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Direct measurements of denitrification in Boston Harbor and Massachusetts Bay sediments

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Direct measurements of denitrification in Boston Harbor and Massachusetts Bay sediments

by

John R. Kelly
Barbara L. Nowicki

prepared by:
Battelle Ocean Sciences
397 Washington Street
Duxbury, MA 02332
(508) 934-0571, and

University of Rhode Island
Narragansett Bay Campus
Narragansett, RI 02882

prepared for:
Massachusetts Water Resource Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA, 02129
(617) 242-6000

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1.0 INTRODUCTION

Denitrification in soft-bottom sediments of shallow coastal marine ecosystems produces nitrogen gas from inorganic nitrogen dissolved in seawater or sediment pore water. In doing so, dissolved inorganic nitrogen that could be available to photosynthetic organisms as a nutrient for primary production is converted to a form that is nonnutritive, unutilized, and exported from the water to the atmosphere by degassing. Studies in the 1980s (cf. Seitzinger, 1988) suggested that sediment denitrification may remove a substantial fraction of the nitrogen load to some coastal waters.

Kelly (1991) raised the issue that a large fraction of the very high nitrogen loading to Boston Harbor may be exported. In investigating this issue, Kelly and Nowicki (1992) made initial direct denitrification measurements in September 1991 at four locations in Boston Harbor. Data showed differences across the stations that were related to organic content of the sediments. A rough extrapolation Harbor-wide to an annual value suggested that only about 8% of the Harbor nitrogen loading might be lost as N_2 gas produced in the sediments. To improve the basis for an estimate of the annual sediment denitrification rate in the Harbor, direct measurements of denitrification were continued into 1992. Two of the original stations of Kelly and Nowicki (1992) were sampled periodically from Spring to Summer 1992, and one also in Fall 1992. Additionally, those two stations and four others in the Harbor were sampled in August to provide wider spatial coverage.

As part of the MWRA outfall monitoring program (MWRA 1991), additional direct denitrification measurements were made at locations near the proposed diffuser site in Massachusetts Bay. Measurements were made in October and November 1992 to gain an initial understanding of the rates and variability in sediments that may be influenced in the future by the outfall effluent discharge.

A synchronous set of benthic nutrient flux (N, P) and metabolism (O_2, CO_2) measurements were conducted and are reported separately by Giblin *et al.* (1993). The pattern of temporal and spatial variation of directly-measured sediment denitrification rates in Boston Harbor and in Massachusetts Bay is examined in this report.

2.0 METHODS

2.1 SEDIMENT CORE COLLECTION

2.1.1 Harbor Stations

In the Harbor, sediments were collected in five months of 1992 (Table 1) to determine seasonal variability at two stations. Stations T3 and T8 (Figure 1) were chosen as representative of two different sediment types. Flux measurements at these locations represented the extremes (upper and lower bounds) of denitrification rates seen in 1991 measurements (Kelly and Nowicki, 1992). T3, off Long Island around the corner from the old sludge outfall discharge pipe (ceased in December 1991), is an organic-rich depositional site with high silt-clay content and abundant macrofauna (Kelly and Kropp, 1992). T8, in Hingham Bay, is in a transitional region, but had low organic content with generally sandier sediments that were hard to core. T8 may be considered a non-depositional, perhaps erosional site (cf. Knebel *et al.*, 1991). Macrofauna at this location are abundant and generally indicative of less enriched conditions (Kelly and Kropp, 1992). Sampling had to be coordinated with tide at both sites, for ebbing currents made sampling difficult, particularly at T8.

Stations T3 and T8 were sampled on April 21, May 13, June 9, and August 17-18. In addition, T3 was sampled on November 2 in conjunction with Massachusetts Bay sampling. In April, May, June, and November, triplicate cores were obtained to provide two "experimental" and one "control" core for laboratory incubations of sediments from each station (see below).

In August, four other sites throughout the Harbor also were sampled (Figure 1). These included T2 (just outside the entrance to the Inner Harbor) and T7 (Quincy Bay), both revisited sites of the 1991 study. Two other stations were sampled to round out geographic coverage and provide other examples of sedimentary communities. These were T4, a very high-organic site near the UMass-Boston Campus, and R4, on Deer Island Flats in a depositional area with spotty pockets of high organic matter. Both T4 and R4 were chosen from the stations occupied by Kelly and Kropp (1992) to be moderate-to-high organic conditions with reduced macrofaunal communities.

The procedures for obtaining the Harbor cores were the same as 1991 (Kelly and Nowicki, 1992). Briefly, SCUBA divers retrieved sediment cores (0.005 m^2) from each station, along with other cores

taken for companion flux studies (Giblin *et al.*, 1993). Cores were carefully pushed into the sediment to a minimum of 10 cm, then capped top and bottom.

2.1.2 Bay Stations

In the Bay, with one exception, sediments were collected by box coring from the R/V *Asterias*, using a box corer (40 x 40 cm). The box core was sufficiently large to obtain, from one successful drop, all the core samples for the direct denitrification measurements as well as other flux measurements (Giblin *et al.*, 1993). After the box core was on deck with a suitable sample, subcores were taken by placing the same types of cores used in the Harbor into the sediment, capping, and removing them. The box corer provides a less disturbed sample than a grab sampler, but is not as undisturbed as diver-obtained cores. In the muddier sites, the box corer took a good undisturbed sample; in general, where higher sand content occurred the sample was, unavoidably, usually a bit more disturbed.

In October (6-7), suitable samples were obtained at stations G8, W1, G6, 11, and C3 (Figure 1). The sediments near the outfall site are very heterogeneous, with patches of gravel and boulders interspersed with sand and muds. Station locations were targeted using maps of Knebel (1992) and knowledge of historical stations; even with this, sampling was difficult. Especially at G6 it was difficult to get a good grab and it took repeated effort. Several other target sites were not successful. C3, from previous macrofaunal studies (Shea *et al.*, 1991) was sandy and we were fortunate to obtain a suitable sample. G8 and G6 were approximate sites of previous flux studies (Giblin *et al.*, 1991). W1 was a USGS site being examined by R. Wheatcroft (WHOI); sampling was coordinated with his study, which is to investigate bioturbation rates. Station 11 was chosen from among those occupied in a 1991 survey by Battelle for MWRA; measurements there had shown very high *Clostridium* counts (K. Keay, MWRA, personal communication).

In November (2-4), we obtained box-corer samples in the Bay again at stations G8, W1, and 11. In addition to the Harbor cores at T3, diver-collected cores were taken at a new station, G9 at intermediately depth between the Harbor and the nearfield sites, in the outer portion of Broad Sound (Figure 1).

2.1.3 General Survey Procedures

The collected cores were maintained in the dark in a cooler filled with seawater at ambient temperatures, and were returned to the University of Rhode Island (URI) laboratory within hours of meeting the sampling boat and divers at the dock. In surveys in the Harbor, a single carboy (from one station) of water taken by a diaphragm pump from throughout the water column, filtered nominally to 1.0 μm, was also returned to laboratory and used to replace overlying water in all of the cores used for flux measurements. In the Bay, water was taken from near-bottom water at each station. Samples also were taken to determine bottom water oxygen at each station in the Harbor and Bay; oxygen determinations used the standard Winkler technique with autotitration to potentiometric endpoint (Kelly *et al.*, 1992).

Samples for sediment grain size analysis were taken from the surface (0-2 cm) of cores after incubations of Giblin *et al.* (1993). These were taken from all August stations in the Harbor, and all Harbor and Bay stations in October and November. Samples were analyzed by GEO/PLAN Associates, Hingham MA (Appendix A). Giblin *et al.* (1993, table 3) determined the total organic carbon (TOC) and nitrogen (TN) contents of the surface (0-2 cm) of cores incubated from each 1992 station.

Stations in the Harbor were located by using a Northstar 800 GPS/Loran C system. The Northstar system automatically chooses between the GPS (Global Positioning System) and Loran C, depending on best accuracy. The GPS has an absolute accuracy of approximately 100 m, and the Northstar automatically corrects the latitude/longitude position when the system is in the Loran mode. Latitude/longitude positions were checked at fixed calibration points in Boston Harbor.

In the Bay (October) Battelle's differential GPS system was used to provide station locations. The system interfaces with the Northstar described previously. In November, a failure was experienced in this system, so the October survey station readings that had been recorded using LORAN C on the R/V *Asterias* were used to revisit stations.

2.2 LABORATORY

2.2.1 Overview of Direct Measurement Approach

The method used here to measure biological denitrification rates was originally developed by Seitzinger *et al.* (1980), improved by Nowicki (1992), and used in prior Harbor studies (Kelly and Nowicki, 1992). The biological production of N_2 from denitrification is very small relative to the background of N_2 gas in the atmosphere and dissolved in seawater, so the flux measurements are made in N_2-free, gastight chambers. The method involves stripping the overlying water and gas phases of nitrogen gas, an action that produces an artifact that must be accounted for by a control. Due to stripping, nitrogen gas dissolved in pore waters degasses from the sediment column because a diffusive gradient has been created between the overlying water and sediment pore waters. Equilibration of pore water and overlying water dissolved N_2 concentrations is not as rapid as equilibration between water and gas phases, and thus N_2 continues to "bleed" out of the sediments into the water over time. The total measured N_2 flux (F_t) estimated by increase of N_2 in the water/gas phase during a sealed (but aerobic) incubation may be characterized as: $F_t = F_p + F_d$, where F_p is the production of N_2 (the flux due to denitrification activity that is of interest) and F_d is the degassing flux, a physical diffusion process induced by maintaining a relatively N_2-free environment in the water and gas phases.

Nowicki (1992) described the use of a replicate core as an anoxic control incubated *in parallel* with experimental cores. The control core is treated in exactly the same fashion as the experimental cores throughout the measurement period in the laboratory; the only difference is that the gas used for sparging and for flushing the control chamber is helium alone, without oxygen. Control cores are maintained without oxygen so that coupled nitrification—denitrification rates are blocked. Thus, N_2 fluxes observed in the anoxic controls are assumed to be due solely to physical degassing of N_2 in sediment porewater (F_d above). This modification allows one to correct for physical degassing *at the same time* incubations are made. Simple subtraction of the anoxic control core flux (F_d) from the rate measured synchronously in an experimental core (F_t) estimates F_p. Two advantages of the improved method are that it allows a direct correction for F_d (rather than assumptions regarding its significance) and it enables measurements to be made with less waiting time (Nowicki 1992).

2.2.2 Incubations

In the laboratory, on the evening of the day of collection, the surface 5 cm of a core was transferred to special incubation chambers. A description of the gastight chambers for denitrification measurements is given by Nowicki (1992). Briefly, the chambers were designed to hold an intact sediment layer, an overlying water column, and an air space above these two. The chambers were constructed of two sections of glass-walled pipe (total height: = 21.6 cm; diameter: = 7.8 cm), joined at the center with an O-ring and a metal clamp. Three glass stopcocks, sealed at the ends with rubber serum stoppers, served as sampling ports.

All sediments, once enclosed in gastight chambers, had their overlying waters carefully replaced with the seawater (ca. 800 mL per chamber) that was collected at the time of core retrieval. The water used in water exchange was maintained at the same temperature as the cores in the laboratory and sparged with He/O_2 to remove 95-99% of the ambient N_2 dissolved in seawater. Removal of nitrogen gas in the overlying water is necessary to detect the flux signal because there is such a large background concentration of N_2 in ambient seawater and the atmosphere (Seitzinger *et al.*, 1980). Following the initial water exchange, the air space (gas phase = 62 mL volume), was replaced with a helium/oxygen (He/O_2) gas mixture in the experimental cores, and with helium (He) alone in the anoxic control core. Flushing with He/O_2 rapidly and effectively removed any remaining nitrogen gas introduced with water exchange, but also kept the oxygen concentration of the overlying water near the intended ambient values (or anoxic, in the case of the control core). Prior to each incubation, the gas phase in each chamber was flushed two to three times daily. This procedure ensured that any N_2 flux from sediments into the overlying water/gas phase in the intervening period was removed, establishing desired initial conditions of low N_2 concentration in the water/gas phase.

The sediment chambers were maintained in the dark at ambient collection temperatures. Each chamber was stirred continuously with a magnetic stir-bar positioned at the interface between the water and gas phases. The stirring rate (approximately 200 rpm) was adjusted to be fast enough to maintain a constant flow of water and particles across the sediments and to resuspend sediments slightly. The magnetic stir-bars mounted inside each chamber were rotated by an air-driven magnet mounted on top of each chamber. The air pressure driving the magnetic stirrers was carefully controlled to maintain constant and equal stirring rates for all chambers. The purpose of stirring is to keep water and gas phases homogeneous and equilibrated with respect to the gases of interest.

Measurements of the concentrations of nitrogen and oxygen in the gas phase of each chamber were made by withdrawing gas samples through the chamber sampling ports. Replicate 50-μL samples were withdrawn using a gastight syringe that was preflushed with helium and then inserted through a rubber serum stopper in the sampling port. To prevent atmospheric contamination of N_2, the sampling port, syringe, and gas chromatography (GC) injection port were flushed continuously with helium during sampling; additionally, chambers were opened only when a slight positive pressure from the appropriate gas mixture was applied (cf. Seitzinger *et al.*, 1980).

Nitrogen (N_2) and oxygen (O_2) were measured by injecting gas samples into a Hewlett-Packard Model 5890A gas chromatograph equipped with a thermal conductivity detector. An 1/8 in. stainless steel column (2 m) packed with 5-Å molecular sieve (45/60 mesh) was operated at room temperature with a He carrier gas flow of 35 mL/min. Calibration curves were run with each set of samples, using a certified standard gas mixture (3% N_2, 20% O_2, balance He). Gas and water phases rapidly equilibrate in the system; therefore fluxes into the water from the sediments may be calculated knowing the changes in N_2 and O_2 sampled in the gas phase during an incubation and the volume of gas in each chamber.

In general, two incubations were done on experimental and control cores of a station. These each occurred over a period of four days and involved measurements at four points in time. During an incubation a chamber was completely sealed; no exchanges of either the gas or water phases were made. The two incubations provided a) two separate flux estimates of F_t from sediment cores (n=1 or 2, depending on the survey) and b) two separate *parallel* estimates of F_d under anoxic conditions from one core at each station.

2.3 DATA ANALYSIS, ERROR ANALYSIS, AND ANALYTICAL QUALITY CONTROL

The slope of the linear regression of the amount of N_2 or O_2 in the gas phase of a sealed chamber versus time provides a direct estimate of flux as mass per unit time. Dividing this slope by the sediment surface area in the chamber yields an area-based rate. Each point in the linear regressions consisted of two or more replicate samples of the gas phase of the sealed chambers at a given time. Initial rates of nitrogen gas production and oxygen uptake were always linear over time in all cores (see Appendix). An analysis of variance was used to calculate 95% confidence limits around the slopes of regressions of N_2 concentration over time.

Observed fluxes of N_2 gas in experimental cores were corrected for the background flux of N_2 observed in the anoxic control core. Since both the experimental core flux and the anoxic control core flux have an error term [95% CI (confidence interval)] associated with them, the error in the resulting corrected N_2 flux was calculated (propagated) according to Ramette, (1981) as follows.

$$R \pm r = (A \pm a) - (B \pm b),$$

$$r = \sqrt{a^2 + b^2},$$

where A and B are N_2 fluxes for experimental and control cores with their associated error terms (*a*, *b*), and *r* is the propagated error in the final corrected N_2 flux.

3.0 RESULTS AND DISCUSSION

3.1 DENITRIFICATION RATES IN BOSTON HARBOR SEDIMENTS

3.1.1 Stations T3 and T8 with Season

Denitrification rates in Boston Harbor estimated by the direct measurement technique varied from about 13 to 169 μmols N_2 m^{-2} h^{-1} across all measurements in 1992 (Tables 2 to 7); this full range was seen at T3 and T8. Fluxes (and uncertainties) are given for each incubation of each replicate core for a station in the Tables. The anoxic control core rate, subtracted to yield the corrected rate, also is given for each measurement. For the most part, there seemed little distinct pattern in the estimates for a given core over the course of two (or three) incubations in the laboratory. For this report describing general trends, note that station mean fluxes have been calculated as simple averages of all replicate measurements, assuming independence of time and space in the one case where there was an unequal number of repeated measurements between two cores of a station (T3, November).

In April, rates at stations T3 and T8 were similar (Table 2). In May, one replicate core at T3 had a much higher rate (Table 3). This core had a large clamworm, *Nereis virens*, that was burrowing intensively throughout the sediments. Higher rates were undoubtedly the result of the worm's activity; note that the *Nereis* density ($\geq$1 per incubation core is $\geq$ 200 m^{-2}) far exceeds the *Nereis* abundance at station T3 ($\sim$7.5 m^{-2} in April 1992; see Kelly and Kropp, 1992). Including the replicate core with the worm makes the mean appear different for T3 and T8 (Figure 2), but the core-to-core and incubation-to-incubation variability was high and thus, the two stations did not appear distinct at this month. Note that the temperature was only about 1 °C different between April and May, due to unseasonably warm temperatures in April and a somewhat cool temperature in May (Figure 2).

Denitrification rates for T3 and T8 became distinct as seasonal warming progressed through mid-Summer. For example, in June temperatures were about 15 °C (a bit unseasonably cool, see Figure 2). The average rate for T3 (72 μmols N_2 m^{-2} h^{-1}, n=4) was about double that of station T8 (35 μmols N_2 m^{-2} h^{-2}, n=4). Each station had reasonably consistent results between incubations and between replicate cores (Table 4). In August, when water temperatures were highest, the estimate of

denitrification at T3 was about three- to four-fold higher than at T8, although no replicate core measurements were made for these stations at that time (Table 5).

A last measurement in the Harbor was made at T3 in November (Table 7). The impetus for this was to estimate the rate as water temperature cooled. This measurement was to provide a seasonal contrast to springtime at similar temperatures and add to the data to describe relations between flux and temperature at T3 (Figure 2). At this time, the sediments were literally carpeted with amphipod tubes (presumably *Ampelisca*). This taxa had been present at this station in 1992 since April and perhaps was expanding its distribution through the northern Harbor compared to 1991 (Kelly and Kropp, 1992), but we appeared to catch an especially large burst in population in November 1992. Whether the growing amphipod presence was part of the first year recovery response of the sediment community to sludge cessation is unknown, but the fluxes measured at this time seemed in part (see below) affected by the presence of the animals. Flux rates in general (see Giblin *et al.*, 1993) and of N_2 in particular (mean 132 μmol m^{-2} h^{-1}, n=3) were the highest measured at any station during either 1991 or 1992.

Overall, denitrification rates at T8, a non-depositional environment with low silt-clay content (<20%, Appendix A) and low organic content (<0.4% C and <0.05% N by weight; Giblin *et al.*, 1993), had little response to season and its concomitant water temperature changes. Rates at T3, an organic-rich (>4% C and >0.39% N by weight; Giblin *et al.*, 1993) depositional environment with >50% silt-clay fraction (Appendix A), diverged strongly from T8 at higher temperatures (June and August 1992, September 1991).

3.1.2 Flux Variability in the Harbor

In August 1992, rates were measured at six locations throughout the Harbor (Figure 1). The range of mean rates (Table 5) was similar to that which we had measured in September 1991 (Figure 3). The rank order of stations varied a bit between the two measurements. However, considering the errors associated with a flux estimate ($\pm$10.8 μmol N_2 m^{-2} h^{-1} on average for 10 estimates in August, Table 5) and that duplicate station cores (spatial replicates) incubated at the same time, or duplicate sequential incubations of the same core (time replicates) may yield replicate estimates that vary by a factor of two (Table 5), there really appear to be two groups of stations in August 1992. The group

with higher fluxes included T7, T2, T3, and T4. Two stations, T8 and R4, had lower fluxes; for each of these there were analytical problems and only one flux estimate (time replicate) was obtained.

Our earlier study (Kelly and Nowicki 1992) had suggested that rates across Harbor sites might be a strong linear function of sediment total organic carbon (TOC) content. Fluxes measured at higher temperatures (above 15 °C, includes mean station data of June and August 1992, September 1991) confirm the pattern (Figure 4). Recognizing there is variability around the mean, it is nonetheless striking that conditions with lower organic content (<2% TOC) characteristically had lower rates (<50 μmol N_2 m^{-2} h^{-1}). The data were described by a functional regression, $Y = 20.8\ X + 6.8$ ($r^2 = 0.55$, significant at 95% level with n = 12). Including the November 1992 station T3 data yielded a similar functional regression, $Y = 24.2\ X + 1.3$ ($r^2 = 0.57$, significant at 95% level with n = 13).

For 1992, there were also data for total nitrogen (TN) in the surface (0-2 cm) sediments (Giblin *et al.*, 1993) at the stations and fluxes could be examined relative to TN (Figure 5). As with TOC, a relation was evident — particularly if the April and May (cooler temperatures) were omitted. Omitting those months, a functional linear regression to describe the data was $Y = 218\ X + 2$ ($r^2 = 0.61$, significant at 95% with n = 9). Also omitting November 1992 station T3 data, the functional regression obtained was similar but slightly less well fit, $Y = 190\ X + 8$ ($r^2 = 0.48$, significant at 95% with n = 8).

Interestingly, for the November flux at T3 (at 10 °C), where very high abundance of amphipods was noted, had the highest recorded N content (>0.5% N) measured for the year. The especially high TN may be in large part due to N in amphipod biomass. Regardless, sediment TN ultimately may prove to be a better predictor of sediment denitrification than sediment TOC, which was not extraordinary for this station at that time.

Scatter in the relationship between surface organic matter and denitrification rates suggests that other factors (including temperature) influence N_2 flux rates. We previously noted that extensive macrofaunal burrowing and extremely high densities of tube-dwelling amphipods that bioturbate the surface sediment were concomitant with higher N_2 fluxes. Station T7 may be in this category, for it has substantial macrofaunal densities and a variety of organisms capable or burrowing and irrigation activities (Kelly and Kropp, 1992). The converse situation, i.e. where less organisms were present to

burrow and irrigate the sediments and therefore lower fluxes result, may be true also. Based on 1991 results we expected station T2 to be such a situation, but 1992 results were quite different in both TOC and fluxes (Figure 4). Perhaps small-scale spatial variability in the benthos complicates resampling and restricts comparisons at this station (see Kelly and Nowicki, 1992; Kelly and Kropp, 1992). Stations T4 and R4 were picked specifically since they were representative of fairly well characterized depositional regions with moderate to high organic content but low macrofaunal diversity and generally smaller, surficial-dwelling taxa, not larger burrowing types (e.g., Kelly and Kropp 1992). Both T4 and R4 sampling regions may have lower dissolved oxygen and the surface sediments appear quite reduced (Giblin *et al.*, 1993). The cores from both stations had low mean denitrification rates compared to other stations with similar organic content (Figure 4). Thus, the station pattern results overall, if not fully, are accord with the notion that certain infauna may influence denitrification rather significantly. The fauna of cores were not examined so it is not possible to explore the notion much further.

The most compelling evidence for animal influence remains the comparison of two cores, with and without *Nereis* (Table 3). However, it is apparent from the data is that the influence of animals, along with temperature and organic matter, should be considered in developing a predictive empirical model of sediment denitrification.

3.2 DENITRIFICATION RATES IN MASSACHUSETTS BAY SEDIMENTS

3.2.1 Spatial and Temporal Variation

Bottom-water temperatures in the Bay in October and November were similar; fluxes were measured at 11 and 10 °C, respectively (Tables 6 and 7). Rates averaged below 50 μmol N_2 m^{-2} h^{-1} for stations (Figure 6); note that station averaging assumes a flux of zero for a replicate measurement where the N2 flux was non-detectable (e.g. Table 6) and that for some stations n=1 measurement. Bay sediment denitrification rates were similar to the range of rates at Harbor station T8 throughout the year and to most Harbor measurements made at temperatures near 10 °C.

The Bay stations had N_2 fluxes that were similar to the group of lower-flux, lower-organic stations in the Harbor (Figure 4), not surprising in that the sediment carbon content at Bay stations was <2.5% (Figure 7). For the Bay stations alone there was no strong trend of flux with TOC (Figure 7) or TN

(not shown), also not surprising given the relatively small *range* of organic content across the stations compared to the Harbor.

The uncertainty of the flux estimate for several measurements included zero, i.e. that no net flux was detectable. For the Bay, this occurred at G8, W1, and C3 at the second incubation in October (Table 6), as well as at G8 at the second incubation in November (Table 7). G6 had highest mean rates in October and W1 in November. Stations with very high sand content (C3, G9) never exhibited very high rates. Without developing statistical tests, but given the variability from incubation-to-incubation in a core and month-to-month at a station, there seems little striking difference among these Massachusetts Bay sites, excepting perhaps the extreme station contrasts like C3 and G6 (October).

For the three Bay stations that were measured in October and resampled in November there was no systematic flux trend by month (Figure 6). The surface organic content varied at the two samplings, as it did for repeated visits to Harbor stations (Figures 4, 5 and 7); the Coefficient of Variation (CV) for TOC ranged from 3 to 28% (n=2 months) for the three resampled Bay stations. Comparing the mean monthly flux rates in October and November at the three stations, the CV for N_2 flux ranged from about 10 to 58% (n=2 months). Duplicate flux measurements on an individual core sometimes indicated CV's that were greater than 100% (e.g., Table 6).

Survey to survey variability in the concentration of surface sediment organics is an inherent feature — arising from the small-scale patchiness in the Bay and time variability, as well as navigation/sampling uncertainties. As has been noted (e.g., Nixon *et al.*, 1980), flux variability in time and space can be greater than variability in sediment concentrations and these data begin to define the level of flux variability that must be expected for the Massachusetts Bay region of interest.

3.2.2 Rates in Context of Sediment Nitrogen Cycling

The mean and standard deviation of measured N_2 fluxes for all stations, incubations, and months in the Bay (n = 17, Tables 6 and 7) was 22.2 μmol N_2 m^{-2} h^{-1} ($\pm$17.1), or 44.4 μmol m^{-2} h^{-1} as *N* (monatomic). Giblin *et al.*'s (1993) average for companion DIN fluxes at this set of stations was 1.995 mmol N m^{-2} d^{-1}, or 83 μmol N m^{-2} h^{-1}. Thus, N_2 gas loss may represent about 35% of the total N flux [i.e., 44/(44 + 83) x 100] from the Bay sediments measured in early Fall when peak annual bottom-water temperatures were reached (Kelly *et al.*, 1992).

For comparison, the same calculation can be made for the Harbor using Giblin *et al.*'s (1993) grand average for 1992 Harbor measurements for DIN (3.77 mmol N m^{-2} d^{-1}) and our average direct estimate of N_2 flux for all 1992 Harbor measurements (56.5 μmol N_2 m^{-2} h^{-1}). About 42% of the N regenerated from the Harbor sediments appeared to be lost as gaseous N_2. As suggested by Kelly and Nowicki (1992) this percentage is expected to vary a bit with sediment type and eutrophication status, but also with season.

3.3 UPDATED STATUS OF THE BOSTON HARBOR NUTRIENT BUDGET

Kelly and Nowicki (1992) presented a tentative nitrogen budget for Boston Harbor. Based on findings of this study, and some changes due to cessation of sludge disposal in the Harbor, amendments to that budget with respect to 1992 input and denitrification terms are discussed. Most other aspects of the budget are assumed to be similar to previous estimates. The interested reader should refer to Kelly and Nowicki (1992) for various assumptions and calculations made for different terms, as well as Giblin *et al.* (1993) for an update of internal DIN recycling by Harbor and Bay sediments.

3.3.1 Input

Menzie *et al.* (1991) estimated the annual total nitrogen input to Boston Harbor from land and air sources to be about 13,086 metric tons. This estimate included sewage sludge (1100 metric tons), the input of which ceased in December 1991. From data for 1992, the MWRA estimates that total nitrogen in effluent load was on the order of 10,691 metric tons (MWRA Discharge Monitoring Reports), which is comparable to the 11,000 used by Menzie *et al.* (1991). Using the MWRA estimate and adding other sources included by Menzie *et al.* (1991), one arrives at a nitrogen load to Boston Harbor of 11,677 metric tons, or roughly 12,000 metric tons $year^{-1}$. Following Kelly (1991), using the area of the Harbor as 1.08×10^8 m^2, the input thus is estimated as 7937 mmol N m^{-2} $year^{-1}$. Note that the new, post-sludge discharge input to the Northern Harbor area (5.1×10^7 m^2) alone can be calculated to be roughly 12,000 mmol N m^{-2} $year^{-1}$. The N input estimate to the Southern Harbor area (5.7×10^7 m^2) remains as before (because sludge was not input there) at nearly 4300 mmol N m^{-2} $year^{-1}$.

3.3.2 Export

Kelly and Nowicki (1992) considered several routes of nitrogen export. Here, an update is considered with respect to the denitrification pathway.

A simple, direct approach to relate denitrification and N inputs is to consider only the period of measurements, in this case through the warmer part of the year from April to August (or November for T3). MWRA effluent N loads to the Harbor do not appear to be very different between summer and winter (M. Hall, MWRA, personal communication); the effluent being the majority of estimated N input to the Harbor it is reasonable to assume, for these calculations, that the annual N load is equally distributed throughout the year. However, fluxes increase with temperature for some sediments, the result being that a comparison of integrated flux and integrated input for the warmer period of the year should provide a percentage (flux/input) that is slightly higher than would be the case for the whole year.

The average rate (all measurements) for the five-month period from April to August 1992 (inclusive) was 50 μmol N_2 m^{-2} h^{-1}, or 100 μmol N m^{-2} h^{-1}. Therefore, the equivalent of about 11% of the annual N input was lost as gas. Using all 1991-1992 data (including high September 1991 and November 1992 rates), and assuming the 7-month period of early April to early November, the average rate was 58 μmol N_2 m^{-2} h^{-1}. This amounts to about 12.8% of the new (1992) N input. For station T3 alone (n = 6 different months, April to November), the average was 76 μmol N_2 m^{-2} h^{-1}. To provide a maximum estimate of sediment denitrification's potential removal of N load, one could assume this very high rate applied over the *entire* Northern Harbor for the seven months. With such assumptions about 766 of the 7000 mmol N m^{-2} delivered to the Northern Harbor region (over 7 months), roughly 11%, could be denitrified.

A second approach to quantifying Harbor denitrification involves calculation of annual N_2 flux by spatial and temporal extrapolations. A common procedure to average across time is to model the relationship between flux and temperature as an exponential (Nixon *et al.*, 1976, 1980) and this was previously used to generate a tentative annual denitrification estimate of about 666 mmol N m^{-2} $year^{-1}$ for Boston Harbor (Kelly and Nowicki 1992). For the April through September months of our Boston Harbor measurements it was possible to develop a flux—temperature relationship for station T3, but T8 was essentially constant in the range of 9 to 17.5 °C. Using all T3 flux—temperature pairings (n= 16 replicate measurements, 1991-1992), the flux data were convolved with data on the

annual temperature cycle (shown in Figure 2; K.Keay, MWRA, personal communication). An integrated value of 772 mmol N m^{-2} $year^{-1}$ was calculated for T3; this value would be about 8% less if the high November values were not included in deriving a flux-temperature relationship. In contrast, an approximation for T8, using the grand average (28.9 μmol N_2 m^{-2} h^{-1}) as a constant for the entire year, would amount to roughly 500 mmol N m^{-2} $year^{-1}$. If rates at T8 dropped to expected lower values as temperature fell below 10 °C, the integrated value for that station would approach 400 mmol N m^{-2} $year^{-1}$. Below we use the value of 450 mmol N m^{-2} $year^{-1}$ for this station.

Knebel *et al.* (1991) characterized Harbor sedimentary regimes (not including the inner Harbor). About 51% by area was "depositional," about 29% was "sediment reworking," and about 20% was "erosional/nondepositional." T3 had high organic content and would fall in the depositional class. T8 is clearly in the erosional/non-depositional class, but a portion of the Harbor bottom area in this class is gravel or bedrock. We here will assume T3 and T8 to be characteristic of 51% and 20%, respectively of the whole Harbor and the remaining 29% of the Harbor to have rates mid-way between these two stations (cf. Figure 4, about 2.5% TOC). The area-weighted average flux for the Harbor can be calculated assuming the rates 772, 450, and 611 mmol N m^{-2} $year^{-1}$ apply to the three classes. The resultant annually integrated, area-weighted value is 660 mmol N m^{-2} $year^{-1}$, or remarkably consistent with Kelly and Nowicki (1992). Note that T3 may have high fluxes for its class and T8 for its. We therefore believe that the 1992 annual estimate is biased to yield a high value, but the assumption of rates diminishing in winter as predicted by the flux-temperature model using presently available data needs verification to increase confidence.

The integrated value 660 mmol N m^{-2} $year^{-1}$ represents about 8% of the annual N input to the whole Harbor estimated for 1992. The many assumptions may be varied in reasonable fashion to yield flux estimates in the range of $\pm$10 to 20% of the calculated value (20% higher being higher than the integrated value for T3). These results reinforce the notion (Kelly, 1991) that most of the N input to the Harbor is exported and they provide a solid empirical basis for rejecting speculation that denitrification may remove a majority of the N input to the Harbor (Christensen, 1991). Moreover, the results are consistent with new results from water column monitoring in Massachusetts Bay in 1992 that show the Harbor as a strong source of dissolved and particulate N into the western Massachusetts Bay region (Kelly *et al.*, 1992). The updated Boston Harbor N budget confirms the

contention that sediment denitrification may not provide enough N removal to alleviate eutrophication effects in coastal waters (Nowicki, 1992).

3.4 NITROGEN LOADING, DENITRIFICATION, AND HARBOR RECOVERY

It has been known for some time that benthic nutrient and denitrification fluxes are sensitive to increases in nutrient loading and organic deposition (Kelly and Nixon, 1984; Kelly *et al.*, 1985; Seitzinger, 1988). Nowicki (1992) has examined rates of denitrification using the direct method with anoxic control correction in experimental enrichment studies. Fluxes were measured at temperatures from <5 to 20 °C in a (5-m deep) control mesocosm with a nutrient input of 1635 mmol N m^{-2} $year^{-1}$ and a DIN-enriched mesocosm receiving 10,045 mmol N m^{-2} $year^{-1}$, and the range of denitrification fluxes was from ≈ 0 to 220 μmol N_2 m^{-2} h^{-1}. The water residence time in the mesocosm was about 1 month, whereas Boston Harbor's is more on the order of a week or two (Signell, 1991). Accordingly, caution is advised in making comparisons of input levels or flux rates in the experiment and in Boston harbor without residence time corrections, but some trends can be directly compared.

Nowicki's enriched-condition sediments showed a sharp exponential flux—temperature relationship, fluxes increasing roughly 10-fold from 4 to 18 °C. The rate of increase was slightly sharper than that seen at T3 in Boston Harbor. In contrast, the mesocosm control sediments (Nowicki, 1992) showed only very slight increase in flux with temperature (maybe a factor of two from 4 to >20 °C). This situation was similar to observations at T8, the non-depositional location in Southern Boston Harbor.

The relationship between sediment organic matter and denitrification observed in Boston Harbor suggests that the direct measure of denitrification (and benthic nutrient fluxes) may well be a faithful indicator of changes in nutrient discharge practices. The simplest prediction from Figure 4 would be that a decreased sediment denitrification rate would ensue in the Harbor as sediment organic content and/or nutrient loading deceases (cf. Kelly and Nowicki 1992, for some additional discussion).

However, recovery due to abrupt loading changes may bring some transitional states. For example, if the appearance of ampelscid amphipods at T3 was indeed related to sludge cessation then perhaps enhanced fluxes will ensue for a period as certain macrofauna recolonize sediments. Characteris-

tically, the progression of benthic recolonization is from very small surficial forms to those which are larger, deeper-dwelling, and influential in bioturbation/irrigation activity and such a progression would likely apply to a substantial area of the Northern Harbor. If this speculative scenario actually occurred, then one of the effects of cuts in loading would be to increase the significance, at least temporarily, of sediment denitrification in the Harbor nutrient budget.

3.5 CONCLUSIONS

The flux of N_2 gas from sediments varied with temperature, sediment organic content, and macrofaunal activity. Within the Harbor, a relationship between denitrification and organic content of the surface sediments was evident. Denitrification in a high organic sediment appeared to be markedly enhanced by seasonal temperature increases, but N_2 fluxes in a sandy, low organic environment varied only slightly over a seasonal temperature range. A role of macrofauna in enhancing denitrification was suggested. In one case, cores with and without a large clamworm were markedly different. In another, cores with a dense population of tube-building amphipods had unusually high N_2 fluxes for the water temperature. Because of the relation between fluxes and sediment quality and the known responsiveness of benthic fluxes and macrofauna to nutrient loading changes, it is recommended that sediment denitrification measurements be continued during the Harbor's transition and recovery with sludge abatement (December 1991) and effluent diversion (1995).

Presently, denitrification rates measured in some parts of Boston Harbor are high and comparable to rates estimated in a few other highly enriched coastal sediments. Most importantly, however, the data suggest that a maximum of about 11-12% of the N input to the Harbor is removed by denitrification in bottom sediments during the warmer part of the year and over an annual cycle it is very likely that less than 10% of the estimated annual N input gets denitrified in the sediments.

In the Bay, measurements were made only during October and November near peak bottom-water temperatures. Sediment denitrification rates in the Bay were in the same range as Harbor rates when and where temperature and sediment organic content were comparable. Both bottom-water temperatures and sediment organic concentrations at the Bay stations peak at much lower values than in the Harbor, so maximum rates in the Bay should not be as high as in the Harbor if the same general

relationships seen in the Harbor apply to the Bay. For the Bay, no station-to-station or month-to-month patterns in the data were particularly striking.

Finally, N_2 flux, directly measured, represented roughly 35 to 45% of the total N regenerated from sediments to the water column, averaged over the periods measured in the Bay and Harbor, respectively.

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Table 1. Stations for Flux Studies.

Station	Months of Sampling	Nominal Depth (m)	Latitude Longitude[1]	Site Description[2]
T2	Au	12	42°20.59 71°00.04	~55% silt-clay
T3	Ap, M, J, Au, N	7	42°19.79 70°57.69	>50% silt-clay
T7	Au	6	42°17.32 70°58.7	~55% sand
T8	Ap, M, J, Au	13	42°17.17 70°54.73	>80% sand and gravel
T4	Au	3.5	42°18.58 71°02.49	~63% silt-clay
R4	Au	5.5	42°21.43 70°59.00	~55% sand
W1	O, N	32	42°24.1617 70°50.1871	~55% silt-clay
C3	O	33	42°23.1634 70°50.0739	~97% sand and gravel
11	O, N	33	42°20.8689 70°48.8977	~55% sand
G6	O	27	42°24.8492 70°52.8152	~66% sand
G8	O, N	33	42°23.5423 70°50.0495	~47% silt-clay
G9	N	21	42°23.02 70°53.92	~90% sand

[1] Target positions based on first site visit
[2] General conditions based on samples collected in 1992 (see Appendix A)

Table 2. Denitrification in Boston Harbor: April 1992
9°C

Station	Incubation #	Days	O_2 Flux (mg O_2 m^{-2} h^{-1})	N_2 Flux	Anoxic Control Flux	Corrected N_2 Flux
				(µmol N_2 m^{-2} h^{-1})		
T-3	1	4- 7	24	79±7	56±7	23±10
	2	9-12	25	56±6	26±3	30± 7
T-3	1	4- 7	35	97±8	56±7	41±11
	2	9-12	39	62±9	26±3	36± 9
T-8	1	4- 7	24	74±7	44±8	30±11
	2	9-12	21	46±5	21±4	25± 6
T-8	1	4- 7	29	79±4	44±8	35± 9
	2	9-12	37	69±4	21±4	48± 6

Errors show 95% CIS around slopes of linear regressions of N_2 production versus time.

Table 3. Denitrification in Boston Harbor: May 1992
10°C

Station	Incubation #	Days	O_2 Flux (mg O_2 m^{-2} h^{-1})	N_2 Flux	Anoxic Control Flux	Corrected N_2 Flux
				(µmol N_2 m^{-2} h^{-1})		
T-3	1	5- 8	27	65±11	52±13	13±17
	2	11-14	32	39± 3	22± 4	17± 5
	3	19-21	26	34± 3	11± 5	23± 6
T-3*	1	5- 8	60	189± 9	52±13	137±16
	2	11-14	50	69±16	22± 4	47±16
	3	19-21	46	101±44	11± 5	90±44
T-8	1	5- 8	26	77±16	48±12	29±20
	2	11-14	25	41± 4	17± 5	24± 6
	3	19-21	20	24±10	N.D.	24±10
T-8	1	5- 8	33	78±19	48±12	30±22
	2	11-14	23	39± 2	17± 5	22± 5
	3	19-21	25	30±12	N.D.	30±12

Errors show 95% CIS around slopes of linear regressions of N_2 production versus time.
N.D. = Non Detectable
*This core contained a large clam worm (Nereis virens) and its extensive burrows.

Table 4. Denitrification in Boston Harbor: June 1992
15°C

Station	Incubation #	Days	O_2 Flux (mg O_2 m^{-2} h^{-1})	N_2 Flux (µmol N_2 m^{-2} h^{-1})	Anoxic Control Flux (µmol N_2 m^{-2} h^{-1})	Corrected N_2 Flux (µmol N_2 m^{-2} h^{-1})
T-3	1	5- 8	39	132±15	37±6	95±16
	2	11-14	39	97± 2	20±2	77± 3
T-3	1	5- 8	55	83±17	37±6	46±18
	2	11-14	55	91± 5	20±2	71± 5
T-8	1	5- 8	40	76± 8	35±7	41±11
	2	11-14	33	47± 2	21±4	26± 5
T-8	1	5- 8	32	77± 5	35±7	42± 9
	2	11-14	25	51± 2	21±4	30± 5

Errors show 95% CIS around slopes of linear regressions of N_2 production versus time.

Table 5. Denitrification in Boston Harbor: August 1992
17.5°C

Station	Incubation #	Days	O_2 Flux (mg O_2 m^{-2} h^{-1})	N_2 Flux (µmol N_2 m^{-2} h^{-1})	Anoxic Control Flux (µmol N_2 m^{-2} h^{-1})	Corrected N_2 Flux (µmol N_2 m^{-2} h^{-1})
T-8	1	7-10	20	43± 4	21±4	22± 6
	2	14-17	15		24±5	-
T-7	1	7-10	43	141±16	25±5	116±17
	2	14-17	30	96±14	22±3	74±14
R-4	1	7-10	30	38± 5	25±5	13± 7
	2	14-17	35	-	17±6	-
T-2	1	5- 8	42	85±10	24±3	61±10
	2	12-15	39	133±17	12±3	121±17
T-3	1	5- 8	42	120±16	35±6	85±17
	2	12-15	24	82± 3	25±3	57± 4
T-4	1	5- 8	40	58±11	18±3	40±11
	2	12-15	39	87± 5	13±2	74± 5

Errors show 95% CIS around slopes of linear regressions of N_2 production versus time.

Table 6. Denitrification in Massachusetts Bay: October 1992
11°C

Station	Incubation #	Days	O_2 Flux	N_2 Flux	Anoxic Control Flux	Corrected N_2 Flux
	#		(mg O_2 m^{-2} h^{-1})		(µmol N_2 m^{-2} h^{-1})	
G-8	1	6- 9	13	54±4	18±6	36±7
	2	13-16	8	13±4	13±3	N.D.
W-1	1	6- 9	17	62±6	33±4	29±7
	2	13-16	9	18±3	19±5	N.D.
G-6	1	5- 8	25	84±3	20±5	64±6
	2	12-15	11	39±3	6±1	33±3
Sta. 11*	1	5- 8	29	-	24±4	-
	2	12-15	6	30±5	7±1	23±5
C-3	1	5- 8	12	31±2	25±3	6±4
	2	12-15	3	9±2	8±2	N.D.

Errors show 95% CIS around slopes of linear regressions of N_2 production versus time.
N.D. = non-detectable
*This core contained a large clam worm (Nereis virens).

Table 7. Denitrification in Boston Harbor (T3) and Massachusetts Bay: November 1992
10°C

Station	Incubation #	Days	O_2 Flux	N_2 Flux	Anoxic Control Flux	Corrected N_2 Flux
	#		(mg O_2 m^{-2} h^{-1})	(µmol N_2 m^{-2} h^{-1})		
T-3A	1	7-10	38	-	20±5	-
	2	14-17	36	113± 7	9±3	104± 8
T-3B	1	7-10	44	142±20	20±5	122±21
	2	14-17	44	178± 5	9±3	169± 6
G-9	1	7-10	14	42± 7	9±2	33± 7
	2	14-17	11	23± 5	8±2	15± 5
W-1	1	7-10	8	51± 2	9±2	42± 3
	2	14-17	15	39± 4	11±4	28± 6
Sta. 11	1	5- 8	19	57± 6	28±3	29± 7
	2	12-15	18	37± 3	13±2	24± 4
G-8	1	5- 8	8	27± 4	14±4	13± 6
	2	12-15	8	13± 4	11±3	2± 5

Errors show 95% CIS around slopes of linear regressions of N_2 production versus time.
T-3 cores were loaded with active Ampelisca

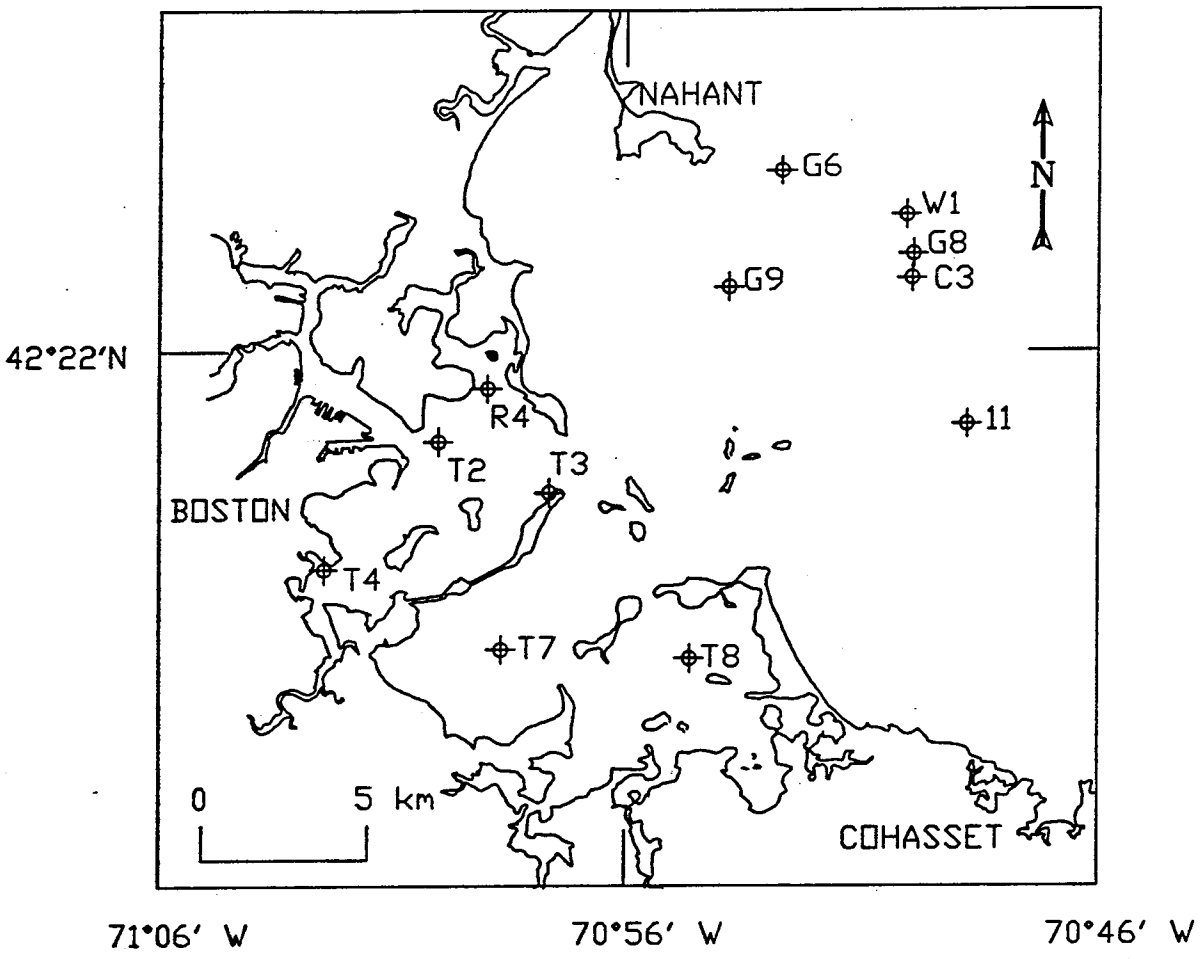

Figure 1. Map of Station Locations.

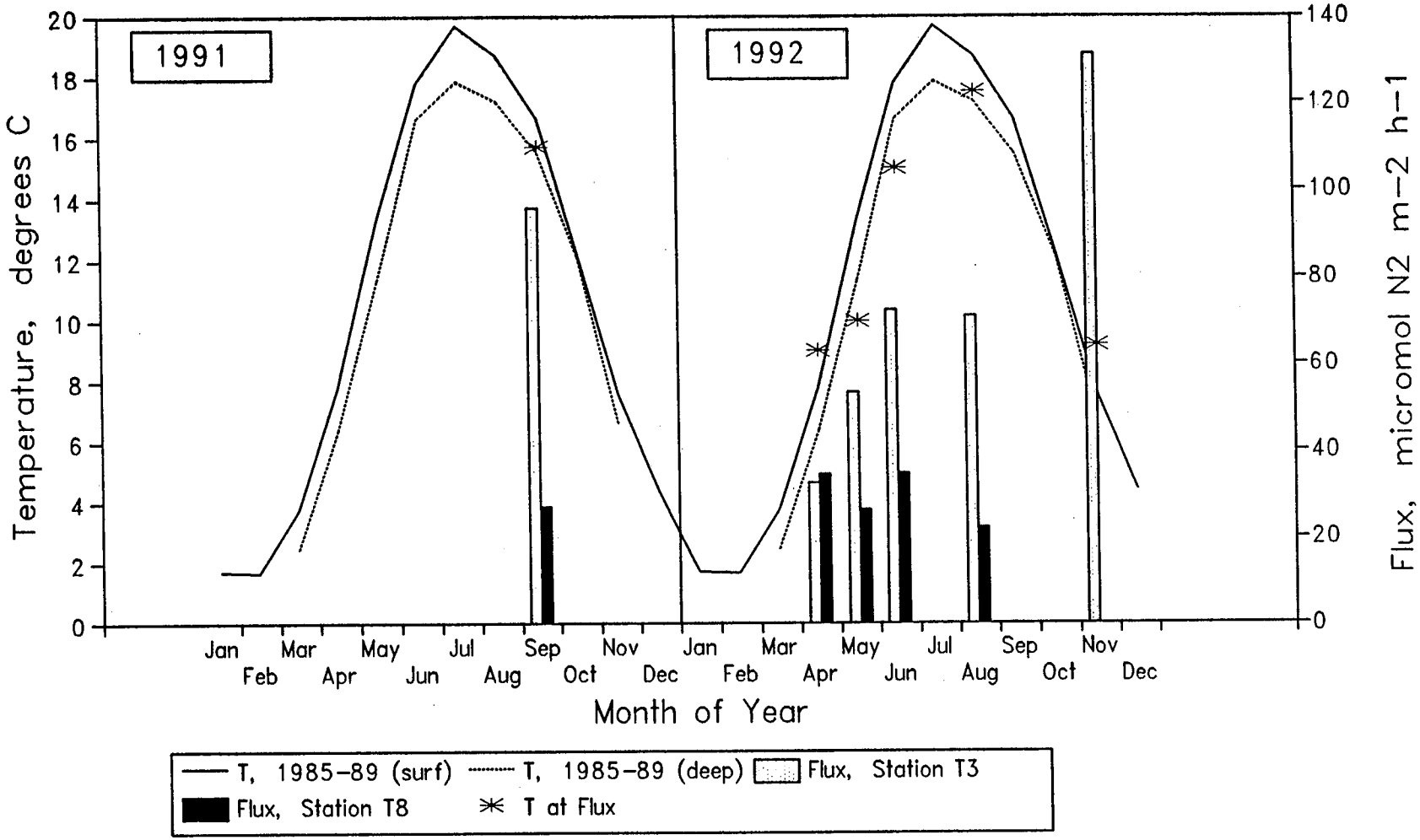

Figure 2. Denitrification at T3 and T8 in Boston Harbor (1991-92).
Fluxes are means of replicates and incubations at a station.
Annual temperature cycle is based on compilation of surface and deep measurements provided by K. Keay (MWRA)

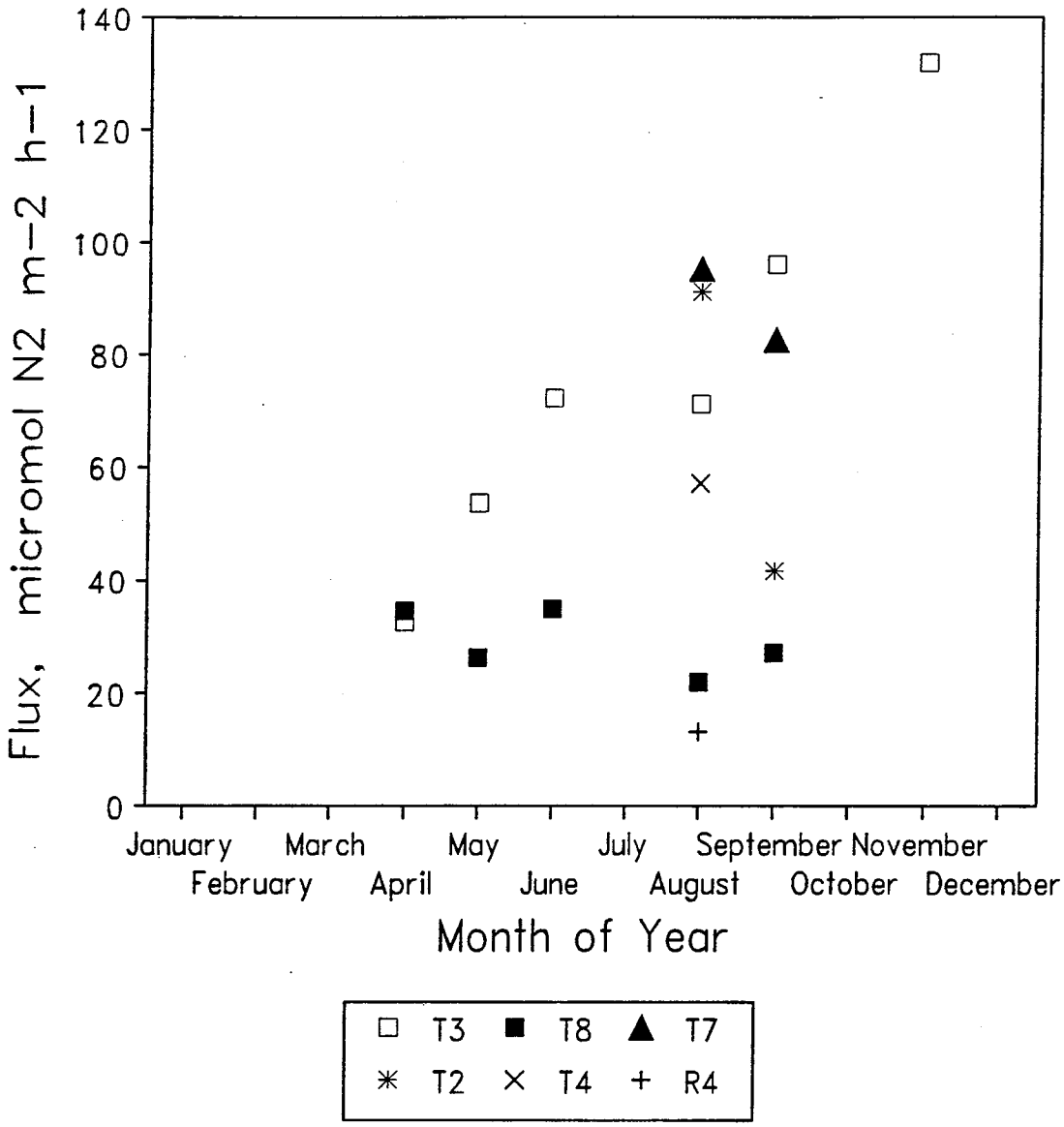

Figure 3. Denitrification in Boston Harbor by Station (Mean) and Month (1991-92).
Note that September is 1991 data, others are 1992 data.

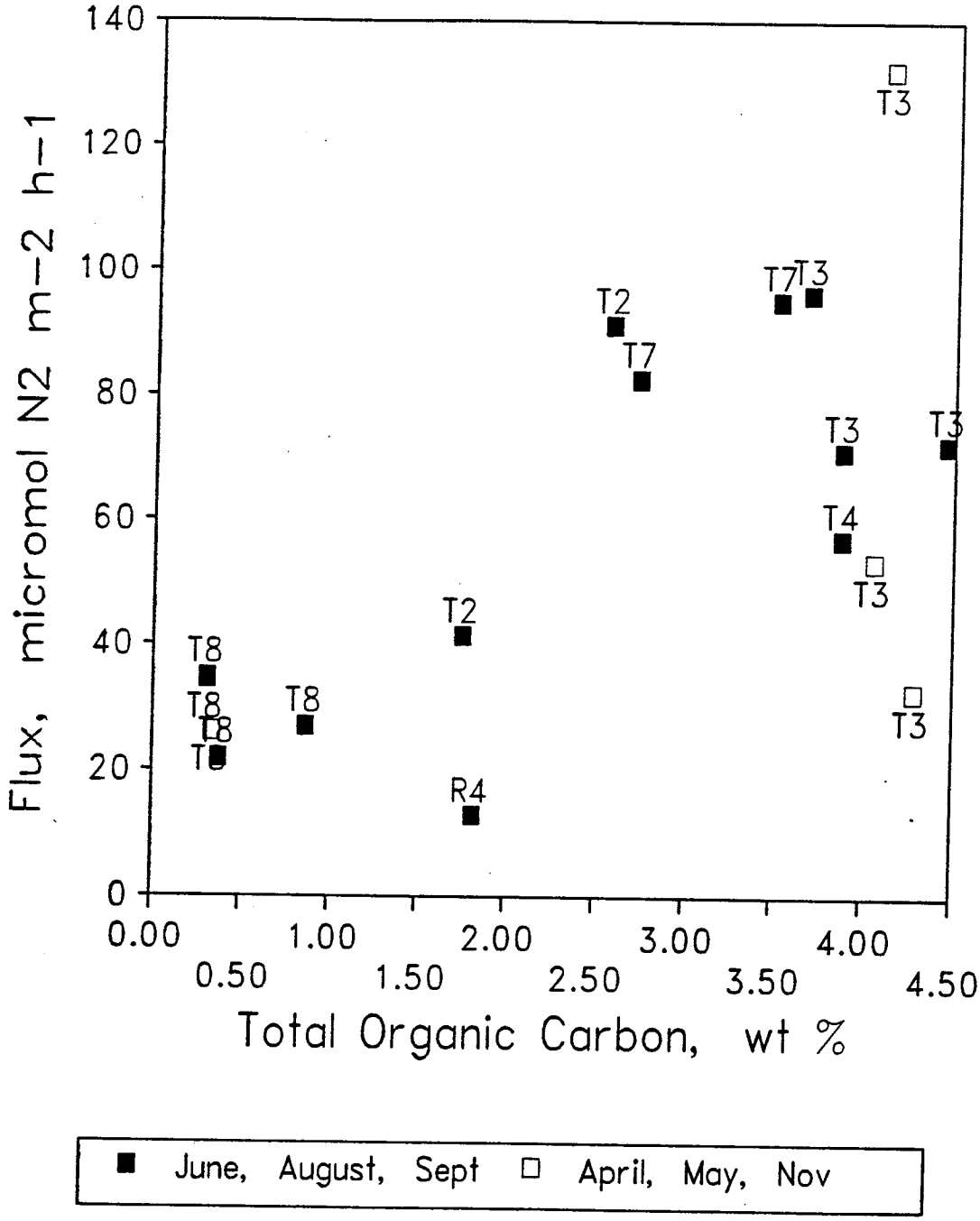

Figure 4. Sediment Denitrification and Total Organic Carbon in Boston Harbor.
Fluxes are means at a station and September 1991 data from Kelly and Nowicki (1992) are included. The TOC data are from Giblin *et al.* (1993) and Kelly and Nowcki (1992).

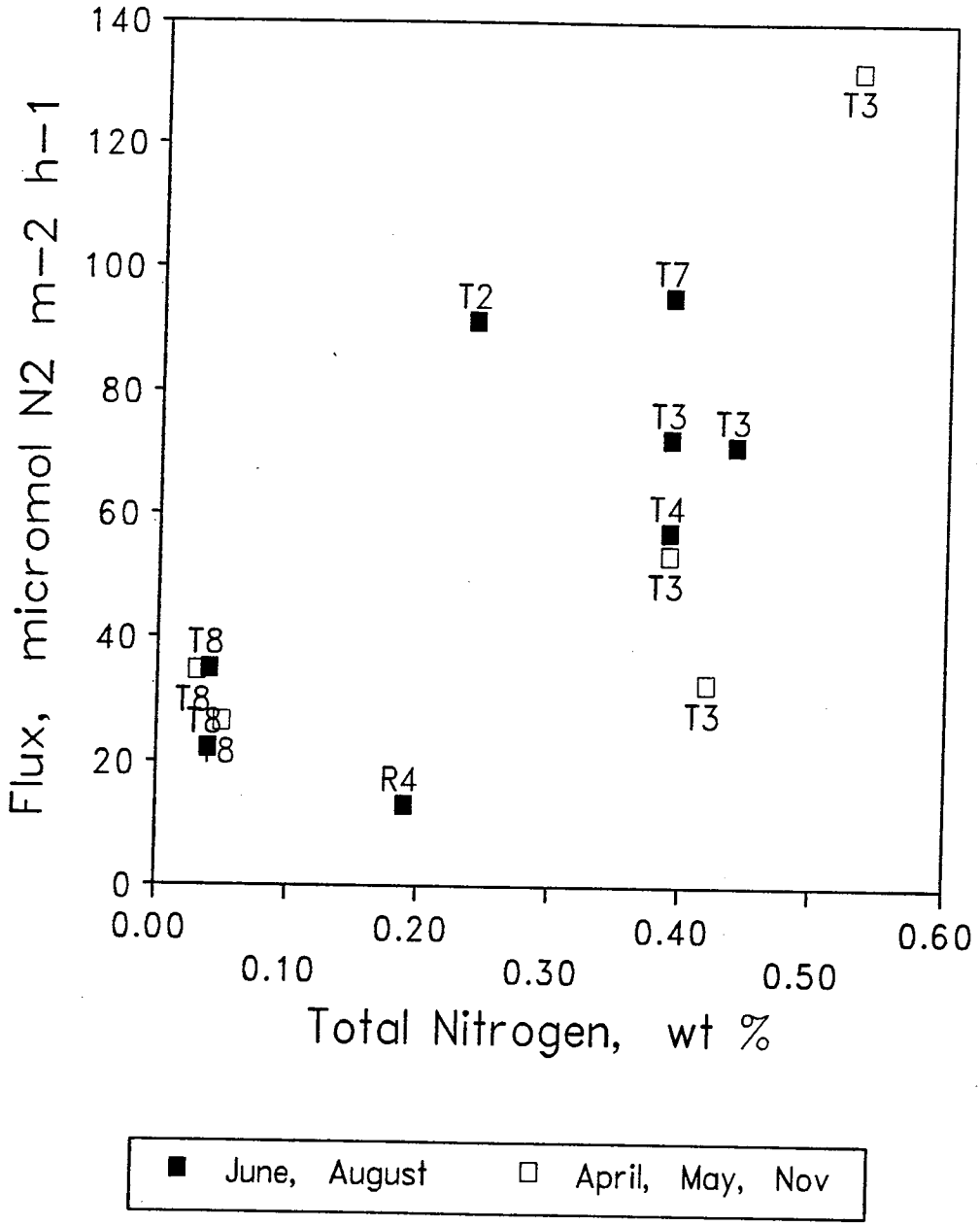

Figure 5. Sediment Denitrification and Total Nitrogen in Boston Harbor.
Fluxes are means at a station. TN data are from Giblin *et al.* (1993).

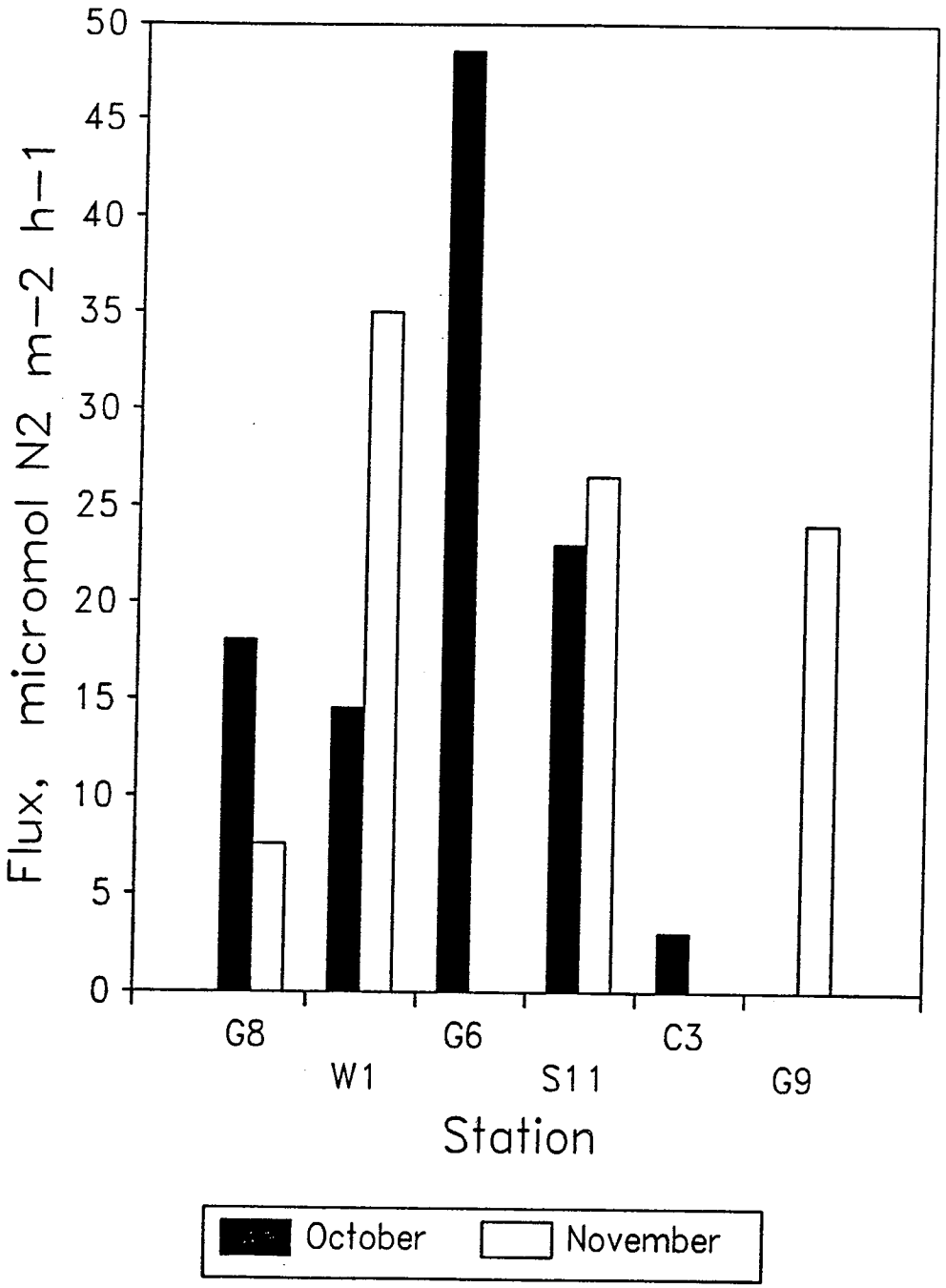

Figure 6. Denitrification in Massachusetts Bay by Station (Mean) and Month (1992).

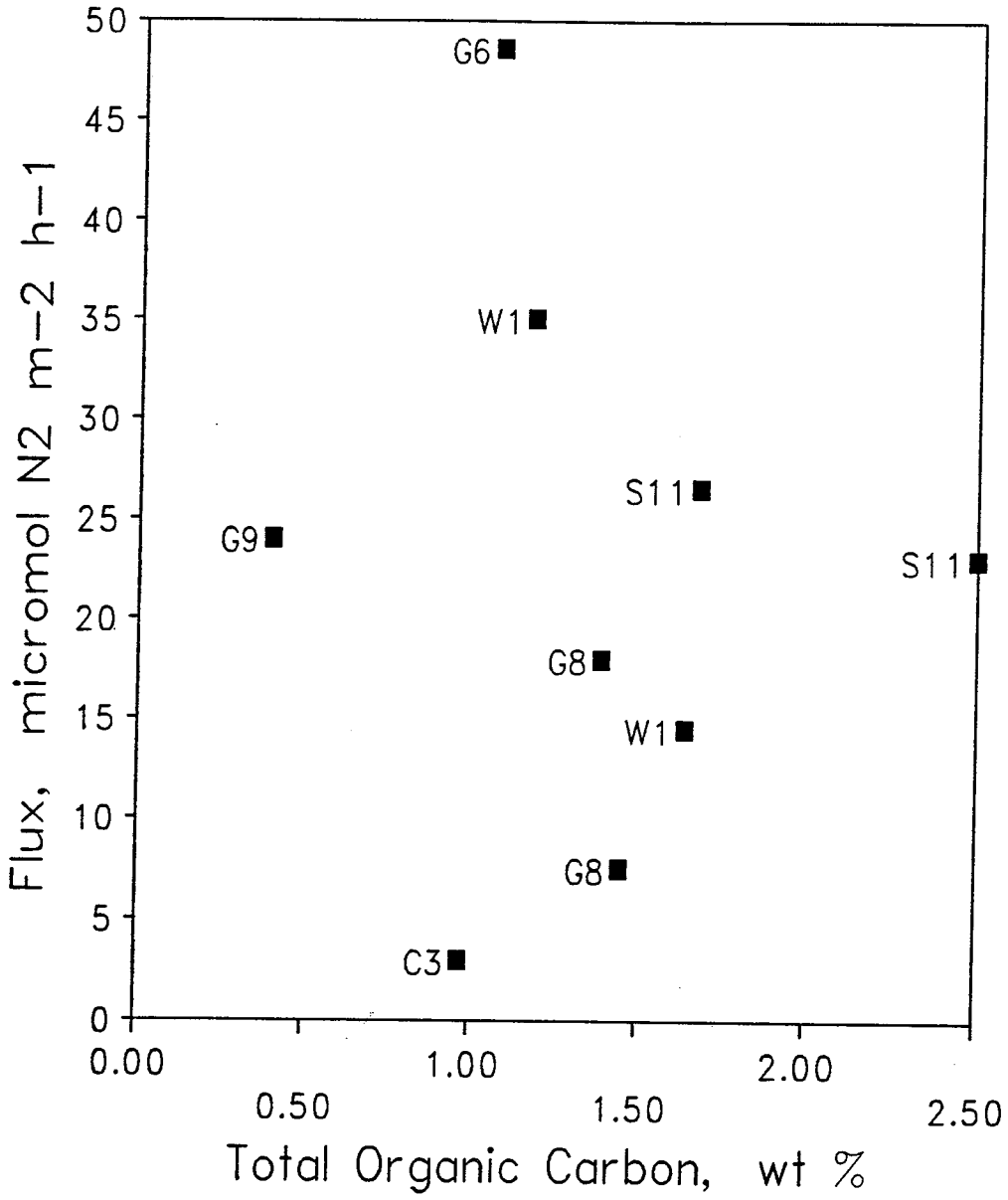

Figure 7. Sediment Denitrification and Total Organic Carbon in Massachusetts Bay.
Fluxes are means at a station.

The Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Charlestown, MA 02129
(617) 242-6000