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Sediment Oxygen Demand and Nitrogen Flux in Massachusetts Bay

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SEDIMENT OXYGEN DEMAND AND NITROGEN FLUX IN MASSACHUSETTS BAY

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EXECUTIVE SUMMARY

We sampled eight stations along a transect from Boston's Outer Harbor through Broad Sound, to the proposed location for the new sewage outfall in Massachusetts Bay. Sediment cores were brought back to the laboratory and the rate of oxygen uptake and nitrogen release were measured.

The benthic fluxes in Boston Outer Harbor are similar to those reported from other areas receiving nutrient inputs from sewage or other sources. Within the Outer Harbor we observed a two-fold difference in rates with the highest rates observed in depositional areas consisting of fine sulfidic muds.

All the stations we sampled in Massachusetts Bay had similar rates and were characterized by low benthic fluxes. On average, the rates of benthic respiration in the Massachusetts Bay were four times lower than rates measured in the Outer Harbor. Rates of nitrogen release in the Massachusetts Bay were nearly ten times lower than those measured in the Outer Harbor.

The two stations samples in Broad Sound were very different. Station 5 in Broad Sound had benthic fluxes more than twice as high as the other four stations in Broad Sound and Massachusetts Bay. We conclude that this area is strongly influenced by the Deer Island treatment plant. This is consistent with the findings of the REMOTS (SAIC 1987) survey. In contrast, Station 4 was characterized by a low benthic respiration rate and an extremely low rate of nitrogen release. This station has fluxes which are more similar to what we observed in Massachusetts Bay.

All stations in the Outer Harbor and Station 5 in Broad Sound took up nitrate from the overlying water. This would indicate that some nitrogen is being removed via denitrification. However, the ratio of oxygen taken up to the amount of nitrogen released (O/N) suggests that these stations do not lose much of nitrogen mineralized within the sediments to denitrification. Therefore, the importance of these sediments as sites of

denitrification probably depends upon nitrate concentrations in the overlying water.

In contrast, sites in Massachusetts Bay, and Station 4 in Broad Sound, were characterized by significant nitrate fluxes out of the sediments and higher O/N ratios. This would suggest that "coupled nitrification/denitrification" is important at these sites and that a significant portion of the nitrogen release by decomposition is lost as N_2.

INTRODUCTION

Sediments of coastal environments play an important role in the recycling of nutrients and in the decomposition of organic matter. In shallow water environments frequently half of the nitrogen needed to support primary production comes from nitrogen which has been recycled back to the water column from the breakdown of organic matter deposited to the sediments. Therefore, in order to understand the magnitude and the timing of primary production it is important to understand how benthic mineralization of nitrogen varies among coastal ecosystems. However, although sediments serve as a source of recycled N to the water column at the system level they also act as a nitrogen sink via the process of denitrification. During denitrification, nitrate is converted to N_2 and thereby lost from the ecosystem. The amount of nitrogen which is lost by denitrification 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 to nutrient regeneration and denitrification.

During organic matter decomposition in sediments there is considerable oxygen uptake from the overlying water frequently resulting in critically low oxygen concentrations. Even occasional anoxic or hypoxic conditions in bottom waters can cause considerable mortality of benthic infauna and lead to fish kills. Therefore, modelling oxygen dynamics in the bottom water is an important part of evaluating effects of organic matter disposal in coastal waters.

The purpose of this study was to measure oxygen uptake and nitrogen release at a series of stations in Boston Harbor and Massachusetts Bay. These stations included locations near the current Deer Island sewage outfall, as well as stations further offshore in Massachusetts Bay where the new Boston metropolitan sewage outfall will be located. This information will provide site-specific values that can be compared to parameters currently being used in models of nitrogen cycling and sediment oxygen demand in Massachusetts Bay.

STATION DESIGN

Station Location

Eight stations were chosen for study (Fig. 1; Table 1). Three of these stations (Stations 1, 2 and 3) are located within the Outer Harbor. Previous REMOTS data (SAIC, 1990) indicated that they are characterized by reducing conditions in the sediments, and low abundances of benthic animals. This suggested that the areas chosen are currently heavily impacted by the Deer Island sewage outfall. Two stations (Stations 4 & 5) are located in Broad Sound. Highly reduced sediments are present is some areas of Broad Sound. Previous investigators have suggested that the presence of these reducing sediments indicates that some material from the Deer Island outfall is being deposited in areas of Broad sound. There is no evidence that the other three stations (Sta. 6, 7, and 8) receive material from the present outfall at Deer Island but these stations may receive nutrients and organic matter from the new outfall in Massachusetts Bay.

Stations 1-6 were chosen using information provided by the August 1987 and the summer 1989 REMOTS survey performed by SAIC for MWRA (SAIC, 1990). The REMOTS survey indicated that the stations varied in sediment types, depth to the RPD layer, and in the Organism-Sediment Indices (see SAIC, 1990 for details). Stations 7 and 8 were chosen using information on bottom types provided by Bothner et al. (1990).

Station Descriptions:

Boston Harbor Stations (Figure 2)

Station 1 is the closest to the Deer Island Sewage Outfall. The actual location sampled is close to REMOTS Station 63 (SAIC, 1990). Station 1 turned out to be a good contrast to the other stations in the harbor. The divers reported that this station had a high percentage of epibenthic animal life (numerous shrimp and crabs). The bottom consisted of shells and cobbles over a layer of fine sand (1-2 cm deep); below the sand, the sediment was black/brown silty/mud. Some of the cobbles were colonized by barnacles. Infauna were visible in the sediment.

Station 2 is near REMOTS Station 58 (SAIC, 1990). The sediment at this station consist of a fine black sulfidic mud. Infauna were not apparent.

Station 3 is located near REMOTS station 32. This sediment also consisted of a black sulfidic mud. In one core some gastropods and a shrimp were present. No large infauna were present.

Broad Sound Stations (Fig. 3)

Station 4 is located just to the west of the August 1987 Massachusetts Bay REMOTS survey. This station was chosen to be at the edge of an area which the REMOTS survey found to contain reducing sediments. We used a grab from the surface to identify suitable sediments. The coordinates for the REMOTS station yielded small rocks. Moving to the north we encountered attached algae on rocks. The location we chose consisted of silty sand with obvious sand ripples, which was difficult to core. The divers landed on a boulder field and found silt several meters away. The sediments in this area are very patchy.

Station 5 corresponds to REMOTS Station 12 in the August 1987 survey. It is located between the A and B stations sampled by Blake et al. (1987). This area was chosen because REMOTS data indicated areas of reducing sediments with low abundances of benthic animals. Based on the REMOTS survey it appeared that some sewage material from Boston Harbor could be reaching this area. These sediments were quite compacted and difficult to core.

Massachusetts Bay (Fig. 3)

Station 6 was chosen to be representative of the low kinetic area (LKA) that Rhodes identified as being a likely depositional area for material from the proposed outfall in Massachusetts Bay (Battelle/SAIC, 1987). This area also appears to be very patchy. Sites to both the north and south were characterized by rocks and cobbles and it took four attempts to find an area of soft sediment. Our sampling here confirmed the previous findings that silt clay facies are located in topographic depressions in this area. Bottom sediments change with differences of only 1-2 meters depths with cobbles present on slight topographic highs. The area sampled consisted of soft sediments which appeared to be heavily reworked by benthic animals. Numerous burrows were evident. Divers noted approximately 5-10 large burrows (1-2 cm dia.) per 1/4 m^2.

Station 7 was chosen to represent a sandy area near the proposed outfall. The station has been identified by the side scan survey of Bothner et al. (1990) as a likely depositional area for material from the new outfall. This area is also quite patchy with the grab retrieving coarse sand, shell and cobbles near by. Sediments from this station contained a fairly high sand content. Infauna were abundant.

Station 8 is a muddy depositional area previously characterized by Bothner et al. 1990. These sediments contained a good infaunal community including large polychaetes.

METHODS

Sampling

Stations 1-6 were all sampled by SCUBA divers between September 7 and 10, 1990. At each station, four replicate sediment cores were taken. At stations 2, 3, 4, and 5 large 15-cm diameter core tubes were used. At station 1 the sediment was too coarse to drive large diameter core tubes into the sediment so smaller, 6.5 cm diameter core tubes were used. Because the smaller diameter core tubes were faster to insert into the bottom we also used them at Station 6 where water depth limited diver time.

Stations 7 and 8 were sampled by a large box core on Oct. 9, 1990. The box core was subcored with 6.5 cm (diameter) core tubes on deck. In order to assess the variability between box cores, two box cores were taken at station 8 and four subcores from each box were removed.

Bottom water temperature at all stations was determined by measuring the water overlying the cores as soon as the cores were brought on board.

Benthic Respiration and Nutrient Fluxes

Cores were transported to Woods Hole and placed in a dark incubator where they were held close to in situ temperatures (which ranged from 12-20 °C; Table 1, 2). The cores were uncapped and held overnight. The flux measurements were begun the next morning. Before making the flux measurements the overlying water of each core was replaced with 0.22 micron filtered seawater. The seawater was obtained from the seawater system of the Marine Biological Laboratory and is typical of the water of Buzzards Bay. Salinity is $32^{\circ}/_{\infty}$, and nutrient concentrations are low, with typical values being: ammonium 1-2 μM, nitrate <2 μM, and phosphate <0.5 μM. The replacement water was held in the same incubator as the sediment cores and was at the same temperature.

After the water had been replaced the cores were sealed and the measurements of benthic flux rates were begun (Table 2). The core tubes were machined to allow them to be sealed with a plexiglass top that was equipped with a magnetic stirrer (Dornblaser et al. 1989). This stirrer gently mixed the water column without resuspending the sediment. We monitored the concentration of oxygen and dissolved inorganic nitrogen species (DIN) in the overlying water throughout an 11-41 hr incubation period (Table 2). Oxygen concentration was measured with a dissolved oxygen meter (Orbisphere 2112 meter) and probe which fit into an opening in the core lid. Incubation duration (see Table 2), was determined by the time required to lower oxygen concentration at least 3 ppm. Oxygen concentration in the overlying water was not allowed to drop lower than 2-4 ppm as benthic animal respiration rates can be affected (for effects of low oxygen concentrations on animal respiration rates see Bishop 1952, for example). At least five samples were taken at regular intervals throughout the incubation period. The benthic respiration rate was calculated as the slope of regression of oxygen concentration versus time. Taking measurements at least five times for each core allowed us to check that 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. At the same time water was removed from the overlying water, replacement water was added through a second syringe. The replacement water was the same water used to replace the water over the sediment. A sample of the replacement water was taken for nutrient analysis at several times throughout the incubation. Water samples were held in the syringes and processed within one hour. Ammonium concentration was determined for duplicate 3-ml sub-samples by the technique of Solorzano (1969) modified for a small sample size. A 2 ml sample was saved for phosphate (see Appendix) and acidified to pH 2 with HCl. The remaining water in the syringe was transferred to clean vials and frozen for later measurement of the nitrate and nitrite concentration. Nitrate + nitrite were determined together using the cadmium reduction method (EPA) on a rapid flow analyzer (Alpkem RFA-300); the limit of detection was $0.2\mu M$. Previous work suggested that the contribution of nitrite to the dissolve 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 + nitrite.

RESULTS AND DISCUSSION

Replication and Accuracy of Flux Measurements

Table 2 shows the details of the incubation procedure. At stations 1 and 7 we obtained only two replicate flux measurements. We had to eliminate two of the four cores from site 1 because of leakage. The sediments contained rocks on the surface and some cobbles at depth making a good seal difficult. Only two sub-cores could be obtained from the box core taken at Station 7. The sand was highly disturbed on one half of the box core.

We obtained four replicates from the rest of the stations. However, we discarded one replicate from station 5 because the oxygen fluxes were not linear over time. Oxygen flux measurements made over short time periods (hrs to a few days) should be linear with time. Several problems can cause fluxes to become non-linear: disturbance of the sediment surface during sampling, leaking or draining of porewater from the bottom of the core, forcing overlying water into the sediment by improper capping, or inadequate and irregular stirring during the incubation. In all of the rest of our incubations the oxygen fluxes were linear (Table 3). The r^2s of the regressions for the oxygen fluxes were always above 0.92 and usually above 0.97.

The r^2s for DIN fluxes are generally good, although not usually as high as those for oxygen (Table 3). For six of the stations r^2s ranged from 0.84 to 1.00. Fluxes at stations 4 and 5 were not as good, and in some cases not linear with time. The low correlation coefficients at station 4 are due to the very low magnitude of the fluxes. At station 4 at least half of the total flux was nitrate and the combined DIN flux averaged less than 200 μmol m^{-2} d^{-1}. We believe that these low, and possibly non-linear fluxes with time may be due to flushing of porewater out of the sediments by bottom currents or storm surges. The presence of bottom ripples at this site indicate that this can be a high energy environment. Porewater nutrients may have recently been flushed out of the sediments, accounting for the low and irregular fluxes. We do not have a simple explanation for the behavior of DIN at station 5. The first three time points indicated a fairly low but linear DIN flux (Table 4). During this time period there was a fairly high nitrate uptake by the cores. After the third time point ammonium fluxes increased four fold (Table 4). This was observed in all three cores. Oxygen uptake throughout this time period was linear which would indicate that problems with sampling or leaking were not responsible for the change in rate. One possibility is that denitrification in this core was very sensitive to changes in the oxygen and/or nitrate concentrations in the overlying waters. After the third time point, nitrate uptake decreased substantially while the ammonium flux increased. If a rate is taken through either time points 1,2,3 or 3,4,5 the fluxes are linear, but a very different rate is obtained. We have chosen to use the combined flux (Table 5; Figs 5,6) but present the data for the shorter time periods (Table 4) so that others can perform their own analysis if they see fit.

Because ammonium in the water column can become nitrified, the r^2s for ammonium or nitrate fluxes alone are sometimes lower than for the total DIN flux (Table 3). At all stations, except 4 and 5 as previously discussed, we observed good r^2 values for ammonium. For the most part, stations which showed nitrate uptake had lower r^2s than those which showed nitrate efflux. This is to be expected because nitrate uptake is very sensitive to changes in the concentration of both nitrate and oxygen in the overlying water. It should be noted that we incubated these cores with filtered seawater of fairly low (all $<3\mu$M) nitrate concentrations. If nitrate concentrations in the outer harbor and Broad Sound are much higher than the concentrations we used to incubate the cores we may have underestimated the importance of nitrate uptake by these stations.

Oxygen Uptake

The average oxygen uptake by sediments from the eight stations ranged from under 10 to over 50 mmol $O_2/m^2/d$ (Fig. 4; Table 5). The highest rates were observed at the two muddy stations in the outer harbor (Sta. 2 and 3). Station 1 in the outer harbor had much lower rates when compared to the other two outer harbor stations. Station 1 was very rocky and had a much lower organic content than the other two harbor stations.

Average oxygen uptake for all stations in Massachusetts Bay were low and very similar ranging from 7.9 to 9.8 mmol $O_2\ m^{-2}\ d^{-1}$. The average oxygen uptake of four cores from two separate box cores (8A and 8B) was nearly identical.

The two sites sampled in Broad Sound were quite different from each other. Station 4 was located on the edge of an area which REMOTS data indicated may receive some influence from sewage. However, in order to find an area soft enough to core we had to move further north and west of the area identified as impacted by the REMOTS survey. This area was very patchy. The divers actually landed on a boulder field and had to swim 5 meters from the buoy to find softer sediments. The area sampled had sand ripples visible on the bottom indicating that this may be a high energy environment. Oxygen fluxes at this site were fairly low and not very different from those we measured in Massachusetts Bay. In contrast, Station 5 had very high fluxes. Although they were lower than the highest outer harbor stations, it is important to keep in mind that these fluxes were measured at 12°C while the outer harbor fluxes were measured at 20°C.

DIN Release

There was a much greater difference in DIN fluxes between stations than there was in oxygen fluxes with fluxes ranging from less than 200 to over 7,000 μmol m^{-2} d^{-1} (Fig. 5; Table 5). Station 2 and 3 in the outer harbor had the highest DIN fluxes. Station 1 also had a high flux averaging around 4,000 μmol m^{-2} d^{-1}.

The average DIN flux from all the stations in Massachusetts Bay were quite similar, averaging just under 1,000 μmol m^{-2} d^{-1}. Again we saw a close correspondence between values taken from the two separate box cores at Station 8.

The large difference between Stations 4 and 5 in Broad Sound is even more pronounced for the DIN flux than it was for the oxygen flux. Station 4 had the lowest oxygen flux of any station we sampled while values at Station 5 are as high as we observed in the outer harbor, even though the incubation temperature was lower.

When the DIN flux is broken down into ammonium and nitrate flux there were some striking differences between the stations (Fig. 6). All of the stations in the harbor consumed nitrate while all the stations in Massachusetts Bay showed a flux of nitrate out of the sediments. Nitrate accounted for 12-37% of the total DIN release from sediments in Mass Bay. In Broad Sound one station consumed nitrate while exhibiting a large ammonium flux while the other station released small quantities of both nitrate and ammonium. All stations released ammonium.

O/N Flux Ratios

One way to compare fluxes across stations is to examine the ratio of oxygen uptake to nitrogen release (Fig. 7; Table 5). This ratio is expressed as the O/N (atom/atom) ratio of the fluxes and is useful in inferring the possible importance of denitrification. When fresh phytoplankton material (C:N of about 7 atom/atom) is being decomposed completely to

CO_2 and ammonium an O/N ratio of 13.25 is expected, and when nitrate is produced a ratio of 17 is expected. When the ratio is substantially greater than 13-17 it may indicate that inorganic nitrogen is being lost by denitrification. This ratio needs to be interpreted cautiously. The ratio frequently varies over an annual cycle. The O/N ratio may change seasonally if carbon mineralization lags behind nitrogen mineralization or due to the seasonal storage or oxidation of reduced compounds.

All the sites in the Harbor show O/N ratios very close to 13.25 which is close to or below that expected from decomposition of algae. This indicates that very little of the nitrogen mineralized within the sediments is denitrified. In many sediments the dominant mode of denitrification is through coupled nitrification/denitrification. In order for this process to be important, ammonium released by mineralization must be converted to nitrate in the oxic portions of the sediment. Some of this nitrate diffuses into anoxic portions of the sediments where it can subsequently be denitrified. We believe this is not an important mechanism for denitrification in these sediments. These sediments are highly reduced and have fairly low rates of bioturbation. As a result, most of the mineralized nitrogen is lost as ammonium, and not converted to nitrate. These sediments did show an uptake of nitrate from the water column, indicating that denitrification of nitrate present in the water column is occurring in the sediments.

All the Mass Bay stations show O/N which are above 13.25 and for the most part above 20. These stations also show a nitrate flux from the sediments. The O/N values indicate that approximately half of the nitrogen mineralized by decomposition is not being released from the sediments as DIN. This is consistent with the data of Seitzinger (1988) who found that 15-70 % of the N mineralized is lost as N_2 via denitrification. The flux of nitrate from the sediments indicates that they are oxidized near the surface and allow ammonium to become nitrified.

Both of the Broad Sound stations show an O/N above 13.25, although the ratio at station 5 is only slightly above 17. In contrast Station 4 has a ratio above 150 indicating a large deficit of nitrogen. We have previously observed very high O/N ratios in sediments subjected to porewater flushing during storm events (Hopkinson, 1987).

Comparison to Other Systems

Oxygen uptake and DIN release along the transect indicates that stations in Massachusetts Bay fall on the low side of values reported for other coastal and estuarine systems (Table 6; Figure 8). The oxygen uptake values we obtained were just a little higher than values from Buzzards Bay obtained in December, when the water temperature in Buzzards Bay was colder (Banta et al. 1990; Table 6).

Oxygen uptake and DIN release at Stations 2 and 3 in Boston Harbor are higher than values reported for most "natural" systems such as Buzzards Bay but similar to other systems receiving substantial inputs of nutrients or sewage such as the Patuxet Estuary and the upper areas of Narragansett Bay and the Neuse River (Table 6). The much lower values obtained at Station 1 in the Harbor may indicate that this is not a depositional area for material from the outfall.

The data from Broad Sound are consistent with the REMOTS survey data which suggested that Station 5 currently receives substantial amounts of sewage inputs from Boston Harbor. This station is behaving similarly to stations in the Harbor and fluxes are similar to other system receiving nutrient inputs (Table 6). The oxygen uptake and DIN release rates at Station 4 were quite similar to those we obtained out in Massachusetts Bay. This would suggest that sewage inputs to Station 4 are much lower than at Station 5. We suspect that Station 4 was not in a depositional area for material from the Harbor.

SUMMARY AND CONCLUSIONS

1) There is a great variety of sediment types in Massachusetts Bay and Broad Sound and the distribution is very patchy. In general, we found similar sediment types in the general area identified by the previous REMOTS surveys (1987 and 1990). However, Loran C navigation may not be accurate enough to assure that a station of a specific sediment type can be revisited.

2) The benthic fluxes in Boston Outer Harbor are similar to those reported from other areas receiving nutrient inputs from sewage or other sources. Within the Outer Harbor we observed a two-fold difference in rates with the highest rates observed in depositional areas consisting of fine sulfidic muds.

3) All the stations we sampled in Massachusetts Bay had similar rates and were characterized by low benthic fluxes.

4) Station 5 in Broad Sound had benthic fluxes more than twice as high as the other four stations in Broad Sound or Massachusetts Bay. We conclude that this area is strongly influenced by the Deer Island treatment plant.

5) Denitrification appears to be occurring at most stations but different mechanisms are important. In the Outer Harbor and at Station 5, nitrate is being removed from the overlying water and presumably being lost as N_2 through denitrification. It is likely that the importance of this mechanism changes as the nitrate concentration of the overlying water changes. We did not evaluate how important this process could be in-situ because cores were not incubated with ambient nitrate concentrations.

In contrast, at Station 4 and in all the stations in Massachusetts Bay we saw nitrate efflux from the sediments. This observation, coupled with the fairly high O/N ratios we measured, suggests that a substantial amount of the nitrogen mineralized within the sediments could be lost as N_2.

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

Site	Depth[1] (feet)	Temp (°C)	Coordinates Latitude	Coordinates Longitude	Date Sampled	Bottom Type
1	55	19	42 20.37	70 58.26	9/7/90	sm rocks over silty mud
2	28	20	42 21.34	70 58.63	9/7/90	very soft black mud
3	42	20	42 20.29	70 59.58	9/10/90	very soft black mud
4	54	14	42 22.89	71 55.09	9/10/90	hard silt/sand, ripples
5	78	12	42 22.96	70 53.20	9/7/90	hard, fine sand & mud
6	96	13	42 24.84	70 52.72	9/10/90	soft clay and mud
7	102	12	42 22.87	70 49.42	10/9/90	mud, fine sand
8A	102	12	42 23.55	71 49.95	10/9/90	mud
8B	102	12	42 23.55	71 49.95	10/9/90	mud

[1] Depth - depth at stations 1-6 is given by depth recorded by the diver's depth gauges. These always agreed within 1-2' with the depth sounder on the Servasa (TG&B). The depths for stations 7 and 8 were taken from the depth sounder on the Asterias (WHOI). The reading varied 5-10'.

Table 2. Details of the incubation protocol for each station.

Station	Incubation Temp (°C)	# Cores	Core Dia. (cm)	Incubation Duration (hr.)
1	18	2	6.5	28
2	21	4	15.0	11
3	21	4	15.0	13
4	12	4	15.0	65
5	12	3	15.0	25
6	12	4	6.5	70
7	12	2	6.5	41
8A	12	4	6.5	41
8B	12	4	6.5	23-41

Table 3. Information on the oxygen, ammonium, nitrate, DIN, and O/N fluxes for each core. Flux is calculated from the slope of 4-6 time points. The regression correlation coefficient (r^2) for each slope is shown. Negative fluxes indicate uptake by the sediments.

		O_2 Flux		NH_4 Flux		NO_3 Flux		DIN Flux		
Site	Core	mmol/m^2/d	r^2	µmol/m^2/d	r^2	µmol/m^2/d	r^2	µmol/m^2/d	r^2	O/N
1	A	-16.93	0.99	3047.0	0.98	-293.9	0.64	2753.8	0.97	12.30
1	D	-20.04	0.92	5419.3	0.98	115.2	0.25	5534.5	0.98	7.24
2	12	-49.87	0.98	8378.6	0.98	-688.0	0.50	7690.6	0.94	12.97
2	2	-42.22	0.98	8141.2	0.99	-1766.4	0.66	6374.8	0.92	13.25
2	3	-47.20	0.98	7241.6	0.96	-647.6	0.97	6593.9	0.95	14.32
2	4	-64.35	0.97	9493.0	0.93	-860.8	0.80	8632.2	0.90	14.91
3	0	-45.08	1.00	7440.5	1.00	-10.6	0.03	7429.9	1.00	12.13
3	6	-48.37	1.00	7942.8	1.00	-84.5	0.78	7858.3	1.00	12.31
3	7	-39.17	0.99	6622.0	0.99	-12.7	0.12	6609.3	0.99	11.85
3	B2	-43.74	1.00	8380.7	0.99	-78.3	0.45	8302.4	1.00	10.54
4	22B	-15.30	0.98	293.0	0.74	60.6	0.77	353.6	0.75	86.54
4	23B	-9.60	0.95	57.3	0.44	70.6	0.84	127.9	0.65	150.12
4	33A	-10.00	0.99	-19.1	0.05	89.1	0.86	69.9	0.26	286.12
4	M7	-9.50	0.98	58.4	0.12	117.5	0.94	175.9	0.48	108.02
5	14	-29.27	0.98	4964.4	0.85	-367.0	0.78	4597.3	0.84	12.73
5	B3	-31.09	0.93	3518.4	0.82	-56.6	0.18	3461.8	0.80	17.96
5	B5	-36.30	0.99	3965.9	0.89	-634.6	0.61	3331.3	0.79	21.79
6	E	-8.63	0.97	836.5	0.97	8.5	0.09	845.0	0.97	20.43
6	F	-9.83	0.99	538.8	0.92	165.5	0.98	704.3	0.96	27.91
6	G	-11.60	0.97	457.8	0.91	250.8	0.98	708.7	0.95	32.74
6	H	-9.13	0.95	579.7	0.96	150.6	0.95	730.4	0.97	25.00
7	B	-9.25	0.98	1879.3	0.99	197.0	0.96	2076.0	0.99	8.91
7	C	-6.46	0.95	416.2	0.80	85.3	0.84	501.5	0.84	25.76
8A	F	-8.94	0.98	474.6	0.88	148.3	0.99	622.8	0.92	28.71
8A	G	-8.84	0.98	716.8	0.92	121.3	0.94	838.1	0.95	21.10
8A	H	-9.64	0.98	817.4	0.94	26.6	0.24	843.8	0.96	22.85
8A	J	-10.32	0.97	789.6	0.98	194.6	0.95	984.1	0.99	20.97
8B	A	-9.49	0.98	380.0	0.94	178.7	0.99	558.7	0.98	33.97
8B	D	-9.59	0.99	525.3	1.00	186.4	0.99	711.8	1.00	26.95
8B	E	-8.55	0.96	442.9	0.79	157.2	0.97	600.0	0.86	28.50
8B	I	-9.79	0.98	388.9	0.94	118.7	0.90	507.5	0.94	38.58

Table 4. Nitrogen Fluxes for Station 5 broken down into first 3 and last 3 time points. Fluxes are in μmol/m^2/d.

		NH_4		NO_3		DIN	
Time	Core	Flux	r^2	Flux	r^2	Flux	r^2
	14	2204.3	0.999	-200.4	0.347	2003.9	0.971
0-16h	B3	2138.2	0.995	-180.5	0.850	1957.7	0.998
	B5	2343.3	0.998	-1101.6	0.708	1241.8	0.809
Mean ± se		2228.6± 60.44		-494.2± 303.8		1734.5± 246.7	
	14	11035.0	0.995	-492.4	0.897	10542.0	0.993
16-25h	B3	7596.2	0.865	215.0	0.655	7811.2	0.859
	B5	7890.2	0.973	-53.6	0.448	7836.6	0.971
Mean ± se		8840.5± 1100.5		-110.3± 206.2		8729.9± 906.1	

Table 5. Averages and Standard Errors (S.E.) of the O_2, NH_4^+, NO_3^-, and dissolved inorganic nitrogen (DIN) fluxes by station. Average O/N ratios are also shown. Oxygen fluxes are in mmol/m^2/d, all other fluxes are in μmol/m^2/d.

Site	O_2	S.E.	NH_4^+	S.E.	NO_3^-	S.E.	DIN	S.E.	O/N	S.E.
1	-18.48	1.56	4233.15	1186.15	-89.35	204.55	4144.15	1390.35	9.77	2.53
2	-50.91	4.75	8313.60	463.15	-990.70	262.67	7322.88	522.80	13.86	0.45
3	-44.09	1.91	7596.50	377.37	-46.52	20.18	7549.98	360.61	11.71	0.40
4	-11.10	1.40	97.40	67.68	84.45	12.50	181.82	61.22	157.70	44.80
5	-32.22	2.11	4149.57	427.41	-352.73	167.01	3796.80	402.00	17.48	3.33
6	-9.80	0.65	603.20	81.79	143.85	50.22	747.10	33.13	26.52	2.58
7	-7.86	1.39	1147.75	731.55	141.15	55.85	1288.75	787.25	17.34	8.43
8A	-9.44	0.34	699.60	77.94	122.70	35.43	822.20	74.55	23.41	1.82
8B	-9.36	0.28	434.27	33.37	160.25	15.17	594.49	43.44	32.00	2.66

Table 6a Summary of studies on benthic respiration and DIN flux measurements in Buzzards Bay (A) and other systems.

CODE	Site	Months	Temperature °C	Benthic Respiration mmoles O_2 m^{-2} d^{-1}	Nitrogen Flux (ΣDIN) mmoles N m^{-2} d^{-1}	O/N Ratio
	A)					
	Buzzards Bay, MA[1]	Jan - Nov	2-16	11.1-44.9	0.29-3.00	28-46
	Buzzards Bay, MA[2]	Aug	--	58.90	--	--
	Eel Pond, MA[1]	July	20	33.60	2.04	32
	B)					
NB	Narragansett Bay, RI[3]	Jan - Dec	0-24	7.5-112.5	0-9.6	27-33
	Long Island Sound, CT[4]	Mar - Nov	4-22	--	-1.0-8.0	--
NY	New York Bight, NY[5]	Aug	--	26.4	0.60	87
PE	Patuxent Estuary, MD[6]	June - Aug	--	94.8	17.04	26
SE	South River Estuary, NC[7]	Jan - Dec	1-25	19.8-75.6	0-6.55	31
NR	Neuse River Estuary, NC[7]	Jan - Dec	1-25	19.6-51.8	0-11.05	13.5
GB	Georgia Bight, GA[8]	July	28	90.6	4.20	22
	La Jolla, CA[9]	June - Aug	11-24	--	0.96	--
KB	Kaneohe Bay, HI[10]	Jan - Dec	--	14.4	1.3	20
LE	Lock Ewe Estuary, Scotland[11]	June - July	6-13	19.2-37.2	0.48-1.92	55
VB	Vostock Bay, USSR[12]	Aug	--	33.6	3.60	19
	Maizura Bay, Japan[13]	July	18-30	--	0.31-0.77	--

Studies:

1. Rowe et al. 1975
3. Nixon et al. 1976
5. Rowe et al. 1976
7. Fisher et al. 1982
9. Hartwig 1975
11. Davies 1975
13. Yoshida and Kimata 1969

2. Smith et al. 1973
4. Aller and Benninger 1981
6. Kemp and Boynton 1979
8. Hopkinson and Wetzel 1982
10. Smith 1978
12. Propp et al. 1980

Table 6b More recent measurements of benthic respiration and DIN flux in Buzzards Bay (Banta et al. 1990)

Station	Temp. °C	O_2 Uptake mmol/m^2/d	DIN flux µmol/m^2/d	O/N
Weepecket				
August 1989	21	23	4,000	13
May 1989	11	22	600	78
Dec 1988	7	6	1,400	9
Station 7				
August 1989	21	28	4,800	12

Note: The Weepecket station is located near Woods Hole in 55′ of water. Station 7 is located in 35′ of water near New Bedford Harbor and receives inputs from the New Bedford sewage treatment plant.

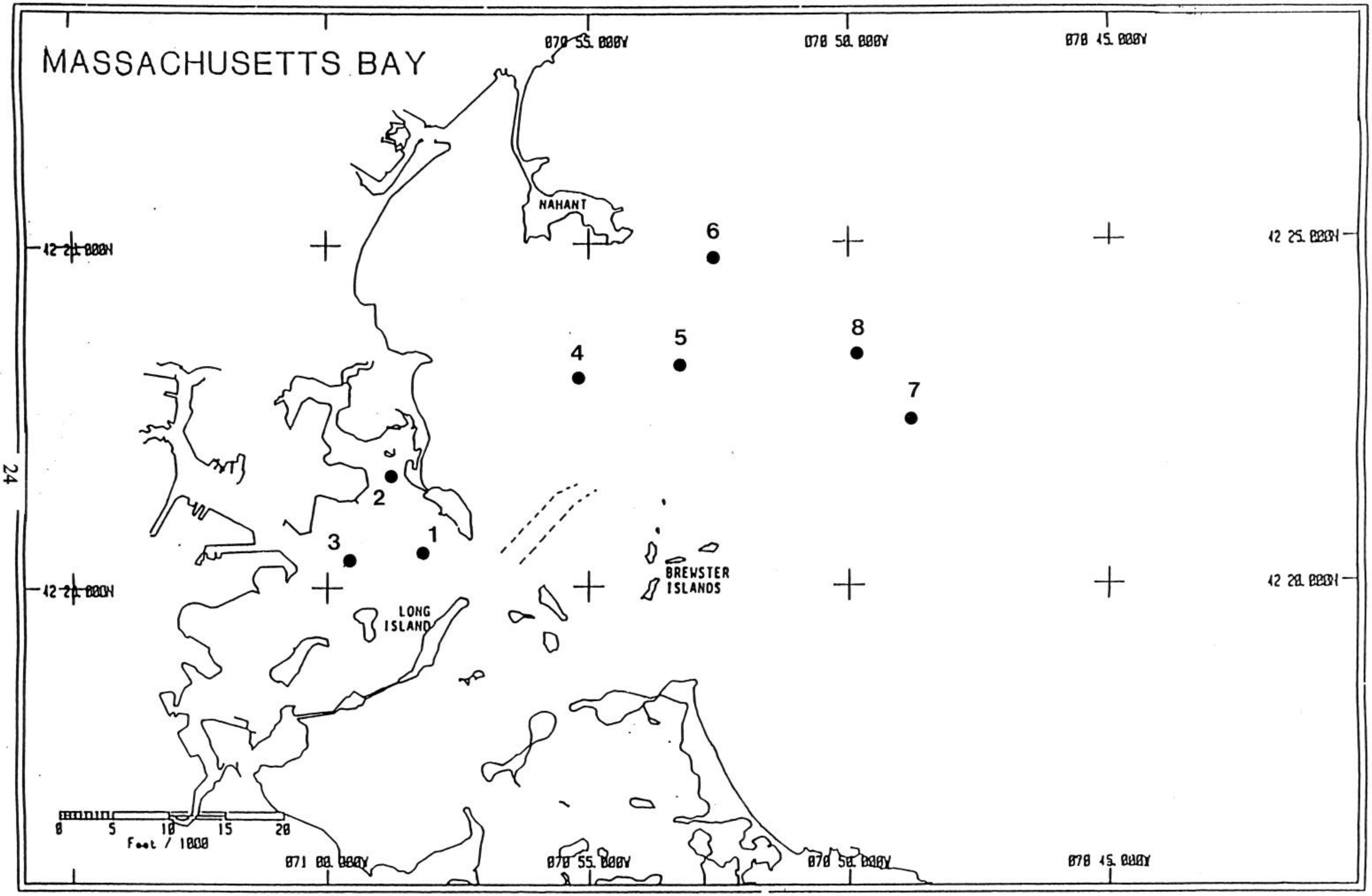

Figure 1. Location of the eight stations sampled in this survey.

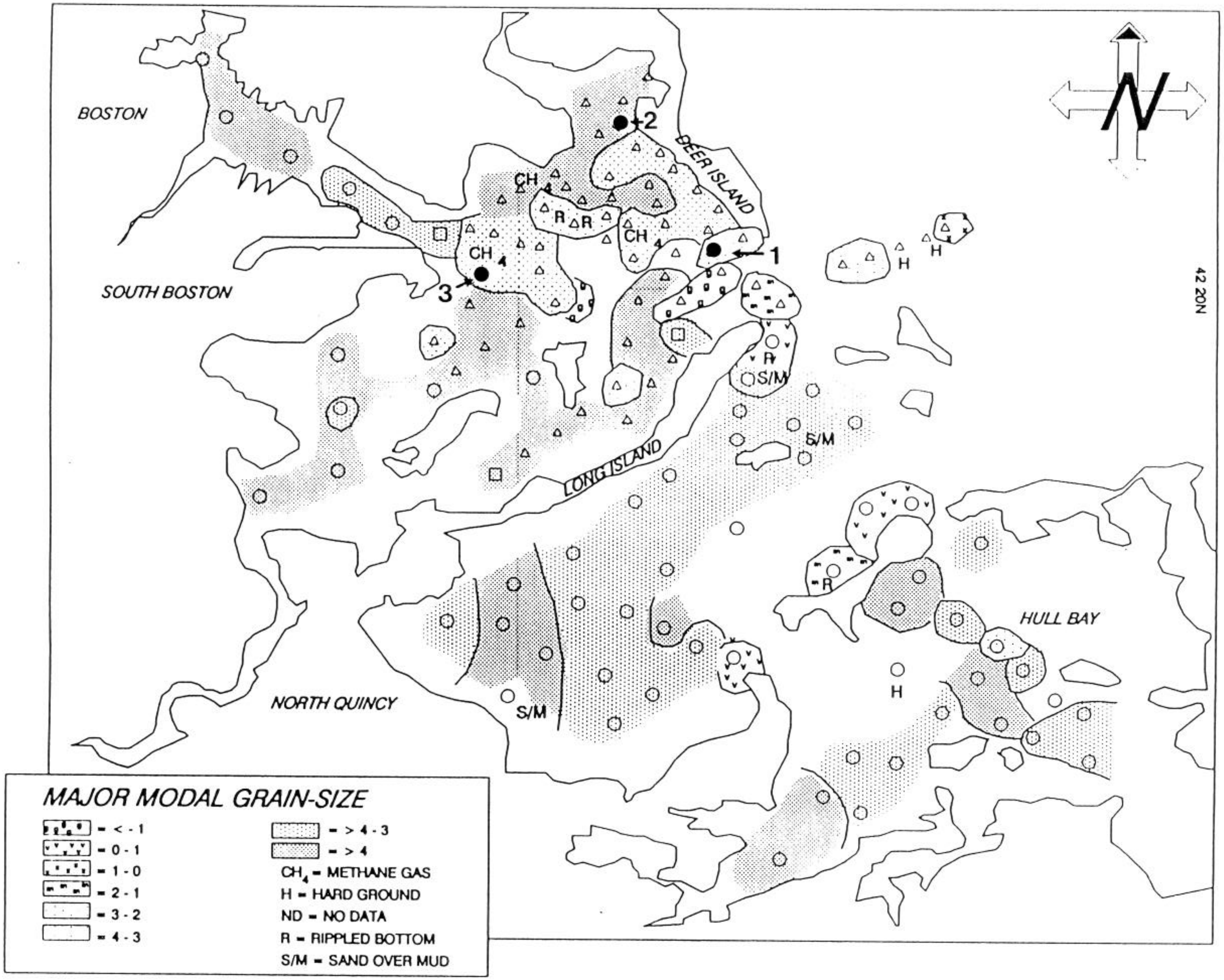

Figure 2. Location of the three stations sampled in Boston Harbor in relationship to sediment types identified using REMOTS.

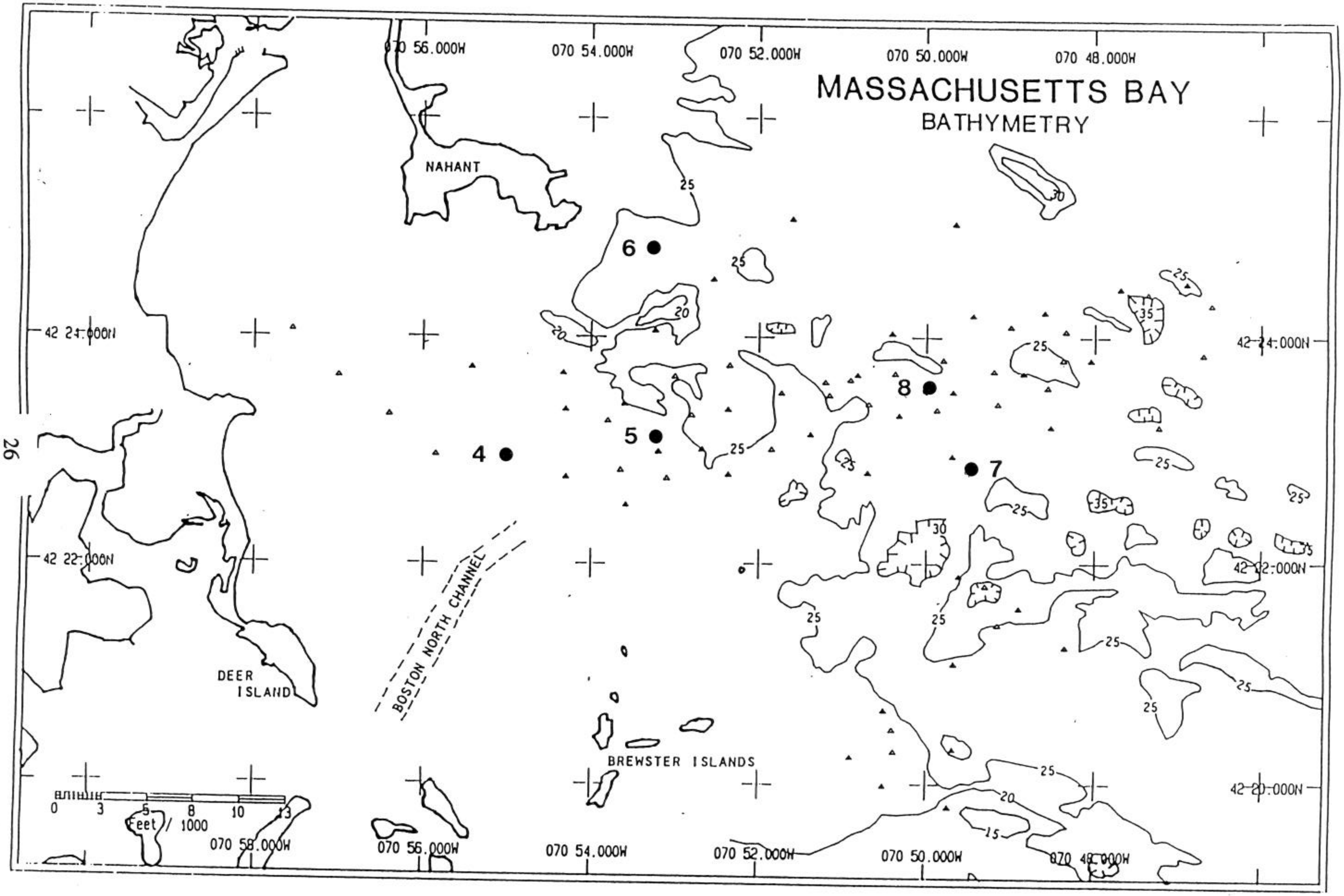

Figure 3. Location of the five stations sampled in Broad Sound and Massachusetts Bay in relationship to those sampled in the 1987 REMOTS survey.

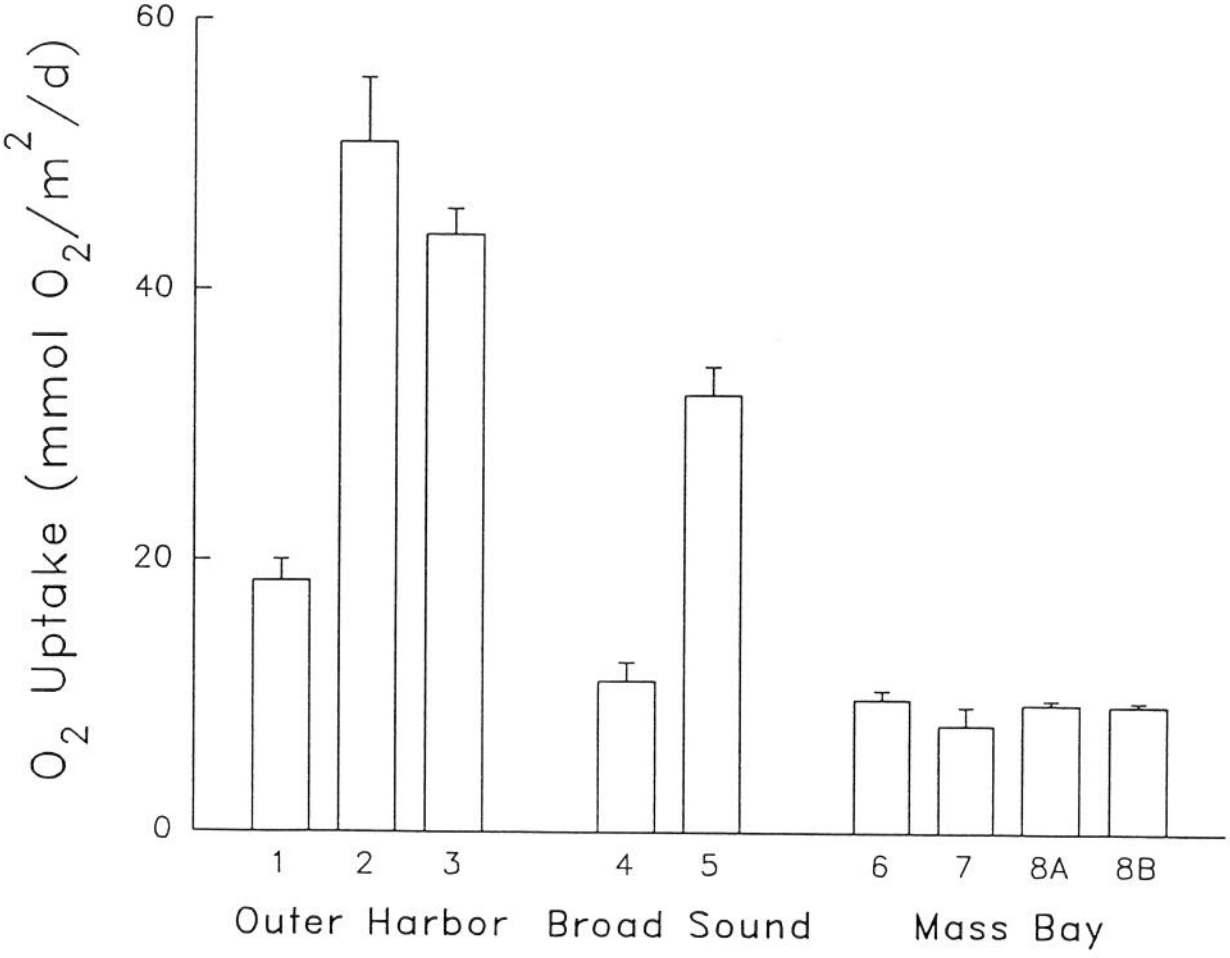

Figure 4. Oxygen uptake (Mean ± S.E.) of sediments from the eight stations sampled.

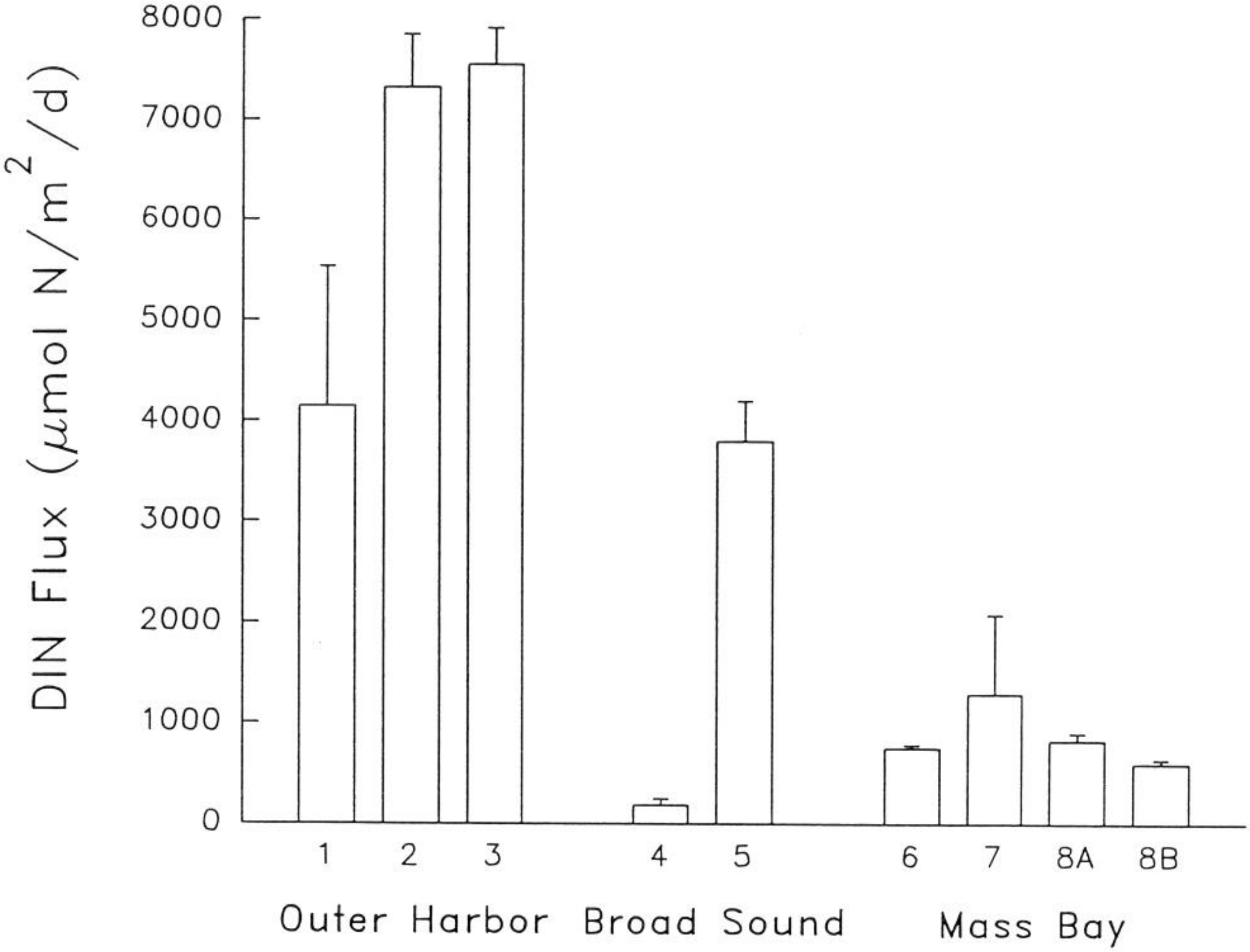

Figure 5. DIN release (Mean± S.E.) of sediments from the eight stations sampled.

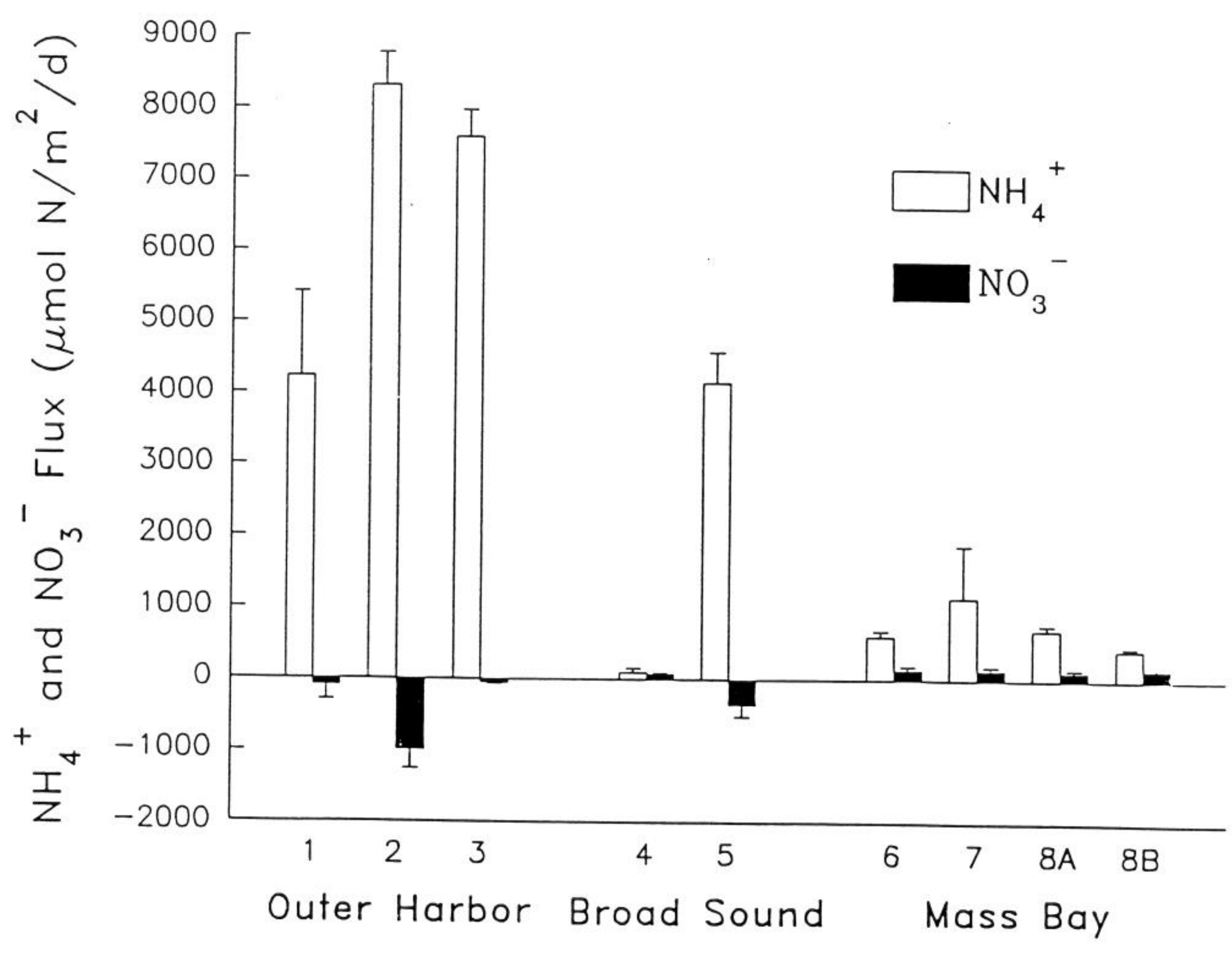

Figure 6. Ammonium and nitrate fluxes (Mean ± S.E.) of sediments from the eight stations sampled. Negative fluxes indicate nitrate uptake by the sediments.

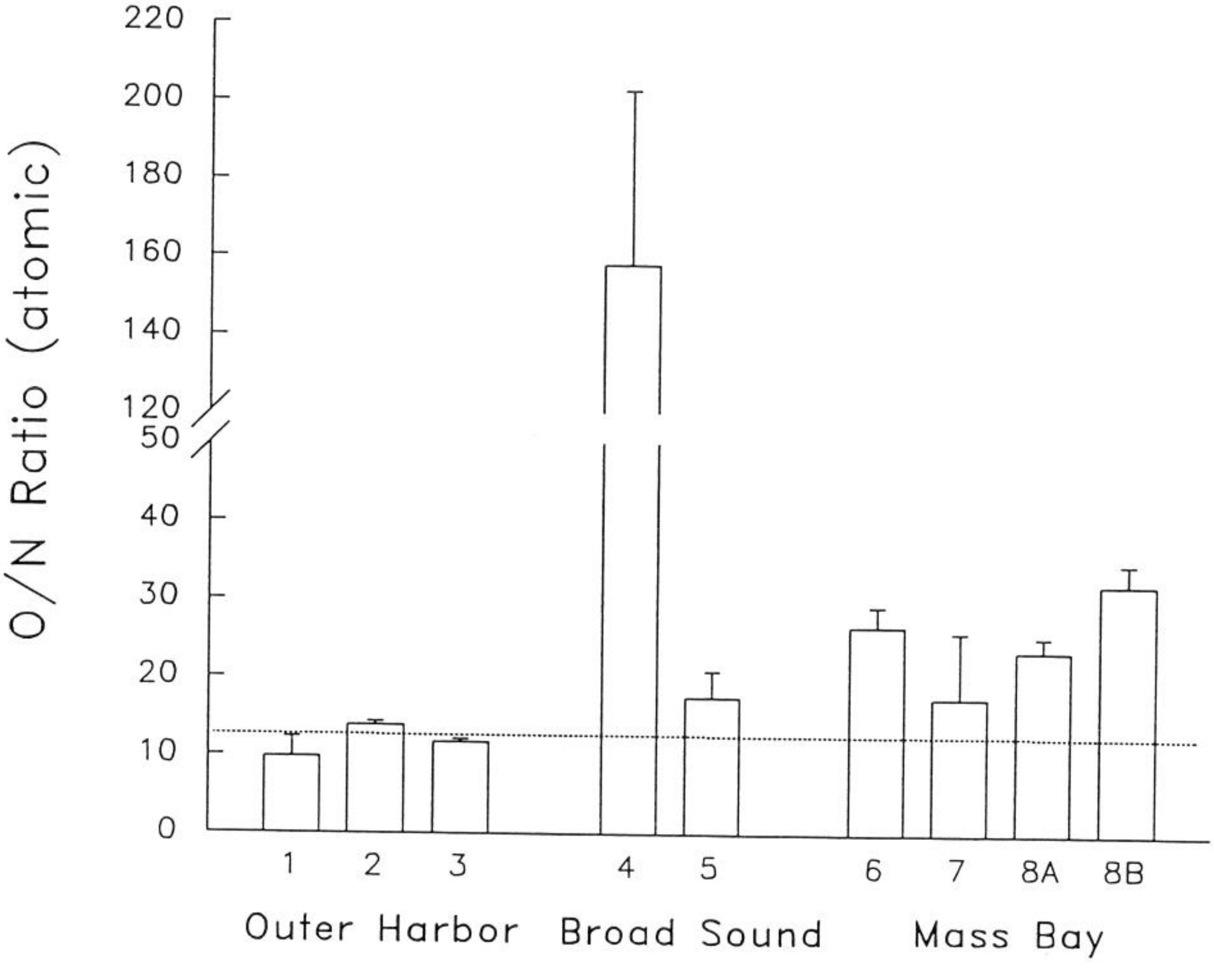

Figure 7. The ratio of oxygen uptake to DIN release (atom/atom) of sediments from the eight stations sampled. The dashed line indicates the ratio to be expected (13.25) from the decomposition of fresh algae to ammonium. (Mean± S.E. of the three ratios are presented to show the variability of the values but should not be used to determine statistical differences in ratios between stations.)

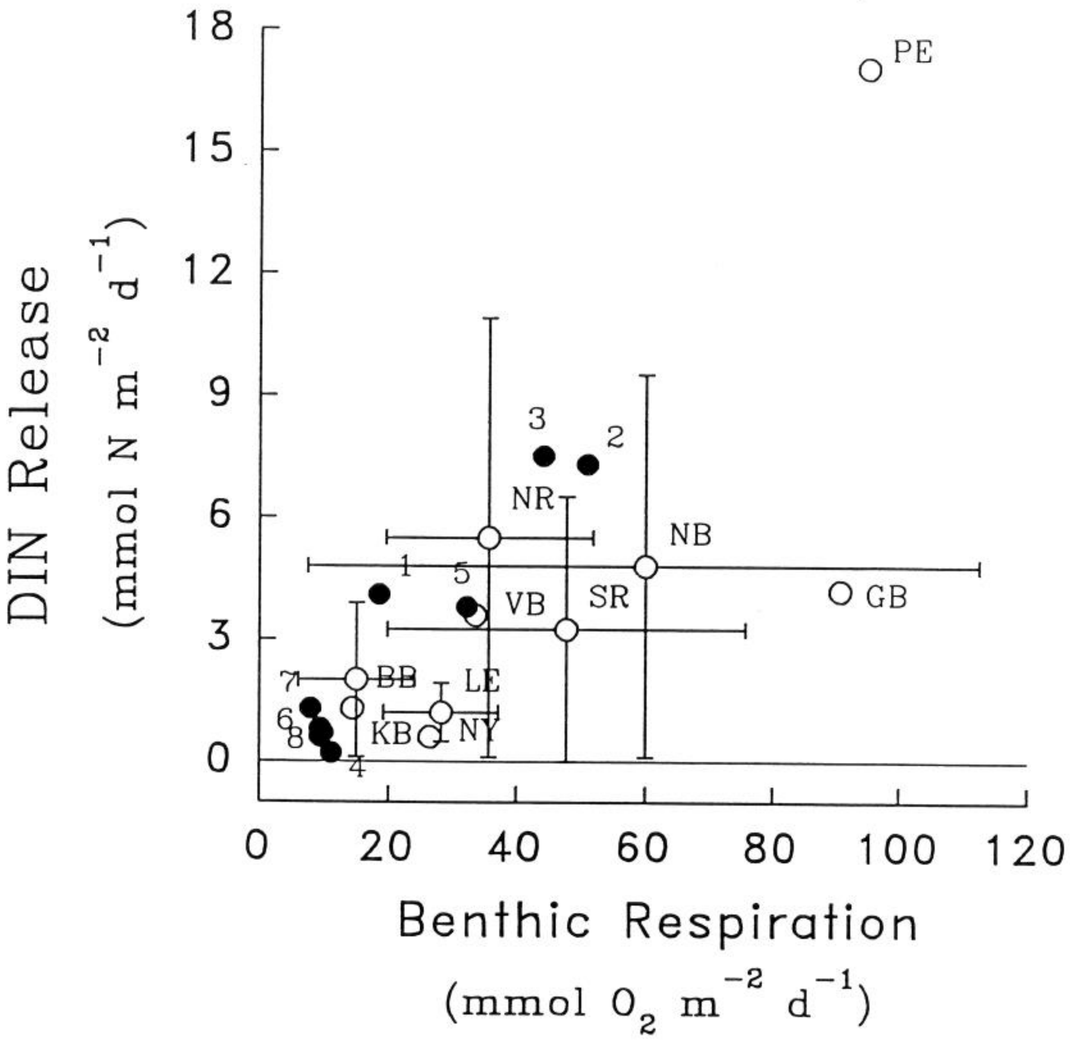

Figure 8. A comparison of the oxygen uptake and the DIN release of sediments from other areas (open symbols) to the sediments we sampled in Boston Outer Harbor, Broad Sound and Massachusetts Bay (closed symbols). The median and range of values from other systems is shown. See Table 6a for an explanation of the codes used to identify the other areas, number indicate Stations locations from this study (see Fig. 1).

PHOSPHATE FLUXES IN MASSACHUSETTS BAY

AN ADDENDUM TO THE REPORT:
SEDIMENT OXYGEN DEMAND AND NITROGEN FLUX
IN MASSACHUSETTS BAY

Report submitted to SAIC
for MWRA

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INTRODUCTION

The purpose of this work was to measure phosphate fluxes in sediments at a series of stations in Boston Outer Harbor and Massachusetts Bay.

METHODS

The flux measurements were made on the same sediments collected for the studies of oxygen and nitrogen fluxes (see Giblin et al. 1991). At the same time samples were taken for nitrogen analysis a sub-sample of 3 ml was saved for phosphate analysis. The sample was preserved with 45 ul of 4.8N HCl and kept at 4°C until analysis. Samples were analyzed using the spectrophotometric method of Murphy & Riley (1962).

RESULTS AND DISCUSSION

Phosphate Fluxes

Phosphate fluxes varied greatly in both magnitude and direction across the 8 stations (Table 1; Fig. 1). The highest fluxes were observed in the Outer Harbor, although there was more than a ten fold difference in the fluxes obtained between the Outer Harbor stations. In all cases the rates were linear over time.

The two Broad Sound stations behaved very differently. Sediments from Station 4 in Broad Sound took up phosphate from the overlying water. This was the only station where we saw a consistent pattern of phosphate uptake. The r^2's of the regressions of phosphate concentration over time ranged from 0.13 to 0.84 indicating that the rates of phosphate uptake were not always linear with time. Station 5 had moderate rates of phosphate releases which were not significantly different from Station

1 in the Outer Harbor, in spite of the lower temperatures in Broad Sound. In general these rates were linear over time.

Stations in Massachusetts Bay had low rates of phosphate release. A single core from Station 7 showed phosphate uptake but all other cores released phosphate to the overlying water. In about a third of the cores the regressions had fairly low r^2's indicating the release of phosphate was not always constant over time.

Even at stations were phosphate flux rates were linear over time we saw a substantial variation between replicate cores. The variation of phosphate flux, as a percentage of the mean, was higher for phosphate than for oxygen or DIN release (Table 2). At most stations the S.E.'s of the Oxygen and DIN flux were less than 10 % of the mean value. In contrast, the S.E.'s of the phosphate flux were seldom below 20% of the mean.

O/P and N/P Ratios

Phosphate uptake and release is strongly determined by adsorption and desorption from the sediments, in addition to mineralization rates. Therefore, the ratio of oxygen uptake to phosphate release ratios may not be simply related to decomposition. An O/P atomic ratio of around 206 would be expected from the decomposition of fresh phytoplankon material if no other processes were important. Phosphate adsorption would increase this ratio. We observed a wide range of O/P ratios. Very low O/P flux ratios were observed from organic rich sediments from the Outer Harbor (Table 2). These ratios would suggest that large amounts of chemically bound phosphate are being released from these sediments at this time of the year. In addition, if much of the organic matter originated from the sewage treatment plant it may be highly enriched in phosphate. Ratios at all other stations were much higher than the Redfield ratio indicating that P adsorption appears to be an important process at nearly all of the stations at this time of the year.

When sediments do not have a large phosphate adsorption capacity the ratio of N/P released from the sediments can be another indicator of denitrification. When denitrification is high the ratio falls below 15. However, the O/P ratios presented above suggest that phosphate fluxes are highly influenced by adsorption and desorption. Two of the Outer Harbor Stations had very low N/P ratios which would normally be assumed to be due to high denitrification rates. However, because these stations also had very low O/P ratios and had O/N values near Redfield values, we feel phosphate desorption, not high denitrification, is lowering the N/P ratio at these stations. Most of the other stations have N/P ratios above 15. The most likely explanation for these high ratios is phosphate adsorption.

CONCLUSIONS

1) Phosphate fluxes were largest in the Outer Harbor and the highest fluxes were observed in the two stations characterized by highly reducing organic rich sediments.

2) Station 5, in Broad Sound, also had moderately high rates of phosphate release when compared to the other stations. This is consistent with the oxygen uptake and DIN release data which showed that this station is more similar to stations in the Outer Harbor than to stations in Massachusetts Bay.

3) O/P ratios deviated greatly from values expected from the Redfield ratio. Two stations in the Outer Harbor had very low ratios suggesting phosphate was being desorbed from the sediments at this time of the year. The other stations all have very high ratios suggesting significant phosphate adsorption.

4) Because it appears that phosphate adsorption and desorption are extremely important in controlling the rate of phosphate release N/P ratios could not be used to assess the importance of dentirification in these sediments.

REFERENCES

Murphy, J. and J.P Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta. 27: 31-36.

Table 1. Information on the oxygen, phosphate, DIN, fluxes for each core. Flux is calculated from the slope of 4-6 time points. The regression correlation coefficient (r^2) for each slope is shown. Negative values indicate uptake by the sediments.
O/P is the ratio of oxygen uptake to phosphate release (atom/atom).
N/P is the ratio of nitrogen release to phosphate release (mol/mol).
No ratio is calculated if the phosphate flux is negative.

		O_2 Flux		PO_4 Flux		DIN Flux		O/P	N/P
Site	Core	mmol/m^2/d	r^2	µmol/m^2/d	r^2	µmol/m^2/d	r^2		
1	A	-16.93	0.99	236	0.94	2753.8	0.97	143.5	11.7
1	D	-20.04	0.92	109	0.98	5534.5	0.98	367.7	50.8
2	12	-49.87	0.98	6331	0.99	7690.6	0.94	15.8	1.2
2	2	-42.22	0.98	6123	0.99	6374.8	0.92	13.8	1.0
2	3	-47.20	0.98	5041	0.99	6593.9	0.95	18.7	1.3
2	4	-64.35	0.97	8250	0.99	8632.2	0.90	15.6	1.0
3	0	-45.08	1.00	2056	0.99	7429.9	1.00	43.8	3.6
3	6	-48.37	1.00	3134	0.99	7858.3	1.00	30.7	2.5
3	7	-39.17	0.99	1695	0.99	6609.3	0.99	46.2	3.9
3	B2	-43.74	1.00	3001	0.99	8302.4	1.00	29.2	2.8
4	22B	-15.30	0.98	-13	0.13	353.6	0.75	-	-
4	23B	-9.60	0.95	-42	0.84	127.9	0.65	-	-
4	33A	-10.00	0.99	-31	0.70	69.9	0.26	-	-
4	M7	-9.50	0.98	-23	0.53	175.9	0.48	-	-
5	14	-29.27	0.98	129	0.92	4597.3	0.84	453.8	35.6
5	B3	-31.09	0.93	126	0.52	3461.8	0.80	493.5	27.5
5	B5	-36.30	0.99	220	0.90	3331.3	0.79	330.0	15.1
6	E	-8.63	0.97	21	0.30	845.0	0.97	821.9	40.2
6	F	-9.83	0.99	28	0.92	704.3	0.96	702.1	25.2
6	G	-11.60	0.97	40	0.64	708.7	0.95	580.0	17.7
6	H	-9.13	0.95	25	0.40	730.4	0.97	730.4	29.2
7	B	-9.25	0.98	73	0.90	2076.0	0.99	253.4	28.4
7	C	-6.46	0.95	-24	0.91	501.5	0.84	-	-
8A	F	-8.94	0.98	26	0.54	622.8	0.92	688.4	24.0
8A	G	-8.84	0.98	36	0.86	838.1	0.95	491.1	23.3
8A	H	-9.64	0.98	54	0.87	843.8	0.96	357.0	15.6
8A	J	-10.32	0.97	71	0.95	984.1	0.99	290.7	13.9
8B	A	-9.49	0.98	14	2 pts	558.7	0.98	1355.7	39.9
8B	D	-9.59	0.99	4	0.14	711.8	1.00	4795.0	178.0
8B	E	-8.55	0.96	45	0.98	600.0	0.86	380.0	13.3
8B	I	-9.79	0.98	15	0.85	507.5	0.94	1305.3	33.8

Table 2. Averages and Standard Errors (S.E.) of the O_2, phosphate and (DIN) fluxes by station. Average O/P and N/P atomic ratios are also shown. Oxygen fluxes are in mmol/m^2/d, all other fluxes are in μmol/m^2/d. Negative fluxes indicate uptake by the sediments. O/P and N/P ratios could not be calculated for Station 4 because P fluxes were negative.

Site	O_2	S.E.	PO_4^{-3}	S.E.	DIN	S.E.	O/P	N/P
1	-18.48	1.56	123	114	4144.15	1390.35	256	31.3
2	-50.91	4.75	6436	667	7322.88	522.80	16	1.1
3	-44.09	1.91	2472	353	7549.98	360.61	38	3.2
4	-11.10	1.40	-20	9	181.82	61.22	-	-
5	-32.22	2.11	92	36	3796.80	402.00	425	26.1
6	-9.80	0.65	29	4	747.10	33.13	709	11.6
7	-7.86	1.39	25	49	1288.75	787.25	>253	>28
8A	-9.44	0.34	47	10	822.20	74.55	457	19.2
8B	-9.36	0.28	20	9	594.49	43.44	1959	66.3

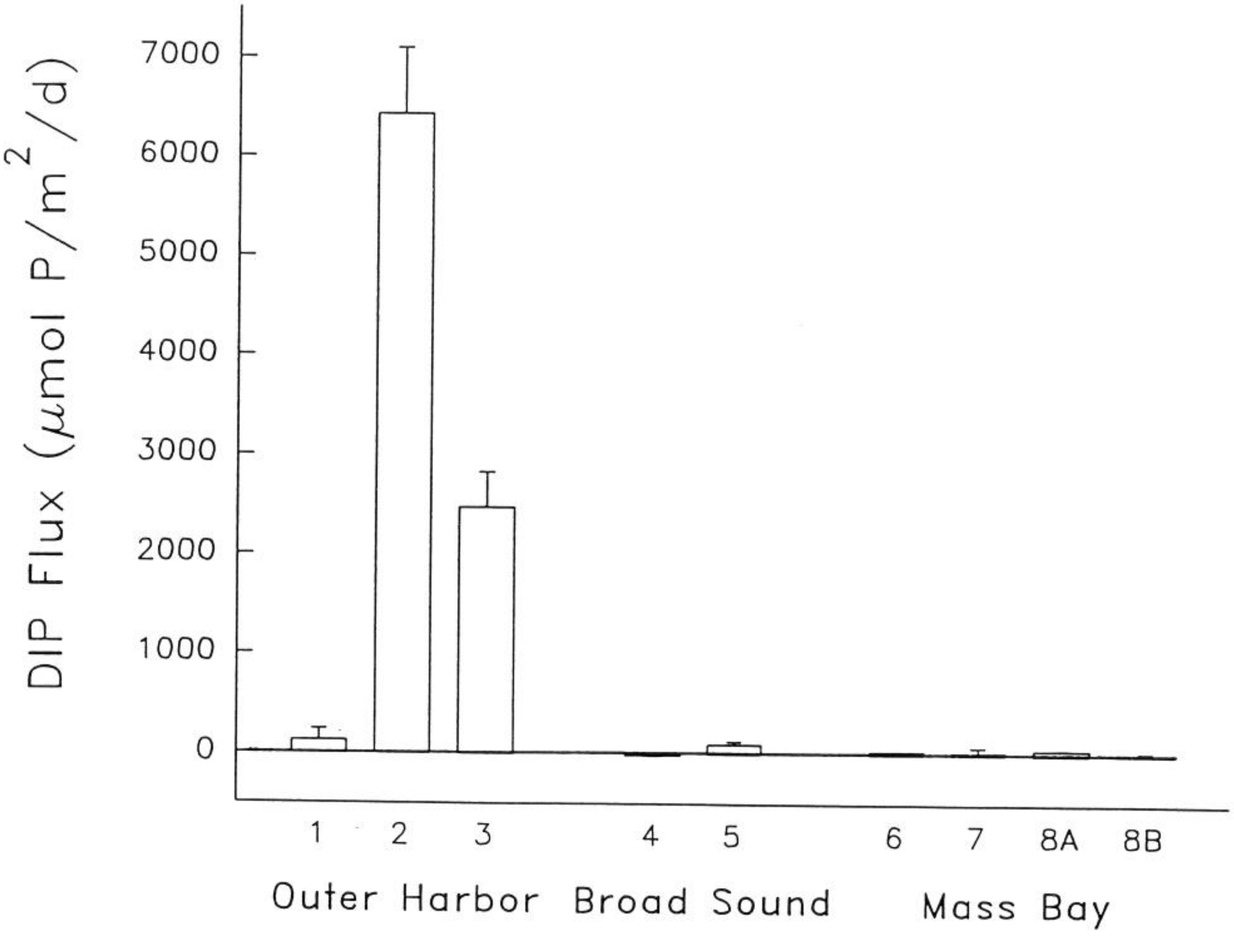

Figure 1. Disolved inorganic phosphate (DIP) release (Mean S.E.) of sediments from the eight stations sampled. Negative fluxes indicate uptake by the sediments.