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Metabolism and Nutrient Cycling in Boston Harbor Sediments

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METABOLISM AND NUTRIENT CYCLING IN BOSTON HARBOR SEDIMENTS

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EXECUTIVE SUMMARY

We sampled four stations in Boston's Outer Harbor in September 1991. Sediment cores were brought back to the laboratory and the rate of oxygen uptake and dissolved inorganic nitrogen, phosphate, and total CO_2 release were measured. Porewater profiles of dissolved inorganic nitrogen, phosphorous, alkalinity and sulfide were measured on separate cores.

Sediment oxygen uptake ranged from 21.6 - 29.0 mmol m^{-2} d^{-1} for the four stations. Porewater profiles of sulfide and alkalinity indicated that oxygen uptake was not integrating total decomposition. Alkalinity fluxes were calculated to range from 1.7 - 27.3 mmol m^{-2} d^{-1}, indicating that oxygen uptake rates were underestimated by a similar amount. Total CO_2 fluxes also showed that oxygen underestimated total metabolism but by a smaller amount, between 0 - 10.4 mmol m^{-2} d^{-1}.

Several lines of evidence suggest that Boston Harbor sediments were more oxidized when we sampled in 1991 than when we sampled in 1990. In contrast to 1990, when all Boston Harbor sediments took up nitrate from the overlying water, in 1991 we observed significant amounts of nitrate release at three out of four stations. It is probable that Boston Harbor sediments were oxidized by a recent storm, Hurricane Bob, and that the conditions we observed were atypical of September conditions.

All stations released measurable amounts of N_2O but the amounts were negligible in terms of the nitrogen budget.

We estimated denitrification using the ratio of oxygen consumption to dissolved nitrogen release. Based on measured rates of oxygen uptake, we estimate that denitrification is of minor importance at most stations. Correcting oxygen uptake to account for total decomposition estimated from alkalinity fluxes, denitrification appears more important. In this case, we would estimate that denitrification removes 0.5 to 3.35 mmols N m^{-2} d^{-1}, with the highest rates being observed off Long Island. The use of total CO_2 fluxes as a measure of total metabolism suggests denitrification is lower, 0 to 1.19 mmol N m^{-2} d^{-1}. Our estimates of denitrification were somewhat lower than those of Kelly and Nowicki (1992), but are in general agreement. Further comparisons of the two approaches, especially at different times of the year, would be extremely valuable.

INTRODUCTION

In this study we measured sediment-water exchanges of oxygen, nitrogen and phosphorus at 4 stations throughout Boston Harbor. This study was undertaken to examine year-to-year variability in benthic processes through comparison to work we conducted during late summer 1990 (Giblin et al. 1991), to augment our limited knowledge on spatial variation in benthic nutrient cycling throughout Boston Harbor, and to provide baseline information on benthic metabolism and nutrient cycling for a series of stations for which Battelle, Inc. has characterized the faunal community. The rationale for measuring benthic fluxes in general was detailed in our previous report; it is summarized briefly below. One of the major goals of this study was to provide a more complete picture of the processes controlling nitrogen cycling within the Harbor and to examine the importance of the benthos in the N budget of Boston Harbor.

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 thus lost from the ecosystem. Denitrification is in essence a cleansing process that can retard eutrophication of heavily nutrient loaded coastal systems. The amount of nitrogen which is lost by denitrification in coastal systems varies greatly, ranging from 15 to 70% of the inorganic nitrogen released by mineralization (Seitzinger 1988). 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.

In previous work in Boston Harbor, we estimated the importance of denitrification using an indirect method based on the deviation of the O/N ratio from expected values. We measured the ratio of sediment oxygen consumption to the sediment-water flux of ammonium and nitrate (the O/N ratio). The deviation between this ratio and the theoretical ratio expected for decomposing phytoplankton (the

Redfield ratio) provides an estimate of the quantity of nitrogen lost via denitrification (discussed more fully in Giblin et al. 1991 and later in this report). In this study we again used the deviation of the O/N ratio from Redfield values to estimate denitrification. We compare these estimates to values measured by Dr. Barbara Nowicki, U.R.I., who directly measured N_2 fluxes on sediment cores taken concomitantly with our cores (Kelly and Nowicki, 1992).

The ratio of oxygen to inorganic nitrogen fluxes can vary substantially over the course of a year due to the storage or oxidation of reduced metabolic end products, such as sulfides, in the sediments (see Giblin & Howarth 1984 for a more detailed discussion). To determine if sulfur was being stored or oxidized within the sediments we used two independent approaches: 1) direct measurement of carbon dioxide flux and 2) calculated alkalinity fluxes. To calculate alkalinity flux we examined the porewater gradients of dissolved sulfides and alkalinity. We then used this information to correct our measures of oxygen consumption to what would have occurred if the total respiration had been accounted for using oxygen.

We also assess the importance of N_2O flux as a component of the benthic nitrogen cycle. Some studies have shown that under eutrophic conditions, N_2O, can be an important end product of denitrification.

STATION DESIGN

Station Location

Four sites within the Boston Harbor area were chosen for study (Fig. 1; Table 1). Station T2 is located on Governors Island Flats near the airport. It is close to Station 3 which we sampled last year. Station T3 is off Long Island in an area which received sludge disposal prior to Jan. 1992. Two additional sites were chosen further to the south. Station T7 is in Quincy Bay and T8 is in Hingham Bay. These stations were sampled by Battelle the previous week as part of a benthic survey (Kelly and Kropp 1992).

Station Descriptions

Boston Outer Harbor

Sediments at Station T2 consisted of silty mud. The surface 1-2 cm of most of the sediment cores were brown but at greater depths the sediment was black. Numerous animal tubes and small snails were evident on the sediment surface. In one core a petroleum smell was noticed below 10 cm. Station T3 had a 1-3 cm thick brown layer on the surface of all cores; below 4-5 cm sediments from all cores were jet black. Snails were present in most cores. In sediments from both T2 and T3, we observed fine tough fibrous material at depth which appeared to be hair.

Quincy Bay

The surface 1-1.5 cm of sediments from station T7 were brown. This was followed by a 5-10 cm thick zone of black mud with some shell fragments. Sediments below this layer largely consisted of shell and sand.

Hingham Bay

Sediments at Station T8 consisted largely of medium sand. It was very hard to core through a dense sand/shell layer at depth at this site. Although the surface 1-2 cm were lighter than deeper sediments, overall there was little color change with depth. Bryozoans as well as numerous tubes were evident on the surface of the sediment. Divers observed crabs, shrimp and lobsters on the bottom.

METHODS

Sampling

All stations were sampled by SCUBA divers on September 23, 1991. At each station several sizes of sediment cores were taken. 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. Two additional cores, approximately 6.5 cm in diameter, were taken for Dr. Barbara Nowicki for her measurements of N_2 flux.

Bottom water temperature at all stations was determined using the thermistor on an Orbisphere Laboratories oxygen meter. No oxygen data were obtained during samplings because the Orbisphere oxygen sensor malfunctioned.

At each station 15 liters of water were obtained with a diaphragm pump from throughout the water column and immediately filtered through a series of cartridge filters (nominally 20 and 1.0 μm). This water was returned to Woods Hole, held at 16 °C, and used to replace the overlying water in the cores used for flux measurements.

Benthic Respiration & 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 16 °C. The flux measurements were begun the day after sampling. Prior to initiating flux measurements, the overlying water of each core was replaced with the filtered seawater obtained from each station. Initial concentrations of nutrients and alkalinity at each of the stations is given in Table 2. Two BOD bottles filled with the filtered water obtained from each station were used to correct for water column respiration and regeneration.

Benthic flux measurements were started shortly after the overlying water was replaced. Machined core tops with magnetic stirrers were used to seal cores from the atmosphere (Dornblaser et al. 1989) and to gently mix the overlying water without resuspending sediment. We monitored concentrations of oxygen and dissolved inorganic nitrogen species (DIN) in the overlying water throughout a 30 hr incubation period. Oxygen concentration was measured with a dissolved oxygen meter (Orbisphere 2112 meter) and a probe which fit into tapered openings in the core tops. Incubation duration was determined by the time required for oxygen concentrations to fall by about 2-4 ppm to below 5 ppm. Oxygen concentrations in the overlying waters were not allowed to drop to below 2-4 ppm as benthic animal respiration rates can be affected (for effects of low oxygen concentrations on animal respiration rates see Bishop 1952). At least five samples were taken at regular intervals from each core throughout the incubation period. The benthic respiration rate was calculated as the slope of oxygen concentration versus time. The values could be corrected for the oxygen uptake by the water overlying the cores by subtracting changes measured in BOD bottle, however, this was not necessary because the respiration rate of the filtered water was essentially zero. Taking measurements at least five times for each core allowed us to determine whether the rate of oxygen consumption was linear over time.

Concurrent with O_2 measurements, samples of the overlying water were withdrawn through syringes to determine the concentration of dissolved inorganic nitrogen. Replacement water was added through a second syringe. A sample of the replacement water was taken for nutrient analysis. Water samples were held in the syringes and processed within one hour. Ammonium concentration was determined for duplicate 3 ml subsamples by the technique of Solorzano (1969) modified for a 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).

The remaining water in the syringe was transferred to clean vials and 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 0.2µM. Previous work suggested that the contribution of nitrite to the dissolved inorganic nitrogen (DIN) pool is insignificant for most sediments so only the combined nitrate + nitrite pool was considered for this study. DIN was calculated as the sum of ammonium, nitrate, and nitrite.

At the beginning of the incubation period, and after 24 hrs, samples of overlying water were taken for N_2O analysis. A 15 ml sample was taken from 2 cores from each station using a gas tight syringe. N_2O was analyzed by Michael LaMontagne (Boston University Marine Program) within 12 hrs. The water samples were equilibrated with a He headspace and analyzed with a Shimadzu gas chromatograph equipped with an electron capture detector.

At the beginning and end of the incubation period, samples were also taken for total CO_2 analysis. A 60 ml sample was taken by syringe and stored in a glass BOD bottle. The samples were kept in the cold (4°C) and the dark until January 1992 when they were analyzed at the Woods Hole Oceanographic Institution by Dr. C. Goyet. Samples were analyzed with a high precision coulometric CO_2 analyzer. The instrument consists of a custom SOMMA instrument from U.R.I. attached to a UIC coulometer and is capable of measuring total CO_2 with a precision of better than 0.05% (1 μmole).

Porewater Sampling and Analysis

Replicate porewater profiles were obtained from stations T2, T3, and T7. Only one core could be analyzed from Station T8 because the porewater from one of the replicates from this station drained during transport to Woods Hole.

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. Each interval was placed into a centrifuge tube and capped. Porewater from stations T2, T3, and T7 was separated from the sediment by centrifuging the samples for 15 minutes at maximum speed on a desk top centrifuge. This technique did not work for sediments from station T8 due to the high sand content. Porewater was removed from these sediments using a "split" centrifuge tube with filter support midway down the tube. A filter is placed on the support and the sediment is placed on the filter. Centrifuging at high speed for 15 minutes forces porewater through the filter. Samples from Station T8 yielded less porewater than other stations so not all analyses were performed at all depths.

Nutrients were analyzed as previously described with the exception that samples for ammonium analysis were diluted between 3 and 30 fold with clean seawater.

Dissolved sulfides in porewaters were trapped in 2% Zn acetate and analyzed the same day using a modification of the technique of Cline (1969). Samples for pH and alkalinity were analyzed immediately. Alkalinity was measured using a Gran titration modified for small sample sizes (Edmond 1970).

Porosity and Solid Phases

Sediment porosity was measured from 2.5 cm diameter cores. Sediments were sectioned in 1 cm intervals to 10 cm and then in 2 cm intervals. Sediment wet weight was measured immediately and dry weight was measured after a minimum of 72 hrs in a 55°C forced hot air 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). Sediment samples have been saved for future analyses of the solid phase.

Calculations of Fluxes from Porewater Gradients

The flux of alkalinity from the sediments was calculated from the 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)).

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

$$J = -\oplus\,{}_oD_s(\sigma\, C/\sigma\, z\,)_{z=0}$$

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

RESULTS AND DISCUSSION

Replication and Accuracy of Flux Measurements

We obtained three replicate measurements of oxygen and nutrient fluxes from all stations. In all incubations the fluxes of oxygen, ammonium, and DIN fluxes were linear over time (Table 3). The r^2s of regressions for oxygen and DIN against time were always above 0.98 and the r^2s for ammonium were always above 0.94. The r^2s for nitrate and phosphate fluxes were also generally high except for station T2. In this case, where we observed a slight uptake of nitrate by the sediments, r^2s were low. This station also had low and non-linear phosphate fluxes both in and out of the sediments in two out of the three cores. At the other three stations, the r^2s for the nitrate fluxes were always above 0.94 and usually greater than 0.98. The r^2s of the phosphate fluxes at the other stations ranged from 0.88 to 0.99.

Oxygen Uptake

The average rates of sediment oxygen consumption for the four stations fell in a fairly narrow range between 21.6 and 29.0 mmol O_2 m^{-2} d^{-1} (Table 3; Fig. 2). Our oxygen uptake data completely overlaps values obtained by Barbara Nowicki (Kelly and Nowicki 1992; values from 24 to 27 mmol O_2 m^{-2} d^{-1}). Oxygen consumption at station T2 was higher than at the other three stations. There was no clear difference between the other three stations.

Maximum oxygen uptake rates observed in 1991 were considerably lower than the maximum rates observed in September 1990 when the fluxes ranged from 18.5 to 50.9 mmol O_2 m^{-2} d^{-1}. For example, oxygen uptake rates at station 3 on Governor Flats, were 50% greater in 1990, than those obtained from sediments from nearby Station T2 sampled this year. One explanation for the lower oxygen uptake in 1991 is the lower water temperature. Water temperatures in early September 1990 were 19-20 °C, as compared to 15-16 °C in late September 1991. However, the 4-5 °C temperature difference does not seem to be large enough to account for the 40% lower oxygen uptake rates observed on Winthrop Flats. Another possible explanation is that sediments were storing substantial amounts of sulfides at this time and therefore oxygen uptake was an underestimate of total respiration. The porewater data (discussed below) tend to support this explanation. It is also possible that sediments in this area are patchy and that we did not sample the same highly reducing areas that we did in 1990. Finally, year-to-year differences, or redistribution of sediments following storms may have caused the differences.

DIN Release

We observed greater station to station spatial variation in DIN release than we did for oxygen consumption. DIN release ranged from 2.82 to 5.04 mmol N m^{-2} d^{-1} (Table 3; Fig. 3). DIN release was higher at station T2 than at the other 3 stations. As with oxygen uptake, there were no clear differences between the other stations.

The percentage of DIN release attributable to nitrate varied greatly between stations. Sediments at station T2 did not release nitrate; and there may have been some nitrate uptake. There was a release of nitrate from all other stations; the percentage of the DIN flux due to nitrate ranged from over 40% at station T3 to less than 25% at station T7.

The fluxes we measured in 1991 differ substantially from those measured in 1990. DIN fluxes, like oxygen fluxes, are lower in 1991. In 1990 all stations within Boston's Outer Harbor took up nitrate from the overlying water. In 1991 only station T2 took up nitrate and the rates were low enough that they were not significantly different from zero. All other stations released substantial amounts of nitrate to the overlying water.

The lack of significant nitrate uptake at any of the stations in 1991 and the presence of a positive nitrate flux out of the sediments at 3 of the 4 sites suggests that the sediments sampled in 1991 were more oxidized than those sampled in 1990. Qualitatively, sediment characteristics are consistent with this idea. In 1990 stations 2 and 3 were black right to the surface. Sediments from each station sampled this year however, had a brown surface layer. We also did not detect dissolved sulfides in the porewater of surface sediments (see below).

Phosphate Flux

Phosphate fluxes ranged from non-detectable at station T2 to a maximum value of 0.54 mmol m^{-2} d^{-1} at station T3 (Table 3; Fig. 4). The range of phosphate fluxes from sediments measured in 1991 is an order of magnitude lower than that measured at Stations 2 and 3 in 1990. A pattern of decreased phosphate fluxes is consistent with the hypothesis that sediments sampled in 1991 were more oxidized than those sampled in 1990.

N_2O Flux

Nitrous oxide fluxes ranged from a low of 0.56 µmol N m^{-2} d^{-1} at station T2 to a high of 4.22 µmol N m^{-2} d^{-1} at station T7 (Table 4). There was no clear relationship between either nitrate flux or total DIN flux and N_20 release. In comparison with other N fluxes, N_2O fluxes were extremely low, amounting to less than 0.1% of the DIN nitrogen flux from the sediments. These values are among the lowest reported for other coastal areas. Seitzinger et al. (1980) measured N_2O fluxes of 4.8 µmol N m^{-2} d^{-1} in Narragansett Bay sediments during summer. In the experimentally eutrophied MERL tanks at the URI Narragansett campus, N_2O release ranged from 13 µmol N m^{-2} d^{-1} in the control tanks to 1224 µmol N m^{-2} d^{-1} in tanks receiving the highest loading rates.

Porewater Constituents

Pore water concentrations of ammonium increased rapidly with depth (Fig. 5). Concentrations near the bottom of the core exceeded 1 mM at all stations except the sandy sediment station, T8. At stations T2, T3, and T7, nitrate in near surface (0-2 cm) porewaters was always less than 1.0 µM. At station T8 nitrate concentrations in the surface centimeter were greater than 3 µM and they exceeded 17 µM between 2 and 4 cm (data not shown).

Dissolved sulfide was not detected in the surface 2 cm of sediment at any of the stations (Fig. 6). However sulfide was detected at depths exceeding 4 cm at all stations except the sandy station, T8.

At all stations, alkalinity was higher at all depths in the sediment, including the surface 0-1 section, than in seawater (Fig. 6). Alkalinity profiles were indicative of considerable alkalinity flux to the overlying water. We used a calculated alkalinity flux as a measure of the "unaccounted for" respiration due to sulfate reduction.

Sulfate reduction is an anaerobic process in which bacteria use sulfate instead of oxygen as a terminal electron acceptor during respiration to decompose organic matter. During sulfate reduction, two moles of carbon are oxidized and two equivalents of alkalinity are produced for every mole of sulfate reduced:

$$2\ CH_2O + SO_4^{-2} = 2\ HCO_3^- + H_2S$$

If the sulfides produced are re-oxidized by oxygen within the sediments, the alkalinity is consumed by the acid produced:

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

It takes two moles of O_2 to oxidize one mole of sulfide so sediment oxygen consumption is a measure of total carbon oxidation taking place within a sediment if all the sulfides are re-oxidized. However, if the sulfides are not re-oxidized, but are stored in the sediments as either FeS or FeS_2, then oxygen consumption does not account for total respiration. In such a situation there is a net flux of alkalinity from the sediments to the overlying water. (These arguments are summarized in more detail in Giblin and Howarth 1984 and Giblin et al. 1990.) Because aerobic respiration produces CO_2 but does not produce alkalinity, alkalinity fluxes measure only the contribution of anaerobic respiration not accounted for by oxygen uptake. It should be noted that both processes contribute to the "total CO_2" pool which is measured on acidified samples so that total CO_2 is a measure of total respiration.

Our calculations indicate that there was a large flux of alkalinity across the sediment-water interface at several stations in Boston Harbor (Table 5). The alkalinity flux indicates that total respiration was underestimated using oxygen alone by less than 10% at station T8 to about 50% at station T3 (Table 6).

The magnitude of the alkalinity flux represents a very large storage of reduced sulfur within the sediments. Such a high rate of sulfide storage is probably not sustainable. We find it somewhat surprising that rates of sulfur storage were this high during autumn. Normally sediments are most reducing at the end of summer when the water temperature is high. As water temperature drops in autumn, respiration generally slows down and the solid sulfur phases are oxidized. We hypothesize that a major storm prior to our sampling date accelerated this process resulting in the oxidation of the top several cm of sediment in Boston Harbor. Hurricane Bob passed through the area the last week in August. Presumably, following this oxidation event, the equilibrium between reduced sulfur production and oxidation shifted back toward production resulting in the accumulation of reduced sulfur that we found.

Total CO_2 Measurements

Total CO_2 measurements were made on triplicate cores from station T2, replicate cores from stations T3 and T8 and a single core from station T7. Total CO_2 concentrations of the initial samples ranged from 2.14 to 2.18 mM.

The total CO_2 flux measurements indicated that oxygen uptake underestimated total metabolism at all stations except station T7 (Table 6). At stations T2 and T8 the total respiration calculated by the total CO_2 fluxes was in good agreement with the total respiration calculations made using alkalinity flux corrections to the oxygen uptake. At stations T3 and T7 CO_2 based respiration measurements were substantially lower than that calculated using oxygen uptake and alkalinity.

Total CO_2 is a direct measure of total respiration, respiration so calculated should be more accurate than our alkalinity calculation because: 1) our alkalinity calculations assume diffusive fluxes and there may be advection losses due to bioturbation; 2) our alkalinity fluxes were measured in separate cores so we can only add in an "average value". However, it is also possible that the total CO_2 samples may have degraded during the long holding time prior to analysis.

Until recently, measuring CO_2 fluxes in seawater was not very accurate due to the large bicarbonate background in seawater. The instrument we used is extremely precise and eliminates this problem. The samples were held in the cold (4 °C) and the dark for 4 months prior to analysis. CO_2 could have been produced during this interval. However, the initial CO_2 concentrations of the samples agreed well with the alkalinity (Table 2) values we measured at the start of the incubations. At the pH of seawater, alkalinity nearly equals total CO_2 in air equilibrated samples. We take this as good evidence that the total CO_2 concentrations did not change much with storage.

O/N Flux Ratios

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 be used to estimate denitrification in sediments (Fig. 7; Table 7). When fresh phytoplankton material (atomic C:N of about 7) 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 may be being lost by denitrification. The expected ratio can be calculated by knowing the proportion of the DIN flux which is ammonium vs. the proportion which is nitrate (Table 7).

The use of these ratios should be interpreted cautiously. The ratio can be expected to vary over an annual cycle. The O/N ratio will change seasonally if carbon mineralization lags behind nitrogen mineralization, if the material being decomposed deviates greatly from the Redfield ratio, or if there is seasonal storage or oxidation of reduced compounds. Ideally, the ratio of the total carbon mineralized to DIN released should be used.

Three of the 4 sites we investigated in the Harbor (the sandy station T8 being the exception) had O/N ratios very close to or below the O/N expected from decomposition of algae (Fig. 7, Table 7). This indicates that a small percentage of the nitrogen mineralized within the sediments is denitrified. However, as explained earlier in the section on porewater constituents, we have evidence of significant rates of sulfate reduction and reduced endproduct storage in these sediments. This indicates that sediment oxygen uptake underestimates total decomposition in these sediments. Using the calculated alkalinity fluxes we can "correct" the directly measured O/N ratio (Table 7). On the basis of the corrected ratio the deviation from the expected O/N is increased substantially at stations T3 and T7 (Table 7) but only slightly at stations T2 and T8.

Total CO_2 fluxes are a direct measure of decomposition and they are not be affected by the storage of reduced endproducts from sulfate reduction. Our estimates of denitrification using the ratio of (Total CO_2)/N are higher than when we use the O/N ratio but lower than our O/N estimates using the "alkalinity corrected" O/N at all stations except T8.

We can use these stiochiometric O/N ratios to estimate the amount of denitrification expected at these stations (Table 8, Fig. 7). The amount of N denitrified is equal to the amount expected by the metabolism estimate (Table 6) times 2 (to convert to O equivalents) divided by the expected O/N ratio (Table 7) minus the actual DIN flux. In most cases our "alkalinity corrected" O/N and our (Total CO_2)/N estimates of denitrification are in much better agreement with Kelly & Nowicki's (1992) directly measured rates of denitrification than with our uncorrected O/N values. Overall, however, our denitrification estimates are somewhat lower than those measured by Nowicki (Table 8). While at some stations the disagreement is more than a factor of two this is not unreasonable considering that totally independent methods were used on different sediment cores held for different lengths of time. All measurements indicate that denitrification rates are low compared to N inputs (estimated by Kelly 1991 to be about 24 mmol N m^{-2} d^{-1}).

O/P, and N/P Ratios

The exchange of phosphate across the sediment-water interface is strongly determined by adsorption and desorption from the sediments, in addition to mineralization rates (Pomeroy et al. 1965; Patrick & Khalid 1974). Therefore, the ratio of oxygen uptake to phosphate release need not be related to decomposition/mineralization. In the absence of sorption phenomena, an O/P atomic ratio of 212 is expected for the decomposition of fresh phytoplankton material. Phosphate adsorption increases this ratio. If total respiration is not fully accounted for by oxygen consumption due to sulfur storage (see above), then a ratio of less than 212 is to be expected. Low O/P ratios can also result from the desorption of phosphate from sediments and the dissolution of phosphate minerals (a completely abiotic process).

We observed a wide range of O/P ratios (Table 9). O/P ratios were close to the Redfield ratio at stations T7 and T8. The ratio was extremely high at station T2 implying P adsorption. In contrast, the ratio at T3 was quite low. Correcting our measured rate of sediment oxygen consumption to total metabolism brings the ratio at T3 closer to a Redfield value but still a bit low suggesting desorption.

In general O/P ratios were considerably higher that those measured within the Outer Harbor in 1990. This is consistent with the hypothesis that the sediments were more oxidized in 1991 than in 1990.

In the absence of significant sorption phenomena deviations in the sediment N/P ratio can be an indication of denitrification (Table 9). When denitrification is high the ratio falls below 16. However, the O/P ratios presented above suggest that phosphate fluxes are highly influenced by adsorption and desorption and thus N/P ratios should not be used for estimating denitrification in Boston Harbor.

SUMMARY AND CONCLUSIONS

1) Average sediment oxygen consumption from the four stations in Boston Harbor ranged from 21.6 - 29.0 mmol m^{-2} d^{-1}. Total CO_2 fluxes and porewater profiles of sulfide and alkalinity indicated that not all of the decomposition was accounted for by oxygen uptake. Alkalinity fluxes were calculated to range from 1.7 - 27.3 mmol m^{-2} d^{-1}, which would mean that oxygen uptake rates were underestimated by a similar amount. Estimates of total carbon decomposition from oxygen and alkalinity fluxes ranged from 23.3 to 49.5 mmol m^{-2} d^{-1}. Measurements of total CO_2 fluxes also indicated that oxygen uptake underestimated total metabolism but by a lesser amount than that predicted by alkalinity fluxes. Total CO_2 fluxes ranged from 20.2 to 34.9 mmol m^{-2} d^{-1}.

2) Several lines of evidence suggest that Boston Harbor sediments were more oxidized when we sampled in 1991 than when we sampled in 1990. In 1991, all stations had a visible oxidized brown layer 1-3 cm thick, and dissolved sulfides were not detected in the top 2-4 cm of the sediments. We observed significant fluxes of nitrate from sediments at three out of four stations. In contrast all stations removed nitrate from the overlying water in 1990. Finally, phosphate fluxes in 1991 were an order of magnitude lower than in 1990, and O/P ratios tended to be greater.

3) It is possible that Boston Harbor sediments were oxidized during the passage of Hurricane Bob. Thus the conditions we observed in 1991 could be atypical of September conditions.

4) All stations released measurable amounts of N_2O but the amounts were negligible in terms of the nitrogen budget.

5) We estimated denitrification using the ratio of oxygen consumed to dissolved nitrogen released. Using measured amounts of oxygen consumption we estimate denitrification to be of minor importance at most stations. Correcting oxygen uptake values to account for the total decomposition occurring in the sediments, using either alkalinity or total CO_2 fluxes, denitrification appears to be more important. We estimate that 0 to 56% of the DIN released by mineralization is denitrified at these stations at this time, with the highest rates being observed off Long Island. This is equivalent to a denitrification loss of 0 to 3.35 mmole N m^2 d^{-1}.

6) In general, our estimates of denitrification were slightly lower than those of made by Kelly and Nowicki (1992). All measurements suggest that denitrification rates are low in comparison to total N inputs to the Harbor. Further comparisons, especially at a different times of the year, would be extremely valuable.

7) The flux and porewater information provide insights into the sediment processes occurring at the time of sampling and help to put the denitrification measurements in perspective. The high nitrate flux we observed in 1991, in comparison to 1990, indicates that denitrification rates in September 1991 were greater than in September 1990.

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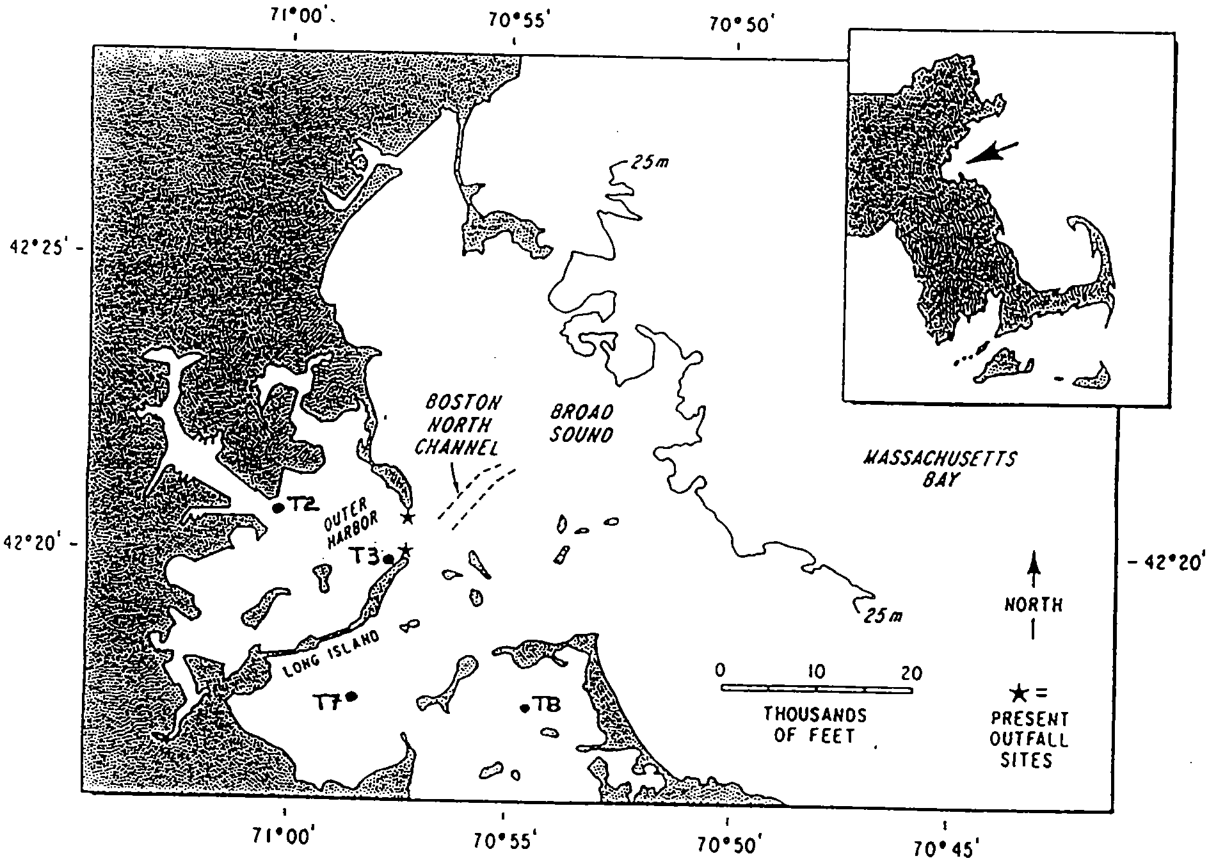

Figure 1. Location of the four stations sampled in this survey.

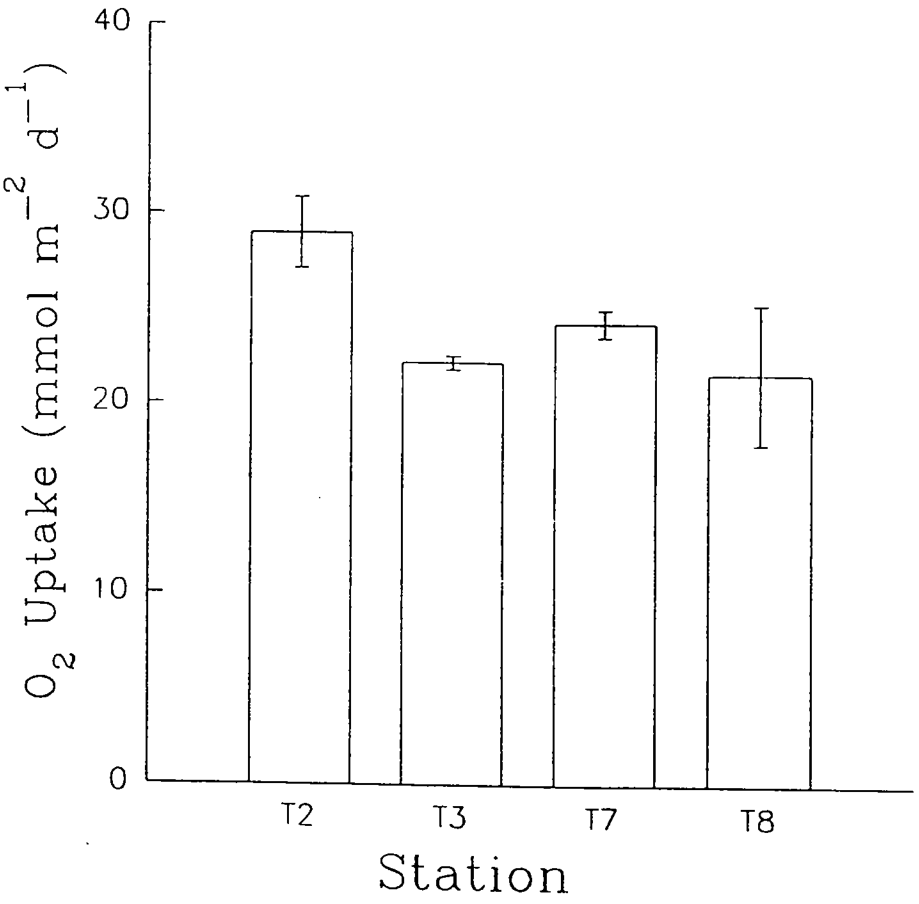

Figure 2. Oxygen uptake (Mean ± S.E.) of sediments from the four stations sampled.

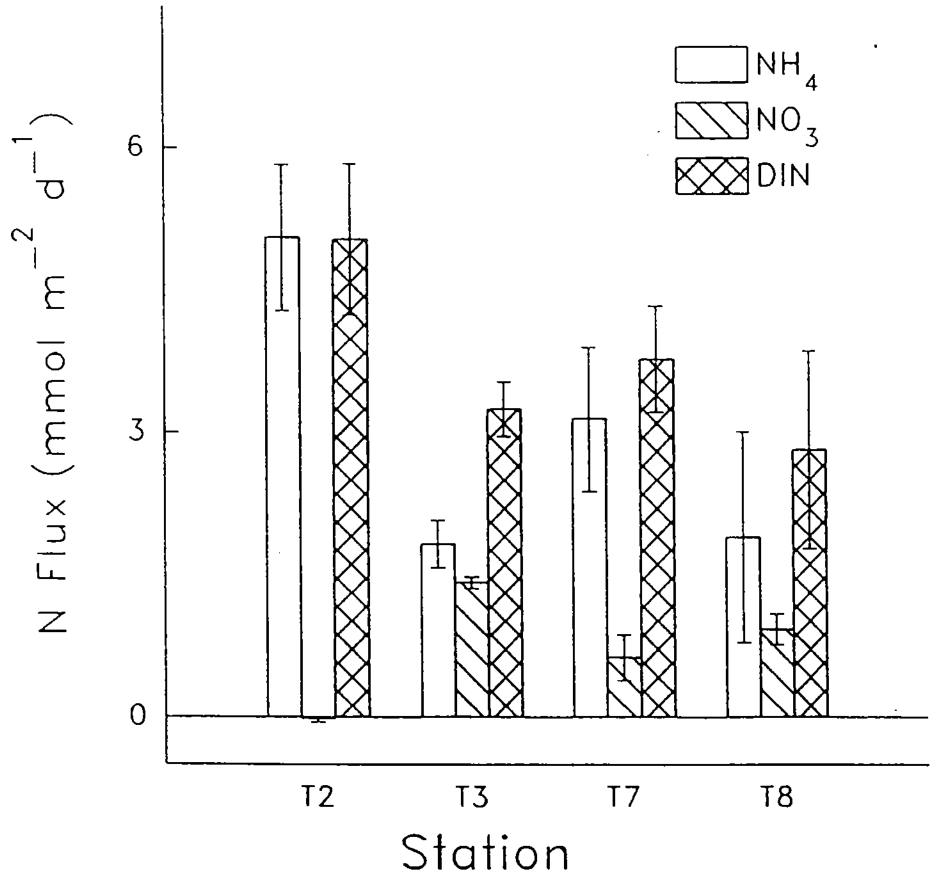

Figure 3. Ammonium, nitrate and DIN release (Mean ± S.E.) of sediments from the four stations sampled. Negative fluxes indicate uptake by the sediments.

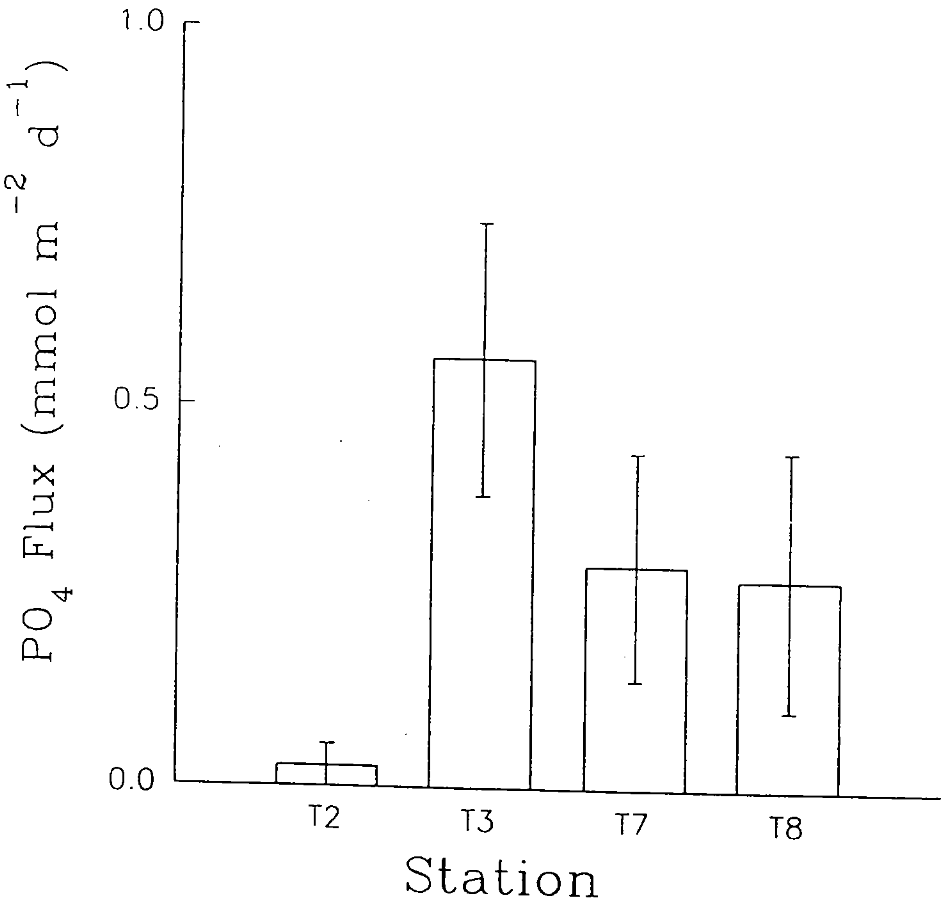

Figure 4. Dissolved inorganic phosphate (DIP) release (Mean ± S.E.) of sediments from the four stations sampled. Negative fluxes indicate uptake by the sediments.

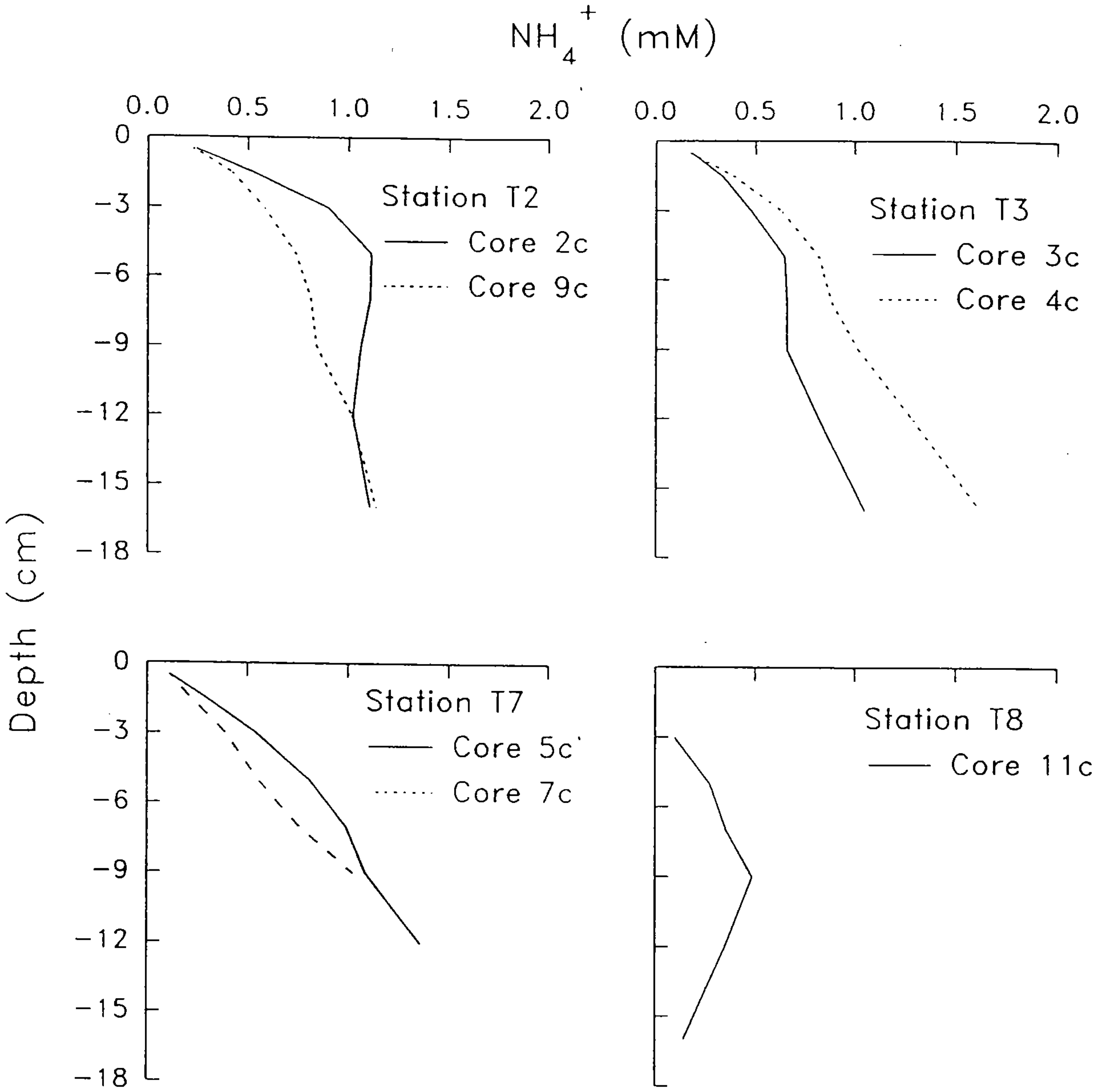

Figure 5. Porewater profiles of ammonium at each of the stations.

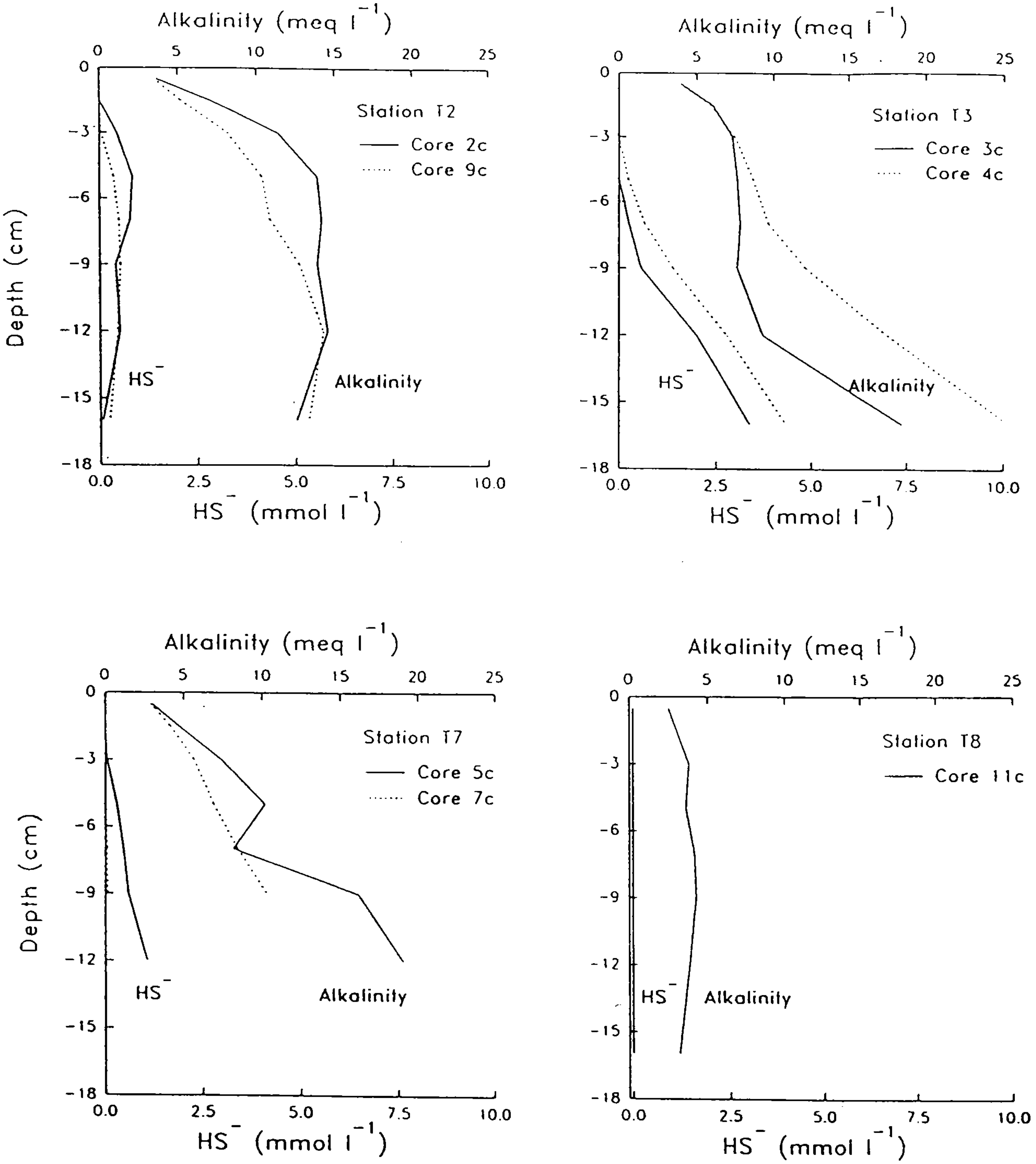

Figure 6. Porewater profiles of alkalinity and sulfide at each of the stations.

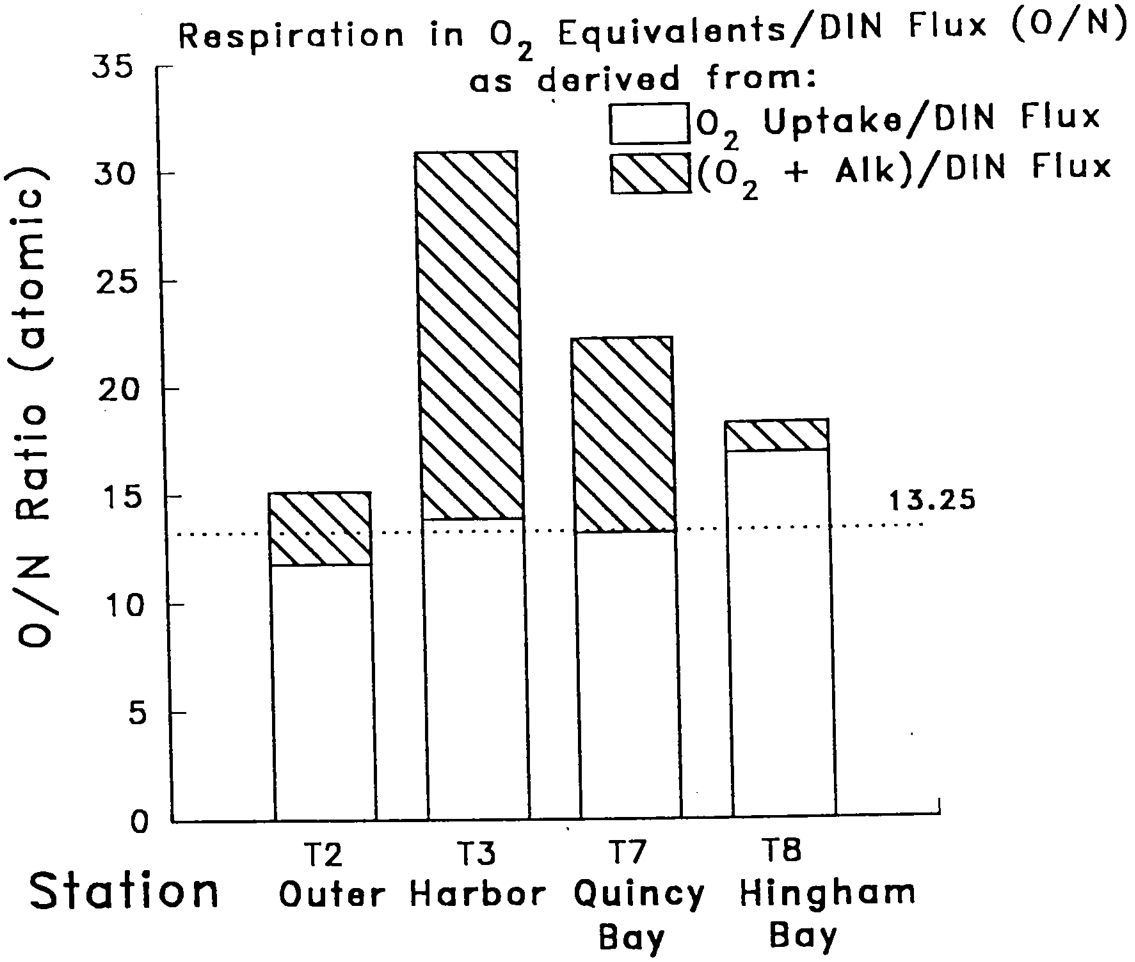

Figure 7. The ratio of oxygen uptake to DIN release (atom/atom) of sediments from the four stations sampled. The ratio was calculated using the oxygen uptake data (open bars) or using the oxygen uptake data corrected for the storage of reduced endproducts (see text for details). The dashed line indicates the ratio to be expected (13.25) from the decomposition of fresh algae to ammonium.

Table 1. Locations, depths, bottom water temperatures of the stations.

Site	Depth[1] (meter)	Temp (°C)	Coordinates[1] Latitude	 Longitude	Loran TD's[1]
T2	12	16.5	42 20.59	71 00.04	14037.96/25867.84
T3	7	15.1	42 19.79	70 57.69	14026.73/25836.36
T7	6	15.9	42 17.32	70 58.70	14045.12/25829.39
T8	13	15.4	42 17.17	70 54.73	14020.24/25799.78

[1] Depths and locations provided by TG&B.

Table 2. Initial nutrient concentrations and alkalinity of the overlying water used for the flux measurements. Water came from the same station as the cores. See text for details.

Station	Amonium umol l^{-1}	Nitrate umol l^{-1}	Phosphate umol l^{-1}	Alkalinity mEq l^{-1}
T2	5.88	3.14	0.31	2.12
T3	5.80	2.79	0.65	2.16
T7	6.19	4.09	0.46	2.14
T8	4.82	3.96	0.36	2.23

Table 3. Information on oxygen, ammonium, nitrate, DIN and phosphate fluxes (mmol m^{-2} d^{-1}) from cores taken from each of the four stations. Flux is calculated from the slope of five time points. The regression correlation coefficient (r^2) for each slope is shown. Negative values indicate uptake by the sediments. For each station the average and standard error (S.E.) is calculated.

Site	*Core*	*O2*	*r2*	*NH4*	*r2*	*NO3*	*r2*	*DIN*	*r2*	*PO4*	*r2*
T2	*12*	*-29.9*	*0.982*	*5.84*	*0.997*	*0.02*	*0.081*	*5.86*	*0.996*	*0.056*	*0.949*
	15	*-31.1*	*0.992*	*5.52*	*0.987*	*-0.03*	*0.200*	*5.50*	*0.988*	*0.053*	*0.613*
	3	*-26.0*	*0.998*	*3.81*	*0.989*	*-0.06*	*0.663*	*3.75*	*0.987*	*-0.031*	*0.507*
Mean		*-29.0*		*5.06*		*-0.02*		*5.04*		*0.026*	
S.E.		*1.9*		*0.77*		*0.03*		*0.80*		*0.035*	
T3	*11*	*-21.7*	*0.997*	*2.02*	*0.990*	*1.37*	*0.997*	*3.39*	*0.997*	*0.419*	*0.980*
	14	*-22.7*	*0.997*	*1.42*	*0.996*	*1.36*	*0.994*	*2.78*	*0.998*	*0.417*	*0.968*
	6	*-22.1*	*0.998*	*2.04*	*0.997*	*1.52*	*0.995*	*3.57*	*0.998*	*0.853*	*0.991*
Mean		*-22.2*		*1.83*		*1.42*		*3.25*		*0.563*	
S.E.		*0.4*		*0.25*		*0.06*		*0.29*		*0.178*	
T7	*10*	*-24.7*	*0.999*	*4.38*	*0.999*	*0.27*	*0.991*	*4.65*	*0.999*	*0.531*	*0.965*
	7	*-23.1*	*0.996*	*2.42*	*0.993*	*0.67*	*0.999*	*3.10*	*0.996*	*0.132*	*0.884*
	9	*-25.0*	*0.998*	*2.62*	*0.996*	*0.94*	*0.992*	*3.57*	*0.997*	*0.213*	*0.981*
Mean		*-24.3*		*3.14*		*0.63*		*3.77*		*0.292*	
S.E.		*0.7*		*0.76*		*0.24*		*0.56*		*0.149*	
T8	*2*	*-21.6*	*0.990*	*0.83*	*0.948*	*1.19*	*0.992*	*2.01*	*0.997*	*0.197*	*0.942*
	4	*-16.4*	*0.992*	*1.15*	*0.979*	*0.76*	*0.998*	*1.92*	*0.993*	*0.087*	*0.956*
	5	*-26.8*	*0.986*	*3.70*	*0.977*	*0.82*	*0.986*	*4.52*	*0.983*	*0.540*	*0.952*
Mean		*-21.6*		*1.89*		*0.92*		*2.82*		*0.275*	
S.E.		*3.7*		*1.11*		*0.16*		*1.04*		*0.167*	

Table 4. Nitrous Oxide (N_2O) fluxes from Boston Harbor cores. N_2O analyses were performed by Michael LaMontagne (Boston University Marine Program). The initial value for core 12 Station T2 was lost. Calculations were made using the average of the initial concentrations of the other Boston Harbor cores (3, 14 and 11). Initial concentrations of the three cores ranges from 11.96 to 12.32 nmol l^{-1}.

Station	Core	N_2O Flux μmoles m^{-2} d^{-1}	Average Flux as N μmoles N m^{-2} d^{-1}
T2	3	0.09	
	12	0.47*	
			0.56 ± 0.38 (SE)
T3	14	2.41	
	11	1.29	
			3.70 ± 1.06
T7	10	1.91	
	7	2.31	
			4.22 ± 0.40
T8	4	0.88	
	5	1.01	
			1.90 ± 0.12

*Initial sample lost

Table 5. Calculations of the alkalinity flux of cores at each station. Porewater profiles were fit using a three parameter model. Cend refers to the concentration calculated at z=infinity, Co is the concentration calculated for z=0 and alpha is the extinction coefficient of the curve. In some cases using all the data points gave very high variances for the coefficients. In these cases several of the bottom points were omitted. The gradient is the slope at z=o. Porosity for each core is shown. J is the alkalinity flux calculated for each core. See text for details.

Station	**Core**	**Fit**	**Cend**	**Co**	**Alpha**	**Gradient umol/cm4**	**Porosity**	**J mmol/m2/d**
T2	**C2**	**1**	**14.79**	**2.40**	**0.10**	**1.239**	**0.685**	**5.73**
T2	**C9**	**1**	**20.06**	**2.51**	**0.11**	**1.931**	**0.685**	**8.92**
							Avg.	**7.32**
T3	**C4**	**2**	**9.75**	**2.64**	**0.39**	**2.773**	**0.950**	**24.65**
T3	**C3**	**1**	**8.68**	**2.55**	**0.55**	**3.372**	**0.950**	**29.97**
							Avg.	**27.31**
T7	**C7**	**1**	**10.40**	**2.03**	**0.20**	**1.674**	**0.980**	**15.84**
T7	**C5**	**1**	**27.99**	**2.06**	**0.07**	**1.815**	**0.980**	**17.17**
							Avg.	**16.50**
T8	**C11**	**2**	**4.31**	**2.15**	**0.36**	**0.778**	**0.470**	**1.69**
							Avg.	**1.69**

Note - Fit = 1, all points used; Fit = 2,1 or more points omitted

Table 6. Estimates of total metabolism at the stations using three methods: total oxygen uptake (oxygen uptake); the oxygen uptake corrected using alkalinity fluxes (O2 + Alk); and the total CO_2 flux. See text for details.

Site	*Core*	*Oxygen Uptake mmol/m2/d*	*O2 + Alk mmol/m2/d*	*Total CO2 mmol/m2/d*
T2	*12*	*29.9*	*37.2*	*33.2*
	15	*31.1*	*38.4*	*51.1*
	3	*26.0*	*33.3*	*20.4*
Mean		*29.0*	*36.3*	*34.9*
S.E.		*1.9*	*1.9*	*10.9*
T3	*11*	*21.7*	*49.0*	*32.5*
	14	*22.7*	*50.0*	*32.8*
	6	*22.1*	*49.4*	
Mean		*22.2*	*49.5*	*32.6*
S.E.		*0.4*	*0.4*	*0.2*
T7	*10*	*24.7*	*41.2*	
	7	*23.1*	*39.6*	
	9	*25.0*	*41.5*	*20.2*
Mean		*24.3*	*40.8*	*20.2*
S.E.		*0.7*	*0.7*	
T8	*2*	*21.6*	*23.3*	*20.1*
	4	*16.4*	*18.1*	*33.9*
	5	*26.8*	*28.5*	
Mean		*21.6*	*23.3*	*27.0*
S.E.		*3.7*	*3.7*	*6.9*

Table 7. The O/N flux ratio (atom/atom) calculated using three different estimates of total metabolism; oxygen uptake (O/N), oxygen uptake corrected for alkalinity fluxes (O + 2*Alk); and total CO_2 fluxes (2*CO2). The expected O/N ratio is the ratio expected from the decomposition of Redfield organic matter making a correction for the percent of the DIN flux which was nitrate. See text for details.

Site	*Core*	*O/N*	*(O+2*Alk)/N*	*(2*CO2)/N*	*%NO3*	*Expected O/N*
T2	*12*	*10.20*	*12.70*	*11.32*	*0.00*	*13.26*
	15	*11.31*	*13.96*	*18.57*	*0.00*	*13.25*
	3	*13.87*	*17.76*	*10.86*	*0.00*	*13.25*
Mean		*11.79*	*14.81*	*13.58*	*0.00*	*13.25*
T3	*11*	*12.80*	*28.91*	*19.16*	*0.40*	*14.87*
	14	*16.33*	*35.97*	*23.58*	*0.49*	*15.21*
	6	*12.38*	*27.68*		*0.43*	*14.95*
Mean		*13.84*	*30.85*	*21.37*	*0.44*	*15.01*
T7	*10*	*10.62*	*17.72*		*0.06*	*13.48*
	7	*14.90*	*25.55*		*0.22*	*14.11*
	9	*14.01*	*23.25*	*11.33*	*0.26*	*14.30*
Mean		*13.18*	*22.17*	*11.33*	*0.18*	*13.97*
T8	*2*	*21.49*	*23.18*	*20.04*	*0.59*	*15.62*
	4	*17.08*	*18.85*	*35.33*	*0.40*	*14.83*
	5	*11.86*	*12.61*		*0.18*	*13.98*
Mean		*16.81*	*18.22*	*27.69*	*0.39*	*14.81*

Table 8. Our estimate of the amount of N which was lost as N_2 in mmoles N m^2 d^{-1} using measured O/N ratios. O/N ratios were calculated three ways: using measured O/N ratios (Denit Est. 1); using our adjusted O/N ratio adjusted by the unaccounted for alkalinity flux (Denit. Est. 2); and using the O/N ratio calculated by the total CO_2 flux (Denit. Est. 3). For comparison we show denitrification measurements reported by Nowicki (per. com.) using a direct N_2 flux method.

Site	*Core*	*Denit Est 1 mmolN/m2/d*	*Denit Est 2 mmolN/m2/d*	*Denit Est 3 mmolN/m2/d*	*Nowicki mmolN/m2/d*
T2	*12*	*0.00*	*0.00*	*1.84*	
	15	*0.00*	*0.30*	*0.00*	
	3	*0.17*	*1.28*	*0.00*	
Mean		*0.06*	*0.53*	*0.61*	*1.73*
T3	*11*	*0.00*	*3.20*	*1.02*	
	14	*0.65*	*3.80*	*1.36*	
	6	*0.00*	*3.04*		
Mean		*0.22*	*3.35*	*1.19*	*4.66*
T7	*10*	*0.00*	*1.46*		
	7	*0.17*	*2.51*		
	9	*0.00*	*2.23*	*0.00*	
Mean		*0.06*	*2.07*	*0.00*	*4.1*
T8	*2*	*0.76*	*0.97*	*0.57*	
	4	*0.29*	*0.52*	*2.65*	
	5	*0.00*	*0.00*		
Mean		*0.35*	*0.50*	*1.61*	*1.15*

Table 9. The O/P and N/P flux ratio for each station. For each station the O/P ratio was also calculated using respiration estimated adjusted for by alkalinity (O + 2*Alk), or total CO_2 flux. See text for details.

Site	Core	O/P	N/P	(O+2*Alk)/P	(2*CO2)/P
T2	12	1067.9	104.6	1328.6	1184.3
	15	1173.6	103.8	1449.1	1927.2
	3				
Mean		1120.7	104.2	1388.8	1555.7
T3	11	103.6	8.1	233.9	155.0
	14	108.9	6.7	239.8	157.2
	6	51.8	4.2	115.8	
Mean		88.1	6.3	196.5	156.1
T7	10	93.0	8.8	155.2	
	7	350.0	23.5	600.0	
	9	234.7	16.8	389.7	189.9
Mean		225.9	16.3	381.6	189.9
T8	2	219.3	10.2	236.5	204.5
	4	377.0	22.1	416.1	779.8
	5	99.3	8.4	105.6	
Mean		231.9	13.5	252.7	492.1

NITROGEN ISOTOPE CONTENT OF SURFACE SEDIMENTS IN THE MASSACHUSETTS BAY AND BOSTON HARBOR REGION

AN ADDENDUM TO THE REPORT: METABOLISM AND NUTRIENT CYCLING IN BOSTON HARBOR SEDIMENTS

Prepared by:
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Submitted on March 17, 1992

NITROGEN ISOTOPE CONTENT OF SURFACE SEDIMENTS IN THE MASSACHUSETTS BAY AND BOSTON HARBOR REGION

In 1990 and 1991 we sampled the sediments at a total of 12 locations in Massachusetts Bay, Broad Sound, Boston Harbor, Quincy Bay, and Hingam Bay (Fig. 1-A; also see Giblin et al. 1991, and this report). Surface sediment samples (0-1 cm) were analyzed for their nitrogen stable isotope composition. A sample of Deer Island Sludge, provided by Bruce Tripp (W.H.O.I.) was also analyzed. Oven dryed samples were analyzed at the Ecosystems Center by Brain Fry using an automated analysis system on a Finnigan MAT delta S isotope ratio mass spectrometer (Fry et al. 1992).

A single sample of Deer Island sludge had a δ_{15}N value of 3.3. This value is similar to the value obtained for particulate material from primary treated sewage from Los Angles (Sweeney et al. 1980). Surface sediment samples ranged from a δ_{15}N of 3.7 near the Deer Island outfall to 7.3 out in Massachusetts Bay. In general the values were closest to that of the sewage sludge within Boston Harbor (δ_{15}N 3.7 to 4.8). The heaviest values were obtained from Massachusetts Bay sediments (δ_{15}N 6.3 to 7.3). The values of the Massachusetts Bay sediments are similar to values we have obtained from Buzzards Bay (δ_{15}N 7.4 to 7.8 Giblin et al. unpublished data). Station 4 in Broad Sound had the lowest δ_{15}N value found outside the Outer Harbor. This is consistent with previous evidence from both the REMOTS survey and the benthic respiration data which suggests this station receives particulate material from the current outfall (see discussion in Giblin et al. 1991).

These results suggest that the δ_{15}N values of sedimentscould provide a useful marker for particulate nitrogen derived from sewage. This approach, especially when combined with other markers such as heavy metals, has been sucessfully used to track material discharged from the Los Angles outfall in southern California (Sweeney et al. 1980; Sweeney & Kaplan 1980).

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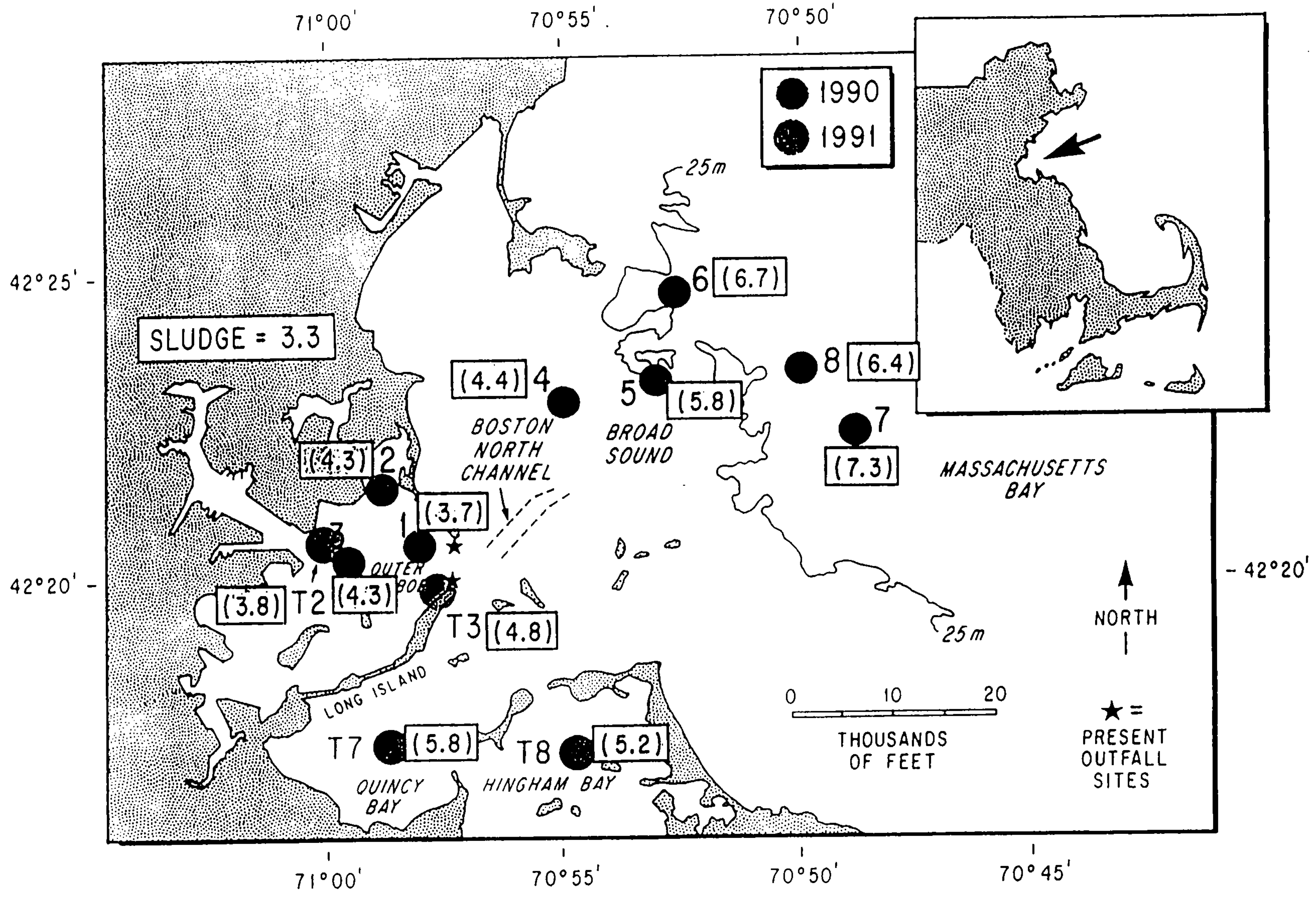
Fig. 1-A

$\delta^{15}N$ OF SURFACE SEDIMENTS FROM OUTER BOSTON HARBOR AND MASSACHUSETTS BAY



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