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

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The Massachusetts Water Resources Authority
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Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments

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ABSTRACT

We sampled stations in Boston Harbor in April, May, June, August, and November of 1992 and stations in Massachusetts Bay in October and November. Sediment cores were brought back to the laboratory and fluxes of oxygen, total CO_2, ammonium, nitrate and phosphate were measured across the sediment-water interface. Porewater profiles of dissolved inorganic nitrogen, phosphate, alkalinity, and sulfide were measured on separate cores.

Sediment oxygen uptake in the Harbor ranged seasonally from 15 to 70 mmol m^{-2} d^{-1}. Respiration at Station T3, near Long Island, was consistently higher than at any other Harbor Stations. Oxygen uptake in the Bay ranged from 12.3 to 30.1 mmol m^{-2} d^{-1}. In most cases carbon dioxide release exceeded oxygen uptake in both the Harbor and the Bay.

A substantial portion of the organic carbon loading to these systems was mineralized by the benthos. In Boston Harbor, the equivalent of 56% of the carbon fixed by phytoplankton, and 36% of the total organic carbon inputs, were decomposed on the bottom. In Massachusetts Bay, between 26% and 37% of the carbon inputs were respired on the bottom.

We calculated denitrification from the stoichiometry of organic matter decomposition and the measured release of dissolved inorganic nitrogen from the sediments. We compared three measures of organic matter decomposition: oxygen consumption, oxygen consumption corrected for anaerobic metabolism using alkalinity, and total CO_2 release.

Denitrification in Harbor sediments, calculated using total CO_2 release as the measure of organic matter mineralization, ranged from 0.56 to 6.38 mmol N m^{-2} d^{-1}. The grand mean of all of the 1992 Harbor denitrification data was 2.5 mmol N m^{-2} d^{-1}. During our study, denitrification removed about 12% of the 21.7 mmol N m^{-2} d^{-1} entering Boston Harbor.

Average denitrification rates in Massachusetts Bay during October and November were 1.6 mmol N m^{-2} d^{-1}.

Our estimates of denitrification agree with those of Kelly and Nowicki (1993). Although there is some scatter in the data at low rates of denitrification, it appears that there is no consistent bias between techniques.

INTRODUCTION

In this study, we measured sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen and phosphorus at stations in Boston Harbor and Massachusetts Bay. This study was undertaken to examine seasonal changes in benthic processes in Boston Harbor and to better characterize fluxes in Massachusetts Bay. It expands, both spatially and temporally, work we conducted in the Bay and in the Harbor during the late summer of 1990 and in the Harbor during September 1991 (Giblin et al. 1991; Giblin et al. 1992). The rationale for measuring benthic fluxes was detailed in our previous reports; it is summarized below. A major goal of this study was to provide a more temporally complete picture of nitrogen cycling within the Harbor and to examine the importance of the benthos in the N budget of Boston Harbor and Massachusetts Bay.

Sediments of coastal environments play an important role in nutrient recycling and organic matter decomposition. In addition to serving as a source of inorganic N to the water column through nutrient regeneration, sediments frequently act as an N sink via denitrification. During denitrification, nitrate is converted to N_2 and lost from the ecosystem. Denitrification is a cleansing process that can retard eutrophication of heavily nutrient loaded coastal systems. The amount of nitrogen lost by denitrification in coastal systems ranges from 15 to 70% of the inorganic nitrogen released by mineralization (Seitzinger 1988). Predicting the response of coastal ecosystems to increased nutrient loading requires an understanding of the importance of benthic processes including organic matter decomposition, nutrient regeneration and denitrification.

An additional goal of this study was to evaluate the "stoichiometric" method of measuring denitrification. In our previous studies, we estimated the importance of denitrification using an indirect method which uses the measured stoichiometry of the fluxes to infer how much nitrogen has been lost. We based our estimate on the deviation of the ratio of oxygen consumption to inorganic nitrogen flux at the sediment water interface (O/N ratio) from the theoretical ratio expected for decomposing phytoplankton (the Redfield ratio) to provide an estimate of the quantity of nitrogen lost via denitrification (discussed more fully in Giblin et al. 1991 and 1992 and later in this report). In our second study we again used the deviation of the O/N ratio from Redfield values to estimate denitrification, but also tried to assess whether or not oxygen was underestimating sediment metabolism by measuring carbon dioxide release and alkalinity fluxes at the same time.

In this study we examined the stoichiometry of the fluxes over several seasons. Because the ratio of oxygen to inorganic nitrogen fluxes can vary substantially over time due to periodic storage or oxidation of reduced metabolic end products, such as sulfides, in the sediments (see Giblin & Howarth 1984 for a more detailed discussion), rates measured over several seasons should be more reliable than rates measured at a single period of time. We also measured total carbon dioxide (DIC) and alkalinity fluxes over several seasons to determine how well oxygen estimated total sediment respiration. We compare our denitrification estimates to N_2 fluxes directly measured by Dr. Barbara Nowicki, U.R.I. (Kelly & Nowicki 1992, 1993) on sediment cores taken concomitantly with our cores.

MEASURING DENITRIFICATION USING THE STOICHIOMETRIC METHOD

The stoichiometric method of measuring denitrification is an indirect method which involves 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.

Measurement of Decomposition

Traditionally the rate of organic material being decomposed has been measured from the rate of sediment oxygen uptake. This method is relatively simple and can be made with high precision and accuracy. Oxygen is a good measure of total decomposition even if terminal electron acceptors other than oxygen are used in respiration provided the reduced end products of anaerobic respiration are ultimately reoxidized. For example, sulfate reduction is an anaerobic process of organic matter decomposition in which bacteria use sulfate instead of oxygen as a terminal electron acceptor during respiration. During sulfate reduction, two moles of organic carbon are oxidized to CO_2 for every mole of sulfate reduced:

$$2\ CH_2O + SO_4^{-2} + 2H^+ = 2\ CO_2 + H_2S + 2\ H_2O$$

If sulfides are re-oxidized within the sediments it requires two moles of oxygen per mole of sulfide:

$$2\ O_2 + H_2S = SO_4^{-2} + 2H^+$$

In this case, the moles of oxygen consumed are equivalent to the moles of carbon dioxide produced so the measured sediment oxygen consumption includes the organic carbon oxidized by sulfate reduction.

While the majority of the sulfides are oxidized on an annual basis there may be times of the year when sulfides are stored in the sediments as either FeS or FeS_2. During other times of the year there may be a net oxidation of FeS or FeS_2. During these specific times oxygen consumption does not account for total carbon oxidation (total respiration); in the first case respiration is underestimated while in the latter it is overestimated.

One way to evaluate the importance of sulfide storage or oxidation is to also examine the flux of alkalinity. Aerobic respiration of carbon neither produces nor consumes alkalinity. Sulfate reduction produces one mole of alkalinity for every mole of carbon oxidized. Sulfide oxidation consumes one mole of alkalinity for every mole of oxygen used. Therefore, the flux of alkalinity can be used to determine if large amounts of sulfide are being oxidized or stored and to "correct" the oxygen uptake values for sulfur storage. However, ammonification and nitrification also affect the alkalinity budget. Ammonium production (either aerobic or anaerobic) produces 0.938 moles of alkalinity for each mole of ammonium produced. The oxidation of ammonium to nitrate consumes 1.0625 moles of alkalinity per mole of ammonium oxidized. Therefore, when nitrogen fluxes are large the alkalinity data needs to be corrected for ammonium and nitrate fluxes.

The difficulty with using alkalinity to measure the respiration not manifested as oxygen uptake is that alkalinity fluxes tend to be small in comparison to the background concentrations in the overlying water and are difficult to measure. One way to try to reduce this problem is to measure the porewater gradients of alkalinity in the sediment and calculate the alkalinity flux. This is the approach we used in our previous report (Giblin et al. 1992).

Many of the problems of using oxygen uptake as a measure of total decomposition can be eliminated by measuring total CO_2 fluxes (DIC) directly. DIC fluxes are not affected by the storage of reduced endproducts from sulfate reduction. However, until recently, measuring CO_2 fluxes in seawater was difficult due to the large bicarbonate background in seawater. The development of a high precision coulometric DIC analyzer, which is precise and accurate to 1 μM, now allows DIC fluxes to be measured directly.

While DIC fluxes should be an accurate measure of total carbon decomposition, artifacts are still possible from carbonate dissolution or precipitation. Very few studies have evaluated this problem. McNichol et al. (1988) found that carbonate dissolution enhanced DIC fluxes 2% in the spring in Buzzards Bay, MA, but that carbonate dissolution was unimportant the rest of the year. 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 lead to an overestimation or underestimation of denitrification.

In some systems, phosphate release appears to be a simple and effective method of measuring decomposition (Dollar et al. 1991; Smith et al. 1991). However, the exchange of phosphate across the sediment-water interface can be strongly affected by adsorption and desorption from the sediments, in addition to mineralization rates (Pomeroy et al. 1965; Patrick & Khalid 1974). Therefore, phosphate release need not be related to decomposition/mineralization in all sediments.

Composition of the Organic Matter being Decomposed

When using flux ratios to calculate denitrification, most investigators have assumed that the material being decomposed in sediments has a composition similar to fresh phytoplankton. A C:N:P ratio of phytoplankton was described by Redfield (1934) as $C_{106}H_{263}O_{110}N_{16}P_1$. The assumption that organic matter undergoing decomposition in sediments has a similar stoichiometry is difficult to test. Typically, sediments have C/N values higher than fresh phytoplankton. However, measurements of bulk sediment ratios are not necessarily representative of organic pools undergoing decomposition because during the early stages of decomposition in the water column and sediments, N and P can be lost preferentially to carbon. It is also possible to observe deviations in the flux ratios seasonally if carbon mineralization lags behind nitrogen mineralization.

When fresh phytoplankton is decomposed the expected ratios of O_2 uptake, CO_2 production, and DIN and DIP release are known:

Aerobic respiration to NH_4^+:

$$C_{106}H_{263}O_{110}N_{16}P_1 + 106O_2 + 15H^+ = 106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O$$

Aerobic respiration to NO_3^-:

$$C_{106}H_{263}O_{110}N_{16}P_1 + 138O_2 = 106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+$$

The deviation between the measured ratio of O_2 consumption to DIN flux (O/N by atoms) and the ratio based on Redfield stoichiometry can then be used to estimate denitrification in sediments. When fresh phytoplankton material is decomposed completely to CO_2 and ammonium, using oxygen, an O/N ratio of 13.25 is expected, and when ammonium is further oxidized to nitrate, a ratio of 17.25 is expected. A ratio substantially greater than 13-17 is an indication that inorganic nitrogen is being lost by denitrification (Nixon et al. 1976). The expected ratio can be calculated by measuring the proportion of the DIN flux that is ammonium vs. the proportion that is nitrate.

Similar calculations can be made when CO_2 or phosphate fluxes are measured (Dollar et al 1991; Smith et al. 1991). Deviations above 6.625 in the DIC/DIN ratio or 16 in the DIN/DIP ratio are used, along with certain assumptions, to quantify the amount of N lost by denitrification.

STATION DESIGN

Station Location

During 1992 we sampled 6 sites within Boston Harbor, Quincy Bay and Hingham Bay (Fig. 1, Table 1). Navigation was provided by Battelle (Kelly & Nowicki 1993). Stations T3 and T8 were sampled intensively, and an additional four stations (T2, T7, R4, T4) were sampled in August. Station T3 is off Long Island, in an area that received sludge disposal prior to Jan. 1992, and was sampled in April, May, June, August, and November. Station T8 in Higham Bay was sampled in April, May, June, and August. Both these stations, along with Station T2, located on Governors Island Flats near the airport, and Station T7 in Quincy Bay had been sampled during our 1991 survey. Station R4 is located near Station 2 in Giblin et al. (1991) and Station T4 is located near Fox Point. All of these stations have been sampled by Battelle as part of a benthic survey (Kelly and Kropp 1992).

We sampled stations in Massachusetts Bay during October and November of 1992 (see Kelly and Nowicki 1992b). During October, Stations 11, C3, G6, W1, and G8 were sampled. Stations W1 and G8 are near the proposed outfall site. Stations G6 and G8 were previously sampled for benthic fluxes (called Sta 6 and 8 in Giblin et al. 1991). During November, Stations 11, G8 and W1 were revisited and Station G9 in Broad Sound was sampled. Station G9 is between Stations 4 and 5 previously sampled for benthic fluxes (Giblin et al. 1991)

Station Descriptions

HARBOR - The stations chosen ranged from organic-rich, fine-grained sediments to hard sand and gravel (see Kelly and Nowicki 1993).

Station T3 sediments were fine-grained and flocculent. During all times of the year Station T3 had a 1-3 cm thick brown layer on the surface of all cores; below 4-5 cm the sediments were black. Small snails were present on the surface at all times. In June the surface was colonized with tube-building ampeliscid amphipods. The tubes were very dense in August and formed a nearly solid mat in November.

Sediments from Station T8 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. During the spring and summer, numerous tubes were evident on the surface of the sediment. Divers observed crabs, shrimp and skates on the bottom.

Stations T2, T4 and R4 had fine grained muds with thin, brown, oxidized surface layers. Sediments from Station T7 were sandier with some shell fragments at depth.

BAY - Sediments from Stations W1, 11, and G8 were fine-grained with a significant clay fraction (Kelly & Nowicki 1993). Stations C3 and G6 had a much higher proportion of sand and were difficult to sample by box-coring. Sediments at Station G9 consisted of hard-packed sand, and ripples were observed on the bottom.

METHODS

Sampling

All stations in Boston Harbor and Station G9 in Broad Sound were sampled by SCUBA divers. The Massachusetts Bay samples were obtained using a box corer (40x40 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 Dr. Barbara Nowicki for her direct measurements of N_2 flux. Bottom water temperature at all stations was determined by measuring the temperature of the water taken from near the bottom using a Niskin sampler (Table 1). 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 1.0μm). This water, which was held at in situ temperatures, was used to replace the water in the cores used for flux measurements.

Benthic Respiration and Nutrient Fluxes

Cores were transported to Woods Hole 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 hours of sampling. Prior to initiating flux measurements, the overlying water of each core was replaced with the filtered seawater obtained from 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.

Benthic flux measurements were made according to the protocols detailed in Giblin et al. (1991) and are given briefly below. 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 analysis. Ammonium concentration was determined from duplicate 3 ml subsamples by the technique of Solorzano (1969) modified for small sample size. A 2 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 & Riley (1962).

Additional water was frozen for later measurement of the nitrate and nitrite concentrations. Nitrate + nitrite were determined together using the cadmium reduction method (EPA) on a rapid flow analyzer (Alpkem RFA-300); the limit of detection was 0.2 µM. DIN was calculated as the sum of ammonium, nitrate, and nitrite.

At the beginning and end of the incubation period, samples were also taken for total CO_2 analysis. Sixty ml samples were stored at 4°C in glass BOD bottles with mercuric chloride as a preservative. Samples were analyzed with a high precision coulometric CO_2 analyzer maintained by C. Goyet at the Woods Hole Oceanographic Institution. The instrument is capable of measuring total CO_2 with a precision of 0.05% (1 µM).

Porewater Sampling and Analysis

Sediment samples for porewater extraction were sectioned into depth intervals in a glove bag under a nitrogen atmosphere (described in Giblin et al. 1992). 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. Porewater was removed from muddy sediments by centrifuging sections of mud for 15 minutes in centrifuge tubes capped under nitrogen. At sandy sites it was necessary to use a "split" centrifuge tube with filter support midway down the tube. Centrifuging at high speed for 15 minutes forces porewater through the filter into the bottom of the tube.

Nutrients, sulfides (Cline 1969), pH and alkalinity (Edmond 1970) in porewaters were analyzed as previously described in Giblin et al. (1992).

Sediment redox potential was measured using a platinum electrode (Bohn 1971). The electrode was pushed into the sediment at 1.0 to 3.0 cm increments and allowed to stabilize for 15 min. The resulting EMF was read on a standard pH meter connected to a saturated calomel reference electrode placed in the overlying water. The calibration of the electrode was checked by measuring the EMF of quinhydrone dissolved in pH 4 and 7 buffers (Bohn 1971). The values reported here have been corrected for the potential of the reference electrode.

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 was measured after a minimum of 72 hrs 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 analysis was performed on a Perkin Elmer 2400 CHN elemental analyzer following carbonate removal. To remove carbonates we placed a small amount of weighed, dry sediment in a humid (100%) atmosphere for 3 days. After the sediments became moist they were placed in a desiccator over fuming HCl for three days. The sediment was then dried, weighed, and ground. The % carbon and nitrogen measured on the sediment was corrected for the weight change due to the procedure.

Calculations of Fluxes from Porewater Gradients

The flux of alkalinity from sediments was calculated from porewater gradients using a procedure similar to that described by Berner (1980). Concentration profiles were fit numerically using a Marquardt (1963) matrix approach to the equation:

$$C_z = C_\infty + (C_o - C_\infty)(e^{-\alpha z})$$

where C_∞ is the concentration at depth infinity; C_o represents the concentration at the interface and C_z is the concentration at depth z. We did not force the fit through the bottom water concentrations at C_o (see discussion in Klump and Martens (1981)).

In cases where a significant fit could not be obtained, we used a linear fit through the data from the surface (0-1) sediment and the bottom water concentration.

The flux (J) across the sediment water interface was calculated by:

$$J = -ø_o D_s(\partial C/\partial z)_{z=0}$$

where $_{øo}$ is the porosity at the sediment-water interface, D_s is the bulk diffusion coefficient at the interface, and $(\partial C/\partial z)_{z=0}$ is the gradient at the interface. D_s is equal to the molecular diffusion coefficient, D_o corrected for temperature and tortuosity by the formula $D_s = D_o ø_o$ (Berner 1980). A value of 1.14×10^{-5} was used for D_o from the published molecular diffusion coefficient for bicarbonate at 20°C (Li and Gregory (1974)).

RESULTS AND DISCUSSION

Replication and Accuracy of Flux Measurements

The measured fluxes of oxygen, ammonium, and DIN appeared linear over time in nearly all cases (Table 2). The regression coefficients (r^2) for regressions of oxygen, ammonium, and nitrate concentrations against time were usually high except when fluxes of oxygen or nitrate were very low. In contrast, phosphate regressions frequently had low regression coefficients and slopes were not consistently unidirectional. DIC analysis was only done at the beginning and the end of the incubation.

During April, May and June, three replicate cores were taken at each station. In June, one replicate from Station T8 was discarded because at the conclusion of the flux measurements we noticed that a small skate had hatched from an egg case present in the sediment. During August, October, and November, flux measurements were made on two replicate cores per station except at G6, where only one core could be taken from the box core.

Oxygen Uptake

HARBOR - Harbor sediment oxygen uptake ranged from approximately 15 to 70 mmol O_2 m^{-2} d^{-1} between April and November 1992 (Fig. 2a; Table 2). Respiration was consistently higher at Station T3 than at any of the other harbor sites during 1992, and overall we observed more difference between stations in 1992 than we did in Sept. 1991 (Giblin et al. 1991). Oxygen uptake rates at Station T3 increased throughout the spring and summer and reached maximal values in August. Respiration at T3 was still very high in November even though water temperature was down to 10°C. These high rates may be due in part to a large population of filter feeding amphipods that appeared in the surface sediments in June. Oxygen uptake at T8 showed much less temporal variation.

During August, the rates of sediment oxygen uptake at Stations T2, T7, R4, and T4 were between that of Stations T3 and T8 suggesting that Stations T3 and T8 span the full range of conditions found in most areas of Boston Harbor.

BAY - Average oxygen uptake rates of the Bay Stations ranged from about 12.3 to 30.1 mmol O_2 m^{-2} d^{-1} (Fig. 2b; Table 2). During both October and November, the highest rates of oxygen uptake were observed at Station W1 with the rest of the stations falling into a lower, narrow range. Respiration decreased slightly from October to November. In general, respiration rates in the Bay during October and November were similar to those measured at Station T8 in the Harbor and averaged slightly higher than the rates for Bay stations sampled in October of 1990 (Giblin et al. 1991).

Total CO_2 Measurements

HARBOR - Total CO_2 fluxes at Harbor stations ranged from approximately 20 to 85 mmol CO_2 m^{-2} d^{-1} between April and November 1992 (Fig. 3a; Table 2). As was observed with oxygen uptake, respiration was consistently higher at Station T3 than at any of the other

Harbor sites, but the difference between stations varied from time to time. Of all the harbor stations investigated, Station T8 always had the lowest rate of total CO_2 production during 1992. Although there was a general increase in respiration rate at Station T3 from April to August as water temperature increased, temperature alone must not be the only factor controlling respiration as the second highest rate of respiration was in November when water temperatures were lowest. There was no seasonal pattern discernible at Station T8.

The total CO_2 fluxes were almost always higher than the oxygen uptake rates at all stations with the exception of Station T7. During June, O_2 fluxes were slightly higher (<5%) than DIC fluxes at Stations T3. Overall, respiration estimated from DIC fluxes was 4% less than that estimated from oxygen uptake at specific times. Over the seasonal cycle the respiration measured using DIC was 14% higher than that measured using oxygen at T3, and 22% higher at station T8.

BAY - In Massachusetts Bay in October and November 1992, total CO_2 fluxes ranged from about 14.7 to 49.7 mmol C m^{-2} d^{-1} (Fig. 2b; Table 2). We attribute our inability to detect any DIC flux from Station G9 to unknown analytical problems. As was observed for DIN, O_2 and DIP fluxes, the release rates of CO_2 were highest at Station W1. On most occasions, DIC fluxes were higher than O_2 uptake although twice (Station G8 and C3 in October) DIC release was lower than O_2 consumption. The largest difference between the two methods was observed at W1 in October when respiration calculated using CO_2 was 65% greater than when using O_2. For the remainder of the stations, respiration estimated from DIC was from 24% lower to 40% greater than when estimated from O_2.

DIN Release from Sediments

HARBOR - The combined flux of ammonium and nitrate from sediments to the overlying water ranged from about 1 mmol N m^{-2} d^{-1} at Station T8 in May to almost 9 mmol N m^{-2} d^{-1} at Station T3 in August (Fig. 4a; Table 2). Rates were higher in the summer and fall than in the spring. Although there were not any consistent spatial patterns to DIN flux, nitrogen release was in general lowest at Station T8 and highest at Station T3. In August, Stations T2, R4 and T4 had release rates approaching that at T3.

The proportion of the DIN flux which was made up of nitrate was consistently greater at T8 than at T3 (Table 2). Both stations always showed some flux of nitrate from the sediments. In contrast, Stations T4 and R4 consumed nitrate during the incubation.

BAY - Release of DIN from Bay sediments in the fall of 1992 ranged from a low of 0.64 mmol N m^{-2} d^{-1} at Station C3 to a high of 4.6 mmol N m^{-2} d^{-1} at Station W1 (Fig. 4b; Table 2). There was little change in rates between October and November. Although rates decreased at Station W1 they actually increased as temperature fell at Stations G8 and S11. DIN flux from Station W1 was comparable to rates observed in the Harbor during warmer months.

We observed nitrate fluxes from the sediments of all Bay stations (Table 2). In October, 14-34% of the DIN flux was nitrate. This is similar to what we observed in October of 1990 (Giblin et al. 1991). In November, a similar proportion (13-22%) of the DIN flux was nitrate at the stations in Massachusetts Bay proper, but the percentage of nitrate was much greater (66%) at G9 in Broad Sound.

Phosphate Flux

HARBOR - There was almost an order of magnitude range in the flux of PO_4^{3-} across the sediment water interface over time in Harbor sediments. Rates were lowest in April (averaging about 0.05 mmol P m^{-2} d^{-1}) and increased substantially as the water warmed (Fig. 5a; Table 2). Phosphate flux reached a level of 1.6 mmol P m^{-2} d^{-1} in August at Station T8. In contrast to the fluxes of C, O_2 or DIN at harbor stations, DIP fluxes were often higher at Station T8 than at T3. There is much large scale spatial heterogeneity in DIP release from Harbor sediments as evidenced by the wide range of release rates observed for the six stations sampled in August 1992. In August, phosphate flux was directed into the sediments at Stations T7 and R4.

BAY - At most stations we observed a release of phosphate from Massachusetts Bay sediments to the overlying water (Fig. 5b; Table 2). However at Station C3, PO_{43-} was taken up. Release rates ranged from a low of 0.05 mmol P m^{-2} d^{-1} at Stations G8 and S11 in October to a high of 0.26 mmol P m^{-2} d^{-1} at Station W1, also in October. As with the DIN fluxes rates changed little between October and November. While DIP release decreased at Station W1 it increased at the Stations G8 and S11 during that time.

The Importance of Benthic Fluxes

In shallow water coastal systems, the benthos is frequently the site where substantial quantities of the organic matter produced in the overlying water column are decomposed. This is certainly true in Boston Harbor and Massachusetts Bay. Organic matter decomposition in the sediments, as estimated from DIC fluxes, averaged 21.16 mmol C m^{-2} d^{-1} in Massachusetts Bay and 41.5 mmol C m^{-2} d^{-1} in Boston Harbor. Levels of primary production have been estimated to be 325 gC m^{-2} y^{-1} in Boston Harbor and 250 gC m^{-2} y^{-1} in Massachusetts Bay (Michelson 1991). By comparing our measured rates of benthic respiration to these estimates of primary production we calculate that 37% and 56% of the organic matter produced in the water column is decomposed on bottom sediments of Massachusetts Bay and Boston Harbor, respectively. In a system as shallow as Boston Harbor, we might expect an even greater percentage of organic matter to be decomposed on the bottom when compared to Massachusetts Bay (Hargrave 1973). However, other sources of organic matter, such as sewage effluent, also enter Boston Harbor and these additional sources probably contribute to the high respiration rate we measured in Boston Harbor sediments. Using a revised estimate for BOD loading for Boston Harbor (Menzie et al 1991; revised using MWRA Discharge Monitoring Reports for 1992), we calculate that sewage effluent and other sources provide an additional 200 gC m^{-2} y^{-1} (46 mmol C m^{-2} d^{-1}) to Boston Harbor. This means that the total amount of organic matter decomposed on the Harbor bottom is about 36% of the total organic matter loading from sewage and primary production.

One way to assess the importance of the benthos to coastal systems is to determine the amount of primary production that can be supported by the remineralization of organic matter and the release of regenerated nutrients. Using published rates of primary production for the water column in Massachusetts Bay and Boston Harbor, referenced above, we calculated that the benthos can provide a substantial amount of the nutrients required to sustain primary production. In Massachusetts Bay, based on the average of DIN and DIP fluxes measured in October and November 1992 (1.995 and 0.12 mmol N and P m^{-2} d^{-1}), the benthos releases enough N and P to provide about 22% of the phytoplankton requirements. If we assume primary production in Massachusetts Bay is as high as 350 gm^{-2} y^{-1} as proposed by Cura (1991), regeneration in the benthos still provides 16% of the N and P required by phytoplankton. In Boston Harbor, the potential role of the benthos in meeting phytoplankton demand is greater (31% N and 22% of P) due to higher N and P fluxes (3.77 mmol N and 0.158 mmol P m^{-2} d^{-1}) from the sediments. In spite of the higher fluxes in the Harbor, regeneration is probably much more important than these calculations suggest in supporting primary production in the Bay than in the Harbor. At the present time new allochthonous nitrogen inputs to the Harbor are nearly ten times greater than the benthic flux and actually exceed phytoplankton N requirements for primary production. This is not the case in the Bay where new allochthonous nitrogen inputs on an areal basis are an order of magnitude lower than into the Harbor and of similar magnitude to the benthic flux.

Sediment Carbon and Nitrogen

Harbor sediments taken for this study ranged from 0.31% carbon at T8 in April to 4.46% carbon at T3 in June (Table 3). The other sediments taken in August had carbon concentrations ranging from 1.82% to 3.88%. Carbon concentrations showed some variation between sampling periods but no clear seasonal pattern. Carbon/nitrogen ratios ranged from 7.0 to 13.35. The ratios also showed variations but again no clear seasonal pattern.

The Bay stations ranged in carbon concentration from 0.40 at G9 in Broad Sound to 2.5% measured at Station 11 in October. Carbon/nitrogen ratios ranged from 7.58 to 14.53.

Porewater Constituents

HARBOR - Alkalinity in the porewaters at Station T3 was much higher than seawater values at depth during all sampling dates (illustrated with June data in Fig. 6; Tucker et al. 1993). In contrast, only a small increase in alkalinity was ever observed in porewaters from Station T8. All the other Harbor stations sampled in August showed a substantial alkalinity increase over seawater values at depth (Tucker et al. 1993). To a large degree, the alkalinity profiles mirrored the profiles of sulfide and ammonium (Fig. 6).

Station T8 is clearly the most oxidized of the Harbor stations as evidenced by higher sediment Eh values, lower sulfide concentrations, and substantial subsurface nitrate maximum values (Fig 6, 7). The only porewater constituents that were higher at Station T8 than at T3 were phosphate and nitrate. The very different alkalinity/phosphate ratios at these stations are a strong indication that phosphate is not acting as a conservative tracer of decomposition.

BAY - The porewater chemistry of the Bay stations was similar to Harbor stations. All stations exhibited low alkalinity values (Tucker et al. 1993), and fairly high and similar sediment Eh values (Fig. 8). Sulfides were below detection.

Alkalinity Fluxes

For nearly all dates and stations we calculated a flux of alkalinity from the sediments to the overlying water (Table 4). This indicates that oxygen is not measuring total decomposition. The calculated flux from sediments from Station T3 was always greater than from Station T8.

The shapes of the sediment porewater profiles were not always representative of steady state diffusive profiles. Profiles frequently indicated that porewater flushing/irrigation was taking place. This was nearly always the case at Station T8 and frequently the case for the Bay stations. When possible, we calculated concentration gradients from the profiles using the non-linear equation for steady state diffusive fluxes. Otherwise the gradients were calculated using a linear fit. When the porewater profiles are heavily influenced by advective removal, our calculation of the diffusive fluxes for these cases will be an underestimate.

We have not corrected our fluxes for alkalinity changes due to nitrogen dynamics, or the diffusion of sulfide into the overlying water. Sulfide diffusion was not important at most stations because sulfide concentrations in the top cm were very low or zero. Ammonium fluxes caused us to overestimate the alkalinity due to DIC while nitrate fluxes lead to an underestimate.

Comparison of Measurements of Decomposition

As discussed above, rates of total CO_2 release exceeded oxygen consumption at nearly all times and sites. Therefore we would calculate higher rates of decomposition when using CO_2 than when using O_2. When we adjusted the oxygen consumption for unaccounted-for respiration using the calculated alkalinity flux (Table 4), the average respiration rate of all stations was nearly identical to what we calculated using total CO_2. Average respiration calculated using alkalinity was slightly greater than average values calculated using CO_2 for

Harbor stations, but lower for the Bay stations.

We feel that total CO_2 fluxes give us the best measure of decomposition within the sediments and is superior to measuring decomposition by correcting oxygen uptake using alkalinity fluxes. One disadvantage of the alkalinity correction is that in order to make our calculations we must assume that alkalinity profiles are at steady state, and that the transport of alkalinity from the sediments is by diffusion. Some of the alkalinity profiles do not meet these assumptions. Another disadvantage of the alkalinity method is that the fluxes are calculated from profiles taken from one set of cores, averaged, and then added to oxygen uptake measurements made on a separate set of cores. The total CO_2 measurement is a direct flux measurement and is made on the same cores from which nitrogen fluxes are measured. However, we have compared calculated denitrification rates using all three measures of decomposition so that the magnitude of the differences can be compared (Table 5).

It has been suggested that P fluxes should be used to estimate denitrification (Christensen 1991). For all stations but one we found that the DIC/DIP release we measured was higher than expected based upon a Redfield ratio (Fig 9). Had we used P instead of DIC to calculate denitrification with this data set we would have calculated much lower denitrification rates. We believe that P fluxes from these sediments are strongly controlled by adsorption and desorption and should not be used to measure decomposition.

Denitrification Rates

Denitrification in Harbor sediments in 1992, calculated using total CO_2 release as the measure of organic matter mineralization, ranged from 0.56 to 6.38 mmol N m^{-2} d^{-1} (Fig. 10). Denitrification at Station T3 increased throughout the year and was highest in November. The very high rates observed at this station may have been related to the dense amphipod population which was actively irrigating the porewater. During 1992, rates at all other stations were either lower than, or not significantly different from, T3. The grand mean of the all the 1992 Harbor denitrification data was 2.5 mmol N m^{-2} d^{-1}. During our study period, denitrification removed approximately 12% of the 21.7 mmol N m^{-2} d^{-1} entering Boston Harbor.

Denitrification rates in Massachusetts Bay during October and November ranged from

1.04 to 2.9 mmol N m^{-2} d^{-1} (Fig. 11). There was no consistent difference between stations. The Bay stations averaged 1.6 mmol N m^{-2} d^{-1}.

Although denitrification in the Harbor is higher on an absolute basis than in the Bay, sediments from both regions denitrify similar proportions of the N remineralized during decomposition. We calculate that 40% of the N remineralized is converted to N_2 in the Harbor, and 44% in the Bay. These percentages are very similar to numbers reported from other bays and estuaries (Seitzinger 1988).

Comparison to Nowicki

Our estimates of denitrification for most stations are in good agreement with those of Kelly and Nowicki (1993) (Fig. 12). There was a large discrepancy between the value we measured at station T7 and that reported by Kelly and Nowicki (1993). We have no explanation for this except to note that this station had the poorest correspondence between our measures and theirs in 1991 as well (Giblin et al. 1992). For the rest of the stations, although there is some scatter in the data at low rates, it appears that neither technique is consistently higher or lower than the other.

SUMMARY AND CONCLUSIONS

1) Sediment oxygen uptake in the Harbor ranged over the seasonal cycle from 15 to 70 mmol m^{-2} d^{-1}. Respiration at Station T3, near Long Island, was consistently higher than any of the other Harbor Stations. Sediment oxygen uptake in the Bay ranged from 12.3 to 30.1 mmol m^{-2} d^{-1}.

2) The release of total carbon dioxide gave a higher estimate of carbon mineralized in the benthos than oxygen uptake for nearly all stations and times. Respiration measured as carbon dioxide fluxes across all stations ranged from 4% less to 65% greater than respiration measured using oxygen consumption during specific sampling times. On a seasonal basis, the average discrepancy between the two techniques was much less with oxygen underestimating respiration by 14% at Station T3 and 22% at Station T8. The overall difference between the two methods at all the Bay stations was 18%.

3) When we use alkalinity fluxes from the sediment to correct oxygen uptake for anaerobic respiration not accounted for by oxygen, the estimate of carbon mineralized was close to the amount measured by total CO_2 flux. We feel that the direct flux measurement of CO_2 has been demonstrated to work well and is superior to using oxygen uptake with an alkalinity correction for the measurement of decomposition. The method is direct, all the fluxes can be measured on the same sample, and fewer assumptions are required.

4) In the Harbor, DIC/P release ratios were almost always much higher than the Redfield ratio indicating that phosphate fluxes are not a good measure of decomposition in this system. A similar result was found for Bay sediments although the differences were not as large.

5) A substantial portion of the primary production is mineralized by the benthos. In Boston Harbor the equivalent of 56% of the carbon fixed by phytoplankton is

decomposed on the bottom. If the organic matter inputs from sewage and other sources are included, about 36% of the total organic matter entering into, and produced within, Boston Harbor is decomposed on the bottom. In Massachusetts Bay, primary production estimates range from 250-350 gC m^{-2} y^{-1}. Given this range, decomposition on the bottom accounts for 26% to 37% of the primary production.

6) Denitrification in Harbor sediments, calculated using total CO_2 release as the measure of organic matter mineralization, ranged from 0.56 to 6.38 mmol N m^{-2} d^{-1} . The grand mean of the all the 1992 Harbor data was 2.5 mmol N m^{-2} d^{-1}. During our study period, denitrification removed about 12% of the 21.7 mmol N m^{-2} d^{-1} entering Boston Harbor. Denitrification rates in Massachusetts Bay during October and November averaged 1.6 mmol N m^{-2} d^{-1}.

7) Our estimates of denitrification are in good agreement with those of Kelly and Nowicki (1992b). Although there is some scatter in the data at low rates, it appears that neither technique is consistently higher or lower than the other.

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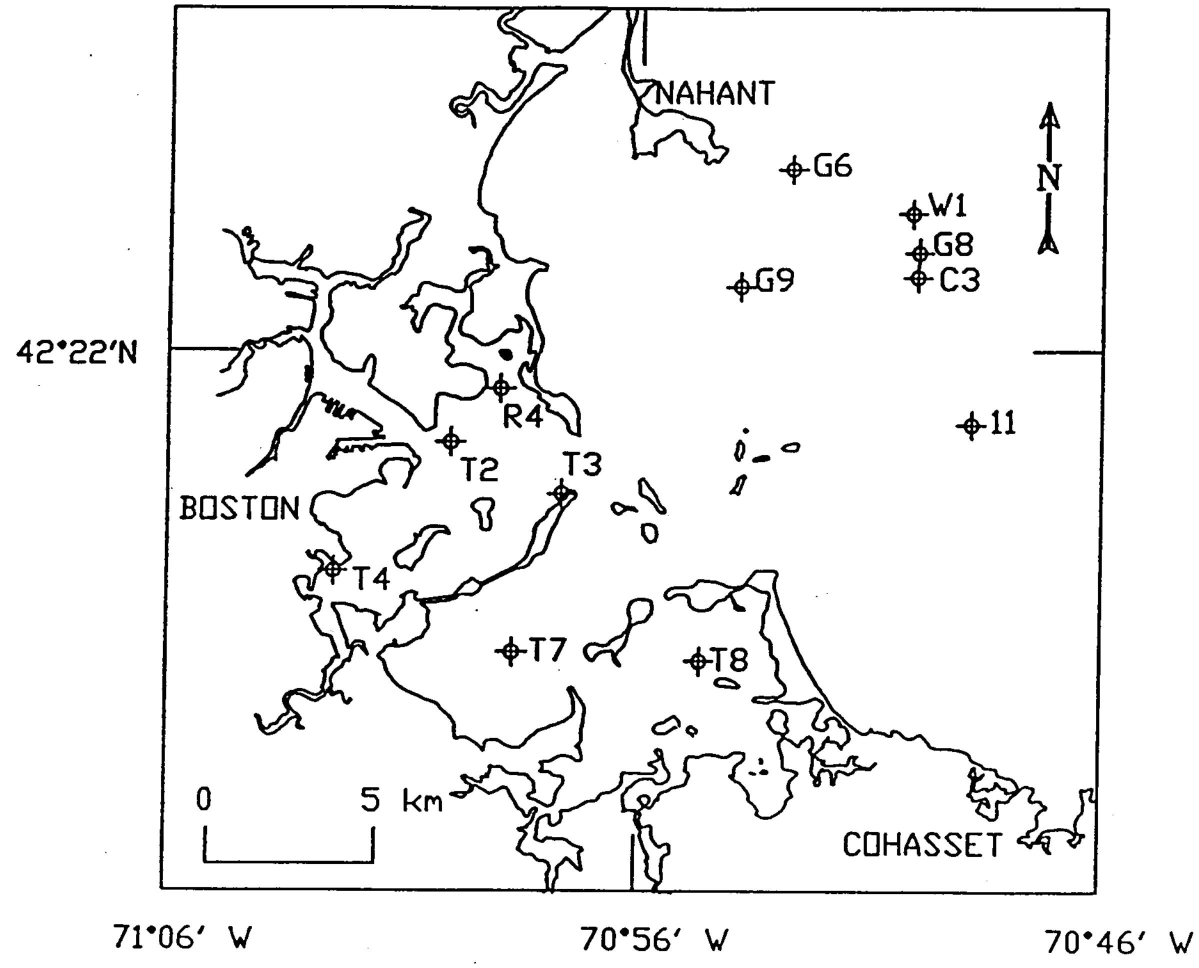


Figure 1. Map of Station Locations

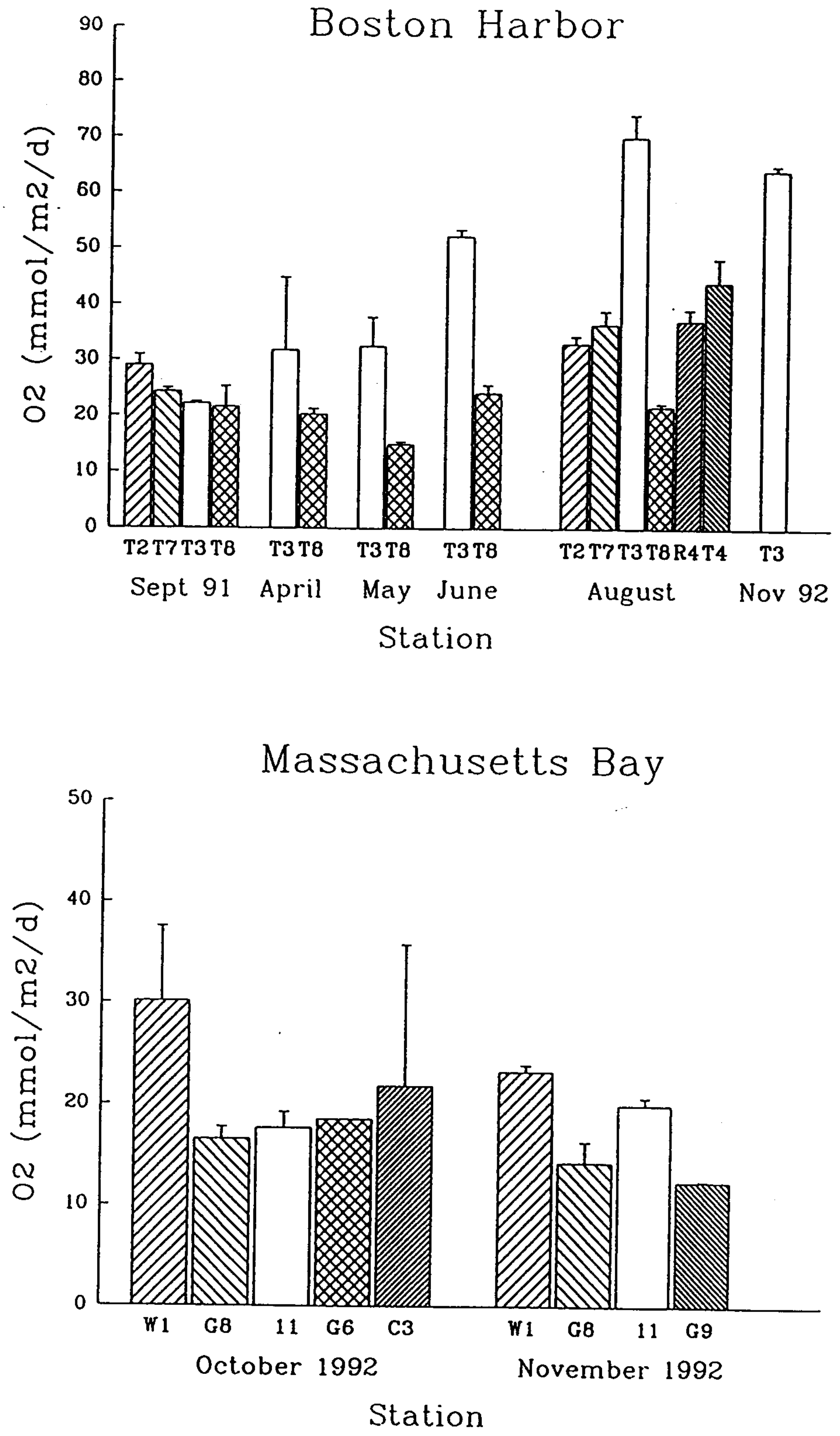
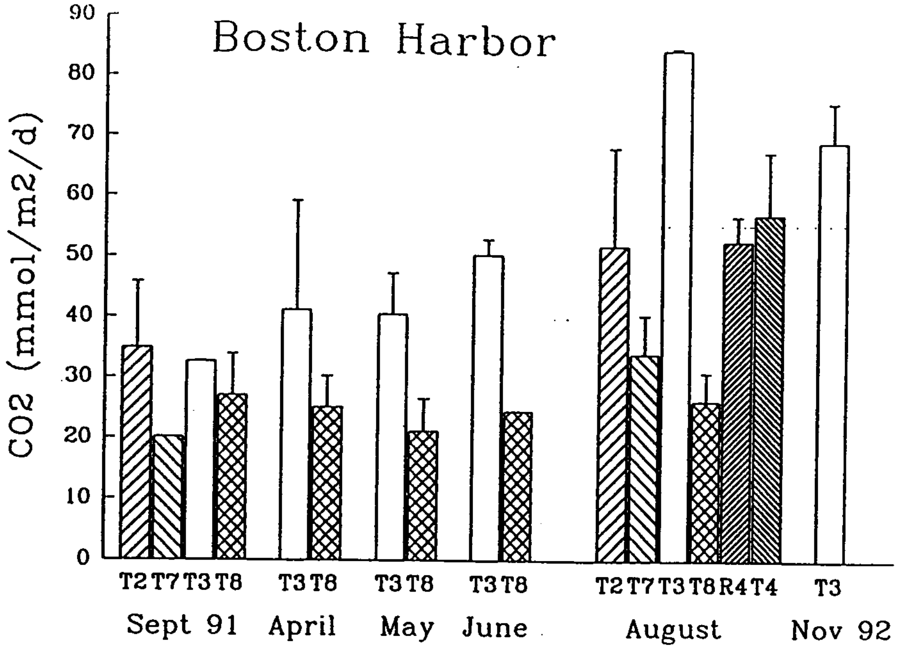


Figure 2. Oxygen uptake (Mean ± S.E.) of sediments from the 1992 survey. Data from Sept. 1991 for the Harbor stations are shown for reference (Giblin et al. 1992).



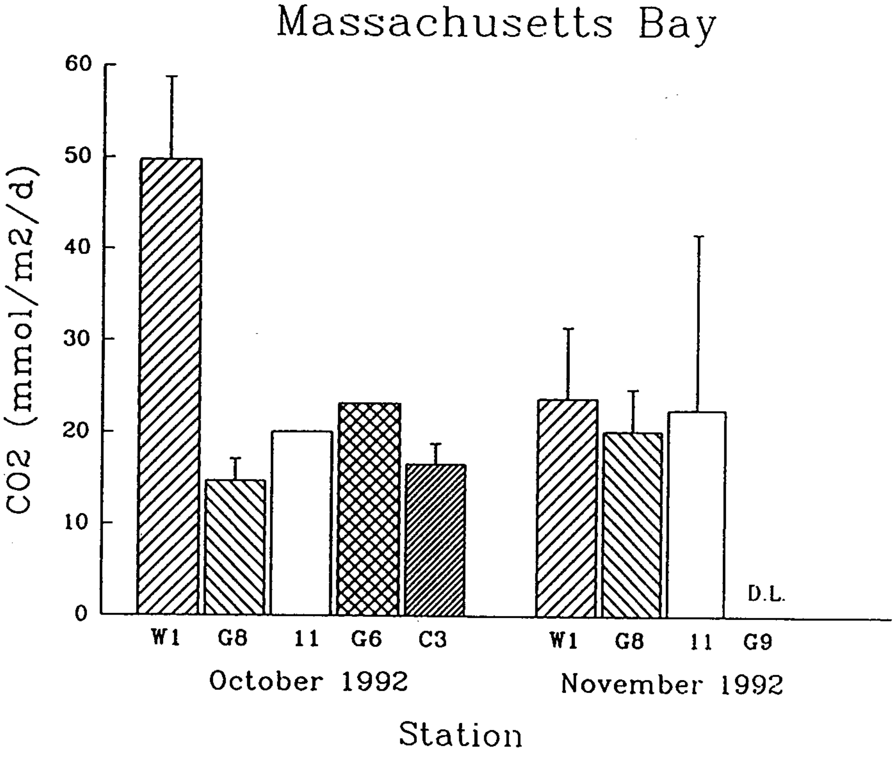
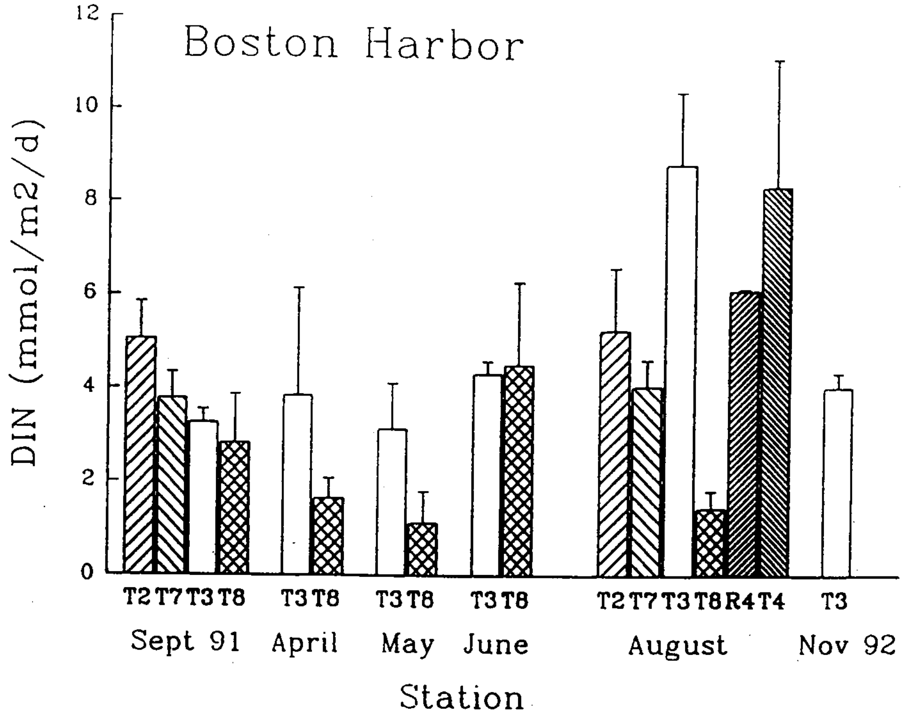


Figure 3. Total carbon dioxide release (Mean ± S.E.) of sediments from the 1992 survey. Data from Sept. 1991 for the Harbor stations are shown for reference (Giblin et al. 1992). D.L. means the data was lost.



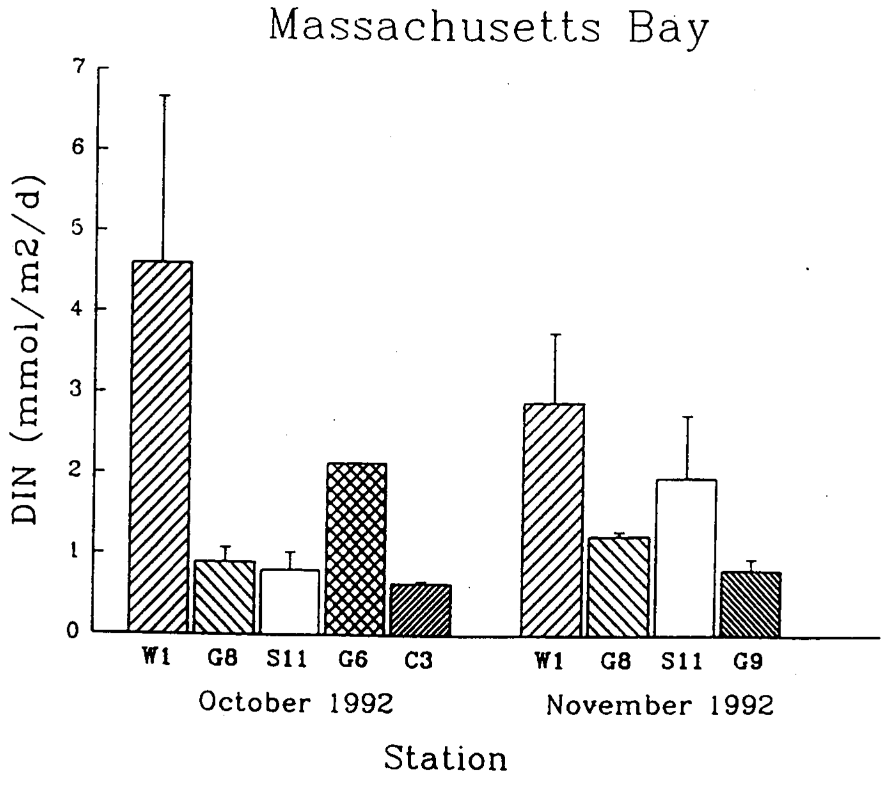


Figure 4. Dissolved inorganic nitrogen (DIN) release (Mean ± S.E.) of sediments from the 1992 survey. Data from Sept. 1991 for the Harbor Stations are shown for reference (Giblin et al. 1992).

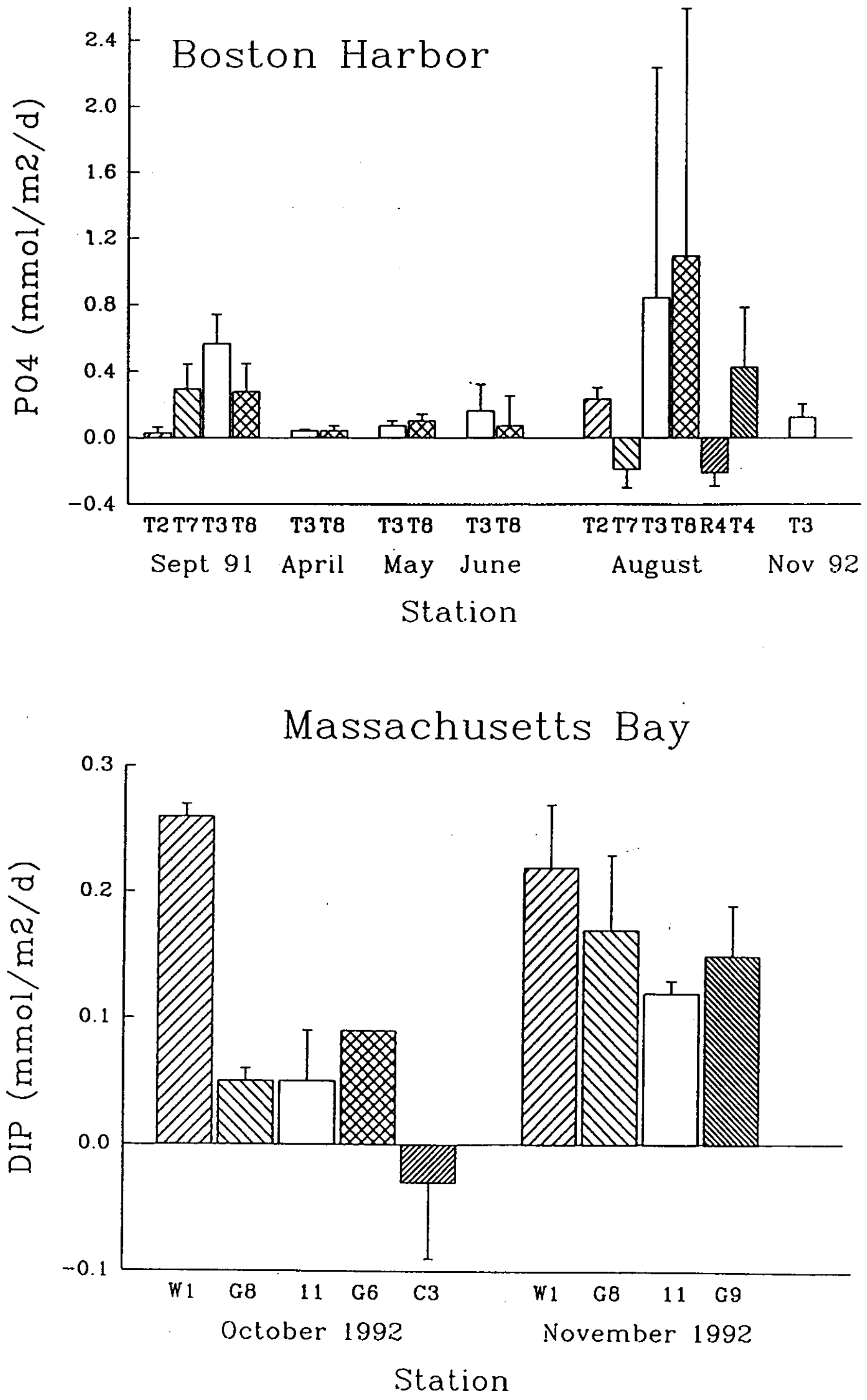


Figure 5. Dissolved inorganic phosphate (DIP) release (Mean ± S.E.) of sediments from the 1992 survey. Data from Sept. 1991 for the Harbor stations are shown for reference (Giblin et al. 1992). Negative fluxes indicate uptake by the sediments.

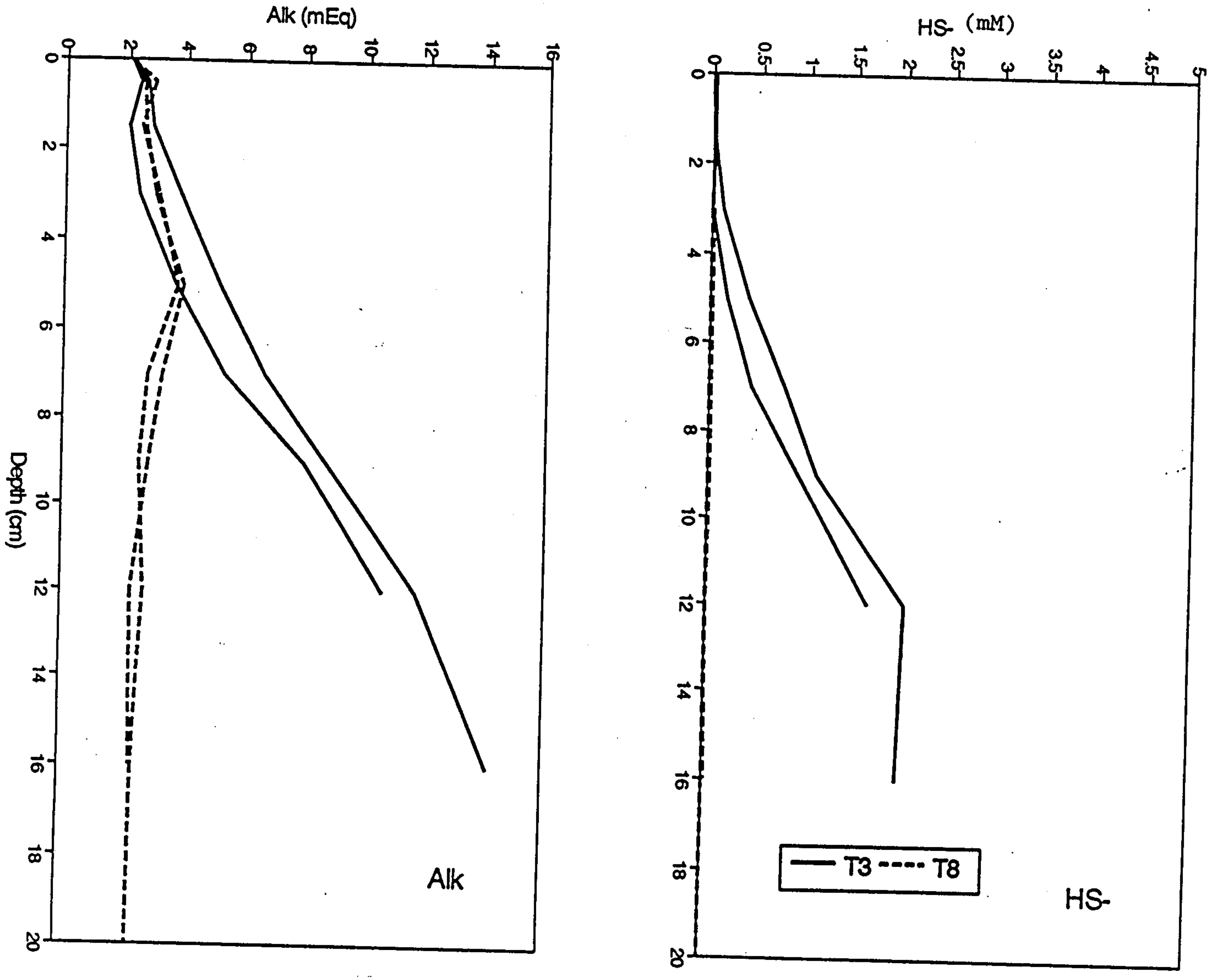
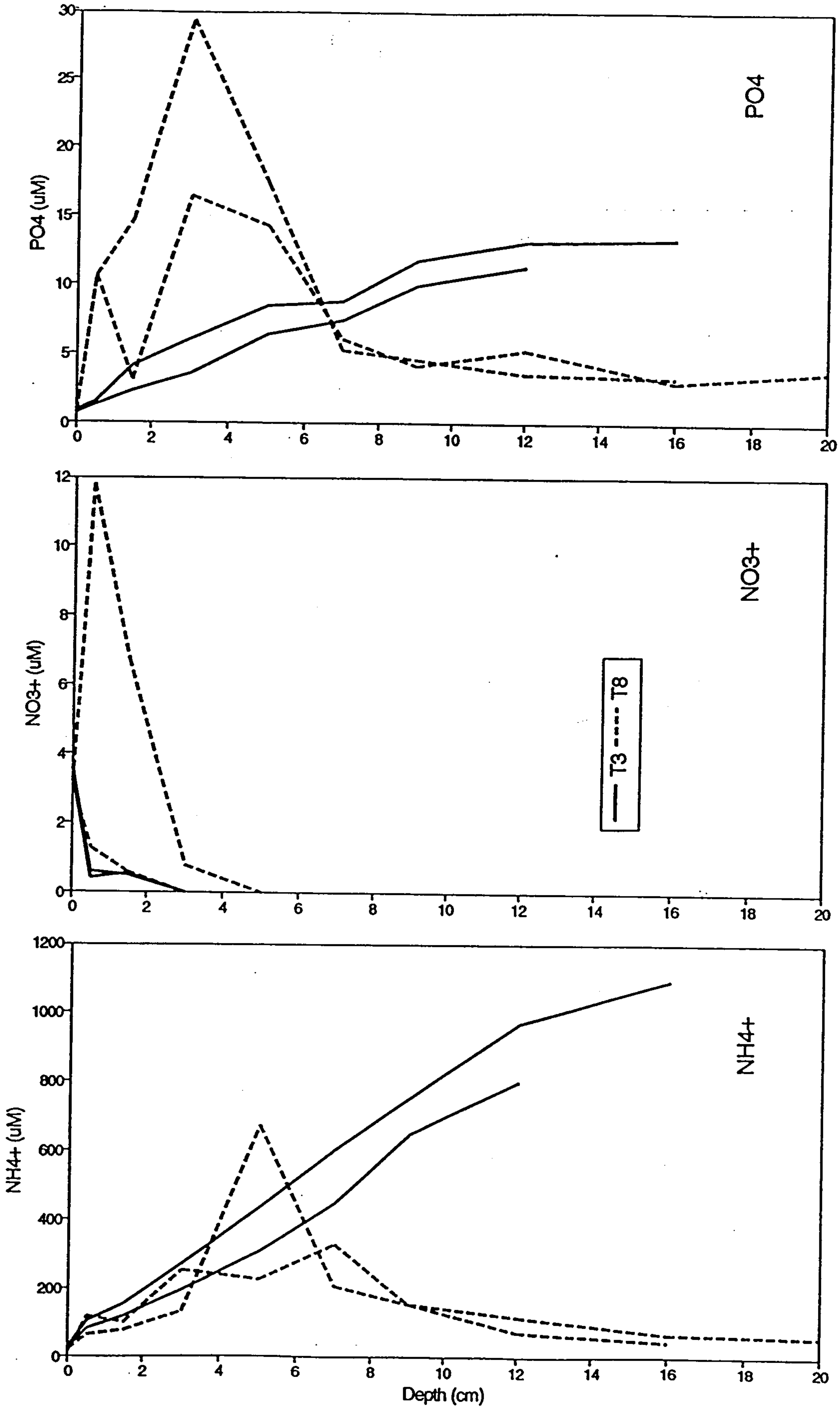


Figure 6. Porewater profiles of alkalinity (Alk), sulfide (HS$^-$), ammonium, nitrate, and phosphate for station T3 and T8. Samples were taken in June. Each line represents data from a separate core.

Fig. 6 Cont.


PO4
PO4 (uM)
0
5
10
15
20
25
30
0
2
4
6
8
10
12
14
16
18
20
NO3+
NO3+ (uM)
0
2
4
6
8
10
12
T3
T8
NH4+
NH4+ (uM)
0
200
400
600
800
1000
1200
Depth (cm)

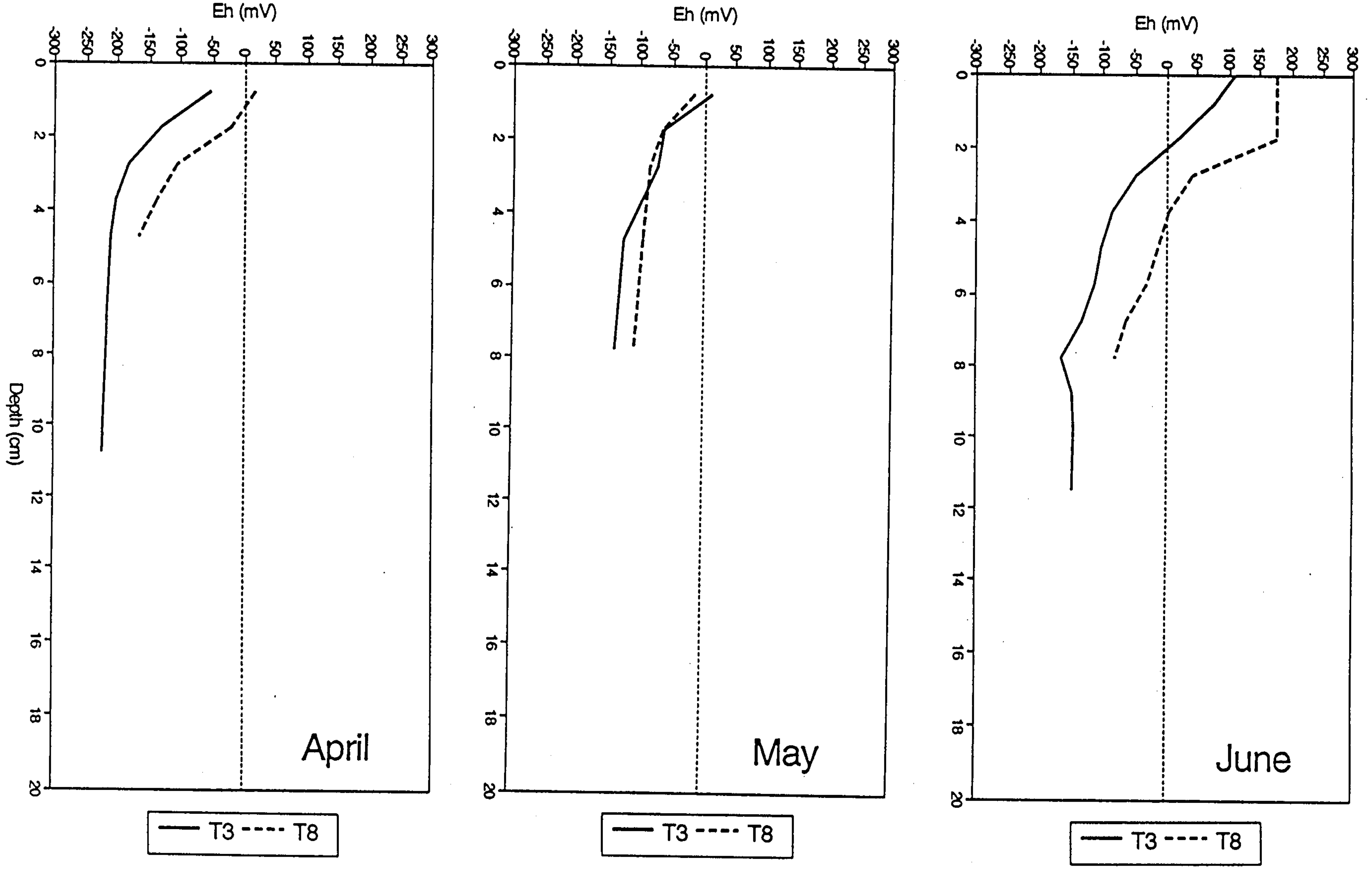
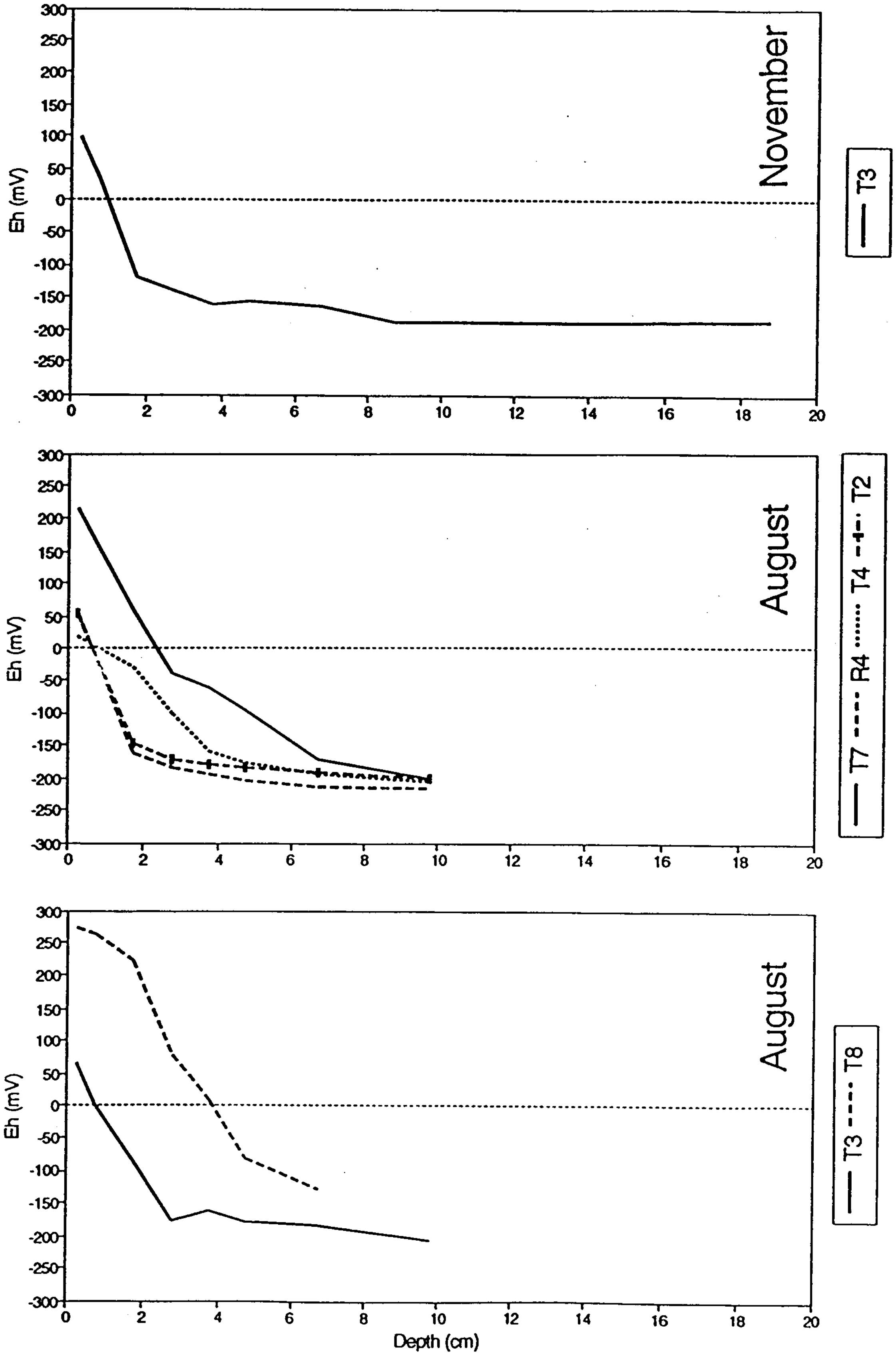


Figure 7. Eh profiles of Harbor sediments. Values have been corrected for the potential of the reference electrode.

Fig. 7 Cont.


November
T3
Eh (mV)
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
0
2
4
6
8
10
12
14
16
18
20
August
T7
R4
T4
T2
Eh (mV)
August
T3
T8
Eh (mV)
Depth (cm)

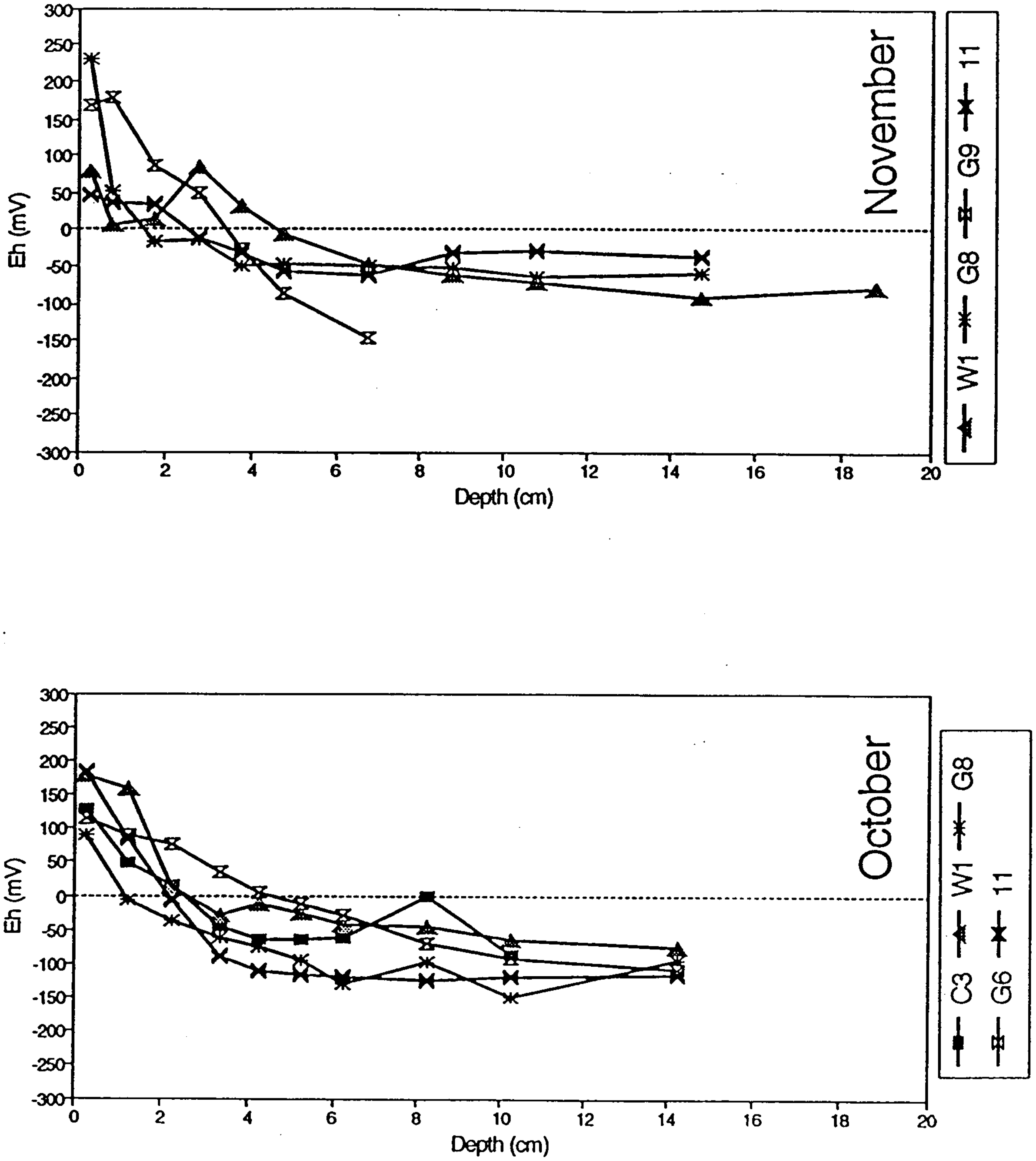


Figure 8. Eh profiles of Bay sediments. Values have been corrected for the potential of the reference electrode.

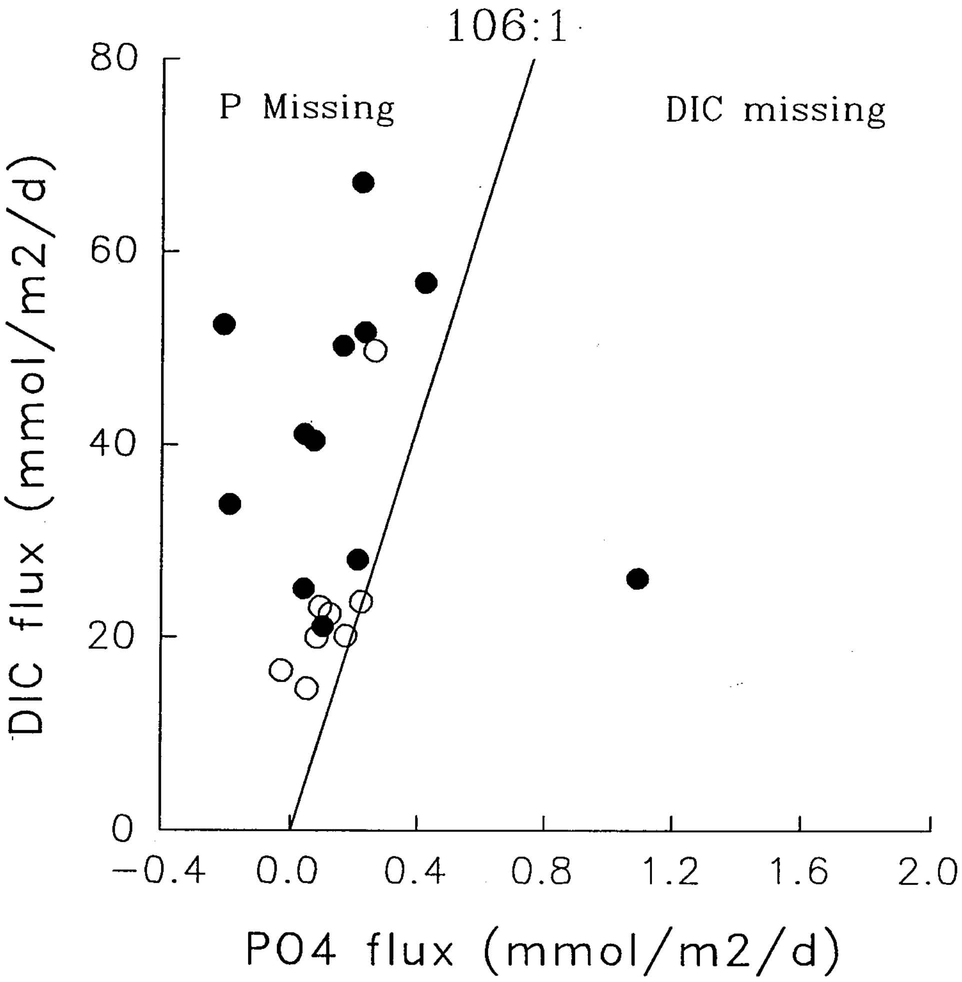


Figure 9. The average flux of phosphate for each station at each time point vs. the average DIC flux. The line indicates the ratio expected if the material being decomposed followed a stiochiometery of 106:1.

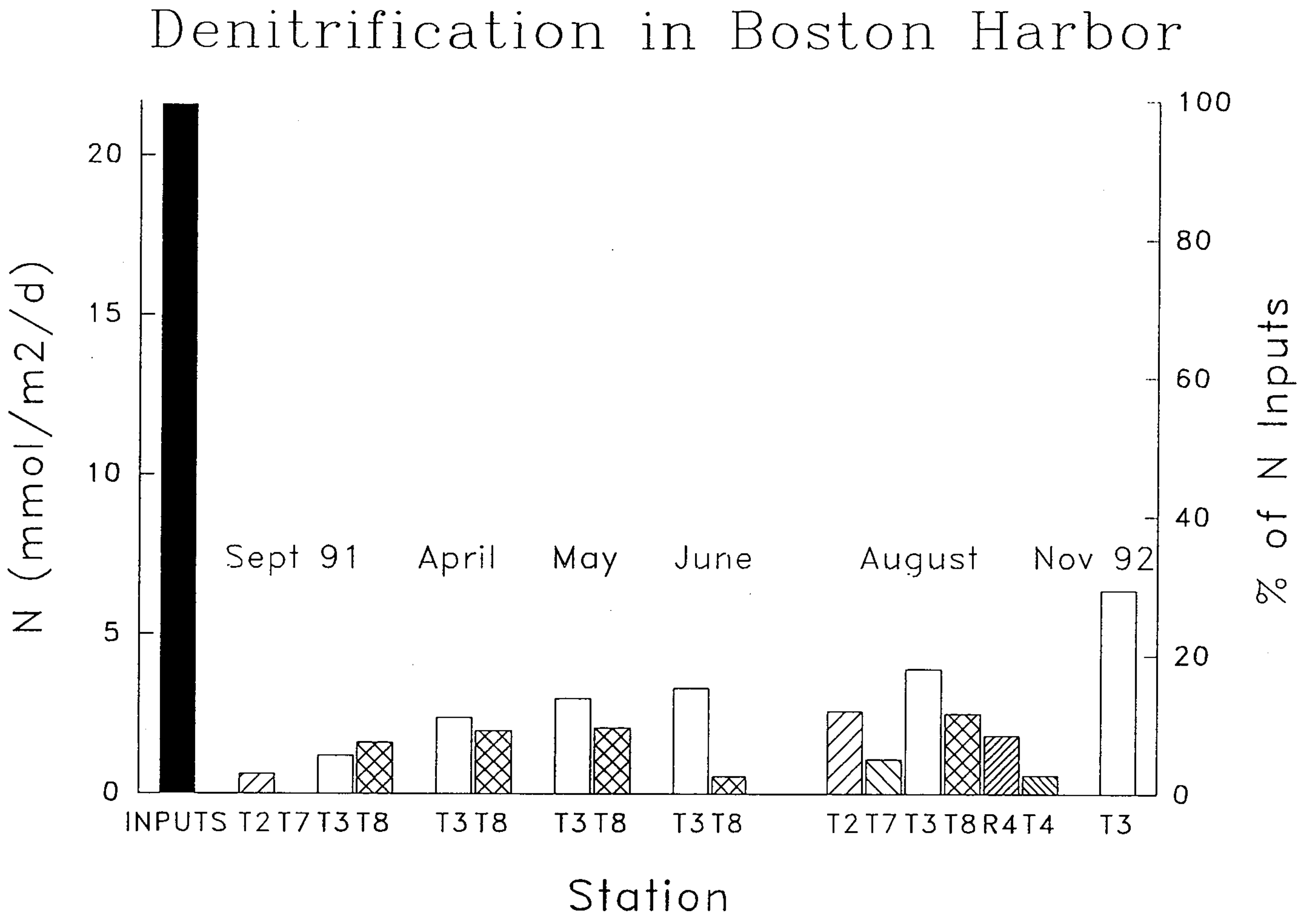


Figure 10. Our measurements of the amount of N denitrified by sediments in Boston Harbor during the study. The means for each sampling are shown. Data was calculated using the DIC/DIN ratio (see table 5). Data from 1991 is shown for comparison (Giblin et a. 1991). The dark bar (inputs) represents the amount of nitrogen entering Boston Harbor from all sources (Menzie et al. 1991; revised by using MWRA Discharge Reports for 1992).

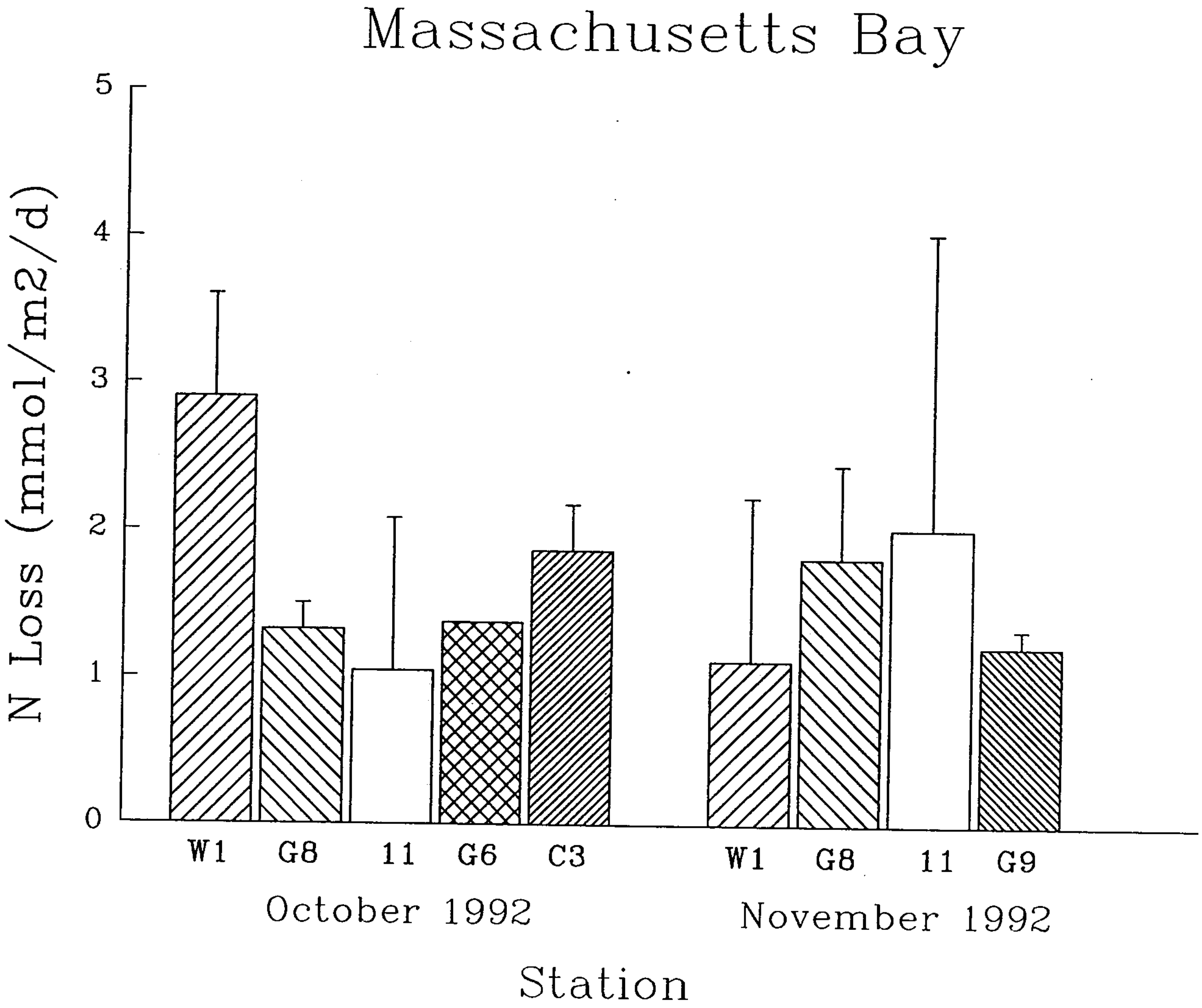


Figure 11. Our measurements of the amount of N denitrified by sediments in Massachusetts Bay during October and November 1992. The means (+ S.E.) for each sampling are shown. Data was calculated using the DIC/DIN ratio (see table 5), except at station G9 where there was no DIC data and (O+Alk)/N was used.

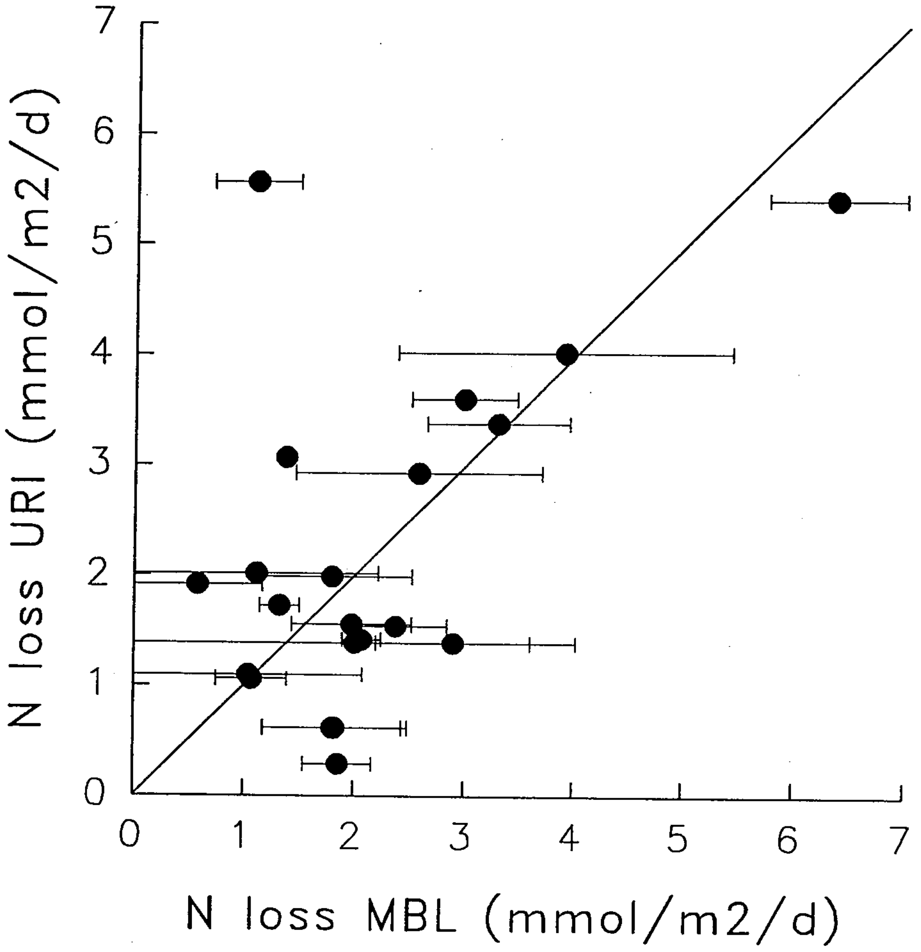


Figure 12. Our measurements of denitrification (N loss MBL) vs. those made by Barbara Nowicki (N loss U.R.I. see Kelly and Nowicki 1992b for details). The line indicates a 1:1 ratio. Error bars are for the S.E. of the station means for our data. No error estimate for U.R.I. is plotted.

Table 1: Station name, date sampled, *in situ* bottom water temperature and salinity, and water depth for stations sampled in 1992. Latitude and longitude are listed in Kelly and Nowicki (1993, Table 1).

STATION	DATE	TEMP °C	SALINITY o/oo	WATER DEPTH feet
T3	4/21/92	10.0	31.5	25
T8	4/21/92	10.0	32.0	38
T3	5/13/92	9.5	30.0	30
T8	5/13/92	9.5	30.5	40
T3	6/9/92	15.0	30.0	25
T8	6/9/92	14.5	30.0	37
T2	8/19/92	17.0	30.5	32
T7	8/17/92	16.0	31.0	16
T3	8/19/92	16.5	30.5	21
T8	8/17/92	16.0	30.0	43
R4	8/17/92	16.5	30.0	18
T4	8/19/92	17.0	30.0	12
W1	10/6/92	11.0	33.5	103
G8	10/6/92	11.0	33.5	108
11	10/7/92	11.0	33.0	108
G6	10/7/92	11.5	33.0	94
C3	10/7/92	12.0	--	107
T3	11/2/92	9.2	31.5	23
W1	11/2/92	10.0	33.5	105
G8	11/4/92	10.0	32.5	106
11	11/4/92	10.0	32.5	112
G9	11/2/92	9.5	33.5	68

Table 2: Fluxes and r2's for Boston Harbor and Massachusetts Bay Stations. Units are in mmol/m2/day.
D.R. = Data removed due to unsatisfactory chemical analysis.
** Data for Core 3, June, were affected by the presence of a baby skate in the core, and were not included in the means.

Date	Stati	Core	O2	r2	DIC	NH4	r2	NO3	r2	DIN	r2	%NO3	DIP	r2
APR	T3	15	20.37	0.9442	28.56	1.81	0.9478	0.14	0.9657	1.95	0.9498	7.18	0.02	0.0635
		9	53	0.9762	70.41	7.42	0.9993	0.17	0.9582	7.59	0.9991	2.24	0.04	0.9287
		6	21.73	0.9636	24.37	1.81	0.991	0.13	0.8922	1.94	0.9889	6.70	0.05	0.1704
	T3	mean	31.70		41.11	3.68		0.15		3.83		5.37	0.04	
		S.E.	13.05		18.00	2.29		0.01		2.30		1.93	0.01	
	T8	1	19.36	0.9854	17.05	0.59	0.9175	0.4	0.9918	0.99	0.974	40.40	0.02	0.0406
		8	19.76	0.9791		0.74	0.8745	0.37	0.9811	1.11	0.9447	33.33	0.04	0.207
		5	19.2	0.9601	27.16	2.29	0.9596	0.51	0.9931	2.62	0.9765	19.47	0.1	0.8524
		13	22.73	0.977	31.06	1.29	0.9432	0.53	0.9892	1.82	0.9744	29.12	-0.02	0.029
	T8	mean	20.26		25.09	1.23		0.45		1.64		30.58	0.04	
		S.E.	0.96		5.11	0.44		0.05		0.43		5.05	0.03	
MAY	T3	15	24.71	0.9888	29.49	0.76	0.9567	0.85	0.9861	1.61	0.9934	52.80	0.02	0.0787
		9	33.31	0.9977	47.03	2.67	0.9657	0.69	0.9843	3.36	0.979	20.54	0.11	0.8747
		6	39.51	0.9983	44.78	3.77	0.9966	0.59	0.9533	4.36	0.9962	13.53	0.09	0.6558
	T3	mean	32.51		40.43	2.40		0.71		3.11		28.95	0.07	
		S.E.	5.26		6.75	1.08		0.09		0.98		14.81	0.03	
	T8	3	15.28	0.9814	17	0.06	0.01	0.71	0.9888	0.77	0.6246	92.21	0.09	0.8828
		2	14.37	0.9723	16.69	-0.09	0.0214	0.5	0.9949	0.41	0.3225	100.00	0.06	0.9151
		1	15.45	0.978	29.78	1.61	0.9767	0.58	0.991	2.19	0.9884	26.48	0.16	0.8934
	T8	mean	15.03		21.16	0.53		0.60		1.12		72.90	0.10	
		S.E.	0.41		5.28	0.67		0.07		0.67		28.56	0.04	
JUNE	T3	15	52.83	0.9983	52.51	3.4	0.9934	0.87	0.9636	4.28	0.9958	20.33	0.08	0.1686
		9	50.28	0.9981	52.29	2.92	0.9791	0.99	0.9675	3.91	0.9809	25.32	-0.01	0.05
		6	53.53	0.9983	45.9	3.98	0.9953	0.69	0.9915	4.67	0.9961	14.78	0.41	0.7481
	T3	mean	52.21		50.23	3.43		0.85		4.29		20.14	0.16	
		S.E.	1.21		2.65	0.38		0.11		0.27		3.73	0.16	
	T8	**3	55.13	0.9992	65.36	5.93	0.9787	1.42	0.999	7.35	0.9851	19.32	0.49	0.9224
		2	23.12	0.9957	D.R.	2.73	0.9581	0.75	0.9852	3.48	0.9749	21.55	0.2	0.8957
		1	25.14	0.9972	24.46	1.97	0.6933	0.65	0.9963	2.62	0.7999	24.81	-0.06	0.4397
	T8	mean	24.13		24.46	2.35		0.70		3.05		23.18	0.07	
		S.E.	1.43			0.54		0.07		0.61		2.30	0.18	

Table 2 (cont'd):

Date	Stati	Core	O2	r2	DIC	NH4	r2	NO3	r2	DIN	r2	%NO3	DIP	r2
OCT	W1	14	24.92	0.9977	43.32	2.56	0.9956	0.58	0.9712	3.14	0.9979	18.47	0.27	0.7682
		7	35.34	0.9954	56.07	5.51	0.9997	0.55	0.961	6.06	0.9994	9.08	0.25	0.9968
	W1	mean	30.13		49.70	4.04		0.57		4.60		13.77	0.26	
		S.E.	7.37		9.02	2.09		0.02		2.06		6.64	0.01	
	G8	6	15.64	0.9921	13.02	0.48	0.8781	0.29	0.9917	0.77	0.9536	37.66	0.04	0.8957
		2	17.4	0.9965	16.4	0.74	0.9775	0.29	0.9906	1.03	0.992	28.16	0.05	0.704
	G8	mean	16.52		14.71	0.61		0.29		0.90		32.91	0.05	
		S.E.	1.24		2.39	0.18		0.00		0.18		6.72	0.01	
	11	8	18.75	0.9972	20.03	0.7	0.9113	0.36	0.938	0.95	0.9689	37.89	0.08	0.9113
		9	16.53	0.981	D.R.	1.4	0.9758	-0.77	0.4583	0.64	0.2914	0.00	0.02	0.34
	11	mean	17.64		20.03	1.05		-0.21		0.80		18.95	0.05	
		S.E.	1.57			0.49		0.80		0.22		26.80	0.04	
	G6	10	18.49	0.997	23.17	1.47	0.8735	0.67	0.9906	2.13	0.938	31.46	0.09	0.8187
	C3	11	11.93	0.9881	14.96	0.27	0.238	0.36	0.9726	0.62	0.5906	58.06	0.02	0.1372
		13	31.64	0.9962	18.13	0.59	0.8995	0.07	0.0489	0.66	0.9728	10.61	-0.07	0.1149
	C3	mean	21.79		16.55	0.43		0.22		0.64		34.34	-0.03	
		S.E.	13.94		2.24	0.23		0.21		0.03		33.56	0.06	
NOV	T3	24	64.65	0.9998	64.13	-0.08	0.0451	3.86	0.9969	3.78	0.9778	100.00	0.06	0.0334
		25	63.29	0.9969	73.39	-0.38	0.7739	4.6	0.9853	4.22	0.9688	100.00	0.17	0.8608
	T3	mean	63.97		68.76	-0.23		4.23		4.00		100.00	0.12	
		S.E.	0.96		6.55	0.21		0.52		0.31		0.00	0.08	
	W1	20	22.72	0.9975	18.22	2.83	0.9962	0.68	0.9993	3.5	0.9979	19.43	0.18	0.9367
		21	23.68	0.9982	29.18	1.7	0.9684	0.58	0.9981	2.28	0.98	25.44	0.25	0.8753
	W1	mean	23.20		23.70	2.27		0.63		2.89		22.43	0.22	
		S.E.	0.68		7.75	0.80		0.07		0.86		4.25	0.05	
	G8	26	12.77	0.9955	23.35	1.05	0.9277	0.22	0.9927	1.27	0.9453	17.32	0.21	0.6208
		27	15.68	0.9963	16.94	1.09	0.9903	0.1	0.9823	1.19	0.9935	8.40	0.12	0.9111
	G8	mean	14.23		20.15	1.07		0.16		1.23		12.86	0.17	
		S.E.	2.06		4.53	0.03		0.08		0.06		6.31	0.06	
	11	29	19.39	0.9962	8.9	2.23	0.9768	0.27	0.976	2.5	0.9779	10.80	0.11	0.5711
		31	20.44	0.991	35.98	1.14	0.9353	0.26	0.9711	1.4	0.9672	18.57	0.13	0.2694
	11	mean	19.92		22.44	1.69		0.27		1.95		14.69	0.12	
		S.E.	0.74		19.15	0.77		0.01		0.78		5.50	0.01	
	G9	22	12.3	0.9924	D.R.	0.28	0.282	0.62	0.8927	0.91	0.8221	68.13	0.18	0.8296
		23	12.46	0.9923	D.R.	0.26	0.2605	0.45	0.8012	0.71	0.5948	63.38	0.12	0.9543
	G9	mean	12.38			0.27		0.54		0.81		65.76	0.15	
		S.E.	0.11			0.01		0.12		0.14		3.36	0.04	

Table 2 (cont'd):

Date	Stati	Core	O2	r2	DIC	NH4	r2	NO3	r2	DIN	r2	%NO3	DIP	r2
AUG	T2	13	33.99	0.9969	40.12	4.22	0.9731	0.06	0.336	4.27	0.9719	1.41	0.28	0.3972
		14	32.06	0.9864	63.22	6.09	0.9922	0.08	0.4049	6.17	0.9891	1.30	0.18	0.0309
	T2	mean	33.03		51.67	5.16		0.07		5.22		1.35	0.23	
		S.E.	1.36		16.33	1.32		0.01		1.34		0.08	0.07	
	T7	6	38.17	0.9914	38.32	3.56	0.8215	0.86	0.9556	4.42	0.8856	19.46	-0.11	0.1235
		7	34.69	0.9888	29.35	2.94	0.9847	0.68	0.934	3.62	0.9915	18.78	-0.27	0.5485
	T7	mean	36.43		33.84	3.25		0.77		4.02		19.12	-0.19	
		S.E.	2.46		6.34	0.44		0.13		0.57		0.48	0.11	
	T3	11	72.93	0.9994	84.4	8.41	0.9889	1.5	0.956	9.91	0.9869	15.14	-0.14	0.0341
		12	67.06	0.9991	83.88	6.15	0.9627	1.52	0.9705	7.67	0.9849	19.82	1.82	0.9582
	T3	mean	70.00		84.14	7.28		1.51		8.79		17.48	0.84	
		S.E.	4.15		0.37	1.60		0.01		1.58		3.31	1.39	
	T8	3	21.35	0.9956	29.38	1.08	0.3065	0.61	0.6865	1.69	0.613	36.09	2.15	0.4366
		5	22.14	0.9992	22.9	-0.27	0.105	1.43	0.957	1.16	0.7283	100.00	0.03	0.0025
	T8	mean	21.75		26.14	0.41		1.02		1.43		68.05	1.09	
		S.E.	0.56		4.58	0.95		0.58		0.37		45.19	1.50	
	R4	8	38.57	0.9974	49.54	6.41	0.9966	-0.3	0.6841	6.11	0.9985	0.00	-0.15	0.1786
		2	35.73	0.9978	55.33	6.46	0.979	-0.41	0.6846	6.05	0.9765	0.00	-0.26	0.6997
	R4	mean	37.15		52.44	6.44		-0.36		6.08		0.00	-0.21	
		S.E.	2.01		4.09	0.04		0.08		0.04		0.00	0.08	
	T4	10	40.94	0.9911	49.46	6.36	0.9909	-0.05	0.0509	6.32	0.9891	0.00	0.16	0.0632
		9	47.02	0.9914	64.07	10.37	0.9928	-0.09	0.6368	10.28	0.9917	0.00	0.67	0.434
	T4	mean	43.98		56.77	8.37		-0.07		8.30		0.00	0.42	
		S.E.	4.30		10.33	2.84		0.03		2.80		0.00	0.36	

Table 3. Carbon and Nitrogen content of surface (0-2 cm) sediments collected in 1992 from Boston Harbor and Massachusetts Bay for this study. Sediment %C and %N was corrected for weight change during the acidification procedure. Elemental percentages are expressed on a weight basis, the C/N ratio is expressed on an atom/atom basis. Sediments collected from Boston Harbor by Kelly during a separate survey in April (designated April-K) are shown for comparison.

Station	Month	%C	%N	C/N (atom/atom)
T3	April	4.29	0.42	11.97
T8	April	0.31	0.03	11.67
T3	May	4.06	0.39	12.12
T8	May	0.34	0.05	7.70
T3	June	4.46	0.39	13.35
T8	June	0.31	0.04	8.75
T2	August	2.58	0.24	12.73
T7	August	3.52	0.39	10.50
T3	August	3.88	0.44	10.30
T8	August	0.38	0.04	10.79
R4	August	1.82	0.19	11.15
T4	August	3.88	0.39	11.54
W1	October	1.64	0.14	13.67
G8	October	1.39	0.15	10.81
11	October	2.50	0.33	8.91
G6	October	1.07	0.11	10.82
C3	October	0.97	0.08	13.42
T3	November	4.13	0.53	9.09
W1	November	1.18	0.14	10.05
G8	November	1.45	0.12	14.53
11	November	1.68	0.20	9.64
G9	November	0.40	0.06	7.58
T3	April-K	4.02	0.44	10.70
T8	April-K	0.25	0.04	7.00
T1	April-K	0.91	0.11	9.23
T2	April-K	3.42	0.44	9.07
T4	April-K	6.06	0.80	8.83
T6	April-K	2.23	0.28	9.42
T7	April-K	3.64	0.45	9.48
R6	April-K	1.29	0.17	8.97

Table 4. Calculation of the flux of alkalinity from sediments. Numbers in boxes are the mean of the values from two cores. The alkalinity gradient across the sediment water interface was fit assuming a linear (Fit 3) or exponential curve (Fit 1 & 2). When fitting an exponential curve sometimes all the data points were used (Fit 1) and in other cases some of the bottom values were omitted (Fit 2). Porosity was measured during each sampling period. The flux (J) across the sediment water interface was calculated by using the porewater alkalinity gradient, the porosity, and a corrected molecular diffusion coefficient taken from the literature. (See text for details.)

Station	Month	Fit	Gradient (umol/cm4)	Porosity (cm3/cm3	J (mmol/m2/d)
T3	April	3	1.78	0.97	16.50
T3	April	3	3.34	0.97	30.95
					23.72
T8	April	1	1.61	0.50	3.95
T8	April	2	2.99	0.50	7.36
					5.66
T3	May	1	0.56	0.92	4.69
T3	May	1	0.86	0.92	7.14
					5.91
T8	May	1	0.69	0.51	1.76
T8	May	1	0.68	0.51	1.75
					1.76
T3	June	3	0.96	0.97	8.90
T3	June	3	0.66	0.97	6.12
					7.51
T8	June	1	0.01	0.48	0.02
T8	June	1	0.19	0.48	0.44
					0.23
T2	August	2	9.86	0.94	85.81
T2	August	2	4.94	0.94	42.99
					64.40
T7	August	3	-1.08	0.98	-10.22
T7	August	3	0.36	0.98	3.41
					-3.41
T3	August	3	0.40	0.98	3.78
T3	August	3	0.18	0.98	1.70
					2.74
T8	August	3	1.10	0.42	1.91
T8	August	3	-0.12	0.42	-0.21
					0.85
R4	August	1	4.36	0.83	29.56
R4	August	2	3.59	0.83	24.38
					26.97
T4	August	3	1.82	0.97	16.87
T4	August	3	3.94	0.97	36.51
					26.69

Table 4 Cont.

Station	Month	Fit	Gradient (umol/cm4)	Porosity (cm3/cm3	J (mmol/m2/d)
W1	October	1	0.05	0.75	0.25
W1	October	2	0.05	0.75	0.26
					0.26
G8	October	3	-0.04	0.67	-0.18
G8	October	3	-0.02	0.67	-0.09
					-0.13
11	October	2	0.10	0.85	0.68
11	October	2	0.08	0.85	0.55
					0.61
G6	October	2	0.07	0.73	0.38
G6	October	2	0.08	0.73	0.43
					0.40
C3	October	1	0.09	0.79	0.58
C3	October	1	0.11	0.79	0.70
					0.64
T3	November	3	0.72	0.98	6.81
T3	November	3	0.60	0.98	5.68
					6.24
W1	November	3	0.18	0.75	1.00
W1	November	3	0.58	0.75	3.21
					2.11
G8	November	3	0.18	0.67	0.80
G8	November	3	0.16	0.67	0.71
					0.75
11	November	2	0.16	0.85	1.12
11	November	2	0.12	0.85	0.88
					1.00
G9	November	3	2.12	0.51	5.43
G9	November	3	0.72	0.51	1.84
					3.64

Table 5: Means of element ratios and stoichiometric estimates of denitrification.

Date	Stat.	O/N	(O+Alk)/ DIN	DIC/DIN	Denitrification Estimates as N/m2/day from:		
		Ratio 1	Ratio 2	Ratio 3	Ratio 1	Ratio 2	Ratio 3
Apr	T3	19.09	37.42	12.16	0.90	4.42	2.38
	T8	28.59	38.44	14.88	1.17	1.89	1.98
May	T3	22.88	27.41	14.19	1.45	2.27	2.99
	T8	41.30	46.22	25.46	0.76	0.97	2.07
Jun	T3	24.44	27.17	11.82	3.15	4.23	3.30
	T8	16.24	16.39	4.67	0.46	0.47	0.54
Aug	T2	13.16	38.68	9.82	0.42	9.43	2.58
	T7	18.22	16.51	8.39	1.18	0.69	1.09
	T3	16.10	16.74	9.73	1.25	1.64	3.91
	T8	31.72	32.96	18.56	1.31	1.42	2.52
	R4	12.22	21.09	8.63	0.00	3.60	1.83
	T4	11.05	17.87	7.03	0.00	2.37	0.57
Oct	W1	13.77	13.89	11.52	0.21	0.23	2.90
	G8	37.20	36.91	16.42	1.37	1.35	1.32
	11	45.56	47.16	10.54	1.72	1.81	1.04
	G6	17.36	17.74	10.88	0.42	0.47	1.37
	C3	67.18	69.18	25.80	2.44	2.53	1.86
Nov	T3	32.10	35.23	17.18	3.42	4.14	6.38
	W1	16.88	18.41	9.00	0.52	0.69	1.06
	G8	23.23	24.45	16.31	0.84	0.95	1.81
	G9	31.07	40.19		0.75	1.21	
	11	22.36	23.47	14.63	0.93	1.07	2.02