Benthic nutrient cycling in Boston Harbor and Massachusetts Bay: 1999 annual report

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BENTHIC NUTRIENT CYCLING in BOSTON HARBOR and MASSACHUSETTS BAY: 1999 ANNUAL REPORT

for

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EXECUTIVE SUMMARY

This study was a continuation of the monitoring studies that have examined the temporal and spatial patterns of benthic processing of organic matter in Boston Harbor and Massachusetts Bay that have been conducted since 1990 (Giblin et al, 1991; Giblin et al, 1992; Giblin et al, 1993; Giblin et al, 1994; Kelly and Nowicki 1992; Kelly and Nowicki, 1993; Howes, 1998a; Howes, 1998b; Howes, 1998c; Tucker et al., 1999). We examined sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen (ammonium, nitrate, urea), silicate, and phosphorus at stations in Boston Harbor and Massachusetts Bay four times in 1999. We also determined the amount of nitrogen lost from sediments via denitrification, both by direct measurement and by stoichiometric calculations. Oxidation-reduction potential (Eh) and pH of porewaters were measured at each sampling time. Sediment characteristics, porewater concentrations of nutrients, and other parameters were also measured on some dates. The data from this study will be added to data from previous years in order to: (1) continue to monitor the recovery of the sludge disposal site and other sites in Boston Harbor as sewage treatment practices continue to improve, (2) continue the baseline monitoring of Massachusetts Bay before sewage diversion occurs, (3) better characterize the variability in conditions in Boston Harbor and Massachusetts Bay prior to wastewater diversion, and (4) provide data for the water quality model developed by HydroQual.

Boston Harbor

Results from the benthic nutrient flux studies in 1999 largely show a continuation of trends related to harbor recovery that have been observed during the monitoring program. However, there were some notable changes in benthic respiration and nutrient flux rates as well as sediment parameters.

The most dramatic changes continue to be reported from Station BH03, the old sludge disposal site. For two consecutive years, 1998-1999, respiration and nutrient flux rates at this station have decreased from the extremely high rates observed in the first three to four years after the cessation of sludge disposal in the Harbor. Respiratory quotients (RQs) have changed from values that were typically much greater than 1.0 in 1992-1994, to values much closer to 1.0 in the last two years, indicating a shift towards a better balance between aerobic and anaerobic processes in these sediments. Fluxes of dissolved inorganic nitrogen include high percentages of NO_3^- relative to NH_4^+, although these percentages have declined somewhat from the nearly 100% NO_3^- fluxes reported in 1995. Sediment carbon and nitrogen content have also decreased.

Benthic infauna, in particular the mat-forming amphipod, *Ampelisca*, remain very abundant at this site, and through their activities, responsible for many of the changes we have seen. However, the mat shows signs of being in decline, consistent with the continuing progression of successional stages with improving habitat (Kropp et al., 2000b). Declining process rates and carbon and nitrogen content are consistent with these results, as it appears that the sediments at this site are being “mined “ of their rich stores of organic matter.

Rates of respiration and nutrient fluxes at Station BH03, as well as the composition of the infaunal community, are approaching conditions we and others (Kropp et al., 2000a) report for Station BH08A in Hingham Bay. BH08A sediments are also heavily colonized by *Ampelisca*, but the community is classified as an equilibrium community rather than a transitional one. In addition, flux rates at BH08A have been constant since 1995. By comparison to Station BH08A, Station BH03 appears to be nearing equilibrium conditions.

At Station BH02, the other station in the northern harbor, we have observed less change, but there are some indications that the sedimentary environment is improving there as well. Fluxes of DIN were lower in 1999, and were comprised of over 40% NO_3^- in late summer/early fall. Similar to results from Station BH03, the RQs at Station BH02 were closer to 1.0 than ever before during the monitoring program. Sulfide concentrations in the sediments were also lower. In addition, the benthic monitoring studies (Kropp et al., 1999b) reported an increase in infaunal diversity at this site. All of these parameters suggest that sediments at BH02 are beginning to change towards a more hospitable benthic environment.

Results from Station QB01 in the southern harbor (Quincy Bay) have shown little change since monitoring began there in 1995. Effects from the diversion of Nut Island effluent to Deer Island were not obvious in 1999, although sediments appeared to be more oxidized than in previous years. Also, early season sediment chlorophyll *a* inventories were elevated in 1998 and 1999, possibly attributable to higher abundances of benthic diatoms that have been noted at this shallow station. Dissolved silica fluxes were maximal following these chlorophyll highs, especially in 1998. It is uncertain whether the slight improvement to water clarity that occurred after the Nut Island diversion is related to these changes.

Massachusetts Bay

In 1999, benthic nutrient cycling studies resumed in Massachusetts Bay after a break in the baseline measurements of one year at Stations MB01, MB03, and MB05, and two years at Station MB02. In retrospect, it was unfortunate that measurements were not made in 1998, as they may have been useful in interpreting the large changes we observed in some measurements of benthic processing in the Nearfield in 1999. Significant changes have not been noted for Station MB05 in Stellwagen Basin.

The fall of 1998 marked the beginning of a very large and sustained phytoplankton bloom in the Bay that persisted into April 1999. Although the bloom declined in April, water column chlorophyll concentrations remained moderately high throughout the summer, and in September, an even larger bloom was underway. In early September, bottom water dissolved oxygen (D.O.)was the lowest recorded during baseline monitoring, falling to less than 6.0 mg/L, the trigger level for D.O.

Events in the water column were apparently translated to the benthos rapidly, although not evenly. Sediment respiration rates were elevated at two of our three Nearfield stations, and at Station MB02, they were the highest recorded during baseline. Fluxes of dissolved silica were also very high at the same two stations, and especially at Station MB02, where again these were the highest rates yet measured. Inventories of total chlorophyll pigments in the top 5 cm of sediment were also higher than typical, especially at Station MB02. All of these measures indicate recent deposition of organic matter, most likely originating from the phytoplankton blooms. This rapid response of benthic processes to water column events continues a pattern that has been observed throughout baseline monitoring.

In contrast to the above results that relate to increased organic matter deposition, we observed decreases in percentages of organic carbon and nitrogen in Nearfield sediments, particularly at Stations MB01 and MB02. We also noted a deepening of sediment RPD in 1999 as compared to earlier measurements. These results, as well as reports of decreases in *Clostridium perfringens*, have also been documented in the benthic monitoring studies (Kropp et al., 1999a)

and may be related to reductions in particulates loading in Deer Island effluent. All of these sediment parameters are consistent with increases in abundances of benthic infauna, and changes towards more Stage II and III communities, which together have increased the importance of biological processes as structuring mechanisms in Nearfield sediments (Kropp et al, 1999).

Although these results apparently present a paradox in terms of classical biogeochemistry, they are reminiscent of observations from the Harbor. Soon after sludge deposition ceased, we began to see the same contrasting results at Station BH03: high sediment respiration rates and increased sediment oxidation. The results have been attributed to increase in infaunal abundance and subsequent increases in bioturbation. The magnitude of the response is quite different between the Harbor and the Bay, however it is in accordance with the level of organic matter inputs. It will be interesting to evaluate whether decreases in particulates loading in Deer Island effluent may account for improvements in benthic sedimentary environments in Massachusetts Bay.

1. INTRODUCTION

Sediments of coastal environments play an important role in nutrient recycling and organic matter decomposition We have discussed the ecological importance of benthic fluxes at length in our previous reports. Briefly, the breakdown of organic material in surficial sediments releases inorganic nutrients (nitrogen, phosphorus, silica) to the overlying water and thereby plays a role in supporting primary productivity. The ratios in which nutrients are released provides insight into the ecological status of the benthos, and may affect phytoplankton dynamics. Benthic processes also consume oxygen, at times contributing to O_2 depletion in bottom waters.

In addition to serving as a source of inorganic nitrogen (N) to the water column through nutrient regeneration, sediments may also act as an N sink via denitrification. During denitrification, nitrate is converted to N_2 and thus effectively lost from the ecosystem. Denitrification may be considered a cleansing process that can retard eutrophication of heavily nutrient loaded coastal systems. The amount of nitrogen which is lost by denitrification in coastal systems varies greatly, generally ranging from 15 to 70% of the inorganic nitrogen mineralized during decomposition (Seitzinger 1988).

This study was a continuation of the monitoring studies that have examined the temporal and spatial patterns of benthic processing of organic matter in Boston Harbor and Massachusetts Bay that have been conducted since 1990 (Giblin et al, 1992; Giblin et al, 1993; Giblin et al, 1994; Kelly and Nowicki 1992; Kelly and Nowicki, 1993; Howes, 1998a; Howes, 1998b; Howes, 1998c; Tucker et al, 1999). We examined sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen (ammonium, nitrate, urea), silicate, and phosphorus at stations in Boston Harbor and Massachusetts Bay four times between May and October in 1999. We also determined the amount of nitrogen lost from sediments via denitrification, both by direct measurement and by stoichiometric calculations. Oxidation-reduction potential (Eh) and pH of porewaters were measured at each sampling time. Sediment characteristics such as carbon and nitrogen content and grain size were also measured each time and chlorophyll *a* and phaeopigment concentrations were measured in May and October. Porewater concentrations of nutrients, sulfides, alkalinity, silicate, and urea were measured twice, in July and August. The data from this study will be added to data from previous years in order to: (1) continue to monitor the recovery of the sludge disposal site and other sites in Boston Harbor as sewage treatment practices continue to improve, (2) continue the baseline monitoring of Massachusetts Bay before sewage diversion occurs, (3) better characterize the variability in conditions in Boston Harbor and Massachusetts Bay prior to wastewater diversion, and (4) provide data for the water quality model developed by HydroQual.

2. SAMPLING DESIGN

The eight sampling sites are shown in Figure 1. Two of the Harbor sites sampled in 1999, BH02 and BH03, have been sampled every year since 1992. The other two, BH08A and QB01 have been sampled since 1995. Surveys were carried out during late May, late July, late August (Harbor)/early September (Bay), and mid October. Survey cruises were planned for two consecutive days, but were interrupted by weather in May, August, and October; all surveys were completed within 3 days. The survey dates and locations, water depths, and bottom water temperatures,oxygen concentrations, and salinities of the sites are shown in Table 1.

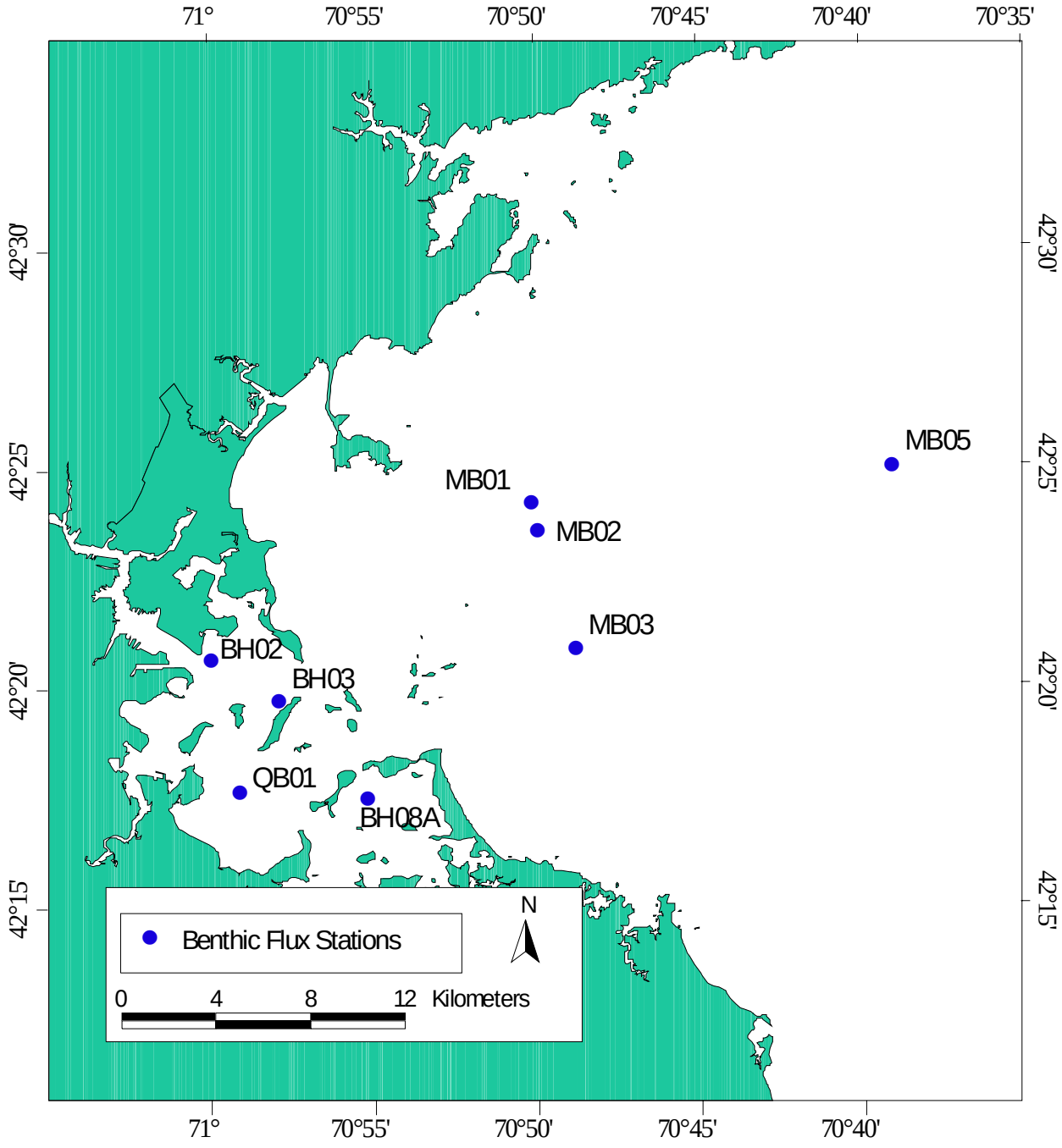


Fig. 1. Boston Harbor and Massachusetts Bay Benthic Nutrient Flux Stations 1999.

Table 1. Station names, survey IDs, date of survey, station locations, water depth, bottom water temperature, dissolved oxygen (D.O.) and salinity for Boston Harbor and Massachusetts Bay stations visited in 1999.

Station	Survey ID	Date	Latitude	Longitude	Depth (m)	Temp (°C)	DO (mg/L)	Salinity (ppt)
BH02	NC991	05/25/99	42.34361	-71.00216	10.5	13.4	10.32	30.3
	NC992	07/28/99	42.34340	-71.00237	11.5	16.6	10.19	32.8
	NC993	08/31/99	42.34198	-70.99982	7.9	18.8	6.9	31.6
	NC994	10/19/99	42.34390	-71.00162	10.0	12.5	7.29	30.0
BH03	NC991	05/25/99	42.33074	-70.96187	8.5	12.8	10.7	31.0
	NC992	07/28/99	42.33028	-70.96140	9.0	17.1	9.95	31.0
	NC993	08/31/99	42.33029	-70.96215	6.6	18.5	6.78	31.6
	NC994	10/19/99	42.33067	-70.96190	8.5	12.3	8.80	30.1
BH08A	NC991	05/27/99	42.29111	-70.92225	8.0	12.1	10.43	31.0
	NC992	07/28/99	42.29128	-70.92212	10.0	16.5	9.98	33.0
	NC993	08/31/99	42.29077	-70.92242	8.0	18.2	7.52	32.2
	NC994	10/19/99	42.29162	-70.92152	9.6	12.3	7.95	30.2
QB01	NC991	05/25/99	42.29380	-70.98815	5.5	13.8	9.63	31.4
	NC992	07/28/99	42.29270	-70.98853	5.3	18.5	9.11	31.4
	NC993	08/31/99	42.29338	-70.98762	2.6	19.4	8.77	32.0
	NC994	10/19/99	42.29348	-70.98772	4.7	12.3	7.98	29.6
MB01	NC991	05/27/99	42.40374	-70.83753	34.4	5.1	10.52	33.5
	NC992	07/27/99	42.40355	-70.83705	33.6	7.9	9.81	33.5
	NC993	09/02/99	42.40300	-70.83768	30.7	10.5	5.15	31.8
	NC994	10/21/99	42.40314	-70.83688	33.0	11.2	6.07	31.3
MB02	NC991	05/27/99	42.39282	-70.83463	35.0	5.4	10.79	33.5
	NC992	07/27/99	42.39292	-70.83432	35.1	7.8	9.98	33.6
	NC993	09/02/99	42.39260	-70.83438	32.0	10.7	4.76	33.4
	NC994	10/21/99	42.39258	-70.83440	34.0	11.2	6.21	31.3
MB03	NC991	05/27/99	42.34880	-70.81558	35.0	5.3	10.37	34.0
	NC992	07/27/99	42.34823	-70.81510	35.5	8.3	9.91	32.8
	NC993	09/02/99	42.34831	-70.81557	33.0	10.9	5.50	33.5
	NC994	10/21/99	42.34780	-70.81580	34.0	11.3	6.87	31.3
MB05	NC991	05/27/99	42.41455	-70.65007	77.0	5.6	12.36	33.7
	NC992	07/27/99	42.41652	-70.65144	76.7	6.4	10.18	33.7
	NC993	09/02/99	42.41655	-70.65127	75.2	8.0	6.95	32.9
	NC994	10/21/99	42.41663	-70.65205	75.0	10.3	6.79	31.6

2.1 LOCATION AND RATIONAL FOR STATIONS

Four stations were sampled in Boston Harbor during 1999. Two of these stations, BH02 and BH03, have been monitored since 1992, although the location of BH03 has varied slightly. During 1995-1997 Station BH03A, located about 200m west of BH03, was sampled; however these two stations are comparable and for the purpose of discussing long term trends will be considered the same. The other two, Stations BH08A and QB01, have been monitored since 1995.

Station BH03, off Long Island and near the old sludge disposal site, has been sampled 4 to 5 times annually since 1992. This site has undergone dramatic changes over this time period, beginning with the cessation of sludge dumping at the end of 1991. In the following years, large numbers of mat-building amphipods colonized the area, peaking in abundance in 1994. In 1998-99, our observations during SCUBA diving suggested the mat at BH03 had begun to show signs of breaking up. Kropp et al. (2000a, 2000b) substantiated our observations in their reports, noting a decline in the area of the harbor colonized by *Ampelisca* in 1997-1998 and continuing into 1999.

Station BH02 is considered more typical of the muddy sediments influenced by the Deer Island sewage outfall. It has experienced less dramatic changes in loading over the monitoring period, although the change in 1995 to new primary treatment certainly represented a significant decrease in solids loading to the central harbor area. Stations BH08A in Hingham Bay and QB01 in Quincy Bay represent depositional areas in the southern harbor. A large change in loading to these two stations occurred in the spring/summer of 1998, when the Nut Island discharge was diverted to Deer Island (Taylor, submitted) (diversion occurred over 4 months, April 27-July 7). The Nut Island diversion coupled with full secondary treatment represented a third major reduction of solids loading to the entire harbor area.

In Massachussetts Bay, three stations were sampled in the Nearfield area of the Bay and one station was sampled in Stellwagen Basin in 1999. The three Massachusetts Bay stations, MB01, MB02, and MB03 have been sampled on a continuing basis since August 1992. Station MB05, in Stellwagen Basin, has been visited since July 1993. Station MB02 was not visited in 1997, and none of these stations was sampled in 1998.

All stations were sampled four times in 1999, from spring to fall, concentrated on the time of the year when the sediments are most biologically active. The first survey of the year was in May when bottom water temperatures are still low. May was also chosen because we anticipate organic matter content of the sediments to be at a seasonal high in spring, both from undecomposed material from the fall bloom, and from recently deposited organic matter from the spring bloom. The next two surveys were in July and August/September, summer months often characterized by the highest flux rates in the Harbor. The last survey was in October, when water temperatures in the Bay are the highest and the fall bloom is underway; we often measure highest flux rates in the Bay in the fall.

3. METHODS

The methods used in this study have been described in Giblin et al. (1997) and in the CW/QAPP (Tucker and Giblin, 1998). They will be only briefly described here. Because the monitoring of these stations in 1995-1997 was carried out by other investigators, we have noted any deviations from the CW/QAPP and discuss specific aspects of the methods which may not be obvious from the previous reports.

3.1 FIELD SAMPLING

For flux measurements, two large, 15-cm. diameter cores were collected per station. Replicate 6.5-cm diameter cores were collected for porewater analysis. Two to three 2.5-cm diameter cores were taken for porosity and solid phase analyses. At BH02 ,BH03, MB02, and MB03, two additional cores, approximately 10.1-cm. in diameter, were taken for direct measurements of N_2 flux. All cores collected from Boston Harbor stations were sampled by SCUBA divers. The Massachusetts Bay cores were obtained using a box corer (50X50 cm). For the

nutrient flux cores, core tubes were mounted inside the box corer before deployment. The additional smaller cores were collected from the filled box core after retrieval.

Bottom water temperature, O_2, and salinity were measured in situ with a water quality monitoring sonde unit (Hydrolab Scout 2 Multiparamenter Water Quality Data System). Water depths at Station MB05 (~75m) exceeded the length of our sonde cable (50m); however, by sampling from below the thermocline we were confident that we collected data representative of bottom water. At each station 15 liters of seawater were collected with a diaphragm pump and immediately filtered through a series of cartridge filters (nominally 20 and 1.0 µm). Water was collected from just above the bottom at all stations except for Station MB05; at this station water was collected from about 33m depth, below the thermocline and equal to the length of our sampling equipment. The collected water was held at in situ temperatures and used to replace the overlying water in cores just prior to flux measurements.

3.2 BENTHIC RESPIRATION AND NUTRIENT FLUXES

Cores were transported to Woods Hole, MA, submerged in water in large insulated containers and maintained at *in situ* temperatures. Before transporting the cores, care was taken to be sure the headspaces of the cores were completely filled with water. This prevented sediment disturbance during handling. Upon arrival cores were placed in a dark incubator where they were held uncapped, overnight, at the in situ temperature of the station. Flux measurements were begun within 12-24 hours of sampling. Prior to initiating flux measurements, the overlying water of each core was replaced with the filtered seawater collected at each station. Two BOD bottles filled with the filtered water obtained from each station were used to correct for respiration in the water overlying the sediments.

Cores were sealed with tops containing magnetic stirrers (Dornblaser et al. 1989) and gently mixed. We monitored concentrations of oxygen in the overlying water throughout the incubation period. Incubation duration was determined by the time required for oxygen concentrations to fall by 2 to 5 ppm (generally 6 to 24 hrs). Water samples were taken periodically from each core throughout the incubation period. Benthic respiration was calculated as the slope of oxygen concentration versus time. The values were corrected for the oxygen uptake in the water overlying the cores by using O_2 changes measured in BOD bottles. Taking measurements over time enabled us to determine whether oxygen consumption was linear.

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

Additional sub-samples were frozen for later measurement of nitrate + nitrite, silicate, and urea concentrations. Nitrate + nitrite were determined together using the cadmium reduction method on a rapid flow analyzer (Alpkem RFA-300). DIN was calculated as the sum of ammonium, nitrate, and nitrite. Silicate was analyzed by reduction with stannous chloride using an autoanalyzer (method of Armstrong 1951 as adapted by RFA, Alpkem Corp 1986). Urea was analyzed using the method of Price and Harrison (1987).

At the beginning and end of the incubation period, 60 mL samples were also taken for total CO_2 analysis. These samples were stored at 4°C in glass BOD bottles with mercuric chloride (10 µL of a $HgCl_2$ saturated solution) as a preservative. Samples were analyzed with a high precision coulometric CO_2 analyzer capable of measuring total CO_2 with a precision of 0.05% (1 µM).

3.3 POREWATER SAMPLING AND ANALYSIS

Sediment samples for porewater extraction were taken from all 8 stations in July and August. Cores were sectioned into depth intervals in a glove bag under a nitrogen atmosphere. Sediments were sampled in 1 cm intervals down to 2 cm, 2 cm intervals to 10 cm and then in 4 cm intervals at greater depths. Nutrients, urea, silicate, sulfides (Cline 1969), pH and alkalinity (Edmond 1970) in porewaters were analyzed as previously described in Giblin et al. (1992). Sediment oxidation-reduction potential (Eh) and porewater pH were measured in a separate core. Eh was measured using a platinum electrode (Bohn 1971). The values reported here have been corrected for the potential of the reference electrode. Porewater pH was measured using an *in situ* pH probe.

3.4 POROSITY AND SEDIMENT C AND N

Sediments from 2.5-cm diameter cores were sectioned in 1 cm intervals to a depth of 10 cm and then in 2 cm intervals to the bottom of the core. Sediment wet weight was measured immediately and dry weight after a minimum of 72 hrs at 105°C. Porosity was calculated as: (volume of water in the depth interval sampled)/(total volume of water + sediment).

Organic carbon and nitrogen content was measured on the dried sediments after carbonates had been removed by acid fuming. Analyses were performed using a Perkin Elmer 2400 CHN elemental analyzer. The % carbon and nitrogen measured on the sediment was corrected for the weight change due to the acidification procedure which was usually 3-7%.

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

3.5 CHLOROPHYLL *a* AND PHAEOPIGMENTS

Sediment samples for chlorophyll *a* and phaeopigments were collected from all eight stations at the beginning and end of the season (May and October) with the intention of capturing inputs from the spring and fall phytoplankton blooms. We also measured sediment pigments from the four Bay stations in August. These additional samples were obtained by taking subcores of the large flux cores after the flux incubation. Pigments were measured in 1 cm increments down to 5 cm from a 2.5 cm diameter core. Each sediment section was placed in a separate centrifuge tube and frozen. Samples were later extracted with cold acetone in the dark. After extraction, samples were centrifuged and the absorbance of the supernatant was measured at 750 and 665 nm before and after acidification (Strickland and Parsons 1972).

3.6 MEASUREMENTS OF DENITRIFICATION

3.6.1 DIRECT MEASUREMENT BY GAS CHROMOTOGRAPHY

Sediment denitrification was measured as the direct flux of N_2 gas from sediment cores in gas-tight N_2-free chambers. These measurement were made in May and August for the Harbor stations, and in May and October for the Bay stations. Two sediment cores were incubated from each site on each sampling date; one was used for measurements of total sediment N_2 flux

("experimental core") and the other as a control for background N_2 de-gassing ("control core"; Nowicki, 1994).

A detailed description of sampling and measurement methods is given in Nowicki et al. (1997) and in the CW/QAPP (Tucker and Giblin, 1998). Briefly, the depth of the sediment in the cores was adjusted to provide equal sediment depths for the experimental core and its anoxic control. Field core stoppers were replaced with gas-tight tops and bottoms so that the core tubes became the incubation chambers. The chambers were filled with ambient seawater and then a gas headspace was created by withdrawing an accurately measured volume of the seawater. The chambers were maintained in the dark, at ambient temperatures, with constant stirring. The overlying seawater and a gas-filled head space in each chamber were sparged with a mixture of helium and oxygen (80 He:20 O_2) to remove nitrogen but to maintain dissolved oxygen concentrations at levels similar to those observed in bottom waters in the field. Control cores were treated in the same manner as the experimental cores, but were maintained without oxygen so that coupled denitrification was prevented. These anoxic control cores were used to monitor and correct for background fluxes of N_2 (due primarily to N_2 in porewater diffusing into the N_2-free headspace) which were not caused by denitrification (Nowicki et al., 1997).

Measurements of the concentrations of nitrogen and oxygen in the gas-filled headspace of each chamber were determined from samples (100 µl) withdrawn with a gas-tight syringe from the chamber sampling port. Concentrations of nitrogen and oxygen in the gas samples were measured with a Shimadzu 8A Gas Chromatograph equipped with a thermal conductivity detector. Calibration curves were run with each set of samples using a certified standard gas mixture. Rates of N_2 gas production and O_2 uptake for sediments in the denitrification chambers were calculated from the slopes of 4-point (or more) linear regressions of N_2 or O_2 concentration in the gas phase of each chamber over time.

3.6.2 ESTIMATION BY THE STOICHIOMETRIC METHOD

The stoichiometric method of measuring denitrification is an indirect method which involves three assumptions. The first is that the amount of organic matter being decomposed within the sediments can be estimated from fluxes of decomposition end products across the sediment-water interface. The second assumption is that the elemental (C:N:P:O) ratio of the material being decomposed is known. The rate of decomposition and the elemental ratio of the material being decomposed are used to calculate an expected N flux from the sediments. The expected N flux is compared to the sum of the measured flux of ammonium and nitrate (DIN) from the sediments. Missing nitrogen is assumed to have been denitrified. For this study we assumed that the organic matter being decomposed had a C/N ratio of fresh phytoplankton and expected to see a DIC/DIN ratio of 6.625 in the absence of denitrification.The third assumption is that denitrification is the major processes removing the missing nitrogen.

3.6.3 DISSOLVED GAS ANALYSIS BY MASS SPECTROMETRY

A second direct measure of denitrification was employed in 1999 for comparison to the gas chromatography technique and to our stoichiometric estimates. We had begun this comparison in 1998 (see Tucker et al, 1999) The method uses a quadropole mass spectrometer to precisely measure N_2/Ar ratios of dissolved gases in water samples. (Kana, et al, 1994) Dinitrogen gas concentrations are affected by both biological and physical processes, whereas Ar is affected only by physical processes. Deviations from equilibrium ratios of these two gases therefore reflect biological activity acting on the N_2. The mass spectrometer is capable of measuring very small deviations in this ratio, thereby providing a very sensitive and precise method for measuring denitrification. Whereas gas chromotagraphy offers a precision of measurement for gas

concentrations on the order of 0.3-1%, the mass spectrometer yields a precision of 0.05% for gas ratios.

Another advantage of the method is that the liquid sample is directly introduced to the instrument through a semipermeable membrane; that is, there is not the added complication of sampling from a gas phase or from degassing the sample. In addition, sample throughput is high, around 20-30 samples per hour, and the requirement for sample volume is small.

Importantly for our benthic flux studies in Boston Harbor and Massaachusetts Bay, samples for dissolved gas analysis (DGA) were taken from the same cores as were used for flux measurements, allowing for direct comparison of fluxes from a given core. Four to five samples were taken over a time course, simultaneously with the nutrient flux samples. Samples were introduced into the bottom of a 7-ml test tube and allowed to overflow the tube for the equivalent of 2 volumes, taking great care to avoid introduction of gas bubbles. Samples were then preserved with $HgCl_2$, and stoppered with a ground glass stopper. Samples were kept submerged and at the ambient temperature of the flux incubations or colder until analysis. Analyses have been performed in the laboratory of Dr. Jeff Cornwell at the University of Maryland's Horn Point Laboratory.

3.7 DATA COMPARISONS

This report adds to an extensive database that has been accumulating since 1991 through field and laboratory efforts associated with the MWRA's Boston Harbor and Massachusetts Bays Monitoring Program. Reference is made to data from long-term studies on benthic metabolism and sediment nutrient cycling in the harbor collected by two sets of researchers. Rather than cite the extensive list at every data comparison, we will use the following convention. Data from 1991-1994 (Giblin et al, 1992; Giblin et al, 1993 ; Giblin et al, 1994; Giblin et al, 1995; Giblin et al, 1997) will be cited as Giblin et al., 199x. Data from 1995-1997 (Howes, 1998a; Howes, 1998b; Howes, 1998c) will be cited as Howes, 1998a-c.

For purposes of comparing long term trends of benthic processes in Boston Harbor in this report, data collected by other investigators (Howes, 1997-1998) were obtained from the MWRA database with the assistance of personnel from Battelle.

4. RESULTS AND DISCUSSION

4.1 BOSTON HARBOR

4.1.1 BENTHIC RESPIRATION AND NUTRIENT FLUXES

4.1.1.1 Oxygen Uptake

Boston Harbor sediment oxygen uptake ranged from approximately 18 to 117 mmol O_2 m^{-2} d^{-1} between May and October 1999 (Figure 2). Highest rates were measured in August at Stations BH03 and BH08A when water temperatures were warmest. These two stations also had the highest average May-October respiration rates, 83 and 79 mmol O_2 m^{-2} d^{-1} respectively; the sediments at both of these stations are densely populated by benthic infauna, primarily the mat forming amphipods.

As has been typical over the monitoring years from 1995 to present, lowest rates of the four Harbor stations were measured at Station QB01 both on individual sampling dates (18 mmol O_2 m^{-}

^{2} d^{-1} in May) and as May to October average (30 mmol O_2 m^{-2} d^{-1}). Stations BH02 and QB01 had similar rates in July and October, but in May and August rates at Station BH02 were nearly double those at QB01; rates at Station BH02 peaked in July at 62 mmol O_2 m^{-2} d^{-1}. As neither of these stations supports appreciable numbers of benthic infauna, respiration rates more directly reflect sediment microbial processes and variable inputs to the sediments, rather than animal respiration.

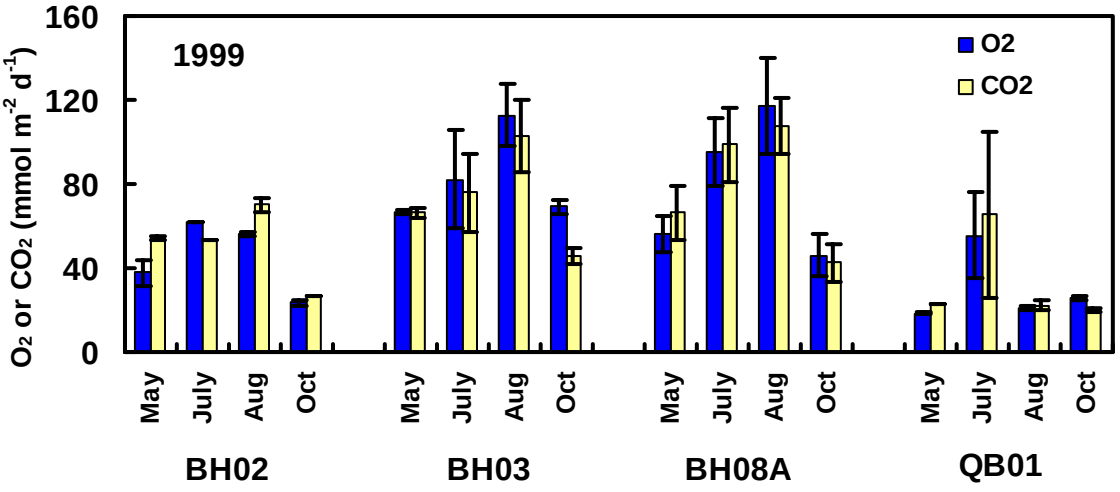


Fig. 2. Sediment respiration as measured by O_2 uptake at a.) BH02, b.)BH03, c.) BH08A, and d.) QB01 for 1999. Error bars represent the standard error of the mean of two cores.

Both rates and the seasonal pattern of respiration at Station BH03 were more similar to those observed in 1992 and 1994 (Figure 3b) than to the very high rates of 1993 and 1995. The year to year differences we have observed in respiration rates at this site continue to be correlated with animal abundances, dominated by amphipods (*Ampelisca*). Although amphipods were still very abundant at this station, the lower rates observed in 1998 and 1999 are consistent with divers' observations that there was a reduced amphipod mat compared to that observed in 1993 and 1995.

The magnitude and pattern of the rates at BH02 were similar to those observed in previous years with the exception of the very high rates measured in May, 1993, and July and August 1995 (Fig 3a). Rates at BH08A in 1999 were somewhat higher than the previous three years, but were lower than those measured in 1995 (Fig 3c). In general, respiration rates at QB01 have remained constant since 1995 (Fig 3d).

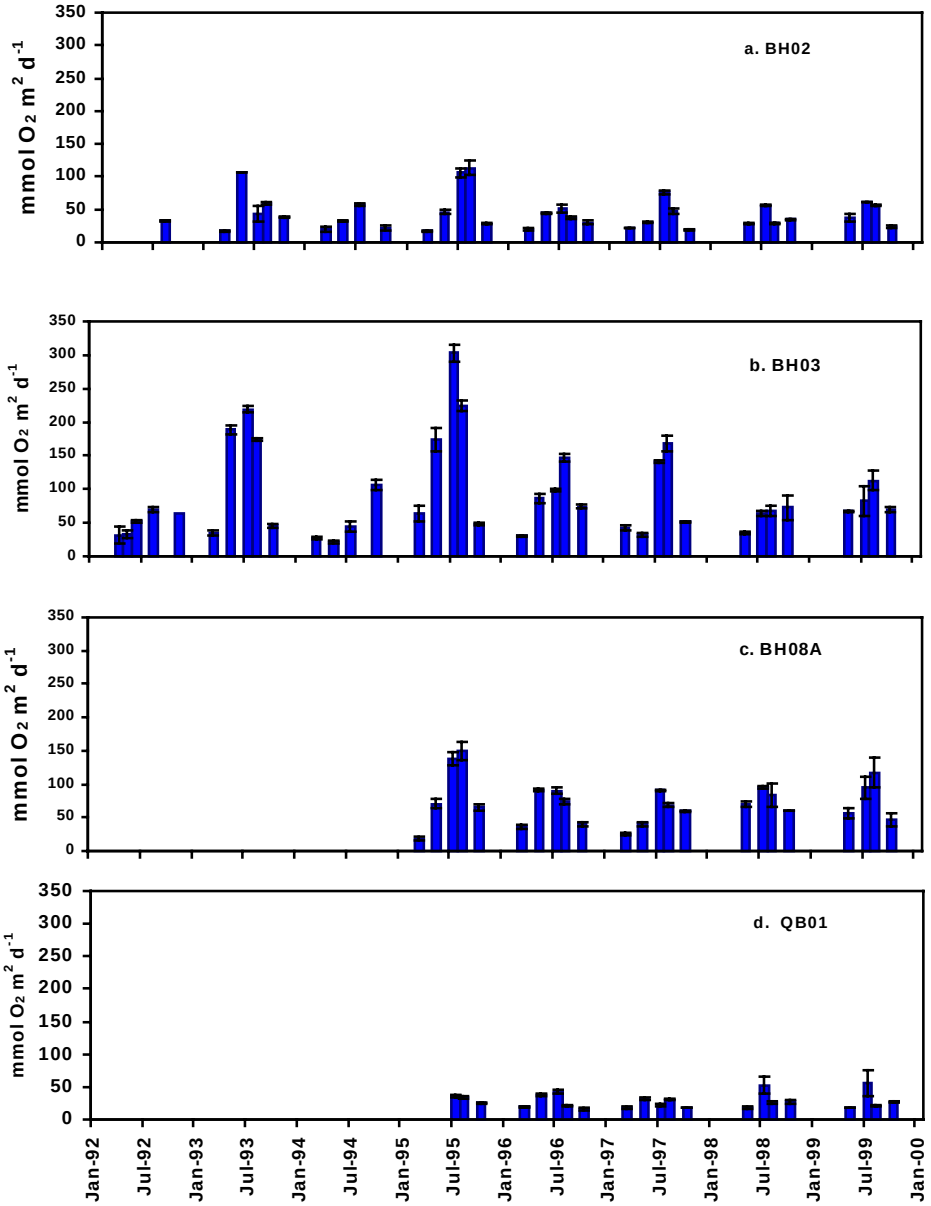


Figure 3. Sediment Respiration as measured by O_2 uptake at a.) BH02, b.) BH03, c.) BH08A, d.) QB01 from 1992-1999. Error bars represent the standard error of the mean of two cores.

4.1.1.2 Total CO_2 Measurements

Total CO_2 (DIC) fluxes at harbor stations ranged from approximately 20 to 107 mmol CO_2 m $^{-2}d^{-1}$ between May and November 1999 (Fig. 2). Fluxes at Station BH08A were higher overall than at the other stations, but only slightly higher than those measured at BH03. The magnitude and seasonal pattern of CO_2 fluxes was similar to that of oxygen uptake.

The largest discrepancy between these two measures of respiration occurred at Station BH03 in October, when O_2 consumption was 69 mmol O_2 m $^{-2}d^{-1}$ and CO_2 release was 46 mmol CO_2 m $^{-2}d^{-1}$. At BH03, the typical pattern has been that the two fluxes balance fairly well, although in 1993 we observed, as in this year, the more unusual circumstance of O_2 flux rates exceeding CO_2

flux rates (Giblin et al, 1997). Instances of excess O_2 uptake compared to CO_2 release were associated with large NO_3^- releases from the sediments in 1993. This was also the case in 1999, especially in October when the NO_3^- efflux was accompanied by an equal NH_4^+ uptake.

CO_2 fluxes at Station BH02 in 1999 more closely matched O_2 fluxes than they had during the previous monitoring years (data for CO_2 fluxes from 1995-1997 are unavailable). The typical pattern at this station had been that CO_2 fluxes exceeded O_2 fluxes, implying that anaerobic respiration, accompanied by storage of reduced endproducts, has been important at this site. The closer balance between CO_2 and O_2 flux, coupled with changes in DIN fluxes (see 4.1.3) and Eh and sulfide measurements, suggest sediments at Station BH02 have become more oxidized.

We now have two consecutive years, 1998-1999, of CO_2 flux measurements from Stations BH08A and QB01. For both years, CO_2 and O_2 fluxes have balanced fairly well; any imbalance has typically been from slightly higher CO_2 fluxes. In 1999, however, in August and October at BH08A and in October at QB01, O_2 fluxes were slightly higher than CO_2 fluxes. As in the case of BH03, this pattern was associated with NO_3^- flux being a significant component of the total DIN flux out of the sediments.

4.1.1.3 DIN Release from Sediments

The combined flux of ammonium plus nitrate and nitrite (DIN) to the overlying water ranged from an uptake of 0.3 mmol N $m^{-2}d^{-1}$ at Station BH03 in October to a release of more than 13 mmol N $m^{-2}d^{-1}$ at Station BH08A in August (Figure 4). The highest average May-October flux, 8.9 mmol N $m^{-2}d^{-1}$ was from Station BH08A and the lowest, 1.4 mmol N $m^{-2}d^{-1}$, was from Station QB01. DIN release at BH03 in 1999 was similar to that of the previous three years, and the very high rates recorded in 1993 and 1995 have not been repeated (Fig. 4b). At Station BH02, DIN fluxes were lower than in the previous six years. DIN fluxes from stations BH08A and QB01 were very similar to those from the previous four years (Fig. 4c, 4d).

At the two stations where there are large abundances of amphipods, BH03 and BH08A, a significant portion of the DIN flux was comprised of nitrate at all sampling times (Fig. 4b, 4c). At Station BH08A (Fig. 4c), 14 to 40 % of the flux was nitrate with the highest percentage, though not the highest flux, occurring in October. Since 1993, DIN fluxes from BH03, the old sludge disposal site, have been dominated by nitrate, coincident with high numbers of benthic infauna. In 1999, about 20-30% of the DIN flux was comprised of nitrate during the May to August period at Station BH03. In October, however, 100% of the nitrogen flux out of the sediments of BH03 was nitrate; at this same time, ammonium was taken up by sediments at an equivalent rate. Although small influxes of NH_4^+ into harbor sediments have been recorded at various times during the monitoring program, the magnitude of this NH_4^+ uptake (7.3 mmol N $m^{-2}d^{-1}$) was unprecedented. Ammonium concentrations in the overlying water were unusually high in October (~20uM), and our measurements may have reflected water column nitrification.

In addition to the observation that DIN fluxes at Station BH02 were lower than in the previous six years, it was also notable that in August and October an average of 40% of the flux was NO_3^- (Fig. 4a). DIN fluxes from Station BH02 have more typically been dominated by NH_4^+, except in 1995 when nitrate did contribute a large proportion, about 25% for March to May and 40% for the July to October period.

DIN flux at Station BH08A has remained fairly constant since 1995, with NO_3^- comprising a significant portion of the flux in all years. Fluxes at Station QB01 in 1999 fell in the middle of the range of measurements made since 1995 (Fig. 4d). Of note in the QB01 fluxes was that all of the DIN flux in October, albeit small, was NO_3^- and NH_4^+ flux was insignificant. This was the same pattern as was seen in October, 1997.

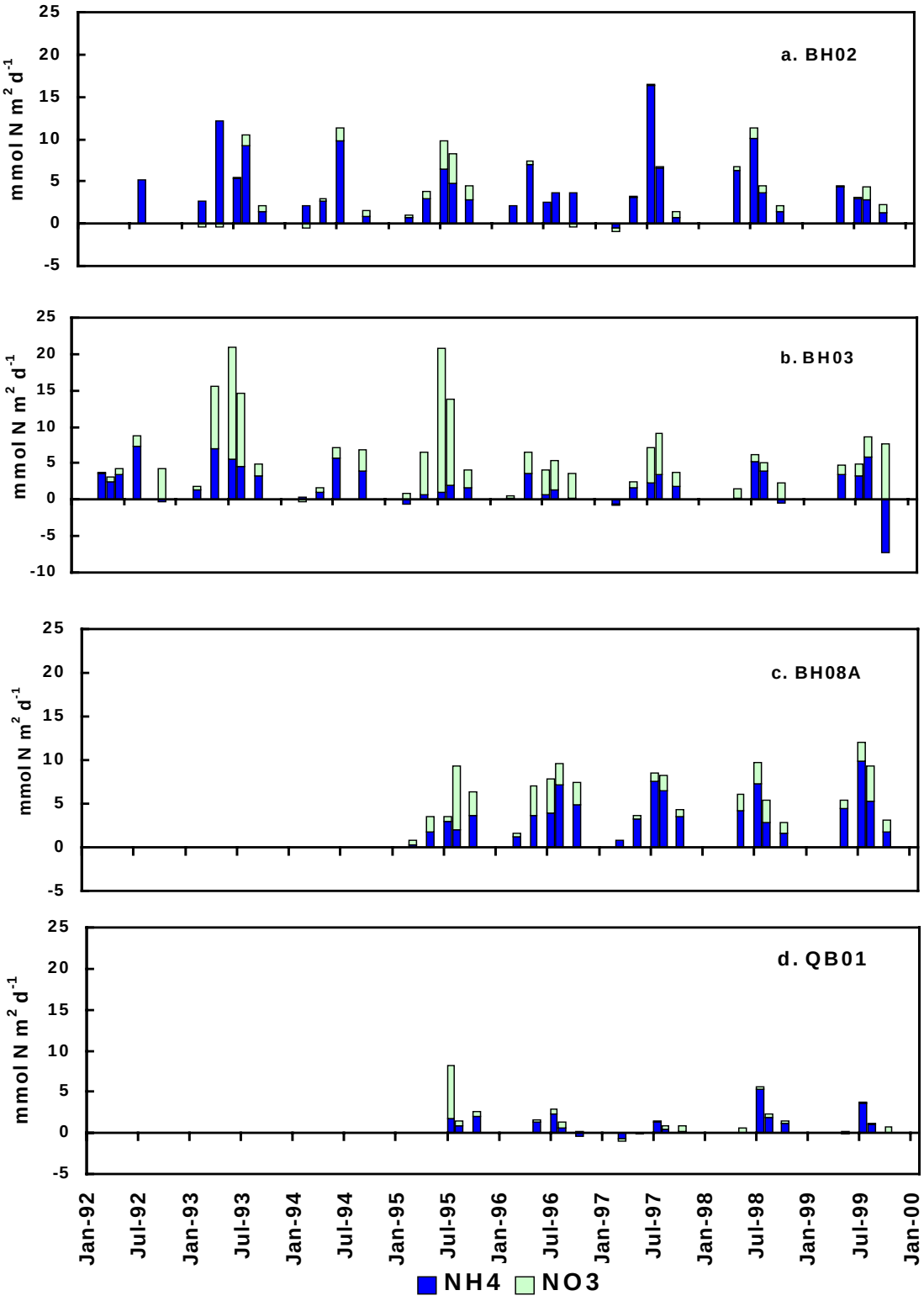


Figure 4. DIN flux, showing relative contributions of NO_3^+ and NH_4^-, at a) BH02, b) BH03, c) BH08A, and d) QB01 from 1992-1999.

4.1.1.4 Urea Fluxes

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

Urea fluxes in the harbor were small and variable. Calculated rates indicated that urea was taken up by sediments as often as it was released. Although some flux rates calculated from individual cores had r^2s greater than 0.5, only once in 1999 did duplicate cores both yield rates with significant r^2s; this was for Station BH02 in May and the rate was 0.2 mmol N $m^{-2}d^{-1}$. The highest r^2 for any rate measurement was 0.91 for a single core from Station BH03 in August and the flux was into the sediments, -1.6 mmol N $m^{-2}d^{-1}$. These results combined with large standard errors around the means of duplicate cores demonstrate the irregularity of these fluxes. The data continue to suggest that urea fluxes, to date, do not account for a significant part of the total nitrogen flux.

4.1.1.5 Silica Fluxes

Harbor silica fluxes in 1999 were similar to rates measured over the monitoring program, but there were some notable differences (Fig. 5a-5d). The highest single rate was measured at Station BH03 in August, almost 20 mmol Si $m^{-1}d^{-1}$. This rate was equivalent to the highest rate measured in the previous year at Station BH08A. The highest May to October average rate was about 11 mmol Si $m^{-1}d^{-1}$, which occurred at both BH03 and BH08A. Overall rates at BH03 were somewhat higher than the previous 4 years, but less than half those measured in 1993. The extremely high and sustained silica fluxes observed during 1993 at Station BH03 (Giblin et al, 1994) have not recurred there or at any of the other stations. Overall rates at Station BH08A were similar to rates in 1998, but higher than 1995-1997. Rates at Station BH02 were exceptional in the fact that May rates were unusually high for that station at that time of year. Lowest overall silica fluxes were measured at Station QB01. Fluxes from this station were similar to the previous year, but both years were higher than rates from 1995-1997.

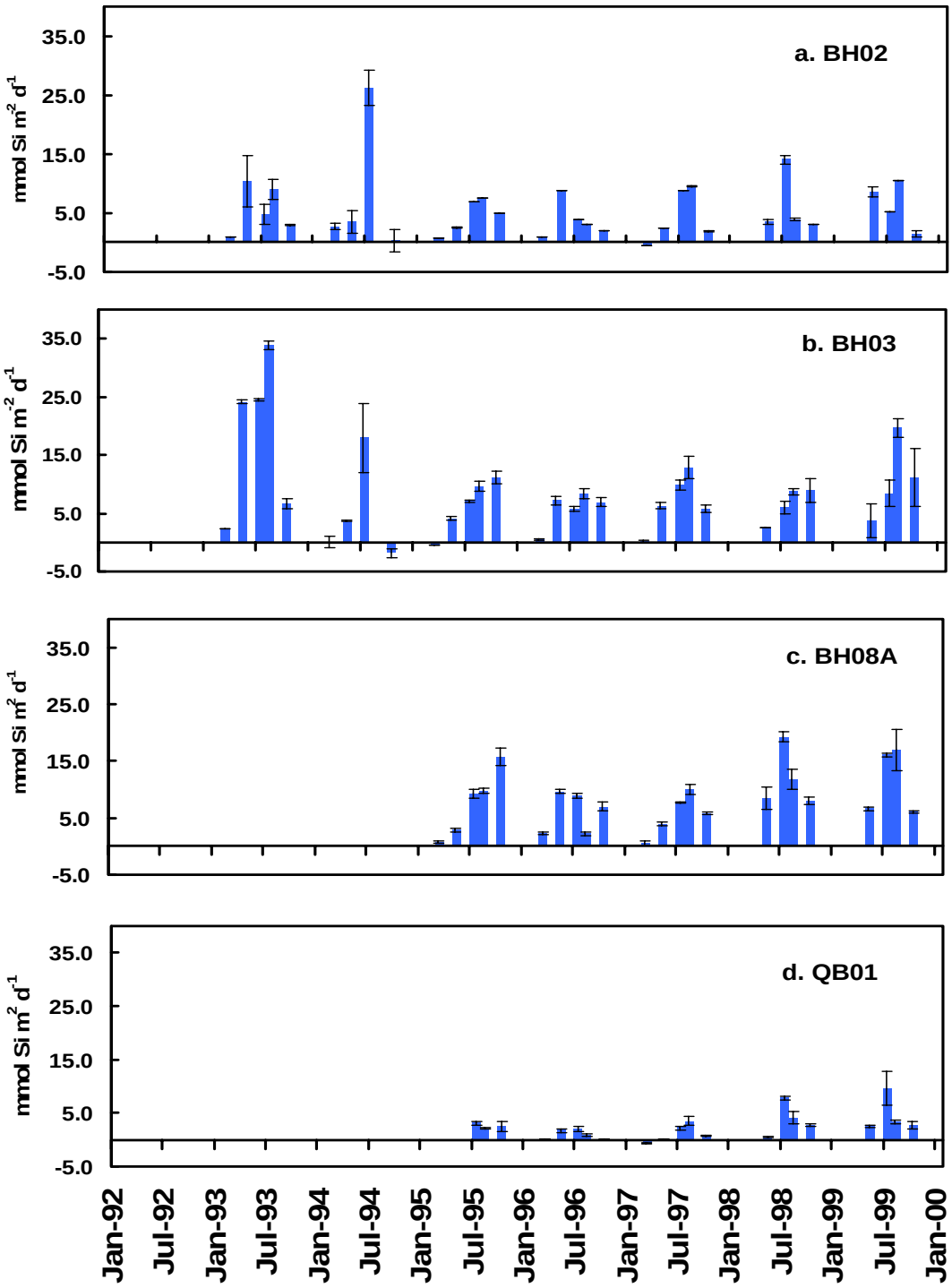


Figure 5. Dissolved silica flux at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the mean of two cores.

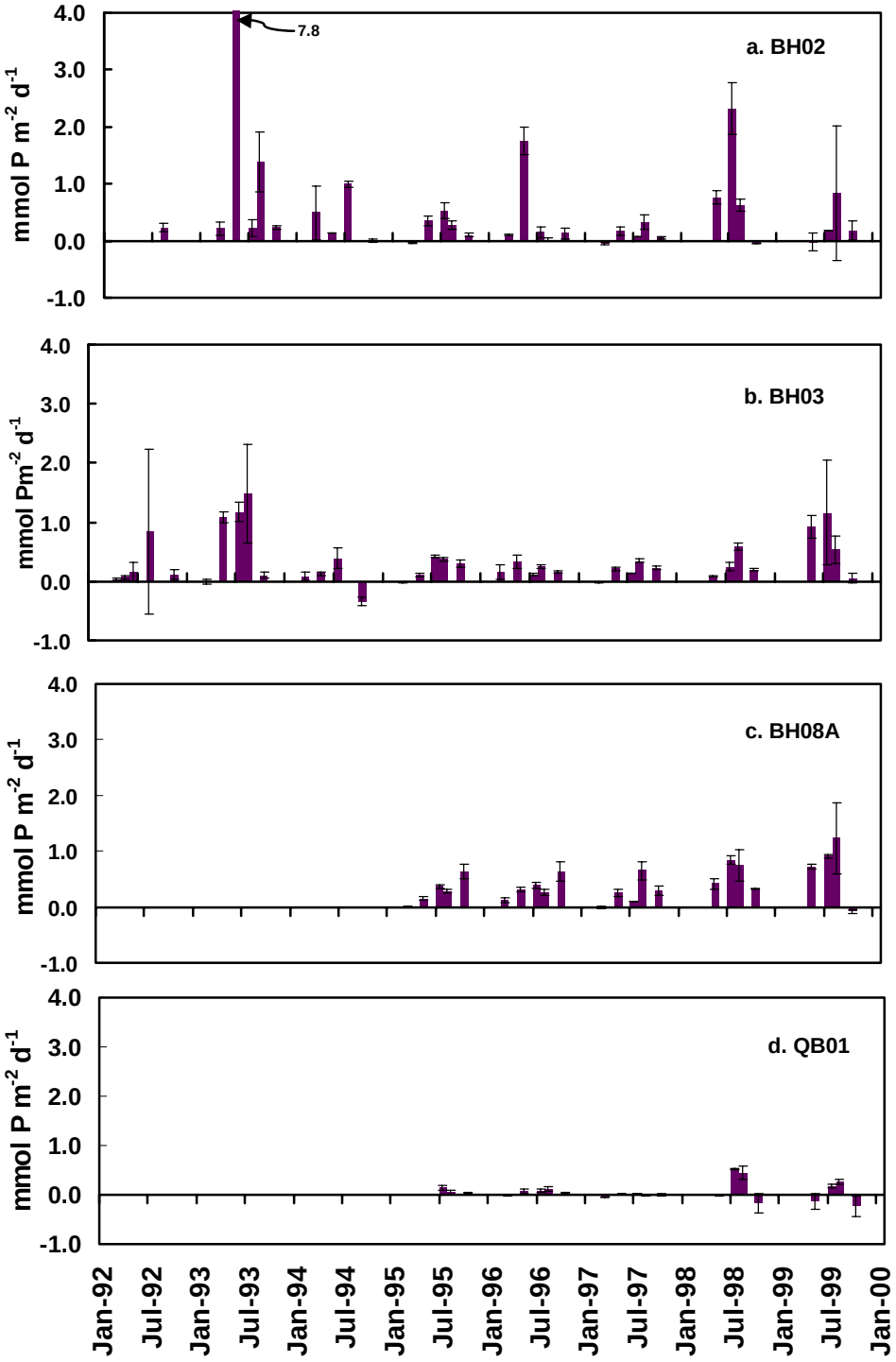


Figure 6. Phosphate flux at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the mean of two cores.

4.1.1.6 Phosphate Flux

Phosphate fluxes from the Harbor stations ranged from -0.2 mmol P $m^{-2}d^{-1}$ at Station QB01 to 1.2 mmol P $m^{-2}d^{-1}$ at Station BH08A, in October and August, respectively.(Figure 6a-6d). Maximal rates at BH03 occurred in July and were equivalent to those from BH08A in August. Overall rates at BH03 were higher than the previous five years but were not as high as those

recorded in 1993. Phosphate fluxes at BH08A were the highest yet measured at this station for the monitoring program. In contrast, rates at BH02 were lower than in 1998, and intermediate those measured in previous years, with the exception of an extreme high, 7.8 mmol P $m^{-2}d^{-1}$, from May 1993 (Fig. 8a). Rates at BH08A were higher than had been reported for the previous four years (Fig. 8c) (Howes, 1998c). At QB01, flux rates of phosphate were lower than in 1998, but higher than previous years. At two sampling dates, May and October, phosphate fluxes were directed into the sediments at QB01. Phosphate uptake also occurred at Station BH02 in May and BH08A in October.

4.1.2 FLUX RATIOS

4.1.2.1 CO_2/O_2 (DIC/O_2)

As discussed in previous reports (Giblin et al. 1993; Giblin et al, 1994; Giblin et al, 1997), the aerobic respiration of organic matter with an oxidation state close to carbohydrates (CH_2O) should have a ratio of CO_2 release to oxygen uptake (RQ or respiratory quotient) of 1. Oxygen is a good indicator of total decomposition on an annual basis even in systems where anaerobic processes such as sulfate reduction are important because most of the reduced end products of decomposition are ultimately reoxidized. On a seasonal basis, however, storage of reduced compounds such as sulfide can change considerably causing oxygen to overestimate respiration at some times of the year and underestimate it at other times. Over an annual cycle, the RQ should be closer to 1. Deviations from an RQ of 1 closely reflect the portion of sulfide which is stored in the sediments as pyrite or FeS.

In 1999, the May-October average RQ was close to 1.0 at Stations BH08A and QB01, but was above 1.0 at Station BH02 and below 1.0 at Station BH03 (Fig. 7a-7d and 8a). The highest RQ from BH02, 1.43, occurred in May, and the RQ was also higher than 1.0 in August and October. The high May value was followed in July by an RQ of 0.85, suggesting at least a short term reoxidation of anaerobic endproducts that had been stored in the spring. For the entire May through October period, the average RQ at this station was 1.29, lower than the previous years' average near 2.0, but still suggesting an overall imbalance favoring anaerobic processes and sulfur storage at this site from May to October.

Station BH03 had an RQ under 1.0 for all months sampled, but substantially less in October (RQ = 0.66) (Fig. 7b and 8a). A large ammonium uptake and equivalent nitrate release accompanied this low RQ, indicating very active nitrification. For the past two years, RQ values have been 1 or less, and the higher values that were common during 1992-1994 have been absent (Fig. 7b)(CO_2 data for 1995-1997 are unavailable).

The May-October average RQ at BH08A was 1.00, balanced by CO_2 release higher than O_2 uptake in May and July, but lower in August and October (Fig. 7c). At QB01, the RQ was 1.08, with CO_2 release exceeding O_2 uptake in all months except July (Fig. 7d). RQ values at these two stations were very similar to those measured in 1998.

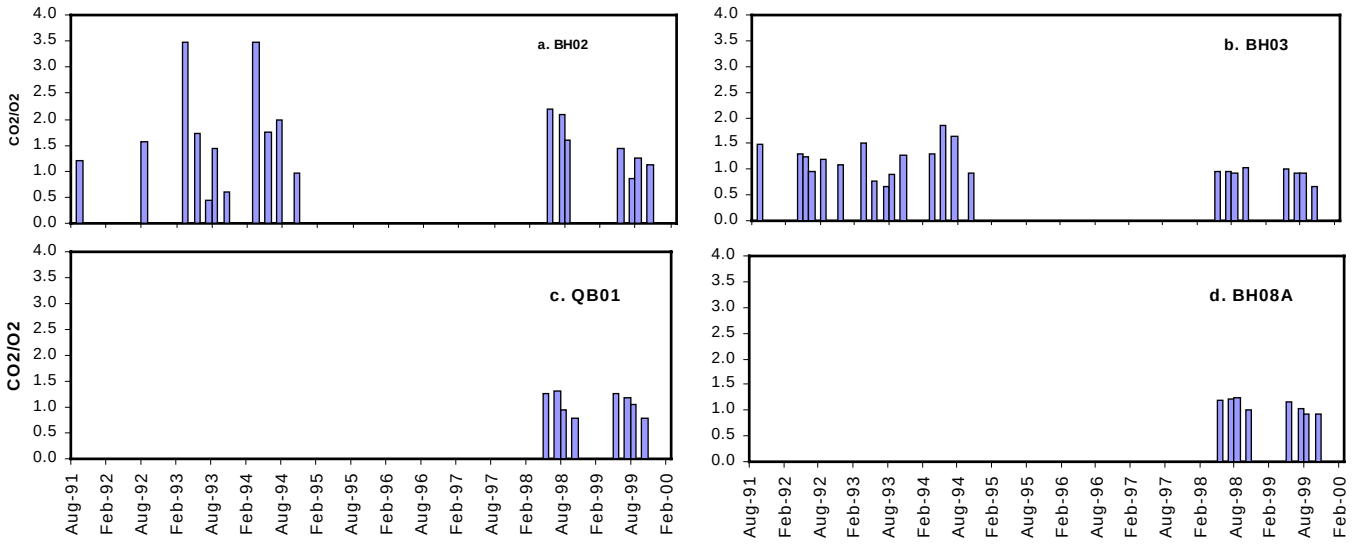


Fig. 7. Respiration Quotients (RQ) as they have changed over time at the Harbor stations.

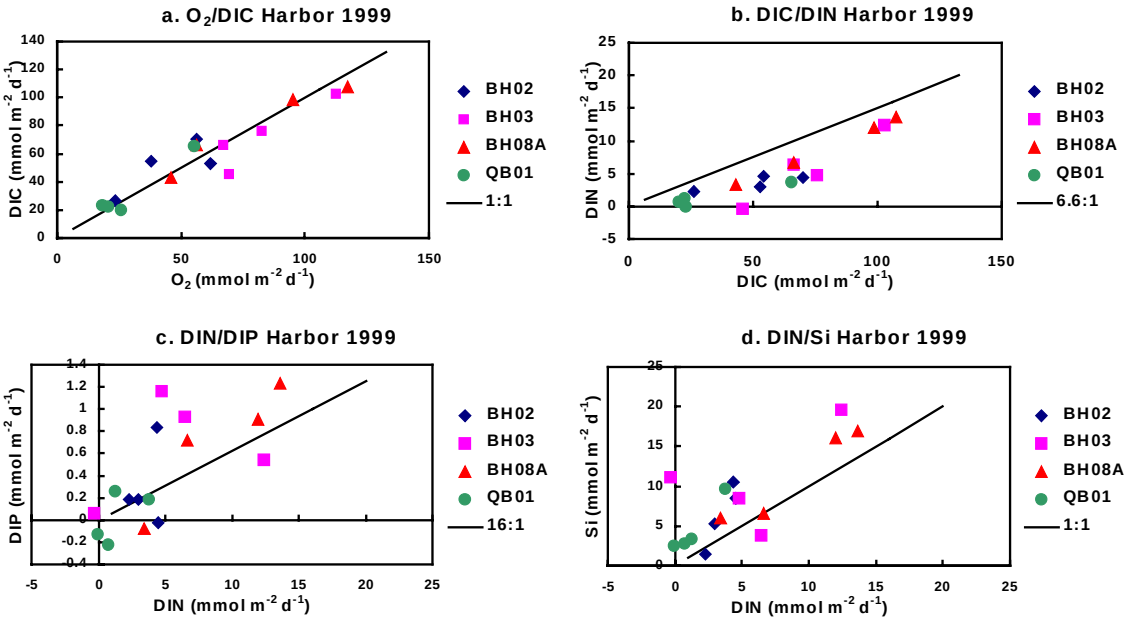


Figure 8. Ratios of element fluxes at all Harbor stations (symbols) relative to theoretical ratios (solid lines). a) DIC/O_2, b) DIC/DIN, c) DIN/DIP, d) DIN/Si.

4.1.2.2 CO_2/DIN (DIC/DIN)

Fluxes of elements derived from decomposition of organic matter in sediments are expected to occur in predictable relationships based on the Redfield composition of phytoplankton, ($C_{106}N_{16}P_1$; Redfield, 1934). In this context, the ratio of CO_2 flux to DIN flux is expected to be 6.6. Ratios higher than expected indicate that less DIN flux was measured than expected from respiration measurements, and it is assumed that the missing nitrogen has been denitrified.

In 1999, CO_2/DIN flux ratios were always higher than 6.6 for Harbor stations, ranging from 7.9 at BH08A in August to 28.5 in October at QB01 (Fig. 8b). A seasonal pattern was not apparent. May to October averages were lowest at Station BH08A (8.84) and highest at QB01 (23.28) (Fig. 9b). These numbers are similar to those reported previously and indicate that denitrification is an active process in the harbor. Rates of denitrification are discussed in Section 4.1.3.

4.1.2.3 DIN/DIP

Following Redfield proportions, the expected ratio of DIN flux to DIP flux is 16. Ratios lower than 16 may indicate a nitrogen loss due to denitrification. However, P flux is strongly affected by abiotic processes in the sediments such that estimating denitrification by this ratio is problematic. A low ratio might be the result of P release from anoxic sediments rather than from denitrification. In contrast, a high ratio might result from P binding in oxidized sediments.

When DIN and DIP fluxes were directed out of the sediments, DIN/DIP flux ratios (Fig. 8c) were less than 16. On two occasions in 1999, IN/DIP was greater than 16. Once was at Station BH03 in August (DIN/DIP = 22.97), and the other was at station QB01 in July (DIN:DIP = 20.64). When DIP fluxes or DIN fluxes were directed into the sediments, the ratio could not be legitimately calculated (becomes negative). This was the case on four occasions. Phosphate fluxes were directed into the sediments in May at Station BH02, and in October for BH08A and QB01; obviously these fluxes were not proportional to DIN fluxes out of the sediments. In October at BH03, DIN flux was negative; again DIN and DIP fluxes were decoupled. May to October averages were less than 16 at all stations except QB01, ranging from 7.65 to 12.78 (Fig 9c). At Station QB01 the average was 67.64. Low ratios are typical of marine sediments and indicate that in Boston Harbor, sediment processing tends to shift the nutrient balance toward N limitation rather than P limitation.

4.1.2.4 DIN/Si

Silica is required by phytoplankton in about a 1 to 1 ratio with nitrogen. Ratios of sediment fluxes may be affected by the silica content of organic matter in the sediments, derived from siliceous phytoplankton, and by denitrification. May to October average DIN/Si flux ratios were less than one at all Harbor stations in 1999 (Fig. 8d). These low ratios indicate that benthic fluxes in the harbor provide nutrients in a ratio that is favorable to diatoms and other siliceous phytoplankton. A ratio greater than 1.0 was calculated on only two occasions, from fluxes at Station BH02 in October, at BH03 in May.

4.1.3 SEDIMENT DENITRIFICATION RATES

4.1.3.1 Direct Measurement of Denitrification

In 1999, direct measurements of denitrification by gas chromatography (Nowicki, 1994) were made on sediment cores from Stations BH02 and BH03 in May and August, the months with the coolest and warmest water temperatures, respectively, during our sampling season. Direct measures were not made at Station BH08A or QB01. Rates ranged from 3.7 mmol N $m^{-2}d^{-}1$ at Station BH02 in May to 15.9 mmol N $m^{-2}d^{-1}$ at BH03 in August (Fig 9). At both stations, rates were higher in August than in May. These rates are among the highest recorded during the monitoring program; in fact, the August rate at Station BH03 was *the* highest recorded. In the past extremely high rates of denitrification at Station BH03 have been measured when there were large numbers of amphipods present (August, 1993; July and August of 1995, 1996, and 1997; October 1998). As amphipod abundances remain high, this pattern appears to be holding.

Although denitrification rates were higher in 1999 than 1998, they accounted for similar percentages of the total benthic N flux. At Station BH02, denitrification accounted for 56% of the total N flux, and at Station BH03 it accounted for 60%.

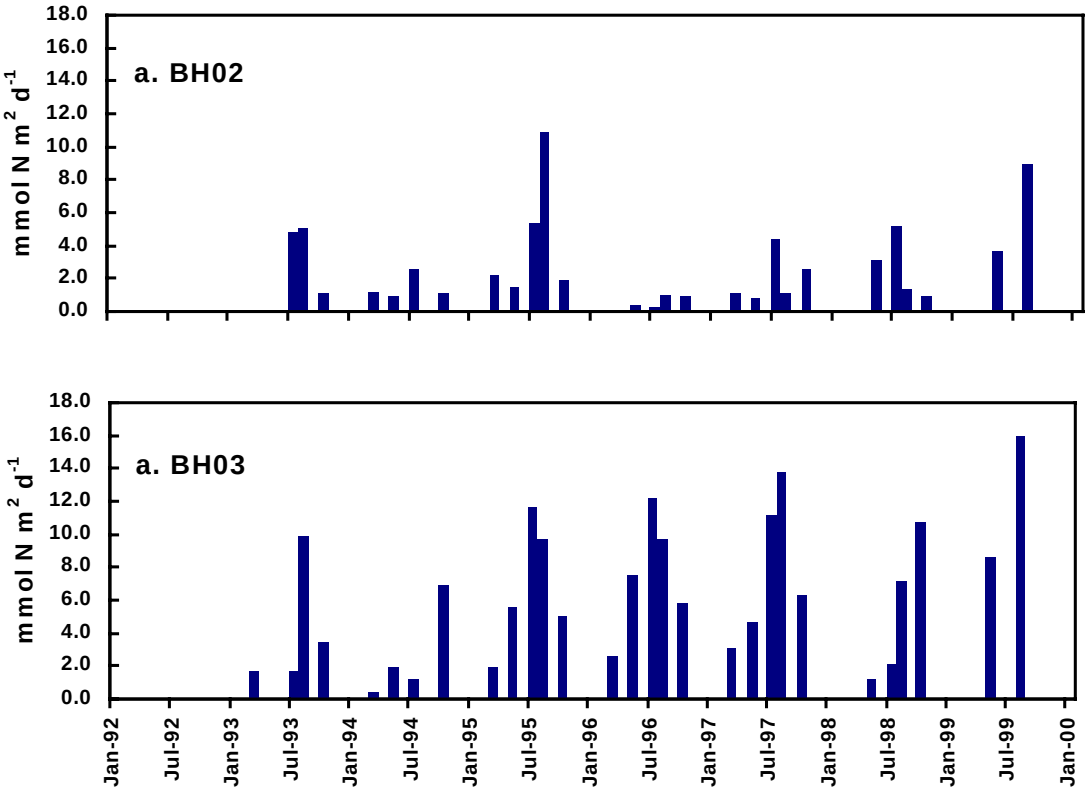


Figure 9. Denitrification as measured by the direct method using gas chromotography (GC) at BH02 and BH03 from 1993-1999.

4.1.3.2. Stoichiometric Measurements of Denitrification

As in previous years, we estimated denitrification from all sites and all dates by calculating stoichiometric relationships between fluxes and comparing them to expected Redfield relationships (see Section 3.6.2). Using this technique, we observed rates and seasonal patterns similar to those of the direct measurements for Station BH02. Denitrification rates estimated by stoichiometry for Station BH02 were 3.7 mmol N $m^{-2}d^{-1}$ in May and 6.2 mmol N $m^{-2}d^{-1}$ in August. These rates compare to 3.7 mmol N $m^{-2}d^{-1}$ and 8.9 mmol N $m^{-2}d^{-1}$, respectively, measured directly. At Station BH03, stoichiometric estimates were much lower than the directly measured fluxes. Stoichiometric rates were 3.6 mmol N $m^{-2}d^{-1}$ and 5.8 mmol N $m^{-2}d^{-1}$ for May and August, whereas directly measured fluxes were 8.6 mmol N $m^{-2}d^{-1}$ and 15.9 mmol N $m^{-2}d^{-1}$.

We also calculated denitrification rates stoichiometrically for Stations BH08A and QB01. Rates at BH08A ranged from 2.9 mmol N $m^{-2}d^{-1}$ in July to 3.4 mmol N $m^{-2}d^{-1}$ in May. These rates were much lower than those calculated in 1998. Seasonal averages of denitrification rates represented only 29% of total N flux at this station. Rates at Station QB01 ranged from 2.1 mmol N $m^{-2}d^{-1}$ in August to 6.1 mmol N $m^{-2}d^{-1}$ in July. At this station, denitrification accounted for over 75% of total May-October N flux .

4.1.4 SEDIMENT CHARACTERISTICS

4.1.4.1 Nitrogen and Carbon

Organic nitrogen and carbon content of surface sediments at Harbor stations in 1999 (Fig 10, Table 2) were within the ranges noted for previous years (Fig. 11) [1991-1994 (Giblin et al, 1997) and 1998 (Tucker et al, 1999) for Stations BH02 and BH03, and as compared to 1998 for Stations BH08A and QB01]. At Station BH03, both carbon and nitrogen content have apparently decreased over the 8 years of monitoring this site (Fig. 11a,b). In 1999, carbon content in the top 2 cm of sediment was nearly constant over the May to October period, averaging 2.7%, well below the annual average of 4.2% from 1992, the year just after sludge dumping ceased. Nitrogen was also lower than the 1992 average of 0.43%, averaging 0.3% and including a May low value 0.2%. Nitrogen content was higher in July through October than it was early in the season. The increase in nitrogen resulted in a decrease in the molar C/N of the sediments, dropping from almost 15 in May to 10 for the rest of the season (Fig. 10).

Station BH02 showed less clear trends towards a reduction in organic matter content of the sediments over all the years of monitoring, however 1999 average values were lower than 1998 Fig.11c,d). Sediments at Stations BH02 showed more seasonal variability in their C and N content than those from BH03, however the range of values measured was narrower than in previous years. Carbon percentages were high at the start of the season and declined over the months between May and August at Station BH02 from 2.0% to 1.2 %; similarly, nitrogen declined from 0.26% to 0.14% (Fig. 10). In October, the concentrations increased somewhat and the higher C and N content suggested new inputs since the summer. C/N ratios changed very little over the sampling season. It has been a consistent pattern that sediments at BH02 experience the widest range in values of the four stations. It is the only one of the four in an area classified as reworking rather than depositional. It is adjacent to Governor's Island Flats, also a reworking environment, but a much shallower one where benthic production may be important. Suspension and redeposition of sediments carrying variable loads of labile carbon may explain the range in C and N we observed at this station.

Sediment organic matter content at Station BH08A and QB01 was very similar to that measured in 1998. At Station QB01, carbon and nitrogen content in the sediments fluctuated such that it was high in May, low in July, highest in August, and lower again in October. The August maximum was 2.9% TOC and 0.26 % TON. The carbon content was as high in August at QB01 as was measured at any time over the season at the other stations. In contrast to the ups and downs of the concentrations, the molar ratio (C/N) calculated for these sediments increased steadily over the 6 month interval from 10.7 in May to 13.9 in October. Sediments from Station BH08 were remarkably constant in both carbon (average 2.4%) and nitrogen (average 0.3%) over the 1999 sampling period. Accordingly, C/N was also constant.

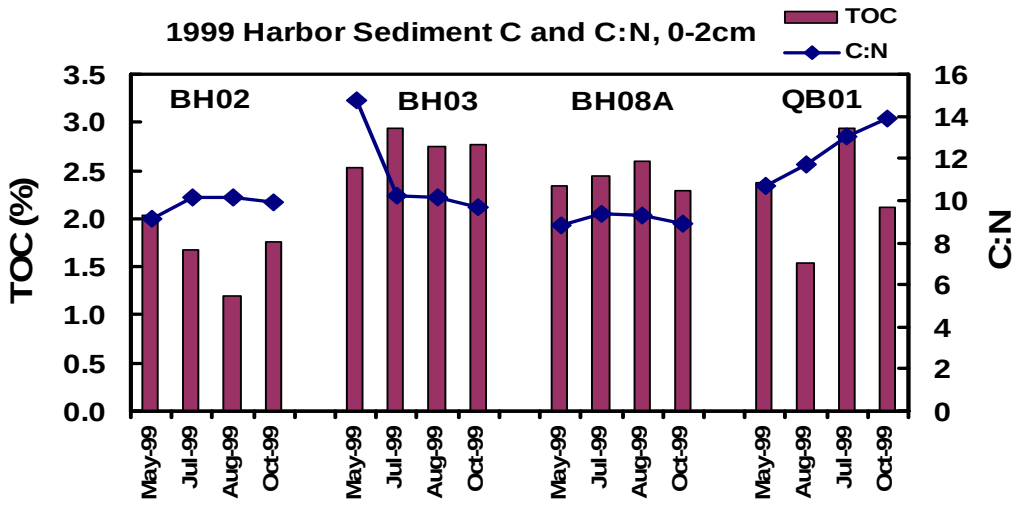
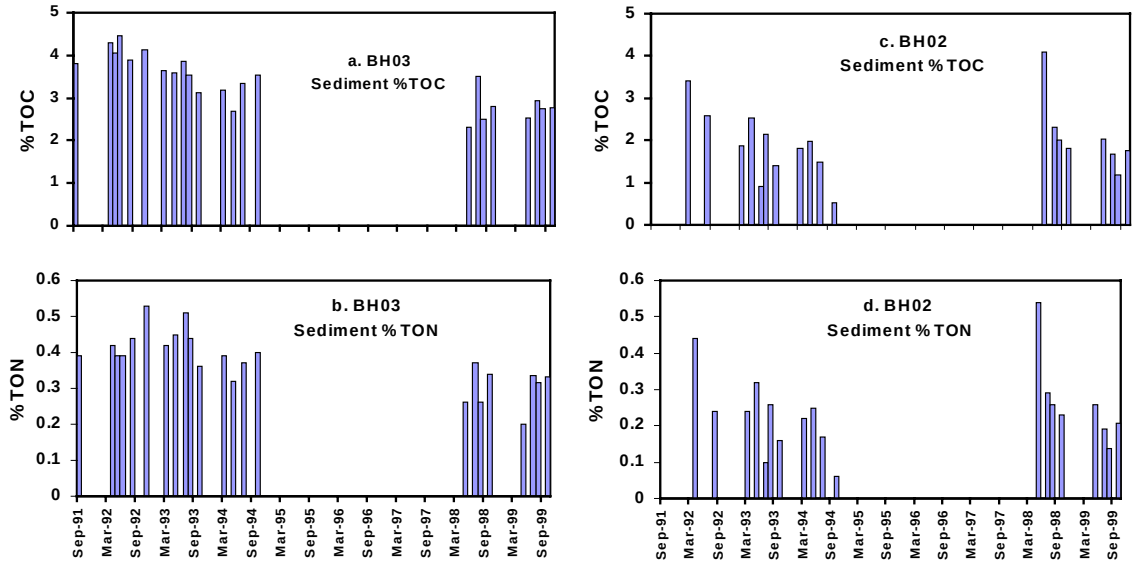


Fig. 10. TOC and molar C:N at the Harbor stations, 1999



.Figure 11. Changes in organic carbon and nitrogen in two harbor stations since 1991. a.) %TOC at BH03, b.) %TON at BH03, c.)%TOC at BH02, and d.)% TON at BH02.

4.1.4.2 Pigments

Sediment pigments were measured at the beginning and end of the sampling season, in May and October, 1999 (Table 2). As in 1998, inventories of pigments, chlorophyll *a* + phaeopigments, summed over the top 5 cm of sediment were higher than they had been in previous years of monitoring (Fig. 12). Much of this increase appears to be in the phaeopigment fraction, except for at Station BH02. At BH02, chlorophyll *a* concentrations have been higher over the past two years with the exception of one high measurement in August of 1997. At the two northern harbor stations, BH02 and BH03, there was not much difference between the early and late season

inventories of chlorophyll *a* (Fig. 12a, 12b). At BH08A and QB01, however, in the southern harbor, May inventories of chlorophyll *a* were approximately double October measurements (Table 2). These differences were also apparent in sediment profiles of chlorophyll concentrations. At Station BH08A, May profiles showed a subsurface peak in chlorophyll around 2-3 cm that had disappeared by October. At QB01, surface concentrations were high in May but absent from the October profile. This early season high was also recorded in 1998. Benthic diatoms have been noted at this station (Tucker et al, 1999), and the chlorophyll results suggest they were present at least early in the season again in 1999.

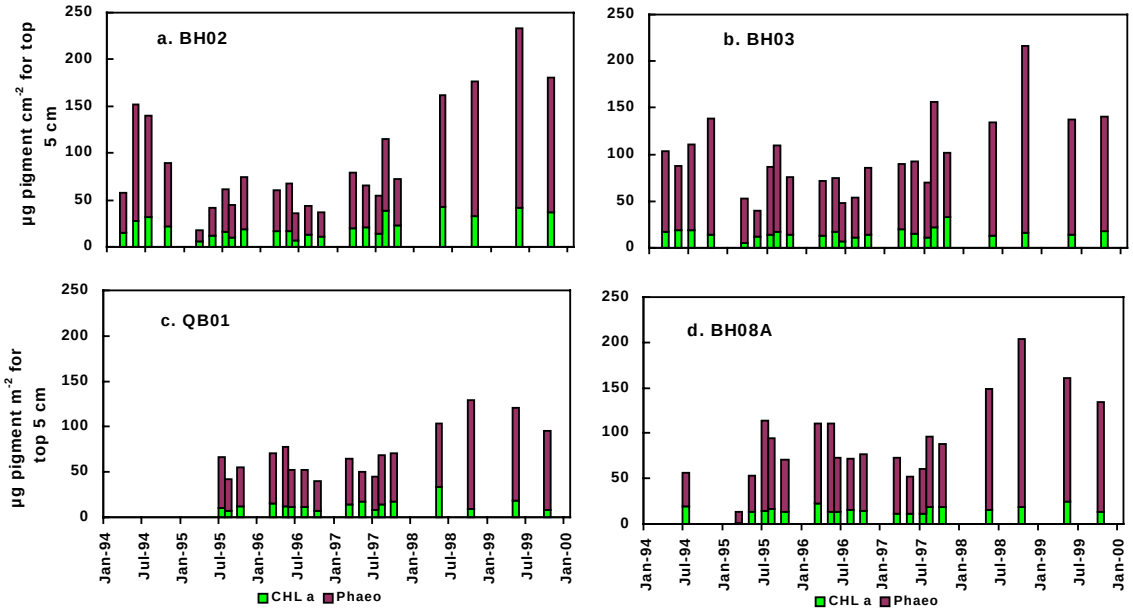


Figure. 12 Inventories of chlorophyll pigments in the top 5 cm. of sediments at Harbor stations a.) BH02, B.) BH03, c.) BH09A, and c.) QB01. green (bottom of bar) = chlorophyll *a*; red (top of bar) = phaeopigments.

Harborwide, it appeared the average for total pigment inventories for the top 5 cm of sediment in 1999 (~150µg cm^{-2}) were similar to that reported from 1998 (~160 µg cm^{-2}) but higher than that from the same stations averaged over the years 1995-1997 (~125µg cm^{-2}) (Howes, 1998c). Apart from real increases in sediment chlorophyll *a* and phaeopigments, higher estimates from 1998 may be partially explained by having only spring and fall measurements, whereas all previous years (1992-1997) included winter and summer measurements. Also, our method for extracting pigments from sediments includes a freezing step which facilitates the extraction of pigments bound in sediment matrices such as fecal pellets or detritus (Sun et al, 1991). Therefore, some of the difference in measurements between 1998 and 1995-1997 may reflect a difference in "free" and "bound" pigments.

Table 2. %Carbon, %Nitrogen, and Pigment Concentrations from Boston Harbor sediments in 1999.

Station	Date	%C[1]	%N[1]	Chlorophyll *a*[2] µg/cm^2	Total Pigments[2] µg/cm^2
BH02	May	2.0	0.26	42.1	233.3
	July	1.8	0.21		
	August	1.7	0.19		
	October	1.2	0.14	36.4	181.0
BH03	May	2.5	0.20	13.7	137.0
	July	2.8	0.33		
	August	2.9	0.34		
	October	2.7	0.32	18.1	140.5
BH08A	May	2.3	0.30	24.2	161.0
	July	2.3	0.31		
	August	2.4	0.31		
	October	2.6	0.33	13.4	134.2
QB01	May	2.4	0.26	18.0	120.4
	July	2.1	0.18		
	August	1.5	0.15		
	October	2.9	0.26	8.6	95.3

1. % C and % N are for the top 2 cm of sediment.
2. Inventory of chlorophyll *a* or total pigments (chlorophyll *a* + phaeopigments) for top 5 cm of sediments.

4.1.5 POREWATER CONSTITUENTS

Oxidation-reduction potential (Eh) was measured at all stations and at all four sampling times (Fig 13 a-d). Patterns in Eh were similar to those of previous years. At Stations BH03, BH08A , and QB01, lowest Eh values were measured in May. At the two stations where bioturbation is very active, BH03 and BH08A, the patterns in Eh were very similar and higher during the rest of our sampling season (Fig. 13 b, 13c). Sediments at these two stations were well oxidized to depths over 10 cm at all times except May, when the redox potential discontinuity (RPD = 0mV) was around 5 cm.

Station BH02 had the most reducing sediments overall, with the RPD occurring at sediment depths less than 3 cm in July and October (Fig. 13a). Lowest Eh values at this station did not occur in May as was the pattern for the other Harbor stations. In August, Eh profiles showed more highly oxidized sediments at this station than are typical for summer. These profiles were measured just after the passing of two hurricane systems off the coast and may reflect sediment resuspension .

In 1999, reducing conditions were never recorded in our measurements on sediments from QB01 (Fig. 13d). May values were lower than those from the other three months, but even at a depth of 18 cm (depth of penetration for these measurements) had not quite decreased to 0 mV. This circumstance was unprecedented for the four previous years of monitoring at this station.

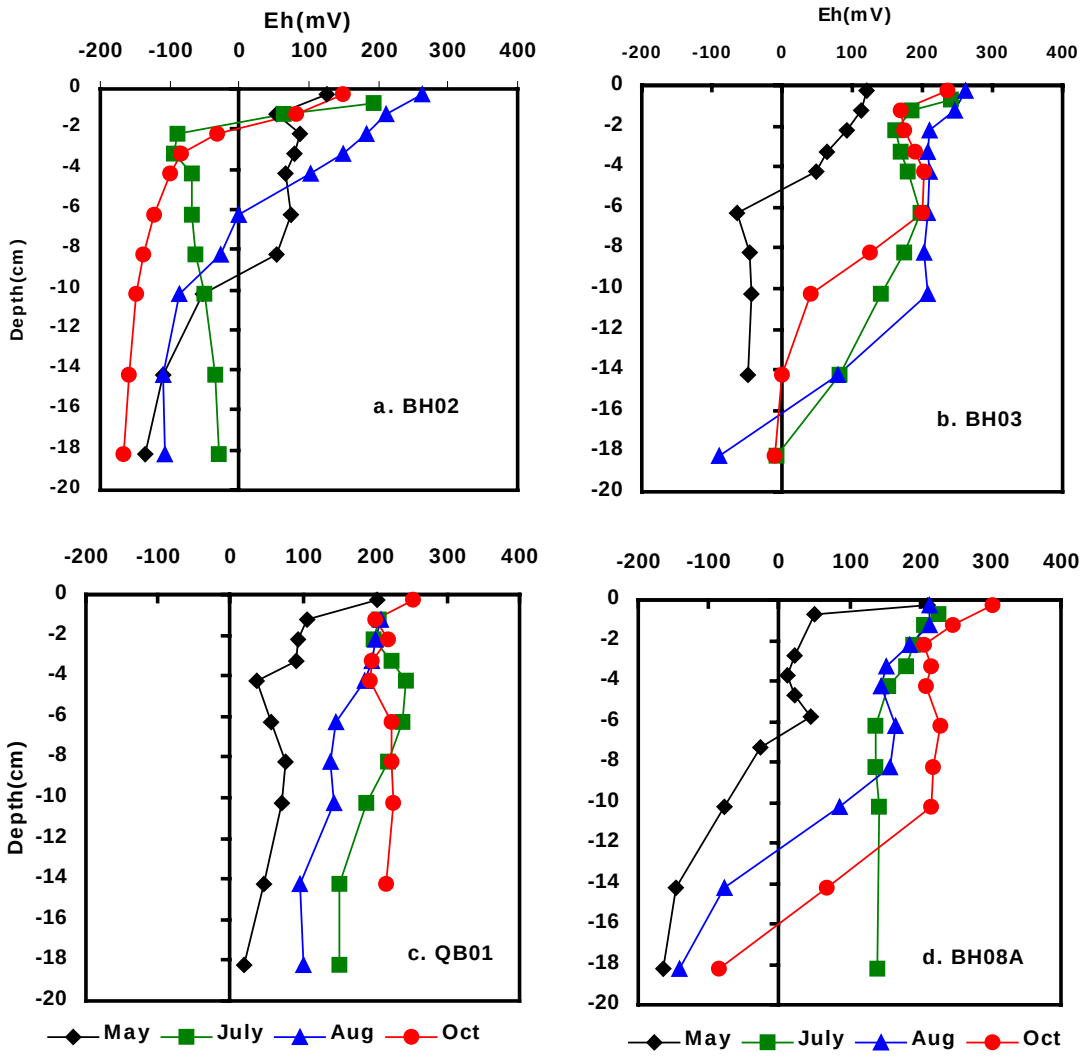


Figure 13. Oxidation-reduction potential (Eh) from sediment cores from each survey for a) BH02, b) BH03, c) QB01, and d) BH08A.

Other porewater constituents were measured in July and August. Porewater profiles continued to suggest that sediments were more oxidized than in previous years. At station BH02, one of the sites that has been characterized throughout the monitoring program as having reducing sediments, the highest concentration measured this year was just over 2 mM at 12 cm depth in August; concentrations twice that high or greater have often been measured at his station. In July highest concentrations were less than 1.0 mM, whereas in 1998 concentrations had reached 4.8 mM.

4.1.6. SUMMARY OF TRENDS IN HARBOR NUTRIENT FLUXES

The reduction of solids loading to the harbor, initially by the cessation of sludge disposal at the end of 1991 and subsequently by treatment improvements at Deer Island and by the diversion of the Nut Island effluent to the Deer Island Plant in the summer of 1998 (Taylor, D. in prep), has been the primary agent of change in Boston Harbor during the past decade. Areas of the Harbor that were directly affected by sludge disposal, such as Station BH03, have undergone large changes in their biology and chemistry. Areas near the Nut Island outfall, such as Station QB01, may have begun to show a response to the diversion of that effluent out of Quincy Bay.

Two of the Harbor stations described in this report, Stations BH02 and BH03, have been studied since 1991. The other two, BH08A and QB01 have been monitored since 1995. Comparisons of these four stations, their physical and biological characteristics, and their histories vis a vis changes to sewage loading in the harbor offer insight into patterns we have reported in nutrient fluxes. Stations BH02 and BH03 have been studied under the MWRA Harbor Benthic Monitoring Program (Kropp et al, 2000) as T02 and T03, respectively. Similarly, stations R46 and R48 in the Benthic Monitoring Program were established at the same coordinates as our benthic flux Stations BH08A and QB01, respectively.

The following summary and Table 4 describing the physical and biological characteristics of the four harbor stations in 1998 are taken from Kropp et al, 2000. The data suggest strong similarities between Stations BH02 (T02) and QB01 (R48), and between BH03 (T03) and BH08A (R46).

Sediments at BH02 (T02) and QB01 (R48) are shaped by physical processes to a higher degree than are those at BH03 (T03) and BH08A (R46). This is reflected in the sediment type at QB01(R48), and although sediment samples from BH02(T02) were very silty in 1998, they have often had a high sand content. Sediment texture at BH02(T02) has varied considerably over time, from 70% sand and gravel in 1994 to 84% fines in 1998. BH02(T02) was classified as a reworking sedimentary environment by Knebel (1993). Other similarities between these two stations were found in their biological characteristics. Both were classified as having infaunal communities in successional stage I/II, or a mix between the poineering and transitional seres. Neither station supported *Ampelisca* mats, although amphipods were present, and both had low organism/sediment indices (OSI), indicating the community was under some form of moderate stress (Kropp et al., 1999b). Both stations had shallow redox potential discontinuities (RPD).

In contrast, Stations BH03 (T03) and BH08A (R46) were both dominated by biological processes, with sediments covered by *Ampelisca* mats. Sediments at these two stations were silts, although some variablilty has been noted at BH03 (T03). Kropp et al. reported that from 1991-1994 sediments at BH03 (T03) were sandier, with less silt and clay, whereas from 1995-1998 they were silty. In fact, in April 1994, sediment samples from T03 were 52% sand. Station BH08A (R46) was classified with a higher successional stage than BH03A(T03), II on III as opposed to II, and had a much higher OSI. Also, the estimated RPD was deeper at BH08A(R46) than at BH03(T03). It appeared that conditions at BH03 (T03) were in transition towards those at BH08A(R46). This is consistent with the history of sludge disposal near Station BH03 (T03).

Table 3 Physical and biological characteristics for the four Harbor stations; excerpted with permission from Kropp et al., 1999b, Table 3-1.

Harbor Monitoring Station **Benthic Flux Station**	**T02** **BH02**	**T03** **BH03**	**R46** **BH08A**	**R48** **QB01**
General location	Northern Harbor	Northern Harbor	Southern Harbor	Southern Harbor
Sediment type	silt	silt	silt	Silt/fine sand w/ shell
Process(es) affecting sediment surface	Physical and biological	Biological	Biological	Physical and biological
RPD	0.9	1.3	3.2	0.7
Successional Stage	I/II	II	II on III	I/II
Ampelisca mat Presence/absence	-	+	+	-
OSI	3.7	5.7	9.0	2.3

Results of the benthic flux monitoring program can be put into context of these changes. The data show that after sludge disposal stopped oxygen uptake rates in sediments at Station BH03 have been among the highest measured in coastal sediments (Giblin et al., 1997). Very high rates were first recorded in the summer of 1993, and the highest (over 300 mmol O_2 m^{-2} d^{-1}) was recorded in the summer of 1995. These high rates corresponded to the dramatic increase and shift in infaunal populations at this site, away from a low diversity, low abundance community present in 1991 - early 1992 to a species-rich community dominated by the amphipod *Ampelisca* spp. present thereafter.

Coincident with the increased sediment oxygen demand at Station BH03 have been large fluxes of nutrients from the sediments and a shift in the components of the fluxes towards more oxidized forms. *Ampelisca* forms dense mats of tubes that penetrate 5-10 cm into the sediment. The activities of the amhpipods as they ventilate their tubes have had several effects. One is simply that advection of porewater nutrients from the sediments has increased. For example, in the early phases of colonization, 1992-1993, phosphate fluxes were high, probably due to a flushing of the sediments, and contrary to expectations of phosphate dynamics in oxidized sediments. Similarly, a large pulse in Si fluxes was recorded in 1993 (Si fluxes were not measured in 1992). The second effect of bioturbation has increased oxidation of the sediments. The proportion of the dissolved inorganic nitrogen flux that is NO_3^- has increased dramatically as nitrification has been enhanced (Fig 4). In turn, denitrification rates have increased (Fig. 9). Another effect has been to increase the access to substances stored in these sediments that were characterized, during the years of sludge deposition, by high accumulation rates of organic matter and resulting anaerobic sediments. This so-called sediment “mining” has contributed to nutrient fluxes by enhancing decomposition of stored organic matter. Its effects have also been to decrease sediment sulfide concentrations at this site, as sulfidic substrates have become exposed to oxidative processes.

These responses seem to have been strongest in the first four years after sludge disposal stopped (1992-1995). Since 1995, flux rates have moderated at this station, and have become very similar to those at Station BH08A, the other of our sites where the amphipod mats are routinely present. The implication is that the stores of organic matter have been reduced and the site is stabilizing. Organic carbon and nitrogen content of the sediments at BH03 have decreased from a 1992 average of 4.2%C and 0.43%N to a 1999 average of 2.7%C and 0.30%N (Fig.11a). These percentages are approaching but still higher than those at BH08A, but support the impression that the conditions at Station BH03 are becoming similar to those at BH08A. Assuming that Station BH08A represents a "normal" depositional site for the Harbor, as is indicated by the equilibrium stage of its benthic community and by the relatively constant nutrient fluxes reported since 1995, it appears that, by comparison, Station BH03 is nearing equilibrium conditions.

The most recent reduction in solids loading to Boston Harbor occurred in the summer of 1998, when all flow from the Nut Island Treatment Plant was diverted to the Deer Island Treatment Facility (Rex, 2000). This change resulted in a decrease in solids loading harbor-wide as secondary treatment in the Deer Island Plant effectively removes over 85% of particulates from the wastewater stream. The diversion also reduced the DIN and DIP concentrations in the southern harbor by over 30% and 15%, respectively, while only slightly (insignificantly) increasing concentrations in the northern harbor (Taylor, submitted).

Results from the first full year of sampling after the diversion reveal that large effects have been observed in only a few parameters (Taylor, submitted). In the north harbor, the most notable change was a 33% increase in annual average chlorophyll *a* concentrations. The number and size of the chlorophyll peaks were higher than any previous measurements with the exception of those from 1995. The south harbor experienced a decrease in total nitrogen (TN), and although changes in DIN and DIP concentrations were not significant, the DIN:DIP ratio decreased from 9.11 to 6.1. There was some tendency towards improved water clarity in the south harbor.

Benthic nutrient fluxes from the Quincy Bay Station QB01 have shown little change since the diversion. In fact, oxygen uptake and nutrient fluxes were somewhat higher in 1998 and 1999 than in the three previous years. However, there was one notable difference in porewater chemistry in 1999. Reducing conditions in the sediments, as measured by Eh, were not observed during the 1999 field season, although in May the RPD (0 mV) would have been reached had our core been a bit deeper (Fig. 12c). These observations may indicate a change in sediment oxidation state, as failure to reach the RPD had not occurred since monitoring of this station began in 1995. Sediments at this site are shaped by both physical and biological processes, and they are not as silty as at the other three sites. It is unclear at this time what mechanism may have contributed to these results. It will be interesting to see if, as has happened elsewhere in the harbor, there has been a change in infaunal abundance at this station. Early spring benthic chlorophyll *a* concentrations were also somewhat higher in 1998 and 1999, and benthic diatoms have been reported at this very shallow station. Although the small increase in water clarity in the south harbor may have contributed to increased benthic production, it is premature to make that correlation.

The fourth harbor station, Station BH02, has also undergone changes over the past 9 years, but they have been more variable (less unidirectional). Sediments at this site support low abundances of infauna and sediment texture may vary considerably. Sediments here typically have very shallow RPDs, sometimes associated with high sediment oxygen demand, and nitrogen fluxes are dominated by NH_4^+. However, there have been two large peaks in infaunal abundances, in 1994 and 1995, coincident with the appearance of *Ampelisca* at this site. In 1995, sediment oxygen demand was somewhat higher than usual, nitrogen fluxes were comprised of larger than typical percentages of NO_3, and denitrification rates were high. These patterns are consistent with

observations at our other amphipod-dominated sites, where nutrient fluxes seem closely linked to animal densities. However, during 1994, the year of the larger peak in infaunal abundances, fluxes were not unusually high, although NO_3^- did make up a significant portion of DIN fluxes in July. Also, sediments collected at this site in 1994 were 70 % sand and gravel, rather than the silt usually associated with higher animal densities. At Station BH02, therefore, there are multiple forcing factors to consider, and correlations made on annual time scales are difficult. On a decadal time scale, it appears that although there has been an increase in infaunal diversity, there has been little change in sediment nutrient cycling at BH02.

4.2 MASSACHUSETTS BAY

4.2.1 BENTHIC RESPIRATION AND NUTRIENT FLUXES

4.2.1.1 Oxygen Uptake

Between May and October 1999, sediment oxygen uptake ranged from approximately 15 to 32 mmol O_2 m^{-2} d^{-1} at our three nearfield Massachusetts Bay stations (MB01, MB02, and MB03) and from about 10 to 14 mmol O_2 m^{-2} d^{-1} at our Stellwagen Basin station (MB05)(Figure 14). As has been typical throughout the monitoring program, the Nearfield rates were approximately 4 to 5 times lower than the Harbor rates, whereas the Stellwagen rates were on the order of 10 times lower. At the Bay stations, highest rates were measured in September, although warmest bottom water temperatures occurred in October. There was no difference in September and October rates at the Stellwagen station. Rates measured in sediments from MB05 were lowest of the four stations at each sampling time and overall for the May to October season, averaging 12 mmol O_2 m^{-2} d^{-1} (Fig. 15d), also typical of the entire monitoring program. Of the three nearfield stations, MB01 and MB03 had very similar seasonal average rates of about 19 mmol O_2 m^{-2} d^{-1}, whereas rates at MB02 were higher, averaging 25 mmol O_2 m^{-2} d^{-1}.

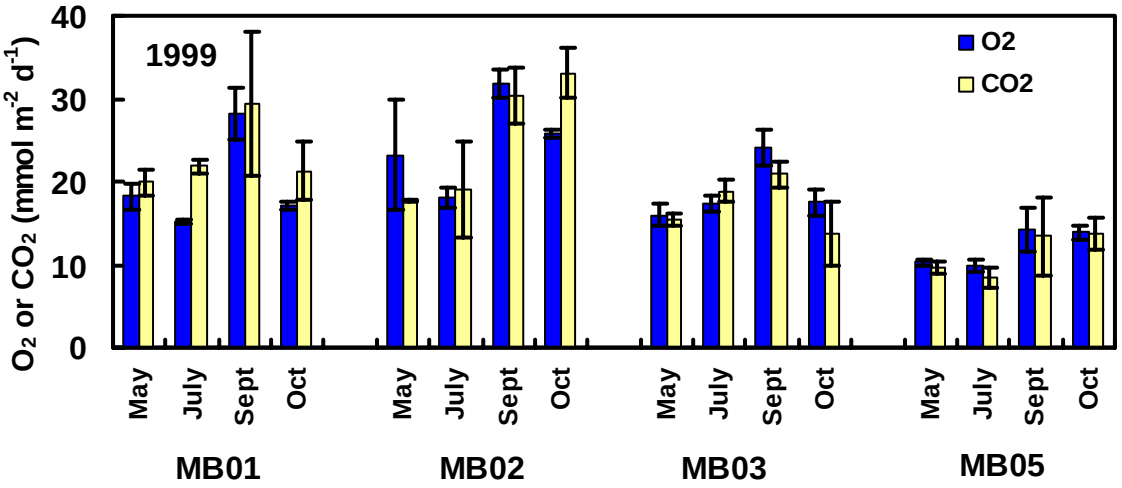


Figure 14. Sediment Respiration as measured by O_2 uptake or CO_2 flux at a.) MB01, b.) MB02, c.) MB03, d.) MB05. Error bars represent the standard error of the mean of two cores.

Annual average oxygen uptake rates in 1999 were higher than for any previous year since 1993 at Station MB01 and MB02 (note: an average winter (March) rate was calculated for each

station using data from 1993-1997, and was included in annual average rates for 1999) (Fig. 15a, 15b). Station MB02 had the highest rates to date of any of the Bay stations. There was also more difference among the three stations than in previous years, except for 1997 during which only MB01 and MB03 were visited. From 1993 to 1995, annual average rates of oxygen uptake in the three Nearfield stations were quite similar across stations and appeared to decline somewhat from about 16.3 (SE = 0.21) to 12.1 mmol O_2 m^{-2} d^{-1} (SE 0.5). In 1996 the three stations were less

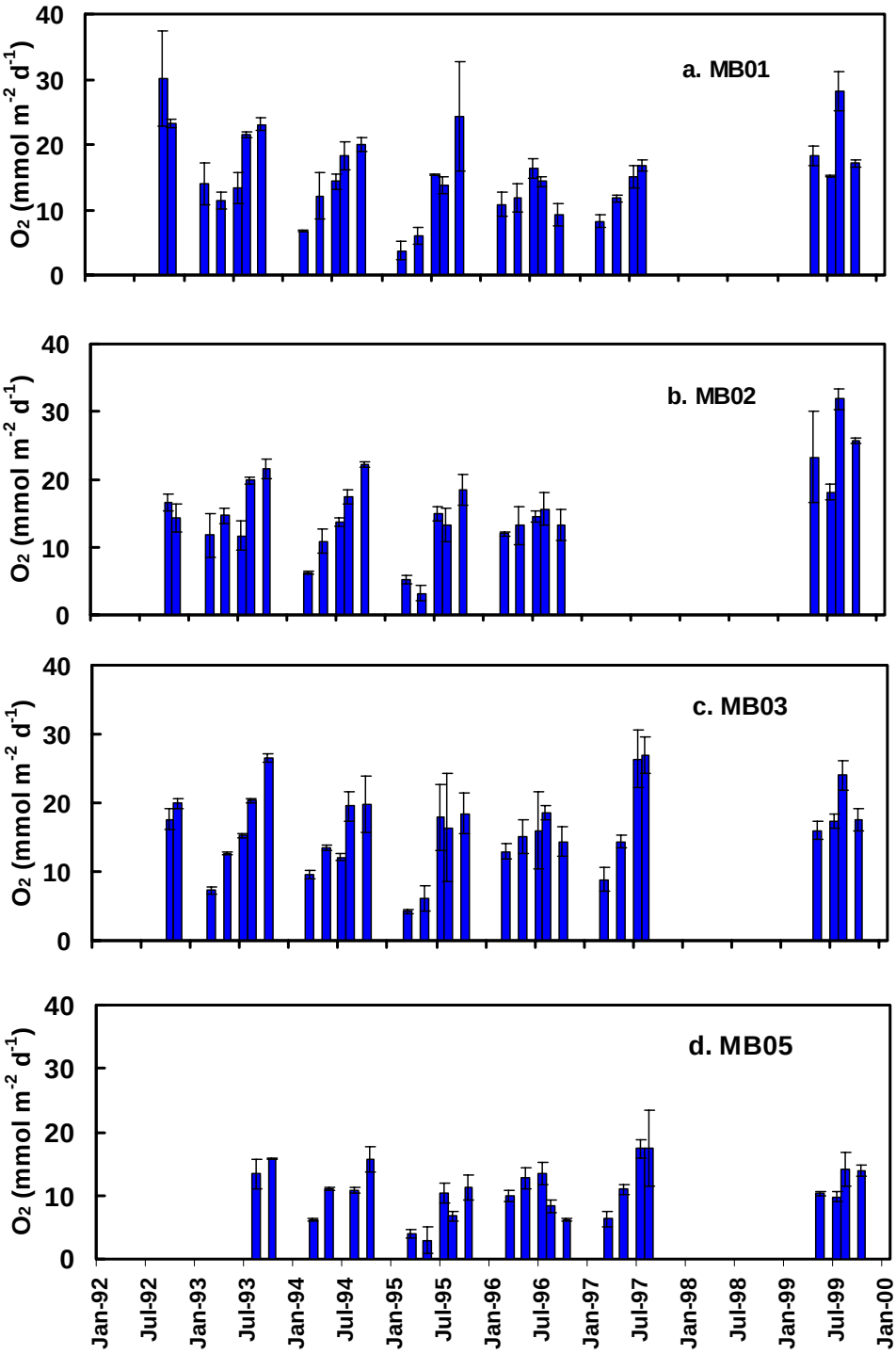


Figure 15. O2 flux from 1992-1998 at a) MB01 and b) MB02, c) MB03 and d) MB05. Error bars represent the standard error of the mean of two cores.

similar, averaging 13.9 (SE 0.84). In 1997, average rates at MB01 and MB03 were quite different (13.0 at MB01 vs 19.1 at MB03), driven mostly by very high rates at MB03 in late summer/fall.

Another difference in 1999 rates at the Nearfield stations was that they did not follow the typical seasonal pattern. In all other years since 1993, except for 1996, the seasonal pattern followed temperature, with maxima in the fall. In 1999, as well as 1996, rates peaked in mid summer (Fig. 14). Seasonal patterns are often less distinct at Station MB05, where water temperatures vary less, but even at this station a mid summer peak was present in 1996 and 1999.

4.2.1.2 Total CO_2 Measurements

Total CO_2 (DIC) fluxes at the Nearfield stations ranged from approximately 14 to 33 mmol CO_2 $m^{-2}d^{-1}$ between May and October 1999, and from 8 to 14 mmol CO_2 $m^{-2}d^{-1}$ at the Stellwagen station (Fig. 14). The magnitude and seasonal pattern of CO_2 fluxes was similar to that of oxygen uptake. As for oxygen uptake, CO_2 fluxes in 1999 were highest at Station MB02.

In general, the two measures of benthic respiration, O_2 uptake and CO_2 release, were in closer agreement at the Bay stations in 1999 than in earlier years of the monitoring program. In the previous years, it was often the case that CO_2 release greatly exceeded O_2 uptake. In 1999, the largest discrepancy occurred at Station MB02 in May when oxygen uptake exceeded CO_2 release, and at the same station in October when the opposite pattern was true. The closest agreement occurred at Station MB05.

CO_2 fluxes in 1999 appeared lower than recorded from 1992-1994 at all stations except Station MB02 (data not available for 1995-1997, and no Bay stations were visited in 1998). At station MB02, CO_2 fluxes were very similar to the previous years; however they came closer to matching O_2 fluxes because the O2 fluxes were high.

4.2.1.3 DIN Release from Sediments

The combined flux of ammonium plus nitrate and nitrite (DIN) to the overlying water at the three Nearfield stations in 1999 ranged from 0.5 mmol N $m^{-2}d^{-1}$ at Station MB02 in May to 1.7 mmol N $m^{-2}d^{-1}$ at the same station in October. (Fig. 16a-d). Rates at MB05 in Stellwagen Basin ranged from an uptake of 0.1 in early September to a release of 0.3 mmol N $m^{-2}d^{-1}$ in July. The highest average May-October rate, 0.9 mmol N $m^{-2}d^{-1}$, was measured in sediments from Station MB01, however the average at the other two Nearfield stations was nearly as high. There was no consistent seasonal pattern of DIN flux across the stations.

In 1999, at the three Nearfield stations, most of the DIN flux was comprised of NH_4^+. Highest NH_4^+ fluxes, 1.8 mmol N $m^{-2}d^{-1}$, were measured in October at Station MB02. In contrast, NO_3^- was the major form of N released from MB05 sediments except in September, when NO_3^- was taken up. The predominance of NH_4^+ was typical from 1992 to 1994 at all four stations. However, from 1995 to 1997, nitrate made up a larger proportion of the total flux. The dominance of NO_3^- at MB05 has only been observed once before, in 1996.

The magnitude of DIN fluxes has varied over the years of the monitoring program. Most of the variability has been in the NH_4^+ fluxes; by comparison, NO_3^- fluxes have been relatively constant, with the exceptions of instances when $NO3^-$ flux was directed into the sediments as noted below. The high NH_4^+ fluxes measured in 1999 were most similar to those from 1992-1994; however the exceedingly high flux measured at MB01 in September, 1992, has not been repeated. Rates of NH_4^+ flux were lower during 1995-1997.

Athough nitrate uptake has been observed in Massachusetts Bay sediments at various times since 1992, it has been infrequent. In 1999, however, nitrate uptake was important at Station

MB02, occurring during all but the July sampling periods. Nitrate uptake had not been observed in sediments from this station since 1993.

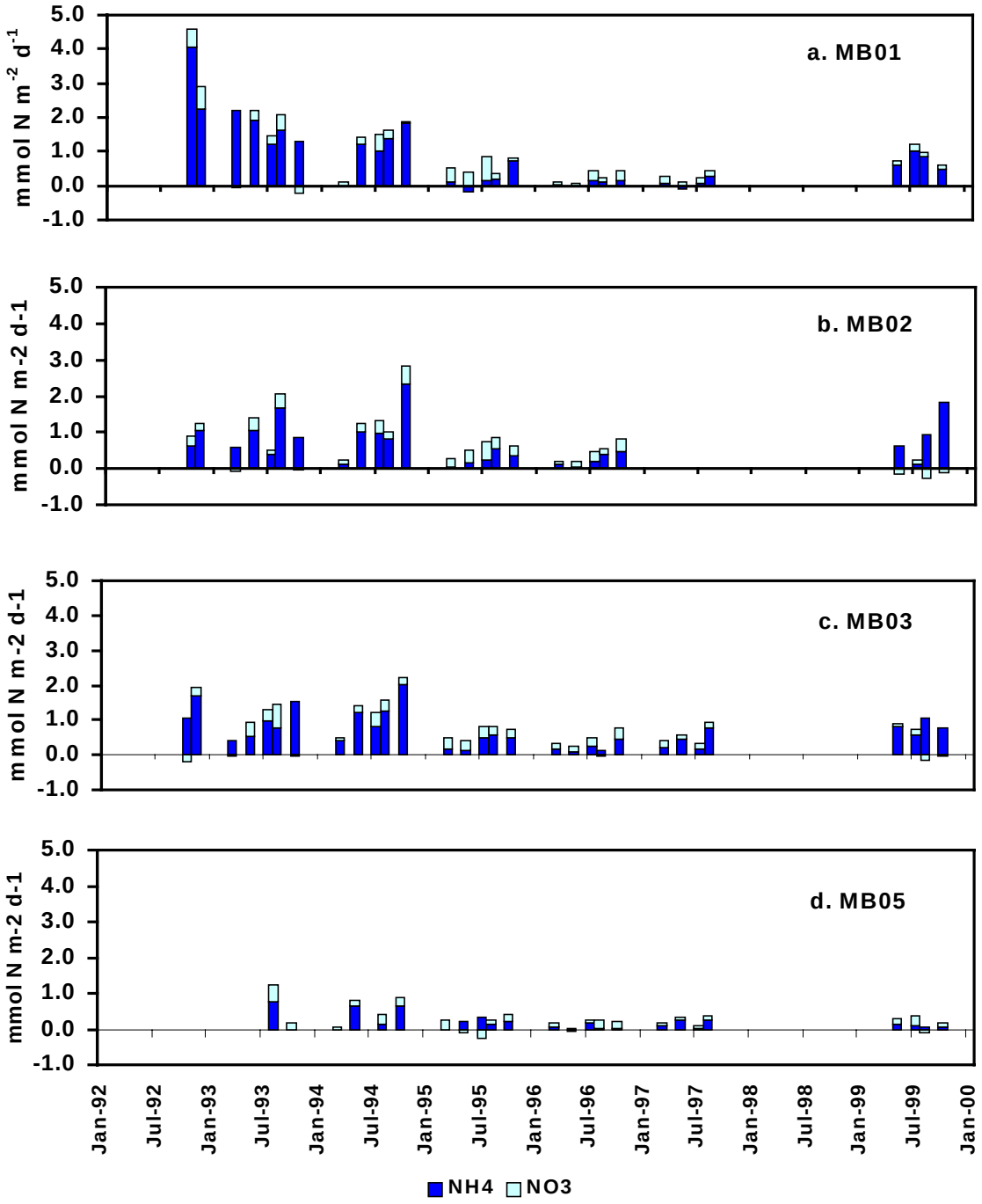


Figure 16. DIN flux, showing relative contributions of NO_3^- and NH_4^-, at a) MB01, b) MB02, c) MB03, and d) MB05 from late 1992 to 1999.

4.2.1.4 Urea Fluxes

Urea fluxes in Massachusetts Bay were small and variable. Calculated rates indicated that urea was taken up by sediments as often as it was released. Although some flux rates calculated from individual cores had r^2s greater than 0.5, at no time in 1999 did duplicate cores both yield rates with significant r^2s. The strongest results were from Station MB05, where at each sampling time one core had a flux with a significant r2; however, its duplicate often had a calculated flux in the opposite direction. The highest r^2 for any rate measurement was 0.96 for a single core from Station MB05 in September and the flux was into the sediments, -0.2 mmol N $m^{-2}d^{-1}$. These results combined with large standard errors around the means of duplicate cores demonstrate the irregularity of these fluxes. The rates, however, are of the same order of magnitude as the DIN fluxes, and may represent, on very short time scales, an important component of the Bay nitrogen fluxes.

4.2.1.5 Silica Fluxes

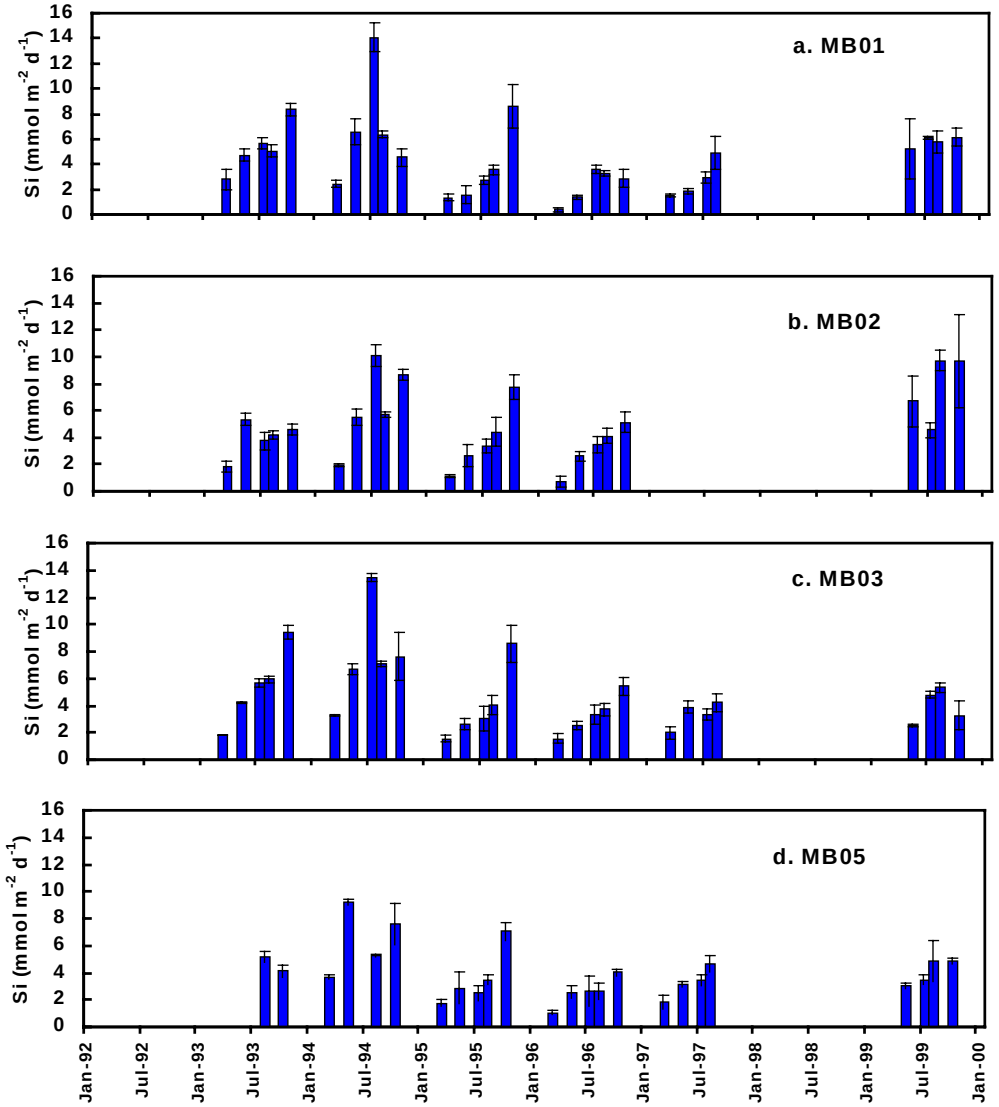


Figure 17. Dissolved silica flux at a) MB01, b) MB02, c) MB03, and d) MB05. Error bars represent the standard error of the mean of two cores.

Silica fluxes in the nearfield stations of Massachusetts Bay in 1999 ranged from a low of 2.5 mmol Si m^{-2} d^{-1} in May at Station MB03 to a high of 9.7 mmol Si m^{-2} d^{-1}, measured in both September and October at Station MB02. Rates at MB05 ranged from 3.0 mmol Si m^{-2} d^{-1} in May to 4.8 mmol Si m^{-2} d^{-1} in September and October. Silica fluxes are the only nutrient fluxes that we measure at the Stellwagen station that are comparable in magnitude to those from the nearfield stations. The largest average seasonal (May to October) flux was 7.7 mmol Si m^{-2} d^{-1} at Station MB02, whereas the lowest was 4.0 mmol Si m^{-2} d^{-1} , shared by Stations MB03 and MB05.

Very high silica fluxes were observed at Station MB02 in 1999. These rates were the highest yet observed at this station, and among the highest overall. Silica fluxes were also elevated at Station MB01 as compared to 1995-1997, and similar on average to the high years of 1993 and 1994. In Massachusetts Bay, Si fluxes have typically shown a strong seasonal pattern associated with increasing temperature such that peaks often occur in the fall (see Giblin et al, 199x; Howes, 1998a-c). However this pattern was not strong in 1999. Departures from this pattern also occurred in 1994, when very high Si fluxes were measured at all four stations.

4.2.1.6 Phosphate Flux

Phosphate fluxes from the Bay nearfield stations ranged from an uptake of 0.3 mmol P $m^{-2}d^{-1}$ at Station MB03 in September to a release of 0.2 mmol P $m^{-2}d^{-1}$ at Stations MB01 and MB02 in September. Fluxes at the Stellwagen site were similar at all sampling times, ranging only from 0.02 to 0.06 mmol P $m^{-2}d^{-}$, with the lower rate in September and the higher in October. There was no consistent seasonal pattern among the stations. MB01 and MB02 were similar in that maximal rates of phosphate flux out of the sediments occurred in September. Maximal fluxes at Station MB03 also occurred in September, but were directed into the sediments. In fact, the seasonal average at MB03 was an uptake of 0.1 mmol P $m^{-2}d^{-}$. At MB05, lowest rates were measured in September.

In general, phosphate fluxes in 1999 did not resemble any particular previous year. At MB01, annual average rates were intermediate the high rates of 1992-1994 and the low rates of 1995-1997. At Station MB02, average rates were among the highest observed at this station with the exception of 1994 which included a very high flux in October. As mentioned above, rates at MB03 were primarily directed into the sediments; this pattern had not been observed before at this or the other stations. Annual average rates at MB05 in 1999 were much lower than those from the high year of 1994, but very similar to those in1995-1997.

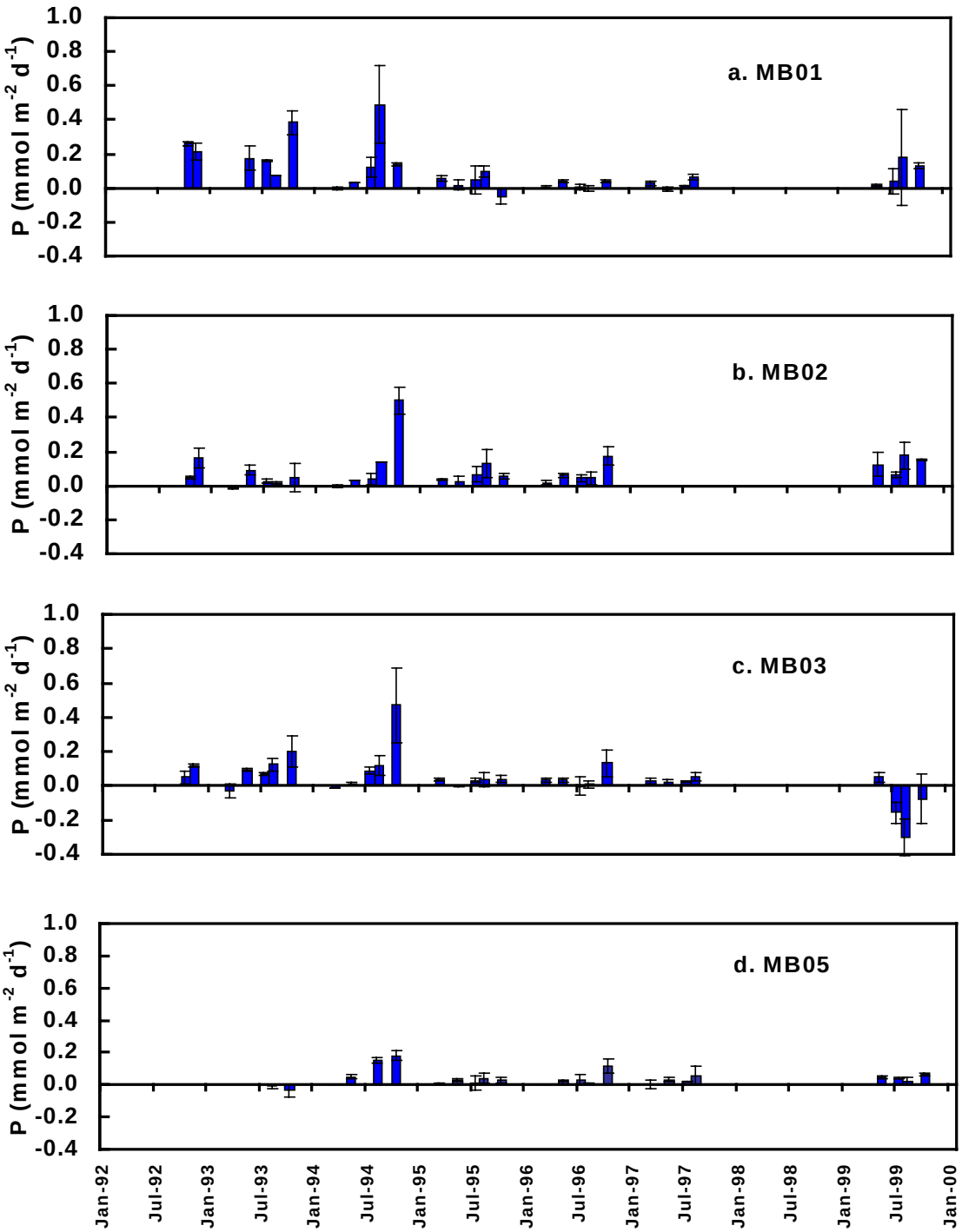


Figure 18. Phosphate flux at a) MB01, b) MB02, c) MB03, and d) Mb05. Error bars represent the standard error of the mean of two cores.

4.2.2 FLUX RATIOS

4.2.2.1 CO_2/O_2 (DIC/O_2)

In 1999, the May-October averageCO_2/O_2 ratio or respiration quotient (RQ) (see Section 4.1.2.1) was close to 1.0 at Stations MB02, MB03, and MB05, but was above 1.0 at Station MB01 (Fig. 19a). Values were significantly above 1.0 at MB01 in July (1.4) and again in October (1.2). A similarly high value was calculated from the October fluxes at MB02 (1.3). Respiratory quotients significantly less than 1.0 occurred in the July fluxes from MB02 (0.8), the September and October fluxes of MB03 (0.9 and 0.8, respectively), and at MB05 in July (0.9). At the nearfield stations, the patterns of change with season in the RQs were similar until October, when the RQ fell to 0.8 at MB03 but was well above 1.0 at the other two stations.

Fluctuations in the RQ reflect variable inputs to the benthos and subsequent sediment processing, and, as we have observed in the Harbor, may be affected by bioturbation. During 1992-1994, it was typical for annual average RQs in the nearfield to be well over 1.0. This suggested that anaerobic processes and storage of endproducts were important. In 1999, average RQs near 1.0 suggest that aerobic and anaerobic processes are currently more balanced. Whether these changes reflect changes in inputs to the Bay and/or possible changes in infaunal communities remains to be determined.

4.2.2.2 CO_2/DIN (DIC/DIN)

In 1999, CO_2/DIN flux ratios were much higher than the expected 6.6 for all Bay stations at all sampling times (Fig. 19b). A seasonal pattern was not apparent, but the highest ratio, 94.9, was calculated from July fluxes at MB02. A meaningful ratio could not be calculated At MB05 in September because the DIN flux was negative (directed into the sediments). However, the absence of N flux to balance the CO_2 suggests that denitrification accounted for all of the inorganic N flux from this station at this time.

Ratios calculated as an annual average for 1999 fluxes were higher than those from 1992-1994. In the nearfield, the ratios fell in a narrow range between 16.1 and 18.5 during 1992-1994. At MB05 in 1994, the average was 23.7. In contrast, the ratios in 1999 ranged from 21.1 to 31.6 in the nearfield, and at MB05 the average was 55.1 (note: annual averages include an estimate of winter flux rates calculated from March data, 1993-1997). The amount of "missing" nitrogen that is implied by these ratios suggests that denitrification is an important process in Bay sediments. Rates of denitrification are discussed in Section 4.2.3.

4.2.2.3 DIN/DIP

DIN/DIP flux ratios were variable from station to station in Massachusetts Bay throughout the 1999 season (Fig. 19c). At Station MB01, ratios were well above the expected Redfield ratio of 16 in May and July (48.1, 29.8) and well below in September and October (5.5, 4.6). At MB02, ratios were below 16 at all times throughout the sampling season, but were lower in May through September than they were in October. At Station MB03, the ratio in May was 17.7, very near Redfield expectations; however during the rest of the season phosphate fluxes were negative, making calculation of the ratio invalid but making apparent that the fluxes were decoupled. At Station MB05, the ratios were below 16 in May, July, and October, but in September, negative DIN fluxes made the September ratio invalid.

As annual averages, all stations in 1999 had DIN/DIP less than 16. As indicated above, the annual average at Station MB03 was negative, driven by the sustained and unprecedented phosphate uptake that occurred in July through October. High average ratios have only infrequently been calculated from Bay fluxes (Fig. 20a) ; at Station MB02 in 1993 (32.2) and at MB03 in 1995 (23.1). On some occasions, ratios have been very close to 16, suggesting that, at these times and

on an annual basis, Bay sediments have been in balance with regard to N and P fluxes (at MB01 in 1995 and 1996 and at MB03 in 1997). Most frequently, DIN/DIP ratios from Bay fluxes are below Redfield expectations, suggesting that the sediments tend towards nitrogen limitation relative to phosphorus, and reinforcing the idea that denitrification is an important process in the Bay.

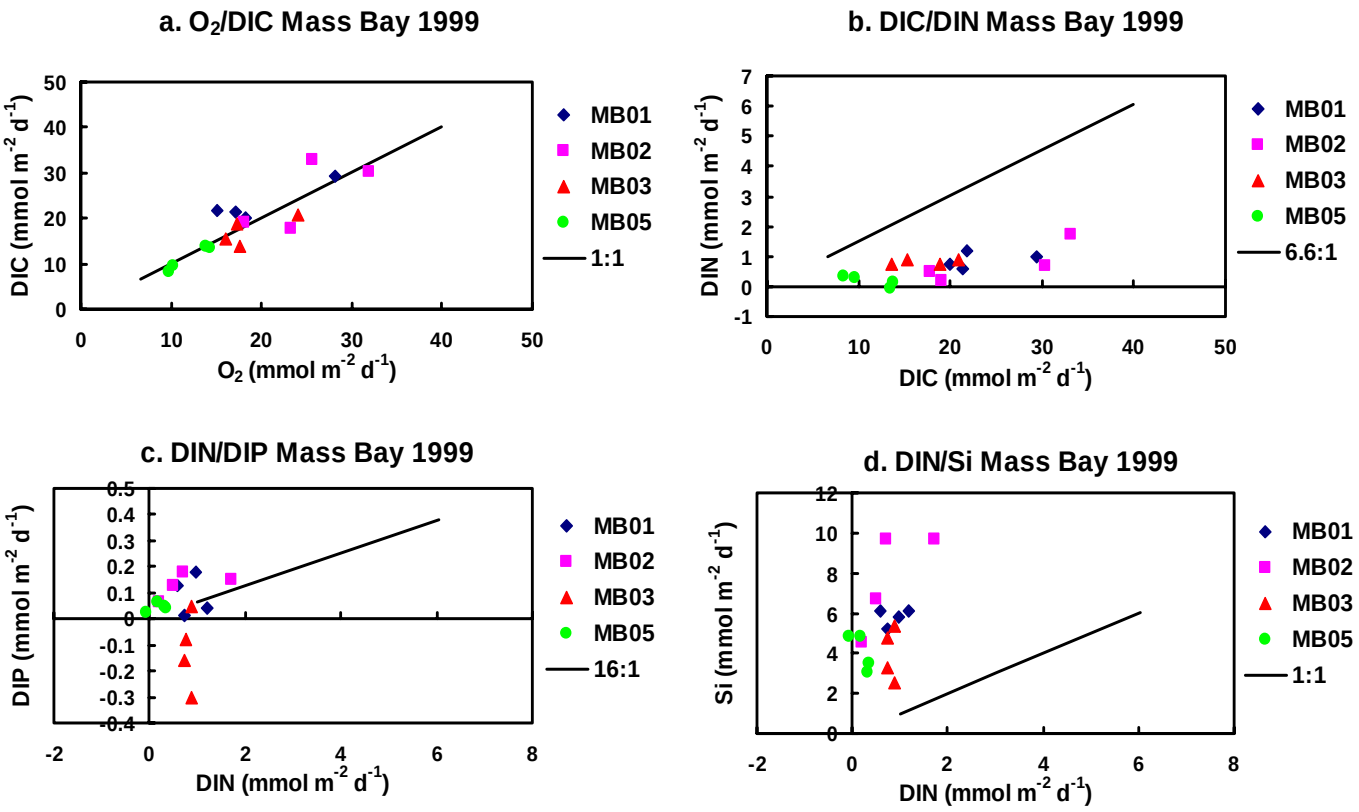


Fig. 19 Ratios of element fluxes at all Bay stations (symbols) relative to theoretical ratios (solid lines). a) DIC/O_2, b) DIC/DIN, c) DIN/DIP, d) DIN/Si.

4.2.2.4 DIN/Si

In Massachusetts Bay and Stellwagen Basin, Si fluxes from the sediments were far in excess of DIN fluxes, leading to DIN/Si ratios much lower than 1.0 (Fig. 19d). The highest ratios occurred at Station MB03, with a maximum value of 0.34 in May. Stations MB01 and MB02 had somewhat lower ratios, and Station MB05 had the lowest. Very low ratios are characteristic for Station MB05 sediments. From 1994 to 1999, the annual average DI/Si ratio at Station MB05 fell in a very narrow range of 0.05 (1999) to 0.08 (1994 and 1997). At the nearfield stations, the ratios were very similar across stations and declined from 1993 to 1996 for all three stations, and until 1997 for Station MB01 (measurements not made at MB02 in 1997). Since then, the ratios have diverged and increased (Fig. 20b).

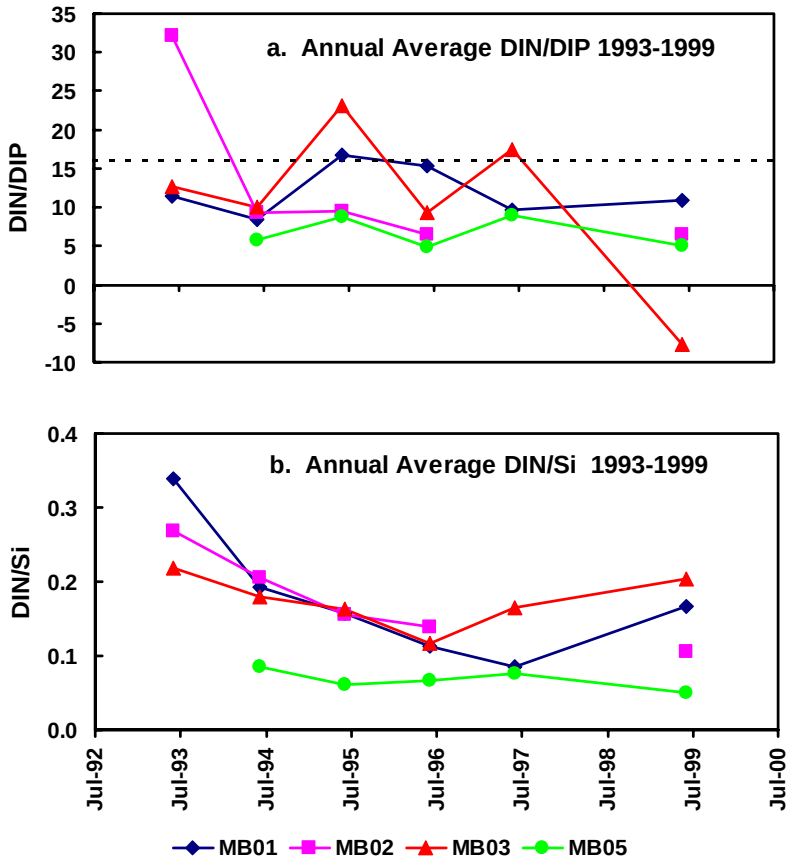


Figure. 20. Changes in annual average sediment flux ratios of a. DIN/DIP and B. DIN/SI at Massachusetts Bay stations, 1993-1999.

4.2.3 SEDIMENT DENITRIFICATION RATES

4.2.3.1 Direct Measurement of Denitrification

In 1999, denitrification rates were directly measured by gas chromatography on sediment cores from Stations MB02 and MB03 in May and October, the months with the coolest and warmest water temperatures in the Bay, respectively, during our sampling season. Direct measurements were not made at Station MB01 or MB05. Rates ranged from 1.3 mmol N $m^{-2}d^{-}1$ at Station MB02 in May to 6.0 mmol N $m^{-2}d^{-1}$ at the same station in October. Although the highest rates were measured in sediments from MB02, Station MB03 sediments had quite high rates in both months, 5.3 mmol N $m^{-2}d^{-}1$ in May and 3.5 mmol N $m^{-2}d^{-}1$ in October. These rates are among the highest recorded during the monitoring program. During 1992-1994, denitrification rates at Bay stations were typically less than 2 mmol N $m^{-2}d^{-}1$. By these measurements and for May and October only, denitrification accounted for almost 75% of the total dissolved nitrogen flux at MB02, and almost 85% at MB03. Denitrification rates were not measured in Massachusetts Bays sediments from 1995-1997.

4.2.3.2. Stoichiometric Measurements of Denitrification

Stoichiometric estimates of denitrification in Massachusetts Bay were lower in general than direct measures. Denitrification rates estimated by stoichiometry for Station MB02 were 2.2 mmol N $m^{-2}d^{-1}$ in May and 3.3 mmol N $m^{-2}d^{-1}$ in October (compare to 1.3 mmol N $m^{-2}d^{-1}$ and 6.1 mmol N $m^{-2}d^{-1}$, respectively, measured directly). At Station MB03, stoichiometric rates were 1.4 mmol N $m^{-2}d^{-1}$ and 1.3 mmol N $m^{-2}d^{-1}$ for May and October (compare to 5.3 and 3.5 mmol N $m^{-2}d^{-1}$, respectively). Using stoichiometric estimates of denitrification that were made for all four sampling months, the seasonal average at MB02 was 3.0 mmol N $m^{-2}d^{-1}$, with a high of 3.9 in early September. At MB03 the four month average was 1.8 mmol N $m^{-2}d^{-1}$, with a high, also in September, of 2.3 mmol N $m^{-2}d^{-1}$.

Denitrification rates calculated for Station MB01 were similar to those from the other two nearfield stations with a seasonal average of 2.6 mmol N $m^{-2}d^{-1}$. Rates from the Stellwagen site were somewhat lower, averaging 1.5 mmol N $m^{-2}d^{-1}$. Highest rates from both of these sites, as for MB02 and MB03, were measured in September: 3.5 mmol N $m^{-2}d^{-}1$ at MB01 and 2.1 mmol N $m^{-2}d^{-1}$ at MB05.

These stoichiometric estimates imply that a very large percentage of the total DIN flux in Massachusetts Bay is accounted for by denitrification, ranging from 62% in May at MB03 to essentially all of the flux at MB05 in September. As a May to early September average, DIN accounts for about 75% of DIN flux at the nearfield stations, and about 85% at the Stellwagen station. These percentages are very high. Estimates from other coastal sediments range from 15 to 70% (Seitzinger , 1988).

4.2.4 SEDIMENT CHARACTERISTICS

4.2.4.1 Nitrogen and Carbon

Organic nitrogen and carbon content of surface sediments in 1999 were higher in Stellwagen Basin sediments than in the nearfield sediments (Fig. 21, Table 4). At Station MB05 in the Basin, sediment %TOC and %TON were quite similar at all sampling times, averaging 1.5%TOC and 0.17% TON. Sediments from the nearfield showed more variability, with concentrations peaking in September at MB03 and in October for MB01 and MB02. C/N ratios were very stable at Station MB05, averaging about 10, whereas they changed over the season at the nearfield stations. Ratios at MB01 and MB02 zigzagged up from May to October from about 11 to 14, and at MB03 increased to 13 in July before declining to 11 by October. Increases in C and N content did not correspond to decreases in C/N, implying that, as expected, the organic matter reaching the benthos was not "fresh" phytoplankton, but had been degraded to some extent during deposition.

Organic nitrogen and carbon content of nearfield sediments in 1999 were lower than in earlier years of the monitoring program. At Stations MB01 and MB03 there was a marked decrease in 1999 compared to 1993-1994, and concentrations seemed less variable across the season. This pattern was also apparent at MB02, but to a lesser degree. In contrast, there was no change in the Stellwagen Basin sediments over the same time period.

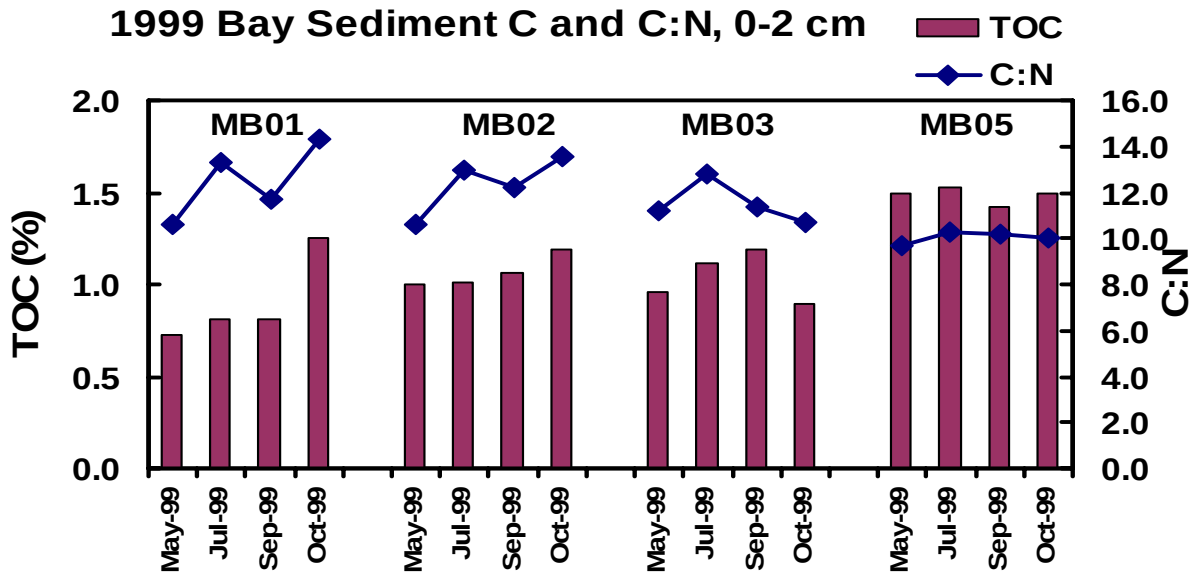


Figure 21,. Sediment %TOC and molar C:N ratios for Bay sediments, 1999.

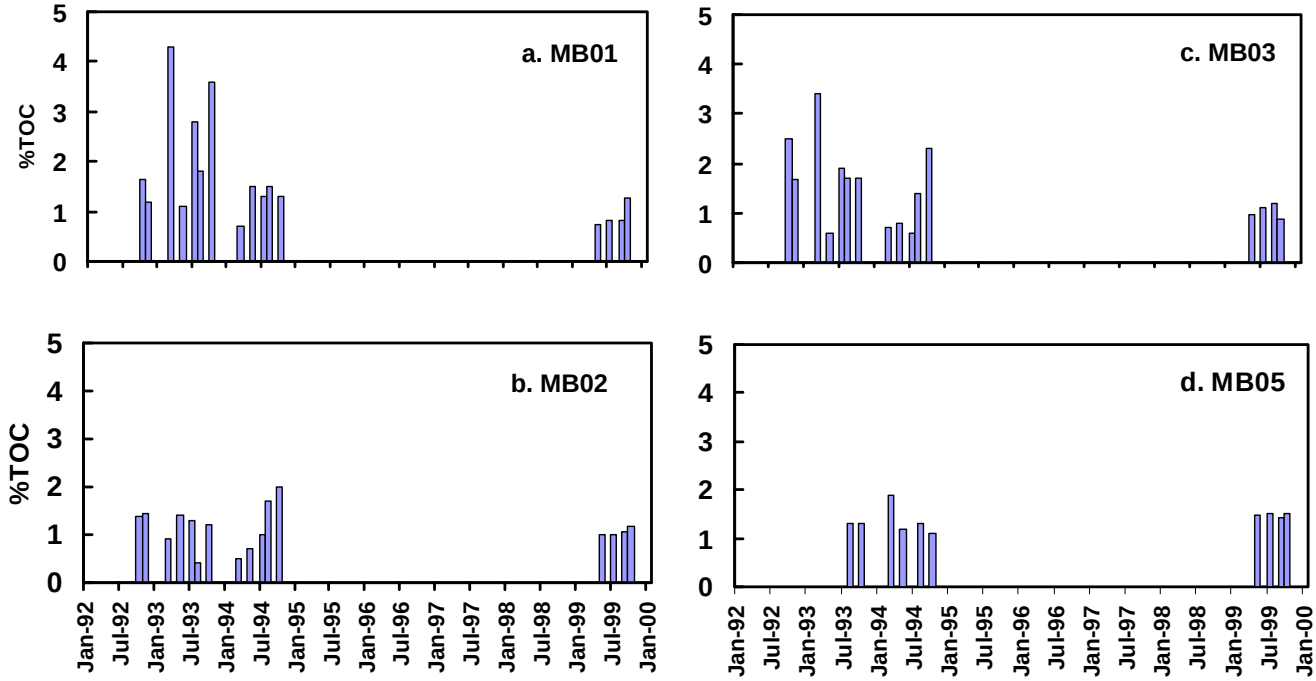


Figure 22. Changes in %TOC in the top 2 cm of sediments at Massachusetts Bay stations since late 1992: a.)MB01, b.) MB02, c.) MB03, d.) MB05.

4.2.4.2 Pigments

Chlorophyll pigments in Bay sediments were measured three times during the 1999 season; in May and October, as planned, and also in early September. The additional samples in September were taken because low bottom water D.O. noted in the field and high sediment respiration suggested fresh inputs of organic matter to the benthos. These samples were taken as subcores of nutrient flux cores, after flux measurements were completed.

Inventories of pigments, chlorophyll *a* + phaeopigments, summed over the top 5 cm of sediment were higher than they had been in previous years of monitoring (Fig. 23). The increase appeared to be in the phaeopigment fraction, as chlorophyll *a* inventories were lower than in previous years. Considering the depths of the nearfield and especially the Stellwagen stations, it is likely that most of the sediment pigment is derived from deposited phytoplankton organic matter rather than from benthic microfauna. As this organic matter is often delivered to the benthos in the form of fecal pellets, it is reasonable that the chlorophyll has been largely degraded to phaeopigments in transit, after which it is further degraded by decomposition in the sediments.

Pigment inventories were in general highest in May for the Nearfield stations, averaging 105 µg cm^{-2}, but equally high inventories were measured in September at MB02 (Table 4). Inventories had been similarly high in 1994, but had decreased through 1995 to 1997. These highs and lows in sediment pigment appear to correlate well with water column chlorophyll *a* concentrations. The highs in sediment pigments in 1994 were preceeded by a fall bloom in 1993 that was the highest recorded during the monitoring program until 1999. Similarly, the high sediment values observed in 1999 followed an unprecedented bloom that started in the fall of 1998 and continued through the winter of 1999. Pigment inventories at Station MB05 in Stellwagen Basin were nearly constant from May to October.

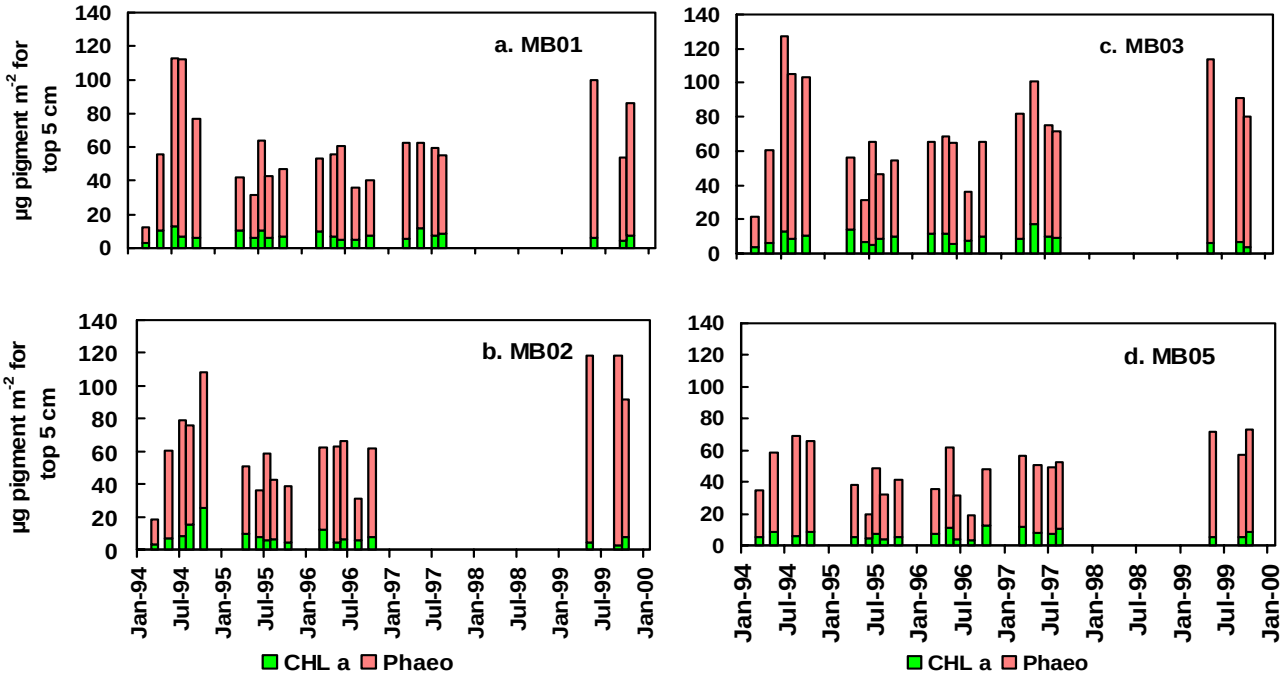


Figure. 23 Inventories of chlorophyll pigments in the top 5 cm. of sediments at Bay stations a.) MB01, B.) MB02, c.) MB03, and d.) MB05. green = chlorophyll *a*; red = phaeopigments.

Table 4 %TOC, %TON, and Pigment Inventories from Bay sediments in 1999.

Station	Date	%C[1]	%N[1]	Chlorophyll *a*[2] µg/cm^2	Total Pigments[2] µg/cm^2
MB01	May	0.8	0.07	6.2	93.6
	July	0.8	0.08		
	September	1.3	0.10	4.5	49.3
	October	0.7	0.08	7.5	78.8
MB02	May	1.0	0.09	4.3	113.8
	July	1.1	0.10		
	September	1.2	0.10	2.4	116.1
	October	1.0	0.11	7.6	84.0
MB03	May	1.1	0.10	6.3	107.2
	July	1.2	0.12		
	September	0.9	0.10	6.7	84.4
	October	1.0	0.10	3.8	76.5
MB05	May	1.4	0.16	5.5	66.4
	July	1.5	0.17		
	September	1.5	0.18	5.5	51.5
	October	1.5	0.17	8.7	64.5

1. % C and % N are for the top 2 cm of sediment.
2. Inventory of chlorophyll *a* or total pigments (chlorophyll *a* + phaeopigments) for top 5 cm of sediments.

4.2.5 POREWATER CONSTITUENTS

Oxidation-reduction potential (Eh) was measured at all Bay stations and at all four sampling times (Fig 24 a-d). In the nearfield, seasonal patterns in Eh were similar to those of previous years (Howes, 1998a): Sediments were most reduced in May, most oxidized in July and were returning to winter conditions through early September and October. At the Stellwagen station, Eh values were higher in October than they had been in early September, suggesting a reoxidization of sediments in these deeper waters that did not occur in the nearfield. At the Nearfield stations, the was little difference between the September and October profiles.

Overall, surface Eh values in 1999 were similar to patterns observed in 1994, but lower than those from 1995-1997. Profiles were unusual in that they changed very little after about 5 cm depth in the sediment, and had not approached the RPD by a depth of 18 cm. In previous years, the RPD had been reached at much shallower penetration. In 1994, the RPD in nearfield stations, calculated as a seasonal average, was within the top 4 cm; in 1995-1997, within the top 5-10 cm. Station MB05 exhibited a similar change in depth of the RPD, going from about 5cm in 1994 to about 20 cm in 1995-1997 (rough extrapolation from data; Howes, 1998a-c). In 1999, profiles from this station had not approached the RPD by 20 cm (Fig. 24d).

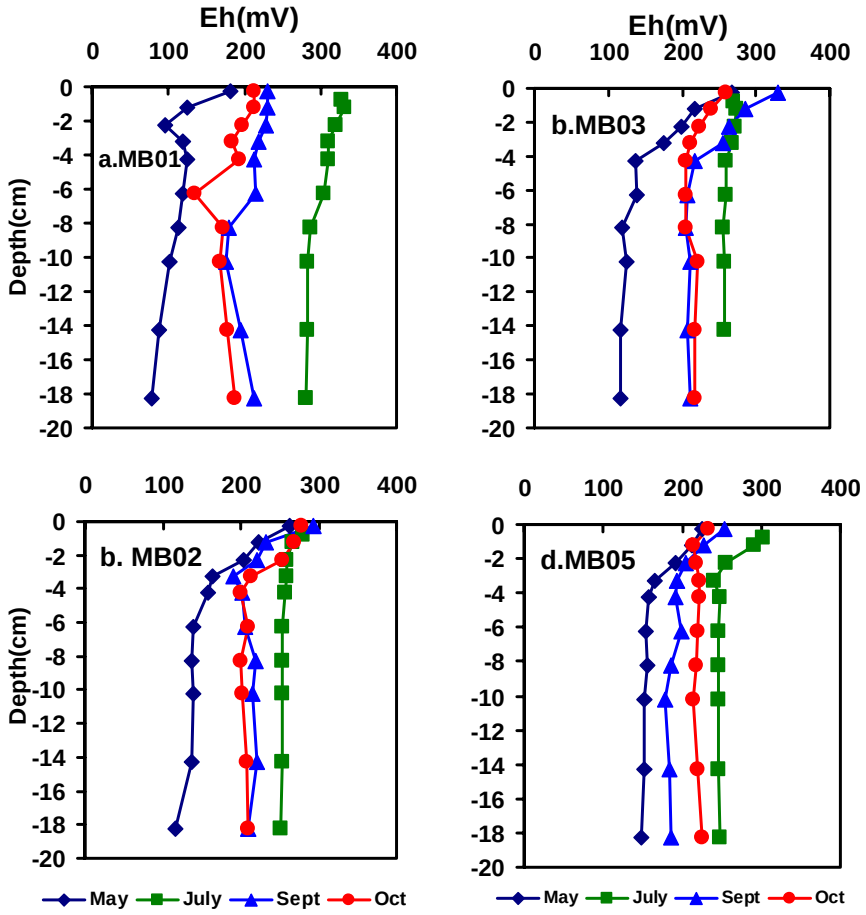


Figure 24. Oxidation-reduction potential (Eh) from sediment cores from each survey in 1999 for a) MB01, b) MB02, c) MB03, and d) MB05.

4.2.6. SUMMARY OF TRENDS IN BAY NUTRIENT FLUXES

1999 was an atypical year for Massachussetts Bay. The 1998 fall phytoplankton bloom persisted into the winter of 1999 and reached average chlorophyll levels of about 7 ug/L by March. The bloom declined in April, but chlorophyll concentrations were moderately high throughout the summer. By September, an unprecedentedly large bloom was under way, such that in October, average water column chlorophyll concentrations were nearly 12 µg/L. (Hunt, 2000). In early September, bottom water D.O. was the lowest recorded during baseline monitoring, falling to less than 6.0 mg/L, the trigger level for D.O.

We measured higher than average sediment pigment content in nearfield sediments in 1999 (see Section 4.2.4.2). Also, hardbottom surveys noted an unusually large amount of drape (Hunt, pers. comm). Both of these measures indicated fresh deposition of organic matter, most likely from the blooms. Similarly high sediment pigment concentrations were reported in 1994, also following a strong fall bloom in the previous year

These results suggest that water column productivity may be transferred to the sediments of the nearfield with only a short lag time, and that we should expect to see a response in sediment processes accordingly. In 1999, this in fact appeared to be the case. For example, annual average sediment oxygen demand was higher than in all previous baseline years (Section 4.2.1.1). This was most pronounced at Station MB02. Howes (1998) described a significant logarithmic relationship between sediment chlorophyll and sediment oxygen demand for the years 1995-1997. Although the trend is apparent, we did not find a similar significant relationship when using data from all the monitoring years. The periods characterized by higher rates are also characterized by higher variability; most likely contributing to the failure to find significant correlations. Massachusetts Bay has been described as a highly variable system by virtually all the researchers working there (Trulli et al., 2000), with multiple drivers including temperature, nutrient inputs, storms, and timing of seasonal events such as phytoplankton blooms and stratification. Describing this complex set of interactions is best accomplished by using a model such as the Bays Eutrophication Model (BEM; Hydroqual, Inc).

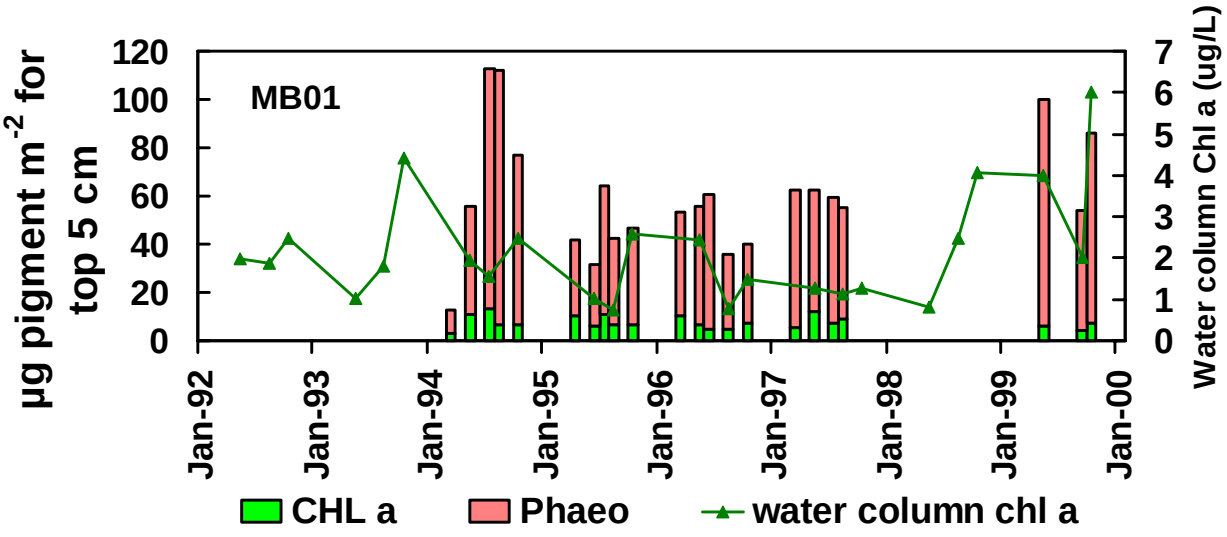


Fig. 25. Comparison of water column chlorophyll *a* concentrations in Massachusetts Bay (Libby et al., 1999a; Hunt, 1999) to sediment pigment inventories from one of the Bay benthic flux stations, MB01; 1992-1999.

The overall pattern since 1992 shows higher flux rates during the first two to three years of the monitoring program. The following three years had lower fluxes. Data were not collected in 1998, but in 1999, flux rates were once again high. This pattern seems to correspond well to the pattern in both annual average water column chlorophyll (Libby et al., 1999a; Hunt, 1999) and sediment pigments. These, too, were higher from 1992-1994, declined in 1995-1997, and were high again in 1999 (Fig. 25).

In addition to highest concentrations of sediment pigments observed in 1994 and 1999, the years following the two largest fall blooms to date, rates of some nutrient fluxes were elevated in these years. Most pronounced was that annual average Si fluxes were maximal for the baseline monitoring in 1994 (Fig. 17). The large fluxes were likely fueled by the deposition of the 1993 fall bloom, which was dominated by the pennate diatom *Asterionellopsis glacialis* (Libby et al., 1999a). This peak in Si fluxes was observed not only in the nearfield, but in Stellwagen Basin as well. Following the 1998-99 bloom, which was a mixed assemblage of microflagellates and centric diatoms (Libby et al., 1999b), Si fluxes were also high in the nearfield, especially at Station MB02, although not as high as the 1994 rates. Other nutrient fluxes were also elevated in the years following the two major fall blooms. In particular, phosphate fluxes were highest for the monitoring program in 1994, and were also large in 1999 (the P flux at MB03, though large, was directed into the sediment) (Fig. 18).

Another possible contributor to high flux rates in the Nearfield in 1999 may be changes in infaunal communities, resulting in increased bioturbation, that have occurred over the baseline monitoring years. The outfall benthic monitoring surveys (Kropp et al, 1999) reported that infaunal diversity in 1998 was significantly higher than it had been for the combined 1992-1997 data, and that infaunal abundance had also increased somewhat. They noted that Stage II communities were prevalent in 1999, whereas up until that time pioneering stage I communities were more common. Stage III communities were also more common in 1998 than previously. Stage II and Stage III communities are characterized by larger infauna, as well as larger tubes, burrows and feeding voids, all of which indicate active bioturbation. Similar to our 1999 findings of higher Eh values, statistical results from trends in RPD showed that the sediment surface oxidized layer was significantly deeper in 1997 and 1998 than it had been in 1992 and 1995. In addition, the sediment profile images indicated that “biological processes increased in importance as a structuring mechanism of the Nearfield communities, a trend that likely began in 1995” (Kropp et al., 1999).

An interesting trend discussed earlier in this report, but that is contrary to expectations from the chlorophyll pigment data and elevated fluxes, was the observation that sediment %TOC and %TON in Nearfield sediments had declined in 1999 compared to previous years (Section 4.2.4.1). Similarly, benthic monitoring surveys (Kropp et al, 1999) reported a decline in sediment TOC between 1997 and 1998 in Nearfield stations located 0-8 km from the diffuser. In parallel, densities of *Clostridium perfringens*, the sewage tracer, were lower in 1998 than had been reported previously. Observations such as these may reflect a decrease in sewage particulates reaching the Bay benthos, a scenario consistent with the reductions in particle loading in the Deer Island effluent.

In 1999, we observed two contrasting trends in Massachusetts Bay sediment processes. One trend was that respiration rates, some nutrient fluxes, and sediment pigment concentrations were all higher than typical for baseline. These results were consistent with unusually low dissolved oxygen concentrations that occurred in the bottom waters of Massachusetts Bay in the summer, and with high water column chlorophyll and primary productivity. In contrast, we report other findings that would more typically occur jointly with lower fluxes and organic matter inputs. Sediments appeared to be more oxidized in 1999 than previously and there was a decreases in

sediment %TOC and %TON, results consistent with data collected by the benthic monitoring surveys. We are unable to reconcile these patterns at this time, however, additional data may help explain them.

5. Denitrification: Methods Comparison

We compared the direct measurements of denitrification by gas chromotography (GC) and by mass spectometry (referred to as dissolved gas analysis, or DGA) to the estimates calculated using the stoichiometric method. All methods were not used at every station or every survey, however. The GC technique was used with cores from Harbor Stations BH02 and BH03 in May and August, and from Bay Stations MB02 and MB03 in May and October. The DGA technique was used for the same four stations, but for all surveys. Unfortunately, samples from Station MB03 in September were lost. The stoichiometric technique was used at all stations for all surveys. Stoichiometric estimates and DGA analyses are made from the same (nutrient flux) cores, whereas GC analyses are made using separate cores. Figure 26 illlustrates the results of the comparison among the three techniques at the four stations.

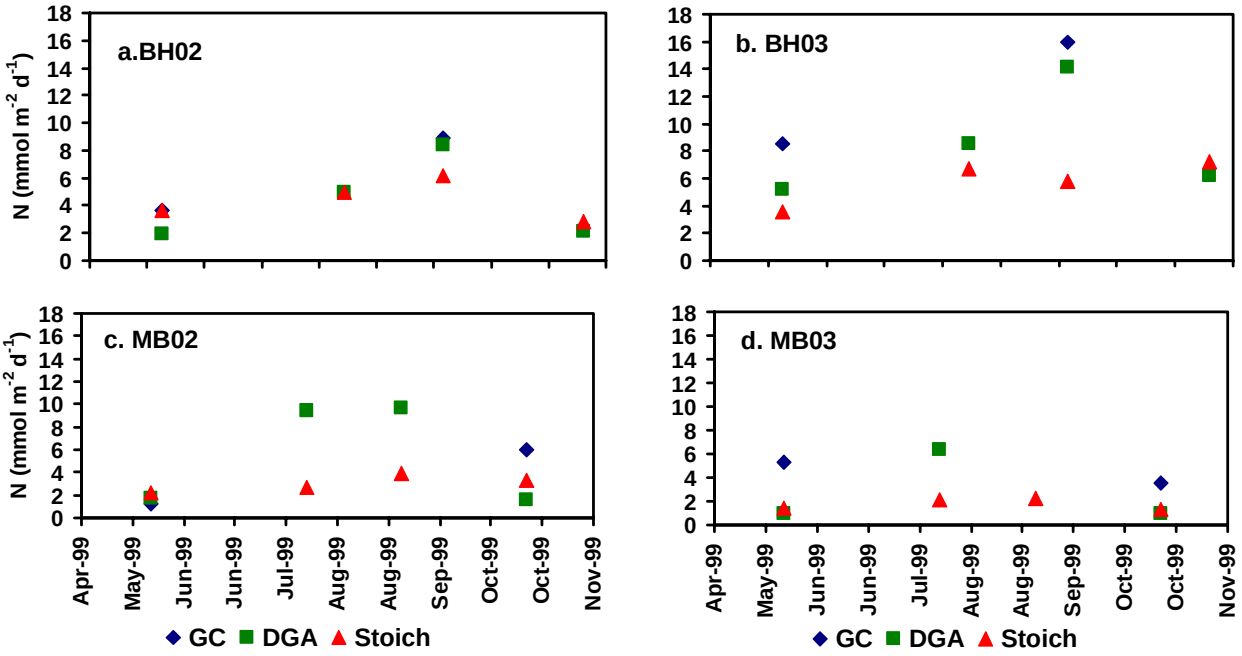


Figure. 26. Comparison of denitrification measurements made by gas chromatography (GC), dissolved gas analysis by mass spectrometry (DGA), and by stoichiometry (Stoich) at Harbor Stations a.) BH02 and b.) BH03, and Bay stations c.) MB02 and d.) MB03 in 1999.

The figure shows mixed results for the comparison. In general, agreement among the three methods was better for the Harbor fluxes than for the Bay, and within the harbor stations, was quite good for Station BH02 (Fig. 26a, 26b). At Station BH03, the largest difference was between stoichiometry and the two direct measures in August, when the direct measures yielded very high rates of denitrification. For the Bay results (Fig. 26c, 26d), agreement was very good among all three techniques in May at Station MB02, and was also good between DGA and stoichioimetry in October at MB02 and in May and October at Station MB03. In July and early September, however, stoichiometric estimates were much lower than DGA direct measurements. When the methods were in disagreement, the pattern was for stoichiometric estimates to be low and for GC estimates to be high. There was also the tendency for larger discrepancies when the direct techniques measured high rates.

The GC and DGA techniques also yield oxygen flux measurements from the same samples that are analyzed for N_2 flux. We compared the oxygen fluxes measured during denitrification analyses to those we routinely measure during nutrient flux incubations, both by oxygen electrode and by Winkler titrations. Because the DGA, oxygen electrode, and Winkler measurements are made on the same cores, we can compare their results directly (Fig. 27a). Because the GC measurements are made on separate cores, station averages are used to make the comparisons to this technique (Fig. 27B).. In both graphs, the oxygen electode measurements, as our routine method, are used on the determinate axis.

The results from this comparison show very good agreement among all measures. In the core to core comparison (Fig.27a) there is a single DGA value that is an outlier. (The corresponding N_2 flux was not, however, an outlier.) In the station average comparison, the GC results seem to deviate somewhat from the one-to-one line as rates increase. The O_2 concentration in the GC technique is allowed to go to lower values than in the flux experiments, so this is not unexpected. Overall, the oxygen results suggest that the two direct measures of gas fluxes, the DGA and the GC techniques, are working well.

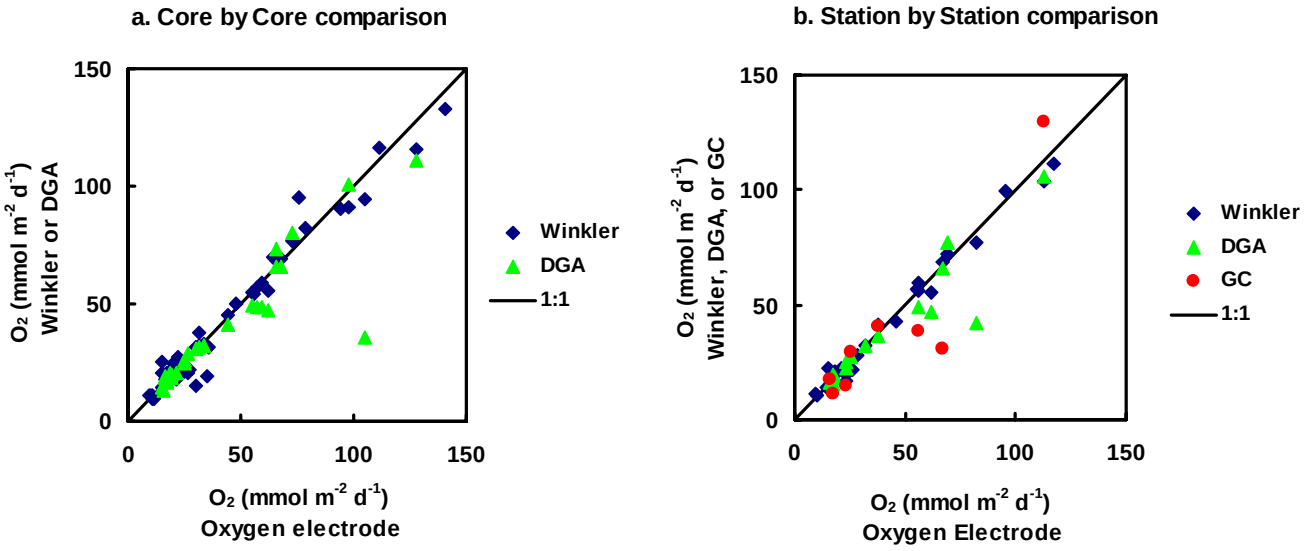


Figure 27. Comparison of oxygen flux measurements made by several techniques: a.) core to core comparison of Winkler titration and DGA measurements vs oxygen electrode measurements; b.) station average comparison of Winkler titration, DGA and GC measurements vs. oxygen electrode measurements.

At this point we are uncertain why the results from the denitrification measurements do not agree as well as do the oxygen measurements. We have discussed the limitations of the various techniques before (Giblin et al, 1993; Giblin et al, 1994; Tucker et al, 1999):

1. For stoichiometry, the primary concern is that the Redfield ratio does not accurately reflect the organic matter that is being decomposed, however we believe the Redfield ratio closely approximates that of the labile carbon pool. Another concern is that $CaCO_3$ dissolution or

precipitation may account for part of the DIC flux; we are currently investigating this possibility.

2. For the GC method, there are three primary concerns. The first two are that the preincubation time is potentially long enough to alter ambient processes, and the incubations are conducted on separate cores that are treated differently than the nutrient flux cores. The oxygen comparisons suggest, however, that conditions and fluxes in the separate cores closely matched that of the flux cores, and that our gas concentration measurements were accurate, although there was some tendency for deviation at higher fluxes. Finally, the anoxic treatment prevents ventilation by infauna and the resulting fluxes may not represent true *in situ* diffusive fluxes.
3. For DGA, the biggest problem is in maintaining a constant temperature in cores and in replacement water during flux incubations, and in storing the samples until they are analyzed. Small temperature fluctuations can cause changes in gas solubilities that in turn alter gas ratios. There is concern over this issue because we must ship these samples for analysis. The results from the oxygen comparison suggest that sample storage and transport have not caused changes in the gas ratios in those samples; that is, they do not explain the differences we see in the denitrification measurements.

Denitrification measurements have long plagued investigators interested in the process. We will continue to compare these techniques in 2000.

7. ACKNOWLEDGEMENTS

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