layer of a few cm near the surface where sulfide was not detected and then sulfide concentrations increased rapidly with depth (Figure 14a). Sulfide concentrations at this station were quite high at depth throughout the spring and summer reaching 4.5 mM at depth in May. Sulfide concentrations fell to below 1 mM in October throughout the profile.

Stations BH08 and BH07 had porewater profiles similar to what we have observed in previous years (Figure 14b). Sulfide concentrations are always low at BH08.

Porewater profiles at stations BH03 continue to change. In 1993 we usually did not detect sulfide in porewater down to 8-10 cm. In 1994, sulfide was frequently detected by 4-6 cm (e.g. Figure 14a, 14b). The 1994 sulfide profiles were more similar to those we measured in 1992 and probably reflect lower animal abundances and less bio-irrigation. This difference in sediment oxidation was also reflected in lower Eh values in the top 6 cm. Profiles in summer 1994 were more similar to those in 1992 than in 1993 (Figure 15a). Sulfide concentrations at depth at BH03 showed considerable variability. In March, May and October they increased rapidly below 10 cm and exceeded the highest values we measured at BH02. However, in July sulfide concentrations were quite low, never exceeding 0.6 mM. We have observed high variability in porewater profiles at depth at this site in the past.

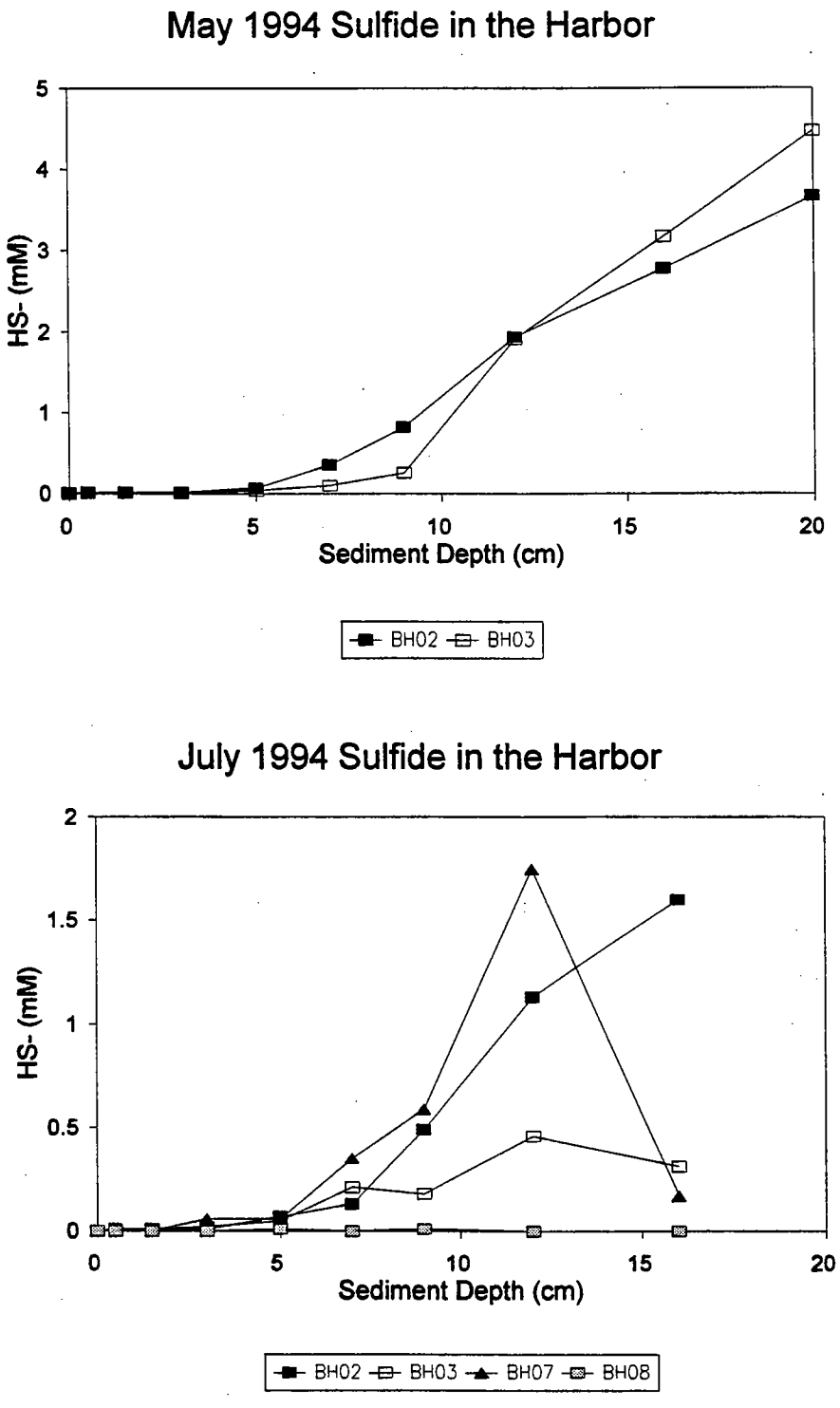
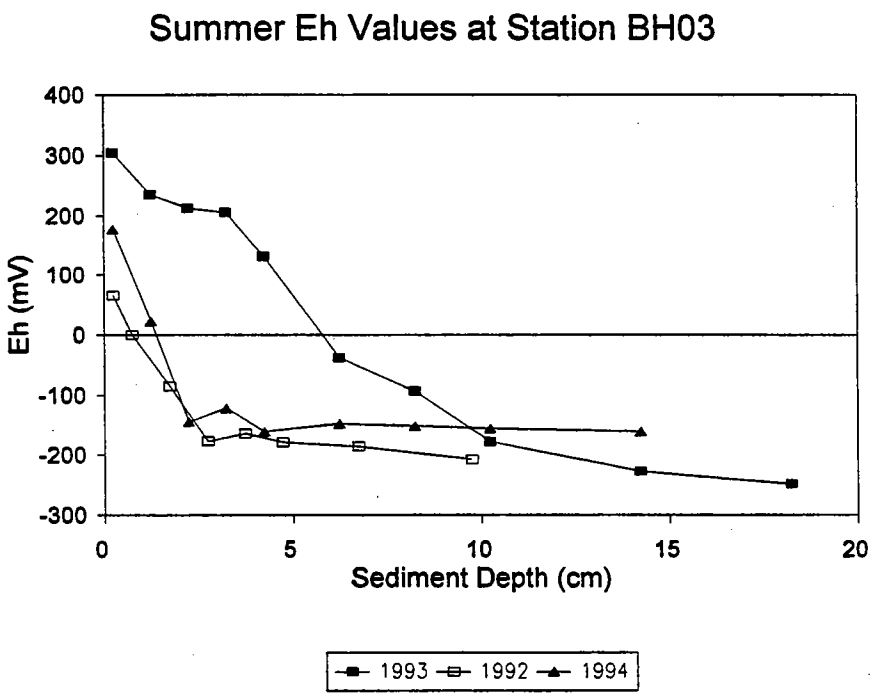


Figure 14. **Dissolved sulfide in the porewater of sediments from Boston Harbor in 1994. (a) May (b) July**



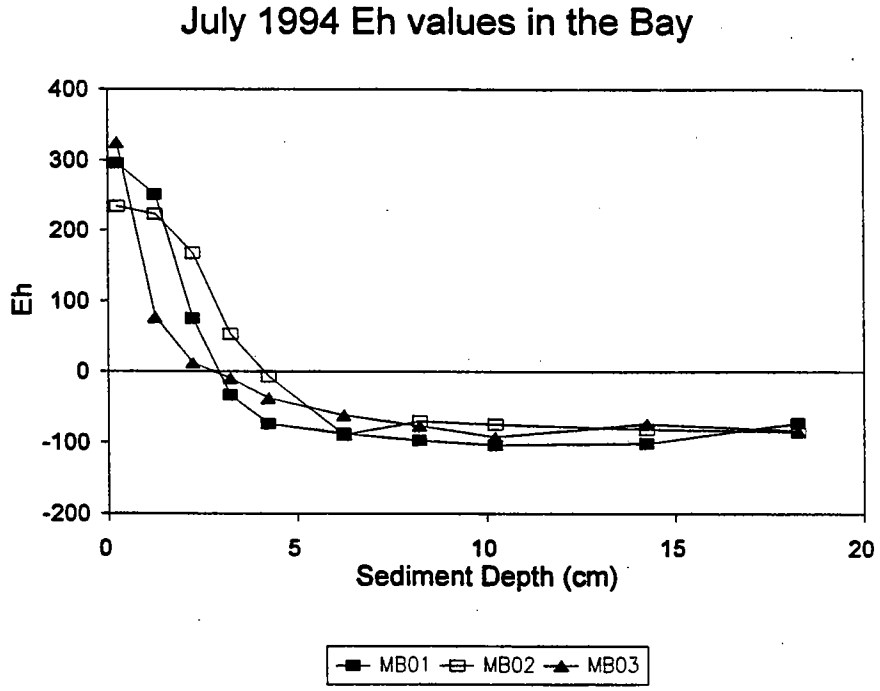


Figure 15. **Eh values from sediments. (a) A comparison of the Eh values at Station BH03 taken during the summers of 1992, 1993, and 1994. (b) Eh values from three nearfield Bay stations in July 1994.**

Porewater profiles in the Bay were very similar to those measured in previous years. Sulfide was seldom detected in the porewater from Bay cores and alkalinity values rarely exceeded 5 mM. Sediment Eh profiles were also quite similar. Eh values were usually positive in the top few cm and then reached an asymptote of -50 to -150 at depth (Figure 15b). The consistency of the Eh and sulfide profiles between different stations in the Bay and between years suggests that these parameters will be sensitive indications of changes in organic matter loading to the sediments.

5.0 COMPARISON TO WATER QUALITY MODEL

The HydroQual water quality model has been run simulating the current conditions in the Harbor and the Bay. The model predicts sediment-water fluxes and porewater concentrations in sediments in addition to a large number of water column processes. We compared our data in harbor and bay sediments to model predictions to help evaluate how well the model mimics current conditions.

Harbor

We have observed a high year to year variability in fluxes at station BH03 which we attribute to: 1) transients from the cessation of sludge dumping and 2) periodic "blooms" of benthic animals, especially tube dwelling amphipods. These periodic benthic colonizations may also be related to the cessation of sludge disposal.

In our report on the 1993 data we predicted that the HydroQual model would probably not capture some of the very high fluxes we observed at station BH03 but that benthic fluxes should decrease over time. In fact this is what seems to have occurred. The very high SOD fluxes we measured at station BH03 (model segment 6/21) in 1993 were not generally observed in 1994. The 1994 data were much closer to the 1990-1992 data and agreed much more closely with the model. The nitrate fluxes from this station were also much lower in 1994, never exceeding about 40 mg N m^{-2} d^{-1} so there was also much better agreement with the model than with the 1993 data. Ammonium fluxes appeared to be in good agreement with model predictions in most years. The direct denitrification measurements were still somewhat higher than predicted but lower than in 1993.

In general, there was better agreement between the model and the data at the other harbor stations than at BH03. The 1994 data from BH02 have a different seasonal pattern than we observed in 1993 (the high May fluxes of 1993 were not repeated) and the model and the data track fairly well. Fluxes matched fairly well at a number of the other muddy harbor stations, sometime observed being a little higher and sometimes running a little lower than predicted. The model tended to predict higher than observed fluxes at BH08 and some of the other sandy stations.

In general, porewater concentrations of ammonium were in the right range for the Harbor overall but tended not to match station to station differences. We have observed that at some of the stations we sampled in 1992, where the sediment quality was very poor (T4 and R4) and macrofuana were not visible, the observed porewater concentrations were much higher than predicted. In contrast, at stations with high porewater turn over such as BH03 where there was very active bio-irrigation or BH08 where there are strong tidal currents, the porewater concentrations we observed were lower than those predicted.

Silica fluxes in most of the harbor stations were higher than predicted in the model. However, at BH08, which is a non-depositional area, they were lower than modelled. This may indicate that Si fluxes calculated by the model are average fluxes and that fluxes will be higher than average in depositional area and less than average in areas where scouring takes place.

Bay

In general, the model and the data agreed very well in terms of timing and magnitude for most fluxes. The agreement with ammonium looked very good and model predicted nitrate efflux, in agreement with the data.

The seasonal pattern of oxygen fluxes matched extremely well. Our measured fluxes were a little higher than the model predicted. One possibility is that the predicted SOD is still a little low because the model productivity is a bit low. The other is that we measured depositional areas that are a little more active than the "average" sediment modeled.

While there is a lot of variability in the measured denitrification data, the overall average of 1.2 mmol N m^{-2} d^{-1} calculated for the shallow nearfield stations was close to that modeled for segments 10/20 and 9/18 which are in the same area.

There is a large difference between the observed and modeled silica fluxes; measured fluxes are 2 to 10 times higher. The 1994 Si flux data are quite similar to the 1993 data so year to year variability does not appear to be a problem. One hypothesis is that the difference between the model and the data is due to the sites which we sampled and the time constants over which Si dissolves. All the Bay sites sampled are depositional and may be accumulating and concentrating material which is more evenly distributed in the model. Because biogenic silica dissolves more slowly than organic matter decomposes, Si fluxes will be more sensitive to the seasonal redistribution of fine particles than O/N/P fluxes. Hence the depositional sites we measure may have much higher fluxes than the model predicts due to sediment focusing. However, this may not be the entire explanation. We have also noted the discrepancy between the high measured Si fluxes and the low build up of Si in the bottom water (Section 4.4.2). This calculation did assume much lower Si fluxes from nondepositional areas and should have taken sediment focusing into account. This suggests that the lower Si fluxes predicted by the model may be appropriate, or that there is a water column Si sink in the bottom waters.

An additional discrepancy between the model and the data is the porewater silica concentrations. The 0-10 cm average Si concentration is less than 6 mg Si L^{-1} while the model predicts 9. The model also predicts higher NH_4 concentrations than we have measured. An alternative hypothesis for the discrepancy in the Si fluxes between model and data is that bio-irrigation in the model is too low and that Si dissolution kinetics are being slowed by too high a porewater Si concentration.

6.0 SUMMARY AND MONITORING DESIGN ISSUES

(1) Sediment oxygen uptake in the Harbor ranged over the seasonal cycle from approximately 20 mmol m^{-2} d^{-1} in the winter to 105 mmol m^{-2} d^{-1} at an organic rich site in autumn. For the first time since monitoring began, oxygen uptake at Station BH03, the former sludge disposal site near Long Island, was not consistently higher than any of the other Harbor Stations. Fluxes at this station still show considerable temporal variability which may be related to the sporadic presence of large numbers of benthic infauna.

(2) Sediment oxygen uptake in the Bay agreed extremely well with data from previous years ranging from 6 to 22 mmol m^{-2} d^{-1}. As was the case in 1993, the three nearfield sites, MB01, MB02, and MB03 had annual average respiration rates that were not significantly different from one another. Two other nearfield shallow stations sampled in August (NF8 and NF12) had similar respiration rates to other nearfield stations. There was a significant relationship between the oxygen uptake rates of all the shallow Massachusetts Bay stations and temperature.

(3) Oxygen uptake rates at deeper Stellwagen Basin sites (MB05 and MB07) had lower respiration rates than other shallower Massachusetts Bay stations for most of the year. Some of the difference between the shallow and deep stations could be correlated with temperature.

(4) Denitrification rates in Boston Harbor ranged from non-detectable to 6.9 mmol N m^{-2} d^{-1}. The rates observed in 1994 were lower than in 1993, largely due to the large decrease in denitrification rates at BH03 in 1994. Highest rates were observed at BH03 in October when exceptional numbers of amphipods were present.

(5) Denitrification rates in Massachusetts Bay ranged from non-detectable to 2.7 mmol N m^{-2} d^{-1}. Rates at the nearfield stations averaged 1.2 mmol N m^{-2} d^{-1}, nearly identical to rates measured in 1993.

(6) Dissolved inorganic nitrogen and phosphate fluxes at the Bay nearfield stations were not as similar to each other as oxygen fluxes but the stations all exhibited similar seasonal trends. The 1994 DIN fluxes were within 20% of the 1993 values but the phosphate fluxes were nearly twice as high. Silica flux rates at all the nearfield stations were very similar. Silica release from the sediments in 1994 was 48% greater than in 1993 mostly due to higher fluxes in July. Silica flux from the sediments of all nearfield stations were very similar. Silica release showed an interannual variation of 48%.

(7) Although there is some spatial and temporal variability in the fluxes from Bay sites, a major change in organic matter delivery to the sediments should be reflected in a measurable change in benthic fluxes. The close correspondence among rates of oxygen uptake and DIC and nutrient fluxes from the shallow Massachusetts Bay stations, and the low inter-annual variability of the oxygen, DIC and DIN fluxes is encouraging. The HydroQual model predicts that benthic fluxes will increase four-fold near the diffuser (Hunt and Steinhauer, 1994). If the depositional nearfield areas experience an increase in the range of 50%, it should be detectable in benthic fluxes.

(8) The release of carbon dioxide over the season gave a higher estimate of carbon mineralized in the benthos than did oxygen uptake for all stations. At two Harbor stations (BH02 and BH03), DIC release exceeded oxygen uptake by about 40%. Over an annual cycle at the nearfield Bay stations (MB01, MB02, MB03). DIC release exceeded oxygen uptake by 54-60%. At the deeper Bay stations (MB05 AND MB07), oxygen uptake and DIC release were nearly equal.

(9) At all stations urea was a very minor component of the total nitrogen flux (urea, nitrate, ammonium, N_2). Over the annual cycle ammonium was the most important component of the nitrogen flux in the Harbor, followed by N_2, and then nitrate. In the nearfield, ammonium and N_2 had nearly identical contributions to the total nitrogen flux with nitrate only making up an average of 6% of the N released. N_2 was the most important component of the nitrogen flux at the farfield stations, making up 66% of the total nitrogen flux.

(10) Respiration at depositional sites in Massachusetts Bay is equivalent to 17% (based upon oxygen) to 28% (based upon DIC) of the production in the overlying water. Benthic nutrient release could supply 11% of the N and 25% of the P required for primary production.

(11) Porewater constituents are important indicators of sediment processes. Porewater sulfide and Eh are dramatically different between the Harbor and the Bay and may be sensitive indicators of changes in organic matter loading.

(12) In general, there is good agreement between measured fluxes and fluxes predicted by the HydroQual model in the Bay. Overall, silica shows the largest consistent difference between measured and predicted fluxes. This may reflect the bias of the sampling toward depositional areas or suggest some problem with the model parameterization.

(13) Station BH03, the former sludge disposal area, continues to exhibit large inter-annual differences in benthic fluxes and porewater chemistry. Fluxes in 1994 were considerably lower than in 1993. High flux rates appear to be correlated with high benthic animal abundance.

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