Benthic nutrient cycling in Boston Harbor and Massachusetts Bay: 2000 annual report

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Final

BENTHIC NUTRIENT CYCLING in BOSTON HARBOR and MASSACHUSETTS BAY: 2000 ANNUAL REPORT

for

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EXECUTIVE SUMMARY

This report documents a continuation of the monitoring studies that have examined temporal and spatial patterns of benthic processing of organic matter in Boston Harbor and Massachusetts Bay. These studies 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; Tucker et al., 2000). We examined sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen (ammonium, nitrate, N_2 gas, urea), silicate, and phosphorus at stations in Boston Harbor and Massachusetts Bay four times in 2000. 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 combine with data from previous years to: (1) extend the record of the recovery of Boston Harbor sites up to and after sewage diversion (2) complete the baseline monitoring data for Massachusetts Bay before sewage diversion occurs and to begin the record after diversion, (3) further characterize the variability in conditions in Boston Harbor and Massachusetts Bay against which future conditions will be compared and (4) provide data for the water quality model developed by HydroQual.

Boston Harbor

Results from the benthic nutrient flux studies in 2000 show a continuation of trends related to Harbor recovery that have been observed during the monitoring program. In general, we have observed lower rates of sediment respiration and nutrient regeneration in the sediments of the Northern Harbor over the past three to five years as compared to rates measured early in the monitoring program. However, DIN fluxes seem to be decreasing more slowly than oxygen uptake. We have not observed similar temporal changes in rates measured at the two Southern Harbor stations.

The most notable changes in 2000 were again reported from Station BH03, adjacent to the previous sludge disposal site. Respiration and nutrient flux rates at this station continued to decrease from the extremely high rates observed in the first three to four years after the cessation of sludge disposal in the Harbor. In fact, 2000 marked the first year that highest flux rates of the four harbor stations were *not* recorded at this station. Instead, highest rates were observed at Station BH08A, in Hingham Bay. Both of these sites support high densities of benthic infauna, in particular the mat-forming amphipod, *Ampelisca*. However, the mat at Station BH03 seems to be in decline, whereas the mat at Station BH08A appears robust. At BH03, declining process rates, as well as decreases in carbon and nitrogen content in the sediments, are consistent with the depletion of the rich stores of organic matter originally present at this site, a process that has been facilitated by very active bioturbation.

At Station BH02, the other station in the northern harbor, we have observed less change. Results in 1999 suggested notable improvements in the sedimentary environment at this site, however these trends were not all repeated in 2000. Although sediment respiration was the lowest ever measured here, respiratory quotients (RQs) were once again well over 1.0, indicating the importance of anaerobic processes at this site. DIN fluxes and %TOC were higher than in 1999. Measurements at this site have traditionally revealed considerable interannual variability, likely due to the location in a dynamic sedimentary environment.

Results from the Southern Harbor stations BH08A and QB01 (Quincy Bay) have shown little change since monitoring began there in 1995. Effects from the diversion of Nut Island effluent to Deer Island have not been obvious, although sediments appeared to be more oxidized at QB01 than in previous years. In fact, sediment respiration rates and nutrient fluxes appear to have increased somewhat at Station BH08A over the last three years. At QB01, early season sediment chlorophyll *a* inventories were elevated again this year as in 1998 and 1999, most likely attributable to higher abundances of benthic diatoms that have been noted at this shallow station.

Nutrient release ratios continue to indicate that denitrification is an important process in Harbor sediments. Denitrification rates, though variable, do not show the decreasing trend we have noted in sediment respiration and nutrient release. Ratios of DIN to Si flux continue to be favorable for supporting diatoms.

With the diversion of the Deer Island effluent offshore, we anticipate further recovery in Boston Harbor sediments. Although we have observed decreases and possibly a stabilization in sediment process at Station BH03 since the cessation of sludge disposal in late 1991, this has not been the case for Station BH02 where changes have been less distinct. With the Bay outfall operational, a large harborwide reduction in DIN load will be realized. Subsequent lowering of primary production should ultimately result in decreasing rates of sediment processes, for example oxygen demand and ammonium flux, which are indicators of the status of the benthic environment.

Massachusetts Bay

Baseline monitoring in Massachusetts Bay was completed in 2000; discharge of effluent through the Bay outfall began September 6. We conducted only one set of benthic flux measurements seven weeks after the diversion, in late October. We did not anticipate any anomalies in the October data because of this short time, especially compared to typical response times in sediment processes, the low-particulate effluent created by secondary treatment, and the limited area projected to be affected by the outfall. In fact, none of our measurements indicated a change in benthic processes, so we have not distinguished the October results from the rest of the 2000 data.

Sediment respiration rates in the Nearfield of Massachusetts Bay in 2000 were very similar to high rates reported for 1999. In particular, the very high rates observed at MB02 were observed again in 2000. Oddly, there was no seasonal pattern in respiration at this station, as had been typical in earlier years, and little at the other two Nearfield stations. The seasonal pattern was damped even at Station MB05, in Stellwagen Basin. Although bottom water temperatures were warmer earlier in the season than normal, they were not high enough in May to explain high rates observed then.

Both 1999 and 2000 were notable for sustained and large phytoplankton blooms. It is tempting to speculate that increased deposition of high quality organic matter fueled the higher and sustained sediment respiration rates. However, direct evidence of increased deposition was lacking. In fact, sediment carbon content appears to have decreased in the last two years, especially at MB01 and MB03. There was little change in average organic carbon content at MB02, where respiration has increased the most, but like respiration, carbon content did not show seasonal variability. Also, sediment chlorophyll *a* content has not increased at these stations, although total chlorophyll pigments may have. An interaction between temperature and substrate availability may be creating the patterns we observe. In addition, changes in benthic fauna may be playing a role not explicitly examined in these studies.

DIN release from Nearfield sediments was higher in 1999 and 2000 than it had been in 1995 to 1997, but similar or lower than in 1993 and 1994. In contrast to respiration, however, a seasonal pattern in DIN fluxes was apparent in 1999 and 2000. Silica fluxes paralleled DIN fluxes. Nutrient fluxes from sediments at our Farfield station, Station MB05, have shown little variability since the somewhat higher rates observed in 1993-1994. The DIN/Si flux ratio indicates that nutrient release from Bay sediments is favorable to diatom production.

Although denitrification rates in Bay sediments have not shown a long-term trend, as a percent of total nitrogen flux, denitrification is very important in the Bay, often accounting for the majority of total remineralization. At the same time, DIN:DIP flux ratios in 2000 suggested that sediment nutrient release would push the Bay towards phosphorus limitation. Phosphate fluxes in 2000 were very small, among the lowest rates measured during baseline monitoring of the Nearfield, and often phosphate was taken up rather than released by sediments.

Several measures indicated that Nearfield sediment redox conditions were more oxidizing than at the beginning of baseline monitoring. In both 1999 and 2000, sediment respiration quotients were closer to 1.0 than in the early 1990s. Sediment redox values have been quite high, with the apparent redox potential discontinuity (ARPD) very weak or absent in most cores. The phosphate uptake observed is also consistent with oxidized sediments. We have yet to observe sulfides in the porewaters of these sediments, the appearance of which would signal a change in the opposite direction, towards more reducing conditions.

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 visited every year since 1992. Station BH03 was also occupied once in 1991, just three months before sludge discharge ceased. The other two Harbor stations, BH08A and QB01, have been sampled since 1995. Surveys were carried out during mid May, mid July, late August, and mid October. Survey cruises were carried out over two consecutive days for all surveys except the October survey. In October, inclement weather forced a 5-day delay between the Harbor sampling (10/18) and the Bay sampling (10/23). The survey dates and locations, water depths, and bottom water temperatures, oxygen concentrations, and salinities of the sites are shown in Table 1.

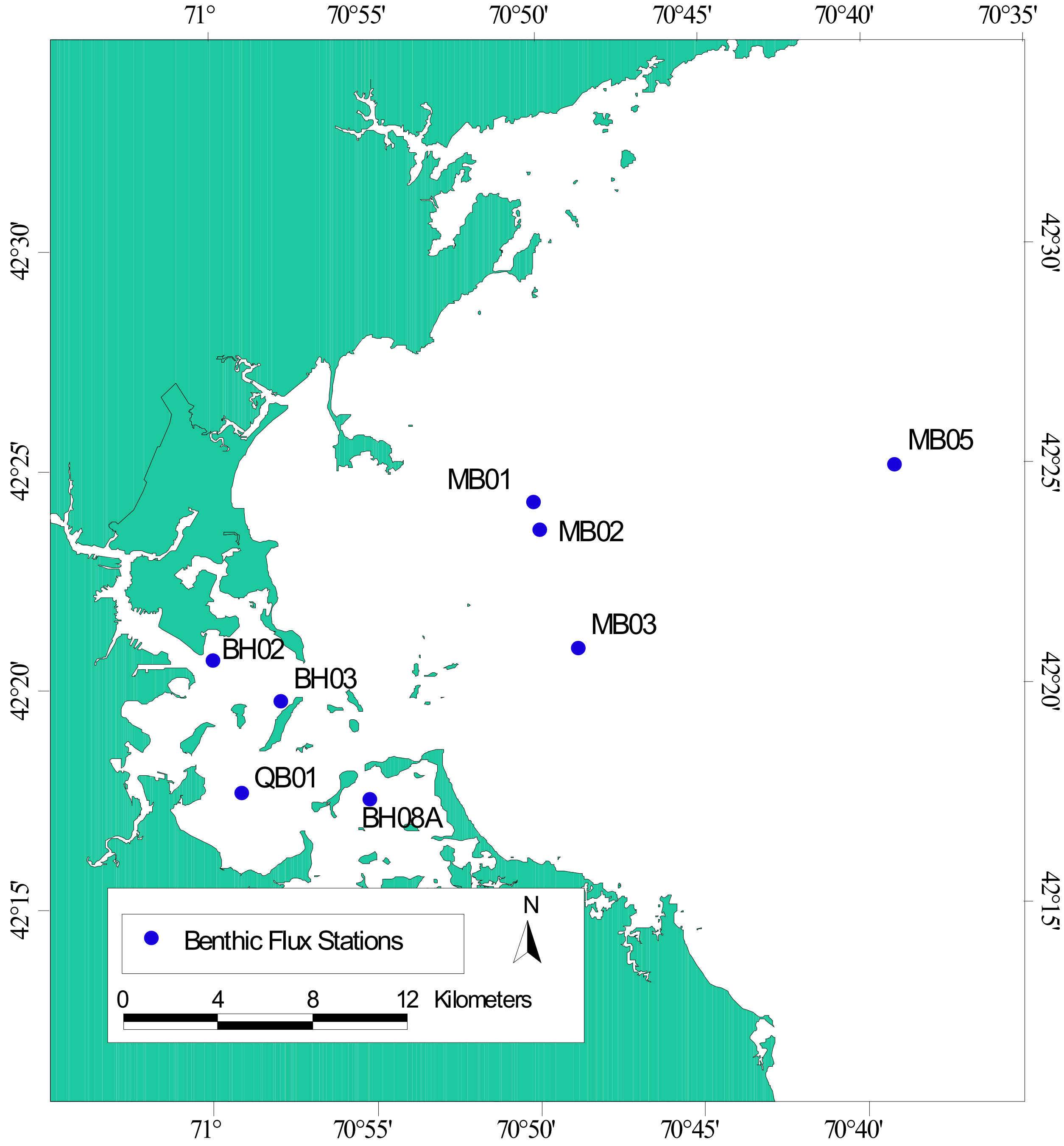

Fig. 1. Boston Harbor and Massachusetts Bay Benthic Nutrient Flux Stations 2000.

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 2000.

Station	Survey ID	Date	Latitude	Longitude	Depth (m)	Temp (°C)	DO (mg/L)	Salinity (ppt)
BH02	NC001	05/15/00	42.34338	-71.00152	10.7	11.3	10.31	30.9
	NC002	07/17/00	42.34362	-71.00227	9.0	17.3	8.23	32.0
	NC003	08/30/00	42.34357	-71.00225	9.1	17.1	7.93	31.3
	NC004	10/18/00	42.34375	-71.00235	8.3	12.5	7.62	32.4
BH03	NC001	05/15/00	42.33038	-70.96156	9.0	11.4	10.29	31.0
	NC002	07/17/00	42.33082	-70.96207	8.9	17.2	8.46	31.7
	NC003	08/30/00	42.33082	-70.96190	7.8	17.2	8.21	30.9
	NC004	10/18/00	42.33067	-70.96212	7.5	12.4	7.65	32.5
BH08A	NC001	05/15/00	42.29133	-70.92205	9.9	11.8	10.55	30.9
	NC002	07/17/00	42.29098	-70.92191	9.5	17.7	8.01	32.1
	NC003	08/30/00	42.29107	-70.92223	9.0	17.5	7.75	31.3
	NC004	10/18/00	42.29095	-70.92243	3.0	12.3	7.86	31.5
QB01	NC001	05/15/00	42.29371	-70.98714	5.0	11.8	10.64	30.5
	NC002	07/17/00	42.29352	-70.98792	4.6	18.9	8.43	31.5
	NC003	08/30/00	42.29332	-70.98820	3.7	18.7	7.80	31.5
	NC004	10/18/00	42.29348	-70.98770	2.8	12.1	7.85	32.6
MB01	NC001	05/16/00	42.40313	-70.83755	31.5	6.8	8.47	33.1
	NC002	07/18/00	42.40304	-70.83727	31.6	8.4	7.70	32.7
	NC003	08/29/00	42.40305	-70.83705	33.0	9.0	8.27	31.7
	NC004	10/23/00	42.40313	-70.83742	32.5	10.8	8.30	33.4
MB02	NC001	05/16/00	42.39251	-70.83418	32.5	6.9	8.53	33.5
	NC002	07/18/00	42.39245	-70.83408	33.2	8.8	8.02	32.8
	NC003	08/29/00	42.39269	-70.83406	31.0	9.2	8.31	33.4
	NC004	10/23/00	42.39243	-70.83615	33.5	11.0	5.58	33.3
MB03	NC001	05/16/00	42.34770	-70.81567	33.5	7.0	8.62	33.8
	NC002	07/18/00	42.34791	-70.81529	34.2	8.9	7.85	33.2
	NC003	08/29/00	42.34822	-70.81517	31.9	9.7	8.31	32.3
	NC004	10/23/00	42.34775	-70.81527	33.5	11.2	6.00	33.3
MB05	NC001	05/16/00	42.41628	-70.65227	40.5	6.3	9.41	33.0
	NC002	07/18/00	42.41640	-70.65182	47.5	7.0	8.05	32.3
	NC003	08/29/00	42.41648	-70.65235	30.3	9.8	7.33	33.4
	NC004	10/23/00	42.41656	-70.65200	46.0	9.9	6.33	33.3

2.1 LOCATION AND RATIONAL FOR STATIONS

Four stations were visited in Boston Harbor during 2000. Two of these stations, BH02 and BH03, have been monitored since 1992, although the location of BH03 has varied slightly. During 1995-1997, a station located about 200m west of BH03 (BH03A), was used; 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 former sludge disposal area, has been sampled 4 to 5 times annually since 1992, and was first occupied in September 1991. This site has undergone dramatic changes over this 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 1998-2000, our observations during SCUBA diving suggested the mat at BH03 had begun to breakup. Kropp et al. (2000, 2001) 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, 1999) (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 Massachusetts Bay, three stations were sampled in the Nearfield area of the Bay and one station was sampled in Stellwagen Basin in 2000. 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

The survey schedule for 2000 followed the pattern set in 1998. Stations were sampled four times, 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; at this time of year bottom water temperatures are typically still low there is potential for “fresh” organic matter input from a spring phytoplankton bloom or remaining from the fall bloom. The next two surveys occurred in July and August, summer months often characterized by the highest flux rates in the Harbor. The last survey was in October, when water temperatures in the Bay typically are the highest and the fall bloom (if present) 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 discussed specific aspects of the methods that 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 pycnocline we were confident that we collected data representative of bottom water. In these deeper waters, stratification below the pycnocline is weak (R. Geyer, pers.comm.) 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 24-48 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, 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 (Lachat 8000). 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; Alpkem RFA-300). 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. Although not specified by the monitoring plan, we also measured sediment in July and August. 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 measurements 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 DIRECT MEASUREMENT BY DISSOLVED GAS ANALYSIS

The dissolved gas analysis (DGA) 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 biologically mediated changes to 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.

We continued to use this method in 1999 for comparison to the gas chromatography method and to our stoichiometric estimates (Tucker et al., 1999; Tucker et al., 2000), however the data were variable and are not reported here. The extreme sensitivity noted above requires very careful handling of samples, both in collection and storage; the preferred procedure is to run samples as close to "real time" as possible, with samples maintained at ambient temperature. Small temperature changes from ambient may cause the formation or introduction of very small gas bubbles, thereby compromising the samples. Because we did not have a DGA system "in house", we had to ship our samples to the laboratory of Jeff Cornwell at Horn Point, Maryland, for analysis. Although precautions were taken to preserve the integrity of the samples, we were concerned that some of the variability we observed in the data might have been introduced in chilling samples for shipping and in the shipping process itself. In 2000, we will have a DGA system "in house" and will continue our comparisons without the complications of transporting the samples.

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 17 to 84 mmol O_2 m^{-2} d^{-1} between May and October 2000 (Figure 2). Harborwide, these rates are much lower than those recorded in 1999, and continue the decreasing trend in sediment respiration rates that have been measured since the very high rates of 1993 and 1995. For comparison, peak rates in 1999 approached 120 mmol O_2 m^{-2} $d^{-1,}$ recorded at both Station BH03 and BH08A in August.

In a departure from the typical pattern, highest rates in 2000 occurred in July. Peak rates are often recorded in August when water temperatures are typically highest. This year, however, temperatures were as high in July as they were in August. Lowest rates were measured in May at Stations BH03 and BH08A, whereas they occurred in October at Stations BH02 and QB01. Bottom water temperatures were similar for the two months (11.3° and 12.0°, respectively).

Highest sediment respiration rates from a single survey (84 mmol O_2 m^{-2} d^{-1}) and as a seasonal (May-Oct) average (72 mmol O_2 m^{-2} d^{-1}) were recorded at Station BH08A. This marks the first time in the monitoring program that highest rates were not attributed to Station BH03.

Sediment respiration remained high through August and October at Station BH08A, whereas it dropped off more sharply at BH03, decreasing to a rather low rate of 25 mmol O_2 m^{-2} d^{-1} in October.

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. We believe this decline in rates at BH03 is related to the waning of the amphipod mat there, noted again this year as in the previous two years (Tucker et al., 2000). In contrast, the mat at BH08A continues to appear quite robust, and although rates at this station were lower than in the previous year, they were typical of those measured at this station since 1995.

Sediment respiration at Station BH02 in the northern harbor was the lowest that has been measured at this site. In fact, rates were as low at BH02 as they were at Quincy Bay Station QB01, traditionally the Harbor station with the lowest rates. The seasonal average for BH02 was 31 mmol O_2 m^{-2} d^{-1}, whereas it was 30 mmol O_2 m^{-2} d^{-1} at QB01. High and low rates for Stations BH02 and QB01 were 47 versus 41 mmol O_2 m^{-2} d^{-1} and 19 versus17 mmol O_2 m^{-2} $d^{-1,}$ respectively. The peak rate at Station BH02 in 1999 was 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.

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 2000 were about average for the station, and the high rates measured in 1995 still have not been repeated. (Fig 3c). In general, respiration rates at QB01 have remained constant since 1995 (Fig 3d).

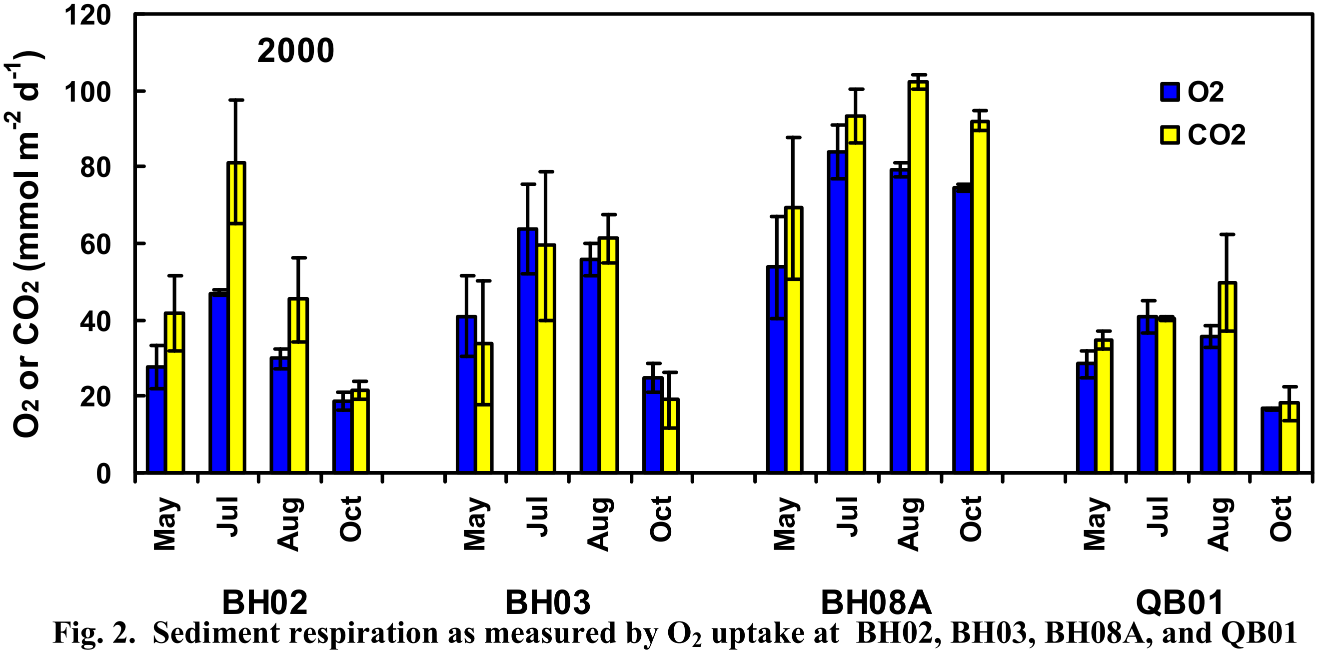

Fig. 2. Sediment respiration as measured by O_2 uptake at BH02, BH03, BH08A, and QB01 for 2000. Error bars represent the standard error of the mean of two cores.

4.1.1.2 Total CO_2 Measurements

Total CO_2 (DIC) fluxes at harbor stations ranged from approximately 18 to 102 mmol CO_2 $m^{-2}d^{-1}$ between May and October 2000 (Fig. 2), a range very similar to that of the previous year. Lowest rates were measured at Station QB01, where the seasonal average was about 37 mmol CO_2 $m^{-2}d^{-1}$. Highest rates were from Station BH08A which had a seasonal average of nearly 90 mmol

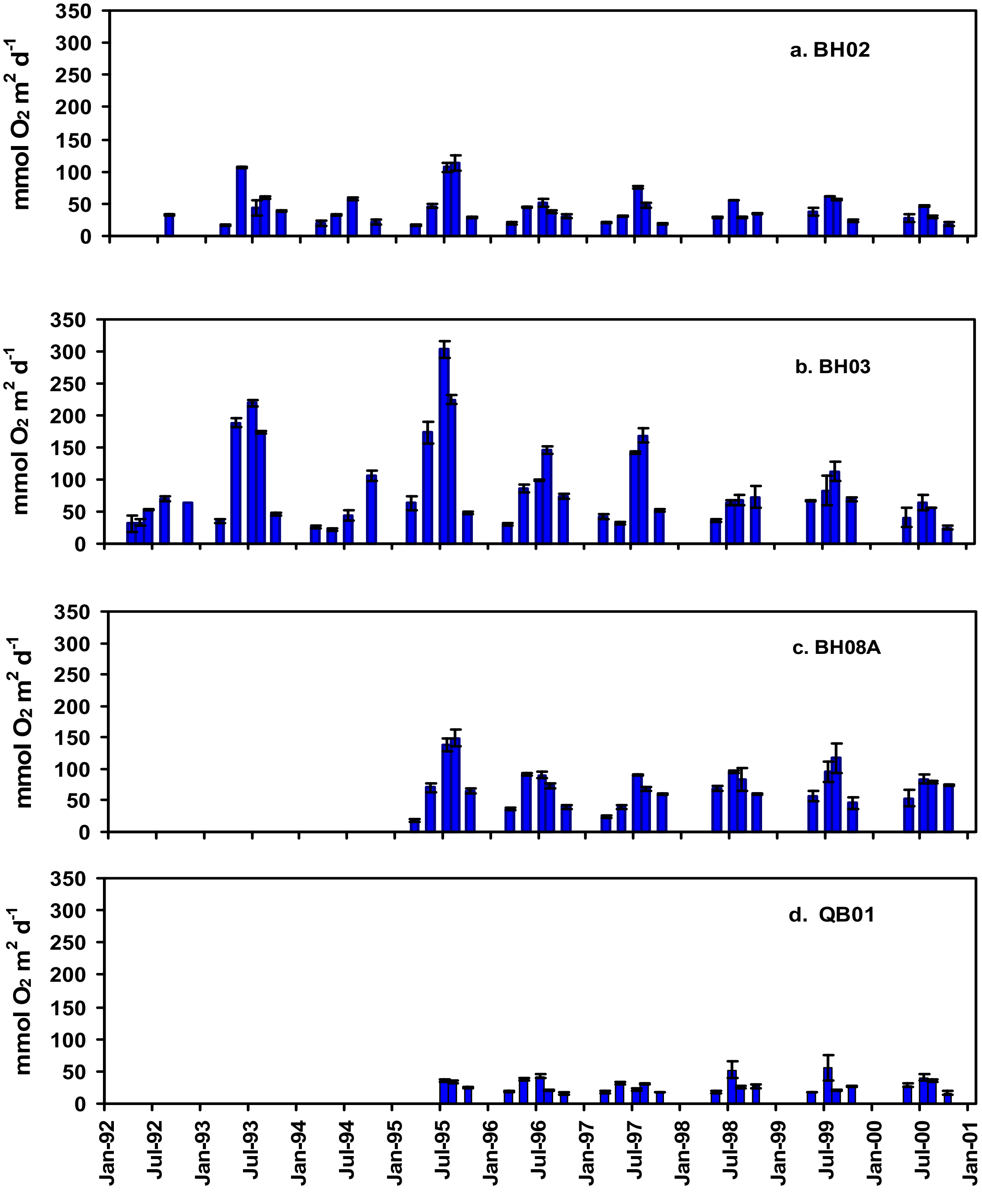

Figure 3. Sediment Respiration as measured by O_2 uptake at a.) BH02, b.) BH03, c.) BH08A, d.) QB01 from 1992-2000. Error bars represent the standard error of the mean of two cores.

CO_2 m $^{-2}$d^{-1} . Fluxes at Station BH08A were about twice as high overall as at the other stations. Unlike the previous year, CO_2 fluxes were poorly coupled to O_2 fluxes. The timing of the seasonal peak in CO_2 release varied across stations and did not correspond to the July peak in O_2 uptake except at Station BH02. At BH03 and BH08A the peak occurred in August, and at QB01 it occurred in October. The largest discrepancies between O_2 consumption and CO_2 release were measured for Station BH02. In May, July, and August, CO_2 release at this station was much larger than O_2 consumption, with the maximal difference occurring in July, when O_2 consumption was 47 mmol m $^{-2}$d^{-1} and CO_2 release was 81 mmol m $^{-2}$d^{-1}. In 1999, these two measures were more closely aligned, although the typical pattern at this station, as in this year, has been that CO_2 fluxes exceed O_2 fluxes. This implies that anaerobic respiration, accompanied by storage of reduced endproducts, continues to be important at this site.

At BH03, the pattern has been that the two fluxes are generally in equilibrium, although in this year as in 1999 and in particular 1993 we observed a tendency for O_2 flux rates to exceed CO_2 flux rates (Giblin et al., 1997; Tucker et al., 2000). Instances of excess O_2 uptake compared to CO_2 release co-occur when a large proportion of the DIN flux is comprised by NO_3^-, as was reported for 1993, 1999 and was again the case in 2000.

We now have three consecutive years, 1998-2000, of CO_2 flux measurements from Stations BH08A and QB01. In the two previous years, CO_2 and O_2 fluxes at these stations were nearly balanced, although in August and October at BH08A and in October at QB01, O_2 fluxes were slightly higher than CO_2 fluxes. In contrast, in 2000 the imbalance was excess CO_2 release compared to O_2 consumption in August and October at BH08A.

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 0.1 mmol N $m^{-2}d^{-1}$ at Station QB01 in October to a release of more than 12 mmol N $m^{-2}d^{-1}$ at Station BH08A in August (Figure 4). The highest average May-October flux, 9.8 mmol N $m^{-2}d^{-1}$ was from Station BH08A and the lowest, 1.8 mmol N $m^{-2}d^{-1}$, was from Station QB01. At Station BH02, DIN fluxes were higher than in the previous year but about average for the monitoring period, and at QB01 were very similar to those from the previous four years. DIN fluxes from station BH08A were the highest (Fig. 4c, 4d) whereas DIN fluxes at BH03 were the lowest on record for these two stations during monitoring (Fig. 4b).

Since 1993, DIN fluxes from BH03, near the former sludge disposal area, have been largely comprised by nitrate, a trend coincident with high numbers of benthic infauna. At times, 100% of the flux of inorganic nitrogen out of the sediments has been NO_3 and at these times, NH_4 flux has been directed into the sediments. In 2000, NO_3 efflux at BH03 accounted for about 45% of the combined flux in July and August, and 100% in both May and October. Ammonium fluxes in May and October were directed into the sediments, however the very large NH_4 uptake recorded in October of 1999 was not repeated.

Long-term changes in DIN flux at the other three harbor stations have been smaller than at BH03. At Station BH08A, it appears there has been a slight increase in DIN flux over the past three years. Most of that increase has been in NH_4 flux, and the contribution of NO_3 has decreased from an average of about 41% in 1998 to 25% this year. DIN fluxes at Station BH02 were higher than in the previous year, but about average for the station since 1993. Fluxes from Station BH02 have typically been dominated by NH_4^+, and this year was not an exception. Although nitrate comprised 45% of the flux in May, it was very minor the other three months (Fig. 4a). Fluxes at Station QB01 in 2000 were lower than at the other stations, as is typical, and fell in the middle of the range of measurements made at this site since 1995 (Fig. 4d). NO_3 fluxes contributed an unusually large amount , for this station, to the total flux in all months except May, ranging from 26-33%.

4.1.1.4 Urea Fluxes

Urea fluxes in the harbor in 2000 continued to be 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 2000 did duplicate cores both yield rates with significant r^2s; this was for Station BH08A in October and the rate was 0.3 mmol N $m^{-2}d^{-1}$. The highest r^2 for any rate measurement was 0.96 for a single core from Station BH02 in

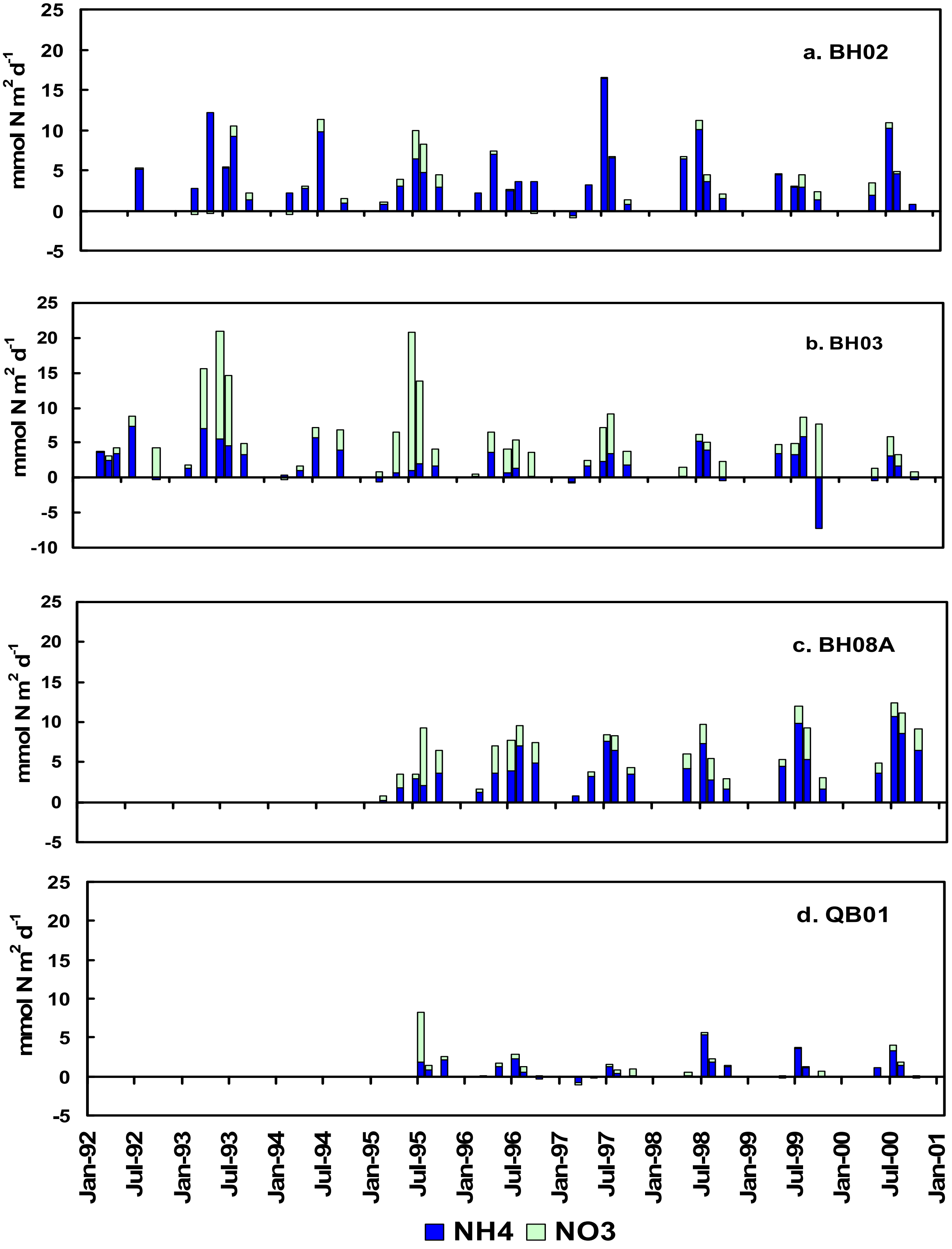

Figure 4. DIN flux, showing relative contributions of NO_3^+ and NH_4^-, at a) BH02, b) BH03, c) BH08A, and d) QB01 from 1992-2000.

August and the rate was 0.6 mmol N $m^{-2}d^{-1}$; the replicate core had a very small flux into the sediments, -0.1 mmol N $m^{-2}d^{-1}$ and the r^2 was 0.03. 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 2000 followed a seasonal pattern that essentially paralleled DIN fluxes, suggesting a close coupling of these two processes. For the first time, rates were highest at Station BH08A, with a May-October average of 16 mmol Si $m^{-1}d^{-1}$ including a July high of 25 mmol Si $m^{-1}d^{-1}$ (Fig. 5a-5d). These rates were the highest measured at this station to date. Similar to DIN fluxes, Si fluxes at Station BH08A appear to have increased over the past three years. At Station BH03, rates were very similar to those measured in 1999, being higher than 1994-1998 but much lower than the extreme rates of 1993. Rates at Station BH02 were low for that station except in July, when rates at 16 mmol Si $m^{-1}d^{-1}$ were approximately five times those measured the other three months. Lowest overall silica fluxes were measured at Station QB01. Fluxes from this station were higher overall than in previous years, mostly attributable to higher rates sustained through October. Si fluxes at QB01 in 1998-2000 mark an increase compared to 1995-1997.

4.1.1.6 Phosphate Flux

Phosphate fluxes from the Harbor stations, like Si fluxes, followed the same seasonal pattern as DIN fluxes. The highest May-October average rate, 0.7 mmol P $m^{-2}d^{-1}$, was observed in sediments from BH08A, but the highest singe rate, 1.4 mmol P $m^{-2}d^{-1}$, was measured at BH02 in July. Lowest rates were recorded at Station QB01; these rates were among the lowest measured throughout monitoring (Figure 6a-6d). Overall rates at BH03 were lower than in 1999 but higher than all other years except 1993. Phosphate fluxes at BH08A were very similar to 1999, which had the highest rates measured at this station for the monitoring program, but the seasonal pattern was quite different. Whereas rates in 1999 increased from May to a peak in August, rates in 2000 peaked in July and decreased thereafter. Rates at BH02 were somewhat higher than in 1999,and this station continues to exhibit the greatest variability in PO_4 fluxes of the four harbor stations. Phosphate uptake by sediments was measured only once in 2000, at Station QB01 in October.

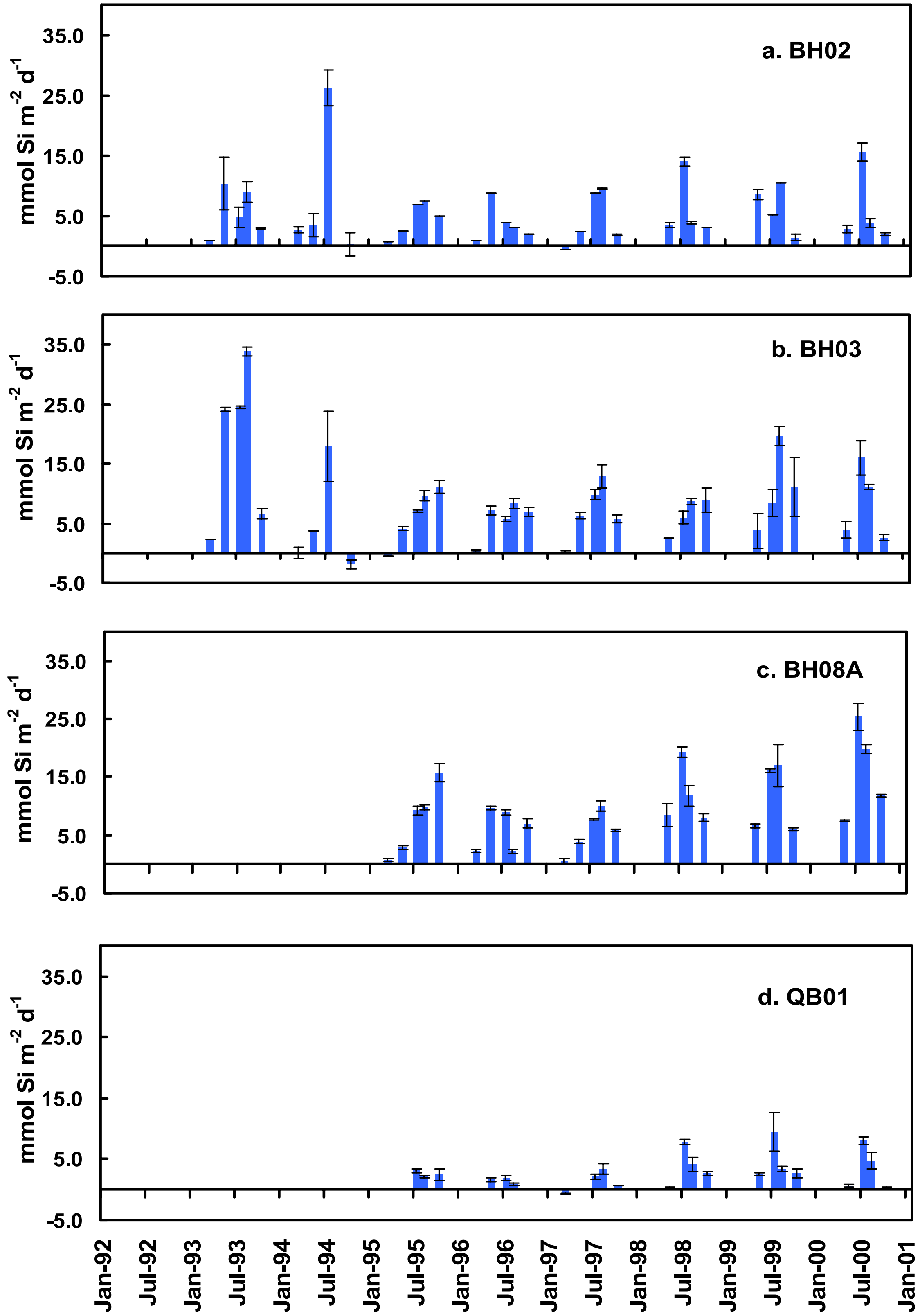

Figure 5. Dissolved silica flux at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the mean of two cores.

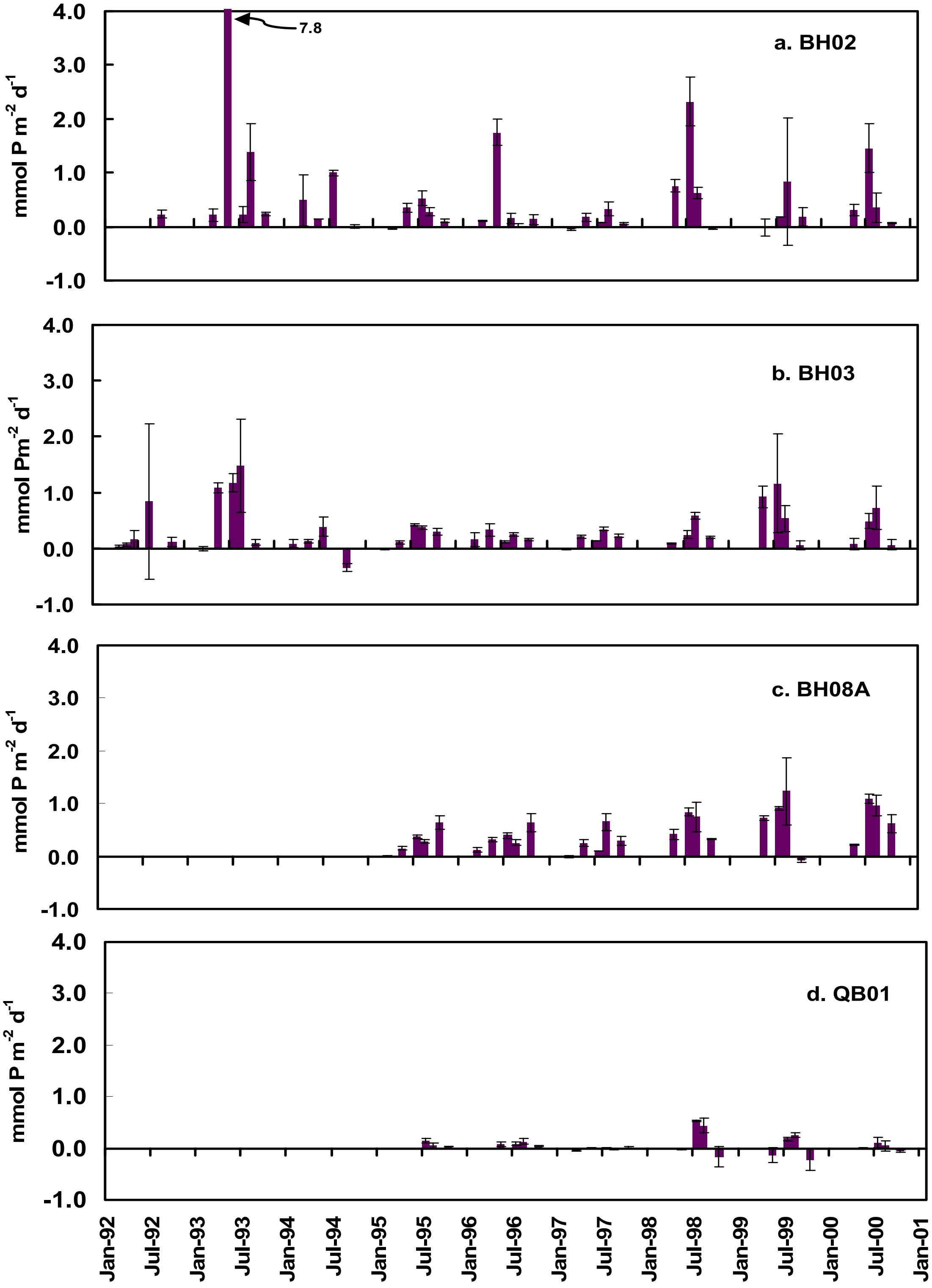

Figure 6. Phosphate flux at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the mean of two cores.

4.1.2 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) is expected to result in a ratio of CO_2 release to oxygen uptake (RQ or respiratory quotient) of 1.0. On a seasonal basis, however, these two processes may be out of balance, and oxygen consumption may over- or under-estimate sediment respiration. When anaerobic respiration is important, the storage of reduced compounds such as sulfide causes oxygen fluxes to underestimate respiration; when these endproducts are ultimately reoxidized, oxygen consumption may over-estimate respiration. However, on an annual basis oxygen is a good indicator of total decomposition because most of the reduced endproducts of decomposition are ultimately reoxidized. Consequently, an annual average RQ should be close to the theoretical 1.0. Deviations from an RQ of 1.0 closely reflect the portion of sulfide that is stored in the sediments as pyrite or FeS.

In 2000, the May-October average RQ for Station BH03 was 0.9. RQs less than 1.0 (i.e. higher O_2 flux than CO_2 release) have been the pattern at this station in recent years and the higher values that were common during 1992-1994 have been absent (Fig. 7b)(CO_2 data for 1995-1997 are unavailable). As in 1999, lowest RQs coincided with the times when all the DIN efflux was comprised of NO_3, and occurred simultaneously with NH_4 uptake, indicating active nitrification. We believe these results reflect the mining (reoxidation) of stored products of anaerobic processes that had accumulated in sediments at this site, a process facilitated by active bioturbation.

Highest seasonal RQs were measured at Station BH02 (may-October average of 1.5), whereas Stations BH08A and QB01 both had seasonal average RQs of 1.2 (Fig. 7a-7d and 8a). A very high RQ, 1.7, was measured from BH02 in July, coinciding with peaks at this station in both NH_4 and PO_4 fluxes. Phosphate fluxes in particular are consistent with anoxic sediment conditions, so the pattern fits well with a predominance of anaerobic processes in these sediments at this time. The high RQs suggest that an overall imbalance favoring anaerobic processes and sulfur storage, at least from May to October, still exists at this site.

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 6.6 indicate that less DIN flux was measured than would be predicted from respiration measurements, and it is assumed that the missing nitrogen has been denitrified.

In 2000, CO_2/DIN flux ratios were higher than 6.6 for Harbor stations at all times but one. Ratios ranged from 6.2 at QB01 in October, the one measurement lower than 6.6, to 40.6 in May at BH03 (Fig. 8b). Ratios at Station BH03 were quite high for the monitoring program, but similar to those from 1998. In these two years there seemed to have been a seasonal pattern, with highest ratios in May and October. A seasonal pattern was not apparent at the other stations. May to October averages were lowest and closest to Redfield expectations at Station BH08A (9.7) and highest at BH03 (24.6) (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.

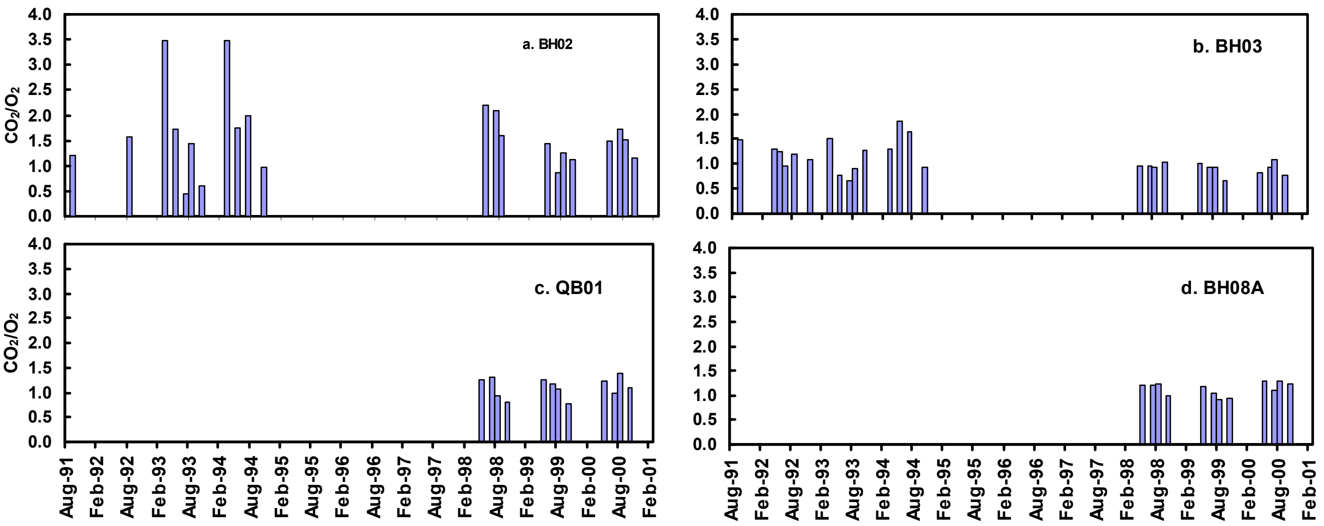

Fig. 7. Respiration Quotients (RQ) as they have changed over time at the Harbor stations.

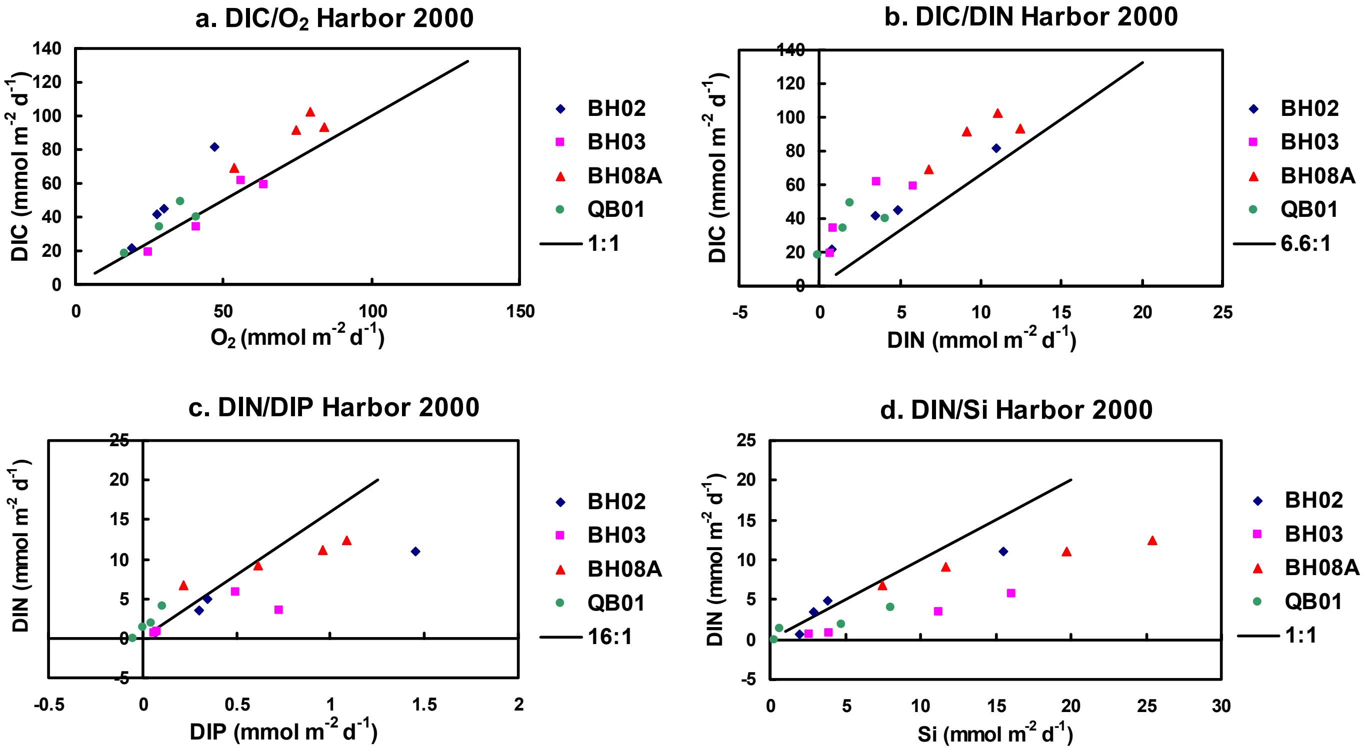

Figure 8. Ratios of element fluxes at all Harbor stations (symbols) relative to theoretical ratios (solid lines). a) DIC/O_2, b) DIC/DIN, c) DIN/DIP, d) DIN/Si.

4.1.2.3 DIN/DIP

Following Redfield proportions, the expected ratio of DIN flux to DIP flux is 16. DIN/DIP flux ratios may indicate relative nutrient limitations to phytoplankton according to Redfield requirements, and 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.

Ratios of DIN flux to DIP flux in Boston Harbor have most often been less than 16, indicating that sediment processes in the Harbor tend to shift the nutrient balance toward N limitation rather than P limitation. This was again the case in 2000, except at Station QB01. At this station, DIN/DIP was greater than 16 in all four months sampled.

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 May and July.

4.1.3 SEDIMENT DENITRIFICATION RATES

4.1.3.1 Direct Measurement of Denitrification

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 that typically have the coolest and warmest water temperatures, respectively, during our sampling season. Direct measurements were not made at Station BH08A or QB01. Rates ranged from 2.8 mmol N $m^{-2}d^{-}1$ at Station BH02 in August to 10.0 mmol N $m^{-2}d^{-1}$ at BH03 in August (Fig 9). These rates are among the highest recorded during the monitoring program but lower than rates measured in 1999. 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 measured denitrification rates were lower in 2000 than 1999, they accounted for similar percentages of the total benthic N flux. At Station BH02, denitrification accounted for 57% and 36% of total remineralization in May and August, respectively; at Station BH03 it accounted for 91% and 74%.

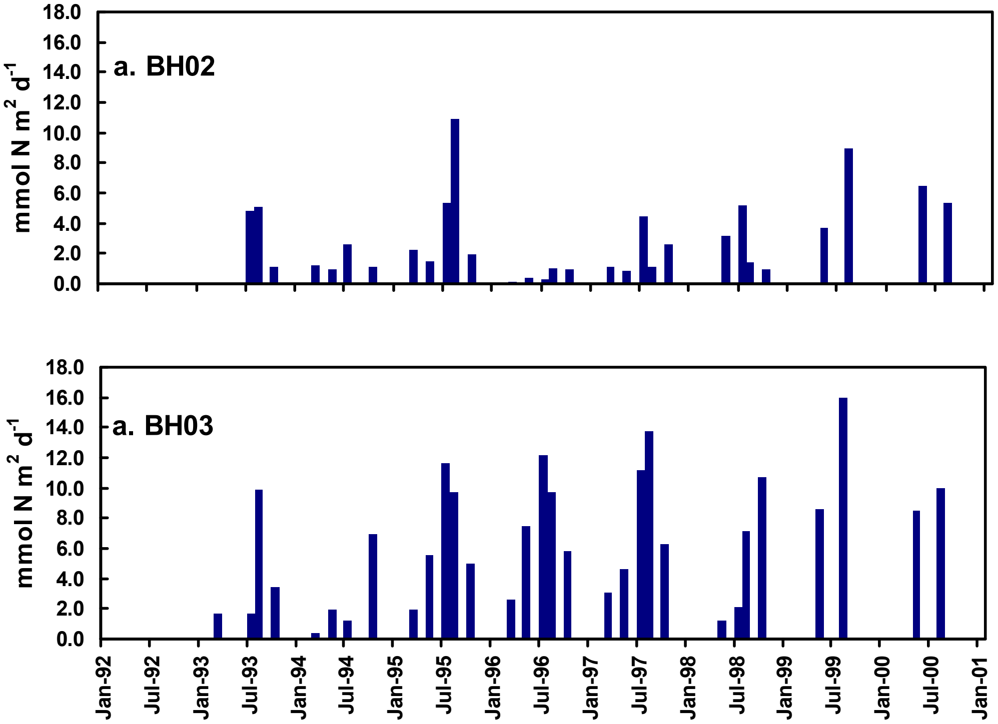

Figure 9. Denitrification as measured by the direct method using gas chromatography (GC) at BH02 and BH03 from 1993-2000.

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). Denitrification rates estimated by stoichiometry were generally lower than directly measured rates. At BH02, rates estimated by stoichiometry were 2.8 mmol N m^{-2}d^{-1} in May and 1.9 mmol N m^{-2}d^{-1} in August compared to 4.6 mmol N m^{-2}d^{-1} and 2.8 mmol N m^{-2}d^{-1} , respectively, measured directly. At Station BH03, stoichiometric rates were 4.2 mmol N m^{-2}d^{-1} and 5.7 mmol N m^{-2}d^{-1} for May and August, whereas directly measured fluxes were 8.5 mmol N m^{-2}d^{-1} and 10.0 mmol N m^{-2}d^{-1}.

Using the stoichiometric calculations augments the direct measures by providing a view of seasonal patterns in denitrification. At Station BH02, stoichiometry indicated that rates were highest early and late in the season, in May and October, and ranged from 1.3 mmol N m^{-2}d^{-1} in July to the high of 2.8 mmol N m^{-2}d^{-1} in May. At BH03, highest rates were in May and August, 4.3 and 5.8 mmol N m^{-2}d^{-1} , and lowest in October, 2.2 mmol N m^{-2}d^{-1} . The percent of total remineralization accounted for by denitrification was highest in October for both stations, accounting for 78% of the flux.

We also calculated denitrification rates stoichiometrically for Stations BH08A and QB01. Rates at BH08A ranged from 1.7 mmol N m^{-2}d^{-1} in July to 4.7 mmol N m^{-2}d^{-1} in October. These rates were similar to those calculated in 1999, and lower than those calculated in 1998. Seasonal averages of denitrification rates represented only 27% of total N flux at this station. Rates at Station QB01 ranged from 2.1 mmol N m^{-2}d^{-1} in August to 5.6 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 2000 (Fig 10, Table 2) were within the ranges noted for previous years (Fig. 11) (Giblin et al., 199x; Howes, 1998a-c). Organic carbon content across all four harbor stations was fairly uniform. May to October averages at BH03, BH08A, and QB01 were nearly identical (2.8%, 2.7%, and 2.7%) and Station BH02 was somewhat lower at 2.3%. Organic nitrogen was slightly more variable. The low value, 0.25%, was from sediments at Station QB01 and the high, 0.33%, was from BH08A. Molar C/N ratios were similar at Station BH02, BH03, and BH08A, averaging about 10; all shared a seasonal pattern of a slight increase after July. In contrast, the lower nitrogen content at QB01 resulted in a higher average C/N of 13, and a seasonal pattern very different from the other four stations. At this station, ratios were constant from May to July, decreased sharply in August, and then increased to a quite high ratio of 17 in October.

At Station BH03, both carbon and nitrogen content have apparently decreased over the nine years of monitoring this site, but may have stabilized at a new level over the past two years (Fig. 11a,b). In 2000, carbon content in the top 2 cm of sediment was nearly constant over the May to October period, averaging 2.8%, consistent with 2.7% in 1999. Both of these values were 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%, again the same as in 1999. Although these seasonal averages were the same between 1999 and 2000, the seasonal pattern was different. In 1999, nitrogen content was higher in July through October than it was early in the season. In this year, nitrogen content was higher in the early season, May through July, and decreased later. *[A note about Station BH03: From July 1995 through October 1997, this station was shifted about 200 m to the west and was renamed BH03A. Site characteristics indicate there is no need to distinguish between the two stations, and we have not done so in any of the long-term data. However, the TOC and TON data from those years suggest a slight difference. TOC and TON appeared higher in 1995-1997 than in 1994, and quite a bit higher than the most recent three years, 1998-2000. The difference appears abrupt between 1997 and 1998 (Fig. 11b). However, TOC was also measured at Station T03 during 1995-1997 under the Benthic Monitoring program. Station T03 is essentially identical to station BH03. TOC at Station T03 (BH03) was not markedly different from values at BH03A, except in spring of 1996. At BH03A, TOC was 4.5% in May 1996, the highest value observed during the 1995-1997 period, whereas at T03 in April 1996, TOC was 2.8%, the lowest value observed during the same period. The comparison of data between BH03A and T03(BH03) supports the assumption that the station shift in 1995-1997 did not cause an appreciable disruption in data continuity. The abrupt decrease observed between 1997 and 1998 remains unexplained, although factors such as strong storms could create that difference.]*

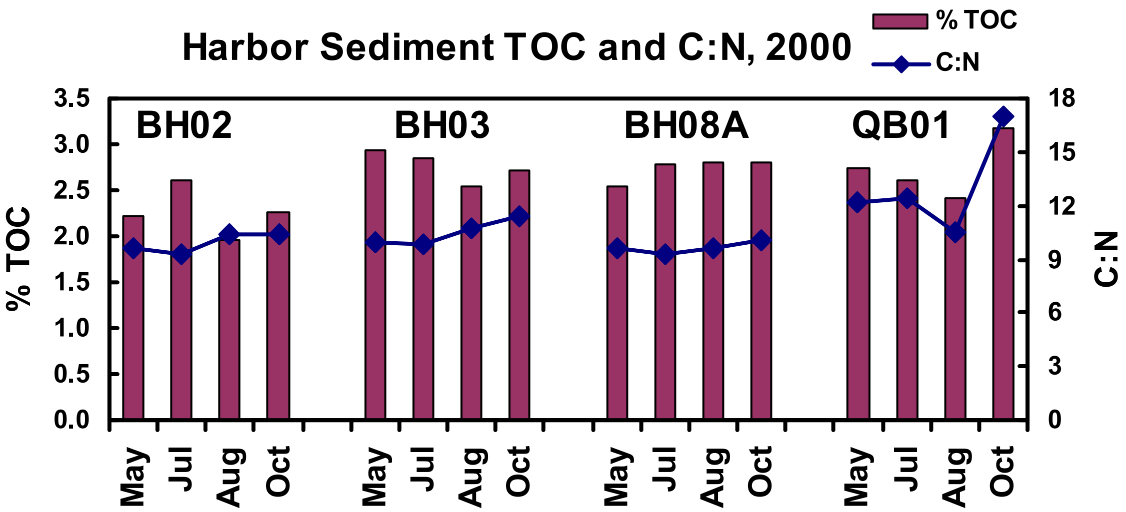

Fig. 10. TOC and molar C:N at the Harbor stations, 2000

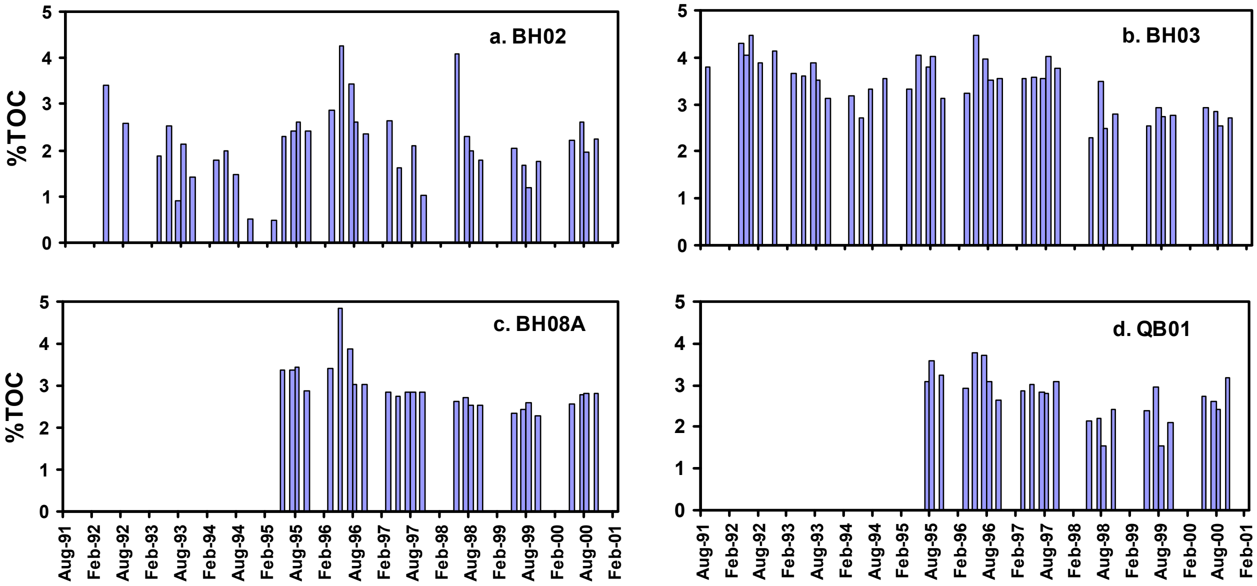

Figure 11. Changes in organic carbon in Harbor sediments since 1991. a.) BH02, b.) BH03, cBH08A and d.QB01.

The other three stations show less clear trends towards a reduction in organic matter content in the sediments. At Station BH02, although 1999 average values were lower than 1998 Fig.11c,d), 2000 values were higher. Sediments at Stations BH02 showed more seasonal variability in their C and N content than those from BH03, however, as was noted in 1999, the range of values measured was narrower than in previous years. At Stations BH08A and QB01, the data through 1999 seemed to suggest a decline in organic matter content at these sites, much as has been noted for Station BH03. However, carbon and nitrogen content in 2000 was somewhat higher than in the previous year. At BH08A, percentages changed very little over the sampling period, whereas QB01 showed more variability. Over the past two years, TOC and TON at BH03 and BH08A have become very similar, suggesting similar levels of input and processing. In contrast, results from BH02 and QB01 suggest different timing, processing, and sources of organic matter to these sediments.

4.1.4.2 Pigments

As in 1998 and 1999, inventories of pigments, chlorophyll *a* + phaeopigments, summed over the top 5 cm of sediment continued to be higher than they had been in previous years of monitoring (Fig. 12). Much of this increase appears to be in the phaeopigment fraction, although at Station BH02 chlorophyll *a* concentrations have apparently increased.

All four stations showed evidence of recent deposition or *in situ* production of chlorophyll *a* in May. At QB01 the chlorophyll *a* inventory was quite high in May, 31.0 µg/cm^{-1}, one of the highest yet measured at this station and among the highest from any Harbor station. This early season maximum at Station QB01 has been observed for the last three years and may be related to benthic diatoms. In October, there was again evidence of fresh deposition, particularly at Station BH02, where concentrations were higher than they had been in May, and to a lesser degree at Station BH08A. At QB01, following the large May concentrations, chlorophyll levels were low and constant.

Seasonal differences were also apparent in sediment profiles of chlorophyll concentrations. At Stations QB01 and BH08A, high concentrations of chlorophyll *a*, around 8 µg cm^{-3}, were present throughout the top three centimeters of sediment in May. BH03 had similar concentrations in the top centimeter, but declined to about 4µg cm^{-3} for the next 4 centimeters, which was still higher than concentrations at these depths the rest of the year. Profiles from Station BH02 did not show elevated concentrations. The profiles also reveal a steady decrease in chlorophyll *a* concentrations in the sediments at these sites until October, when concentrations became higher again. Elevated surface concentrations in October were observed at Stations BH02 and BH08A.

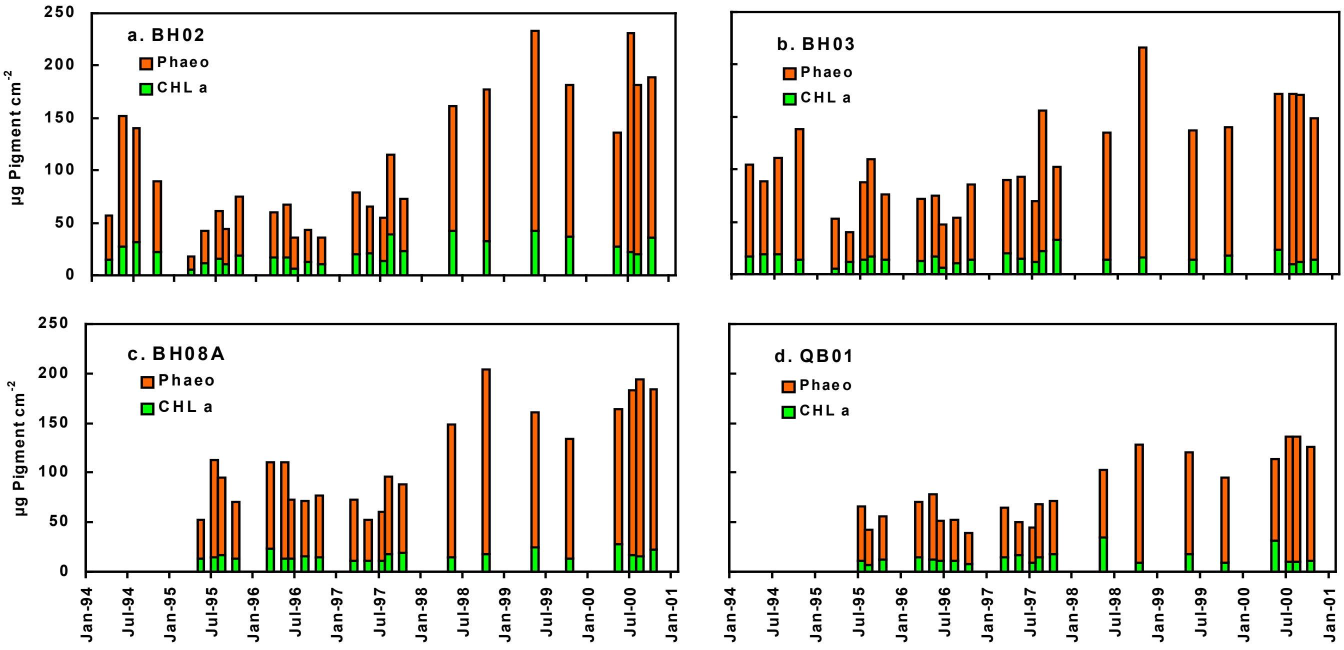

Figure. 12 Inventories of phaeopigments and chlorophyll *a* in the top 5 cm. of sediments at Harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01, 1994-2000.

Harborwide, the average for total pigment inventories for the top 5 cm of sediment in 2000 (~165 µg cm^{-2}) was similar to that reported from the previous two years (~150µg cm^{-2} in 1999 and ~160 µg cm^{-2} in 1998) but higher than that from the same stations averaged over the years 1995-1997 (~125µg cm^{-2}) (Howes, 1998c). As noted, most of this difference is in the phaeopigment fraction. 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). One would expect chlorophyll in such matrices to be largely degraded. Therefore, some of the difference in measurements between 1998 and 1995-1997 may reflect a difference in "free" and "bound" pigments.

Table 2. % Organic Carbon, %Organic Nitrogen, and Pigment Concentrations from Boston Harbor sediments in 2000.

Station	Date	%TOC[1]	%TON[1]	Chlorophyll *a*[2] µg/cm²	Total Pigments[2] µg/cm²
BH02	May	2.2	0.27	27.7	135.8
	July	2.6	0.33	22.1	231.0
	August	2.0	0.22	19.7	181.1
	October	2.2	0.25	36.2	189.0
BH03	May	2.9	0.34	23.1	172.2
	July	2.8	0.34	10.0	171.6
	August	2.6	0.28	11.7	171.0
	October	2.7	0.28	13.2	149.1
BH08A	May	2.6	0.31	28.0	163.7
	July	2.8	0.35	16.5	183.1
	August	2.8	0.34	15.8	194.4
	October	2.8	0.33	22.5	184.3
QB01	May	2.7	0.26	31.1	126.2
	July	2.6	0.25	10.3	136.1
	August	2.4	0.27	9.7	135.9
	October	3.2	0.22	11.0	125.8

[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). In contrast to the previous year, when lowest Eh values, or most reducing conditions, were recorded in May, in this year, sediments were most highly oxidized in the early season, May –July. In general, Eh values decreased into August, and then returned to more oxidized conditions by October. At station BH08A, however, there was little difference between the August and October profiles. Sediments at Station BH03 and QB01 were well oxidized all season. Only in August did Eh values become significantly negative, with the redox potential discontinuity (RPD = 0 mV) occurring fairly deeply at 8 cm. At BH08A, the RPD was reached at shallow depths(< 2 cm) in August and October, but the values did not decrease further with depth after that point.

Station BH02 had the most reducing sediments overall, however conditions at this station were more highly oxidized than in most earlier years and similar to conditions in 1999. In May, the

RPD was below 8 cm, and in July and October it was at 5 and 4 cm, respectively. In August, the RPD was the shallowest, 2 cm, and the transition from oxidized to reducing conditions the sharpest. In July, August, and October, Eh values at depth in the core dropped to their lowest levels of about –200 mV. It is at about this point that one expects to detect sulfides in the porewaters of these sediments (Stumm and Morgan, 1996), and in fact that was the case. In July and August, the two months when porewater constituents are measured, sulfide concentrations became detectible as the Eh reach –200, and reached concentrations of 4.3 and 3.4 mM, respectively. Although sulfides were not measured in October, Eh values nearing –200 suggest that measurable concentrations would have been present. These sulfide levels were higher than in 1999 but similar to concentrations measured in 1998.

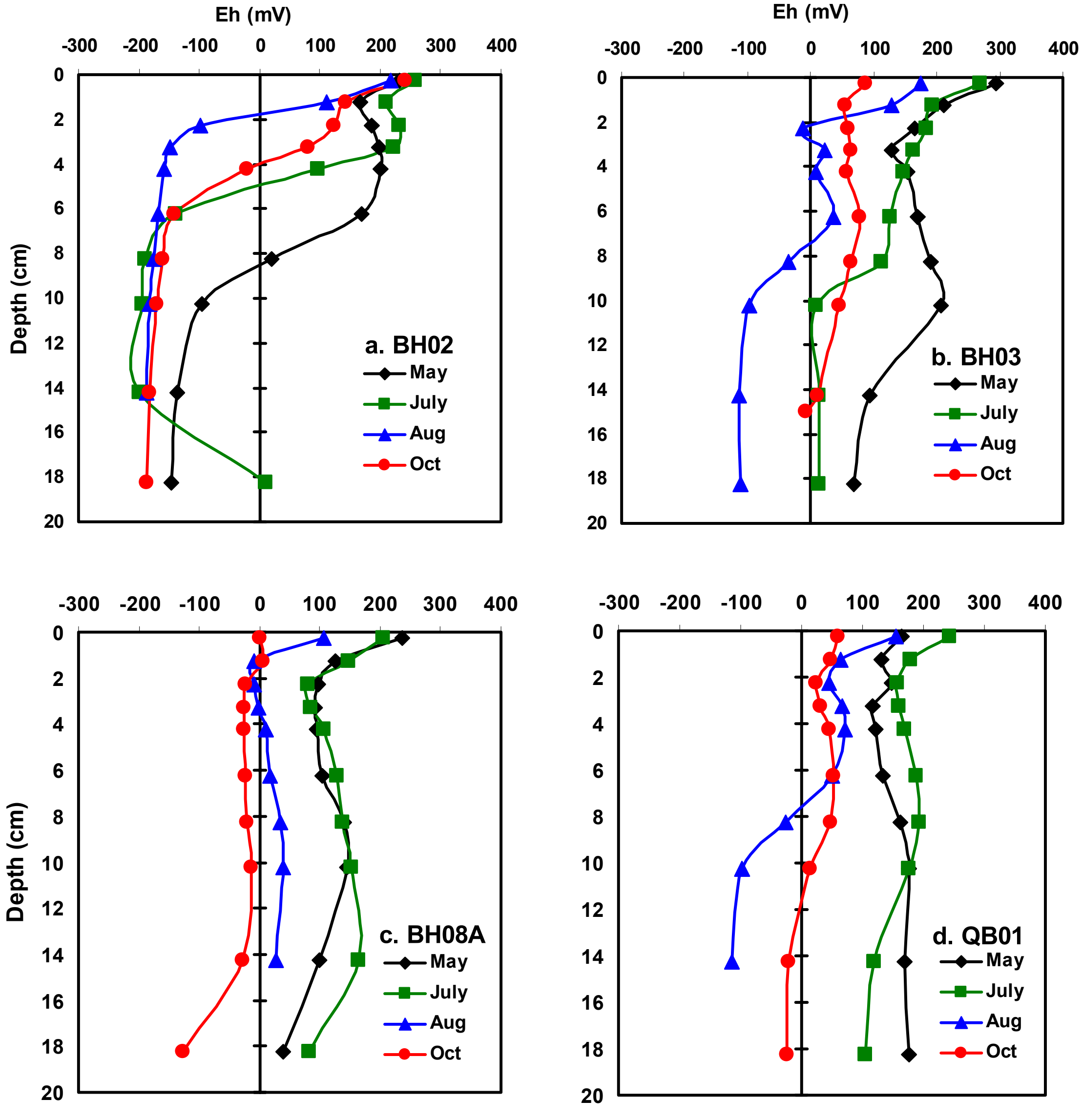

Figure 13. Oxidation-reduction potential (Eh) from sediment cores from each survey for a) BH02, b) BH03, c) QB01, and d) BH08A.

4.1.6. SUMMARY OF TRENDS IN HARBOR NUTRIENT FLUXES

The most notable change in benthic nutrient cycling in Boston Harbor in 2000 was that for the first time since monitoring began, highest sediment respiration and nutrient flux rates were *not* recorded at Station BH03, the site notable for its proximity to the previous sludge disposal site. In earlier reports we have noted the decrease in rates at this site linked to the depletion of stored organic matter and the waning of the amphipod mat in the area. This year continued that trend with further decreases in the rates of most processes from the very high rates reported in 1993 and 1995.

The station that had the highest flux rates overall was Station BH08A in Hingham Bay. This site is also densely colonized by benthic infauna, but the mat here seems quite robust. Although rates of nutrient release (DIN, DIP, and Si) at this site appear to have increased somewhat over the past three years, sediment respiration has changed little.

In last year's report, we noted some improvements in the sedimentary environment of Station BH02 in the northern Harbor, the station we have traditionally considered the most degraded of our four sites. The improvements were suggested by decreases in sediment parameters such as DIN flux and sediment %TOC, as well as by respiratory quotients (RQs) approaching 1.0. This trend did not continue into 2000, however. Although sediment respiration was the lowest ever measured at this site, RQs were well over 1.0, and DIN fluxes and %TOC were higher than the previous year. Conditions in this area of the harbor vary from year to year and do not seem to respond directly to improvements in water quality.

Nutrient release ratios continue to demonstrate that silica and phosphate are released from Harbor sediments in excess of Redfield requirements to balance nitrogen. These ratios indicate that sediment processes would act to shift nutrient status in the Harbor towards nitrogen limitation, and that release ratios are favorable for supporting diatoms. They also indicate that denitrification is an important process in the Harbor. However, measured rates of denitrification have been variable and have not followed the same trends observed in respiration and nutrient fluxes.

Other sediment properties that show a long-term trend include organic carbon content and redox values. Organic carbon content has apparently decreased in sediments at Station BH03, and possibly at BH08A and QB01 as well. Sediment carbon at Station BH02 is variable, possibly due to the station's location in a reworking environment. Sediment redox values are generally higher than at the beginning of the monitoring program, and porewater sulfides are often below detection.

Overall, results from 2000 add to observations from the last few years of lower rates of sediment respiration and nutrient regeneration in the sediments of the northern harbor compared to measurements made early in the monitoring program. These changes are certainly the result of improvements in sewage treatment and disposal from the Deer Island Treatment Plant. At Station BH03, where the cessation of sludge dumping occurred in late 1991, we have observed large decreases in sediment processes, possibly approaching a new stabilization. Further decreases in particulate organic matter (POM) input harborwide, effected by secondary treatment, contributed to these improvements. However, unambiguous "recovery" has not been observed at all sites (e.g. station BH02).

At the two stations in the southern harbor, we have detected little change in sediment processes since 1995, even after the diversion of the Nut Island Plant effluent to Deer Island in 1998. Respiration rates at Station QB01, in particular, are not atypical of rates observed at sites such as Buzzards Bay, Massachusetts, that do not receive large wastewater inputs (Banta et al., 1995). Although respiration rates at BH08A are higher, they have remained relatively stable throughout the monitoring period. Therefore, any response to reduced sewage inputs at these sites may be difficult to detect.

In 2001, with all inputs from the Deer Island Sewage Treatment Plant diverted offshore, we anticipate further improvement in northern Harbor sediments and possibly some response in the southern harbor sediments. The most significant change that will result from the outfall relocation will be the large reduction in DIN loading to the Harbor. Results from the Bays Eutrophication Model (BEM; Hydroqual, 1995) predict that DIN will be lowered to nutrient limiting conditions by early spring and throughout the summer in the area of the Deer Island outfall. A 50% reduction in surface water DIN is predicted for the inner harbor. We expect the resultant lowering of primary production to ultimately decrease rates of sediment processes by further decreasing POM flux. For example, we anticipate reductions in oxygen demand and ammonium flux, which are indicators of the status of the benthic environment.

4.2 MASSACHUSETTS BAY

4.2.1 BENTHIC RESPIRATION AND NUTRIENT FLUXES

4.2.1.1 Oxygen Uptake

Between May and October 2000, sediment oxygen uptake ranged from approximately 13 to 31 mmol O_2 m^{-2} d^{-1} at our three Nearfield Massachusetts Bay stations (MB01, MB02, and MB03) and from about 10 to 13 mmol O_2 m^{-2} d^{-1} at our Stellwagen Basin station (MB05)(Figure 14). 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 11.5 mmol O_2 m^{-2} d^{-1} (Fig. 15d), typical of the entire monitoring program. For the three Nearfield stations, seasonal average rates were 16.5 mmol O_2 m^{-2} d^{-1} for MB01, 21.8 mmol O_2 m^{-2} d^{-1} for MB02, and 19.6 mmol O_2 m^{-2} d^{-1} for MB03.

In most years, sediment respiration rates follow a seasonal pattern that correlates closely with temperature. In 2000, peak rates occurred at different times of the year at different stations. At MB01 and MB05, rates peaked in August, when for this year bottom water temperatures were the warmest of the times we sampled. At MB02, the highest rates occurred in July, however there was no significant difference in rates at this station across the four months sampled. Peak rates at MB03 occurred in July as well. These rates were unusually high for this station, but the measurements were influenced by the presence of a burrowing anemone in one of the core samples.

Average oxygen uptake rates at the three Nearfield stations in 2000 were not as high as they were in 1999. However, rates at MB02 continued to be quite high for the baseline period. Station MB01 and MB03 had high uptake rates in August and July, respectively, but otherwise were typical of baseline. Unlike most years, oxygen uptake rates at Stellwagen station MB05 showed little variability from May to October.

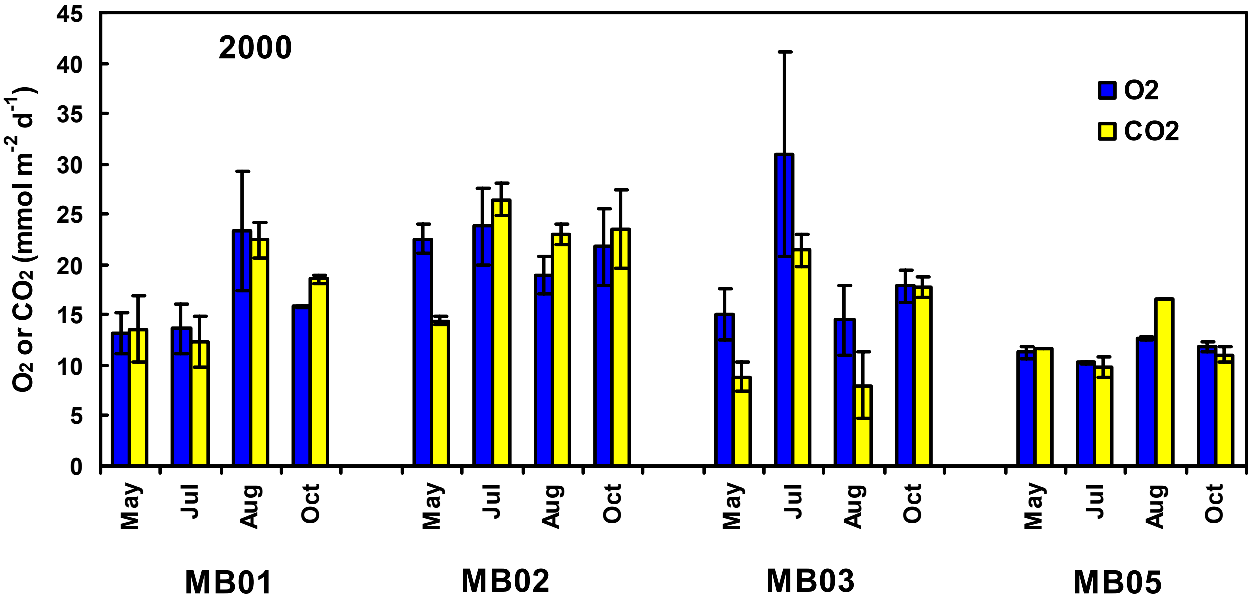

Figure 14. Sediment Respiration as measured by O_2 uptake or CO_2 flux at a.) MB01, b.) MB02, c.) MB03, d.) MB05. Error bars represent the standard error of the mean of two cores.

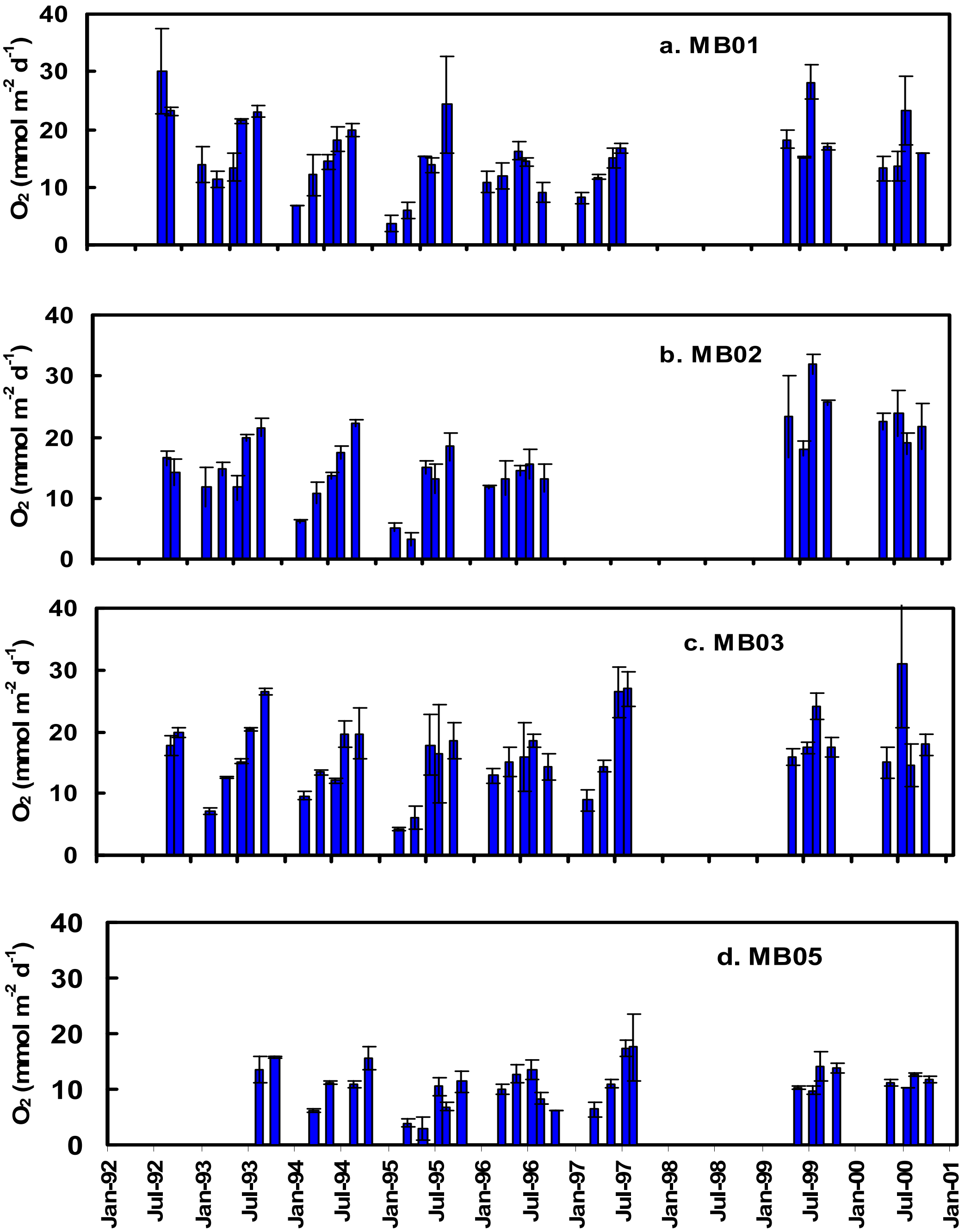

Figure 15. O_2 flux from 1992-2000 at a) MB01 and b) MB02, c) MB03 and d) MB05. Error bars represent the standard error of the mean of two cores.

4.2.1.2 Total CO_2 Measurements

Total CO_2 (DIC) fluxes at the Nearfield stations ranged from approximately 8 to 26 mmol CO_2 m $^{-2}$d^{-1} between May and October 2000, somewhat lower than the previous year. At the Stellwagen station, MB05, rates ranged from 10 to 16 mmol CO_2 m $^{-2}$d^{-1}, very similar to 1999 (Fig. 14). CO_2 release was highest at Station MB02, and peaked in July. As reported for 1999, CO_2 fluxes 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 have remained similar throughout baseline.

During the earlier years of measurements in the Bay, CO_2 release often greatly exceeded O_2 uptake. In 1999, we reported the two measures of benthic respiration had come into closer agreement. In 2000, again there was close agreement between the two measures, both in magnitude and timing, except at Station MB03. At this station, O_2 uptake exceeded CO_2 release in May, July, and August; only in October were the two measures in balance. At Station MB01 in 1999 and 2000, and Station MB03 in 1999, the closer agreement was the result of decreases in CO_2 fluxes. At Station MB02, however, the agreement was derived from increases in O_2 fluxes; as noted above, CO_2 fluxes at this station have changed little.

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 2000 ranged from 0.3 mmol N $m^{-2}d^{-1}$ at Station MB01 in July to 2.5 mmol N $m^{-2}d^{-1}$ at MB03, also in July. (Fig. 16a-d). Rates at MB05 in Stellwagen Basin ranged from an uptake of nearly 0.3 in July to a release of 0.2 mmol N $m^{-2}d^{-1}$ in October. Average May-October rates were highest at Stations MB02 and MB03 (1.1 mmol N $m^{-2}d^{-1}$). The high rate at MB03 was influenced by a single core sample from July which contained an active animal burrow; otherwise the rates at this station appeared about average for the entire baseline period. When compared only to 1995-1997, DIN fluxes for the last two years at all the Nearfield stations have appeared high, however they are similar or lower than rates reported in 1993-1994.

At the three Nearfield stations, NO_3 flux accounted for between 20% and 40% of the total DIN flux at all times except August. In August, NH_4 comprised essentially all of the DIN efflux from the sediments at the three stations and NO_3 was taken up by sediments at Stations MB01 and MB03. At Station MB02, having NO_3 comprise a significant part of the DIN efflux represented a return to the pattern most typically seen throughout the baseline period. In 1999, we reported the unusual pattern that NH_4 comprised nearly all the DIN efflux, with NO_3 often taken up by sediments at this station.

DIN fluxes at station MB05 were small, and in May and August there was essentially no DIN flux out of the sediments. In these two months, the flux was directed into the sediments and comprised entirely of NH_4. We also recorded NH_4 uptake in July, but this was balanced by a nearly equal efflux of NO_3. NH_4 uptake by sediments at this station has been reported only three times before during the baseline period (October 1993, and March of 1994 and 1995) , but rates at those times were an order of magnitude lower than those for this year. Also unusual in this year was that NH4 uptake was apparently sustained from May through the summer. By late October, DIN flux at MB05 was comprised entirely of NO_3, and the flux was directed out of the sediments.

The magnitude, composition, and sometimes the direction of DIN fluxes has varied over the years of baseline monitoring with most of the variability in the NH_4^+ fluxes. The relatively high DIN fluxes measured in 1999 and this year were most similar to those from 1992-1994, especially for Stations MB02 and MB03. DIN fluxes at MB01 have not been as high as they were in the early years of the program; Rates of DIN flux at all Nearfield stations were higher than recorded during 1995-1997.

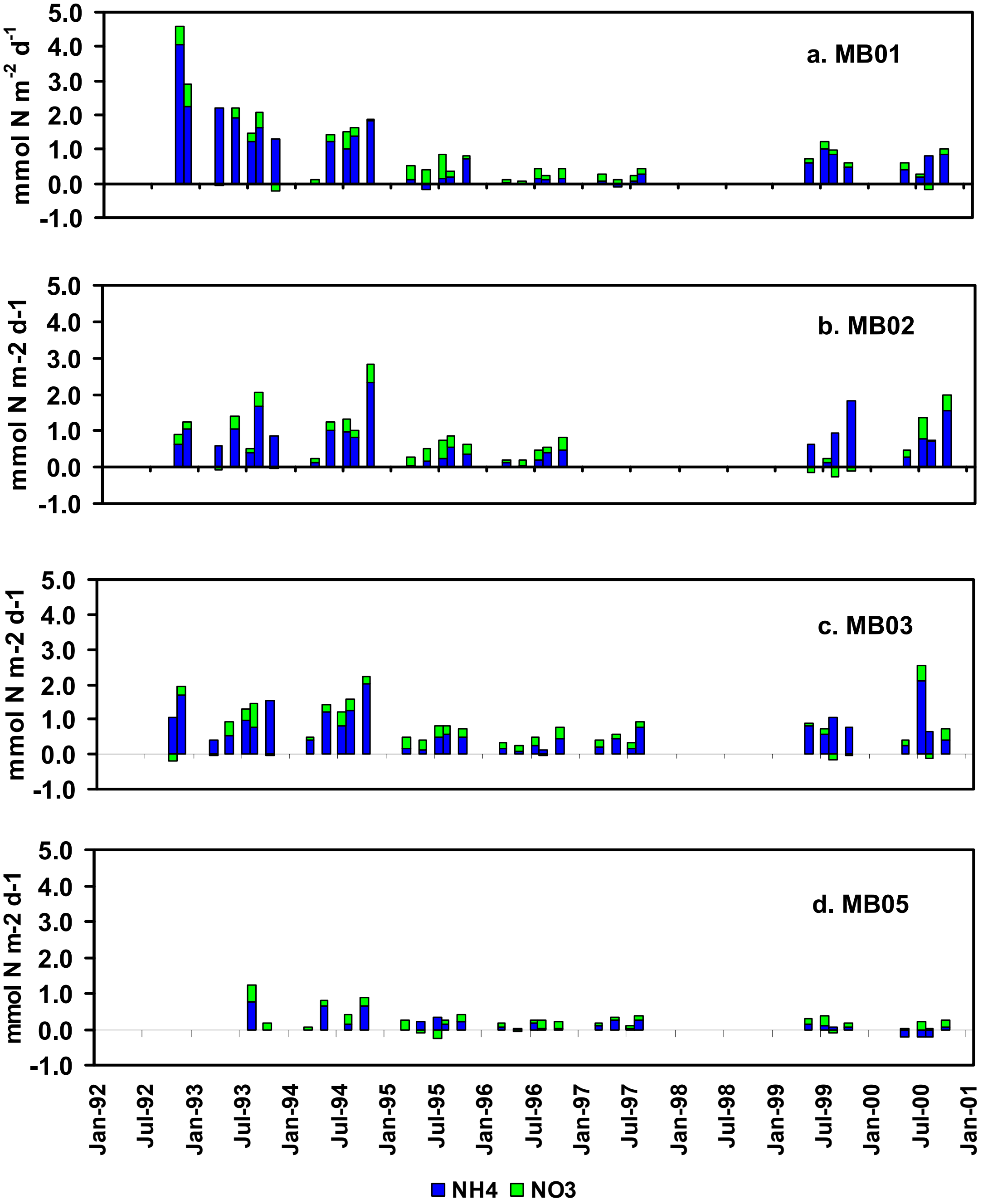

Figure 16. DIN flux, showing relative contributions of NO_3^- and NH_4^-, at a) MB01, b) MB02, c) MB03, and d) MB05 from late 1992 to 1999.

4.2.1.4 Urea Fluxes

Urea fluxes in Massachusetts Bay were small and variable and indicated that urea was more often taken up by sediments than released. The coefficients of determination (r^2s) for these fluxes are often quite weak, and it has been rare for both cores of a duplicate pair to yield strong linear fluxes. In 2000, this occurred on four occasions. Linear rates were measured twice at Station MB05, in May and October. In May, the magnitude of the urea flux was 15% that of the DIN flux, but both fluxes were directed into the sediments. The October urea flux at Station MB05 was also into the sediments, whereas the DIN flux was directed out; the magnitude was 21% that of the DIN flux. At Station MB02 in October, both cores yielded urea fluxes with significant r^2s and were of equal magnitude; however one flux was out of and one was into the sediments, resulting in no net flux. The fourth instance occurred at Station MB01 in August. The average urea flux was 0.24 mmol $m^{-2}d^{-1}$, and although the r^2s for the replicates were fairly high (0.74 and 0.79), the standard error for the two replicates was large (S.E. = 0.18). Even so, the magnitude of the flux compared to the DIN flux (ratio of 0.38), marks this as a noteworthy urea flux for the baseline period. Generally low rates and low r^2 values combined with large standard errors around the means of duplicate cores continue to make interpretation of urea fluxes difficult. In some cases, however, the rates 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

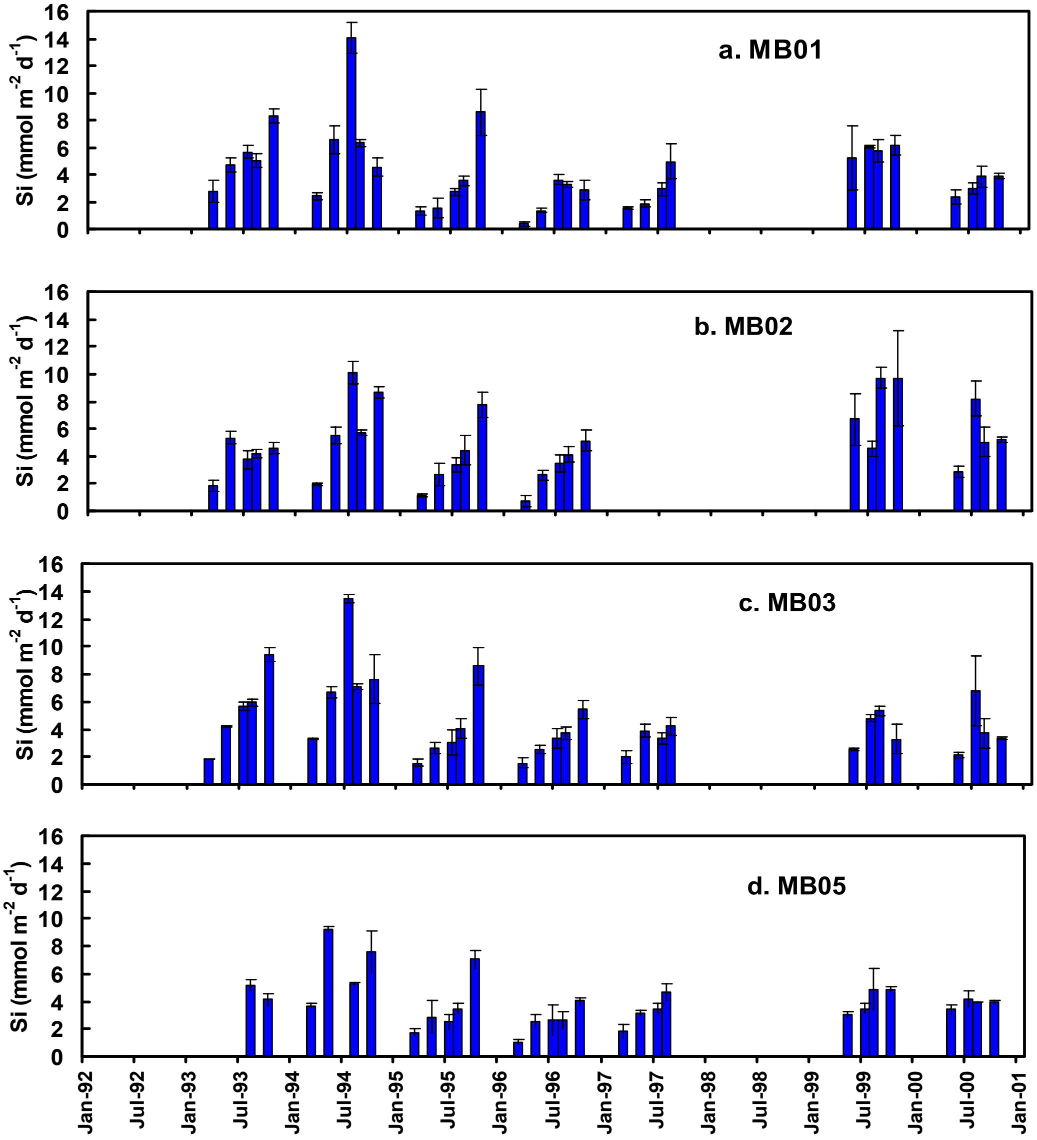

Figure 17. Dissolved silica flux at a) MB01, b) MB02, c) MB03, and d) MB05. Error bars represent the standard error of the mean of two cores.

Silica fluxes in the Nearfield stations of Massachusetts Bay in 2000 ranged from a low of 2.1 mmol Si m^{-2} d^{-1} in May at Station MB03 to a high of 8.2 mmol Si m^{-2} d^{-1}, in July at Station MB02. Rates at MB05 ranged from 3.4 mmol Si m^{-2} d^{-1} in May to 4.1 mmol Si m^{-2} d^{-1} in July. 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 seasonal (May to October) average flux was 5.3 mmol Si m^{-2} d^{-1} at Station MB02, whereas the lowest was 3.3 mmol Si m^{-2} d^{-1}, at Station MB01.

The average Si flux of 5.3 mmol m^{-2} d^{-1} at Station MB02 represents a decrease from the baseline high of 7.7 mmol m^{-2} d^{-1} observed at that station in 1999. Silica fluxes also decreased at Station MB01 compared to 1999 rates and were more similar to rates reported in 1995 through1997 although lower than rates from 1993 and 1994. At MB03 and MB05, Si fluxes were comparable to 1999 and the 1995-97 period, although lower than in 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). In 2000, however, as for 1999, this pattern was not strong. Peak fluxes, as a baywide average, occurred in July, whereas highest bottom water temperatures were measured in August. . Departures from the typical pattern also occurred in 1994, when very high Si fluxes were measured at all four stations, and bay wide peak rates occurred in July.

4.2.1.6 Phosphate Flux

Phosphate fluxes in Massachusetts Bay in 2000 were very small, rivaling the lowest rates measured during baseline monitoring, and variable across stations and surveys. Calculated rates often had very low r^2s, and standard errors around the mean of duplicate cores were large. Sediments often took up PO_4, and fluxes ranged from an uptake of less than 0.1 mmol P $m^{-2}d^{-1}$ at Station MB03 in August to a release of 0.09 mmol P $m^{-2}d^{-1}$ at Stations MB02 in October. The only consistent pattern in 2000 was that in August, fluxes at all four stations were directed into the sediments; at best, however, only one core per duplicate yielded a rate with an r^2 greater than 0.5. Only in October at Station MB01 did we observe good duplicate linear PO_4 release from sediments, and the rate was only 0.03 mmol P $m^{-2}d^{-}$.

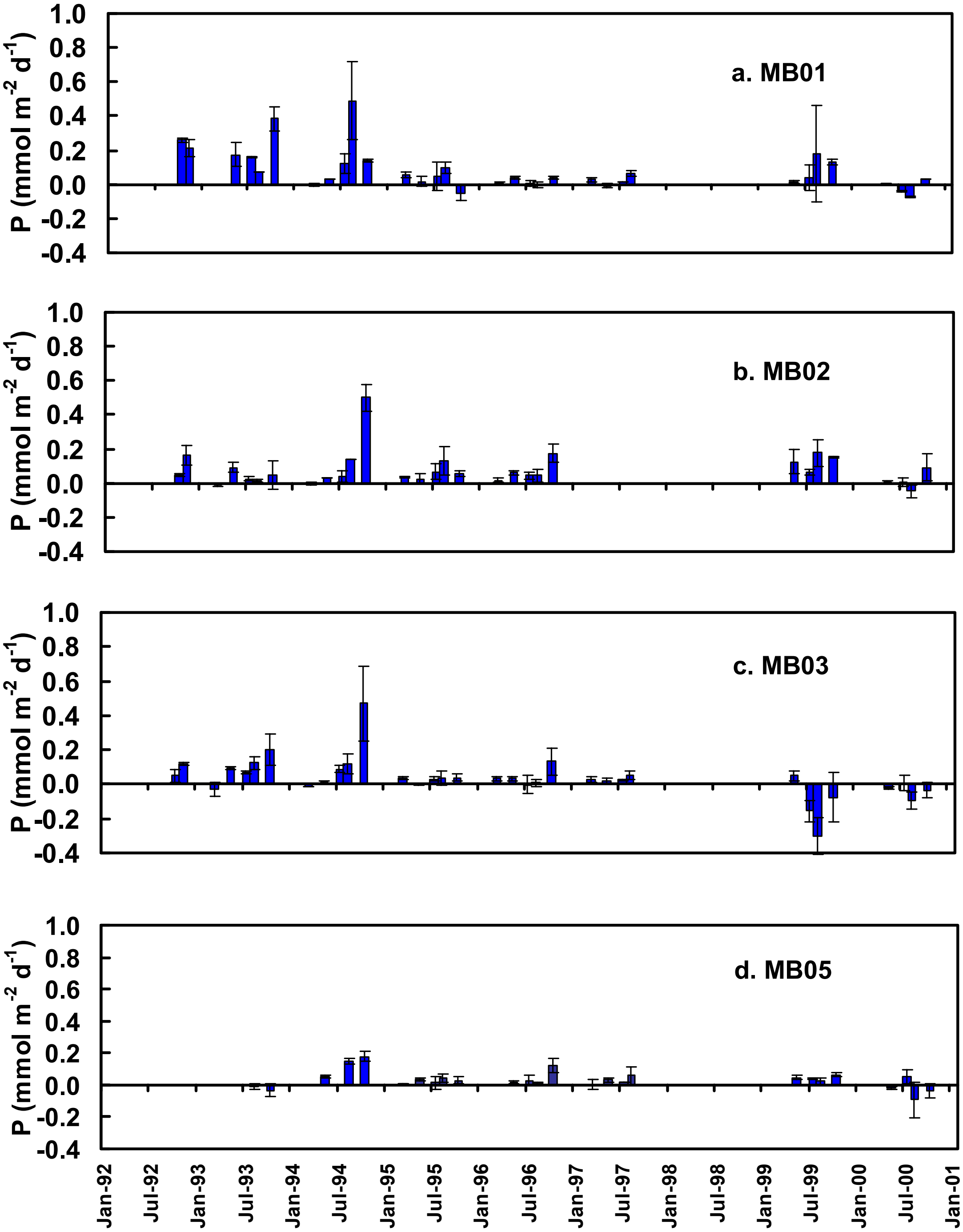

Figure 18. Phosphate flux at a) MB01, b) MB02, c) MB03, and d) Mb05. Error bars represent the standard error of the mean of two cores.

4.2.2 FLUX RATIOS

4.2.2.1 CO_2/O_2 (DIC/O_2)

May-October average CO_2/O_2 flux ratios or respiration quotients (RQ) (see Section 4.1.2.1) were very close to 1.0 at Stations MB01, MB02, and MB05, and the ratio was fairly constant across the season except for one low value at MB02 in May. (Fig. 19a). There were no values significantly higher than 1.0. At Station MB03, however, the seasonal average was 0.7, well under 1.0; only in October were O_2 and CO_2 fluxes in balance at this station.

Deviations from an RQ of 1.0 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 and 2000, average RQs near 1.0, wtih the exception of the unusual low RQs at Station MB03 in 2000, suggest that aerobic and anaerobic processes have become 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)

As has been typical throughout the baseline monitoring, CO_2/DIN flux ratios in 2000 were higher than the expected 6.6 for all Nearfield stations at all sampling times (Fig. 19b). A seasonal pattern was not apparent, but the highest ratio, 43.4, was calculated from July fluxes at MB01. During 1992-1994, annual average ratios in the Nearfield fell in a narrow range between 16.1 and 18.5. Last year, in 1999, these ratios were higher, ranging from 21.1 at MB03 to 31.6 at MB02 (note: annual averages for 1999 and 2000 include an estimate of winter flux rates calculated from March data, 1993-1997). In 2000, DIC/DIN ratios returned to values more like those in earlier years, ranging from 13.9 at MB03 to 20.0 at MB01. The amount of "missing" nitrogen that is implied by these ratios suggests that denitrification is an important process in Bay sediments.

A meaningful ratio could not be calculated at Stellwagen Station MB05 except in October because the DIN fluxes in May through August were negative (directed into the sediments); the ratio in October was 44.9. However, the absence of NH_4^+ or $NO_3^-+NO_2^-$ flux to balance the CO_2 flux suggests that denitrification accounted for essentially all of the inorganic N flux from this station at this time. Rates of denitrification are discussed in Section 4.2.3.

4.2.2.3 DIN/DIP

DIN/DIP flux ratios in Massachusetts Bay have been variable throughout the baseline period, however most typically the annual average for the ratio has fallen below the expected Redfield value of 16:1. In 2000 we observed a different pattern (Fig. 19c, Fig. 20a). Firstly, phosphate uptake by sediments was recorded frequently at all Nearfield stations. At Station MB05, either DIP or DIN or both fluxes were directed into the sediments. Although nutrient uptake, as opposed to release, by sediments contradicts the rationale behind calculating the ratios, the ratios may still provide some useful insights. Secondly, when fluxes of both DIN and DIP were directed out of the sediment, in all cases DIN/DIP was greater than 16:1. Although it is not unprecedented to calculate ratios above 16 at some sites and some times, it is unprecedented to observe no ratios lower than 16. These high ratios would indicate that sediment processes in 2000 tended towards phosphorus limitation rather than in the more typical direction of nitrogen limitation.

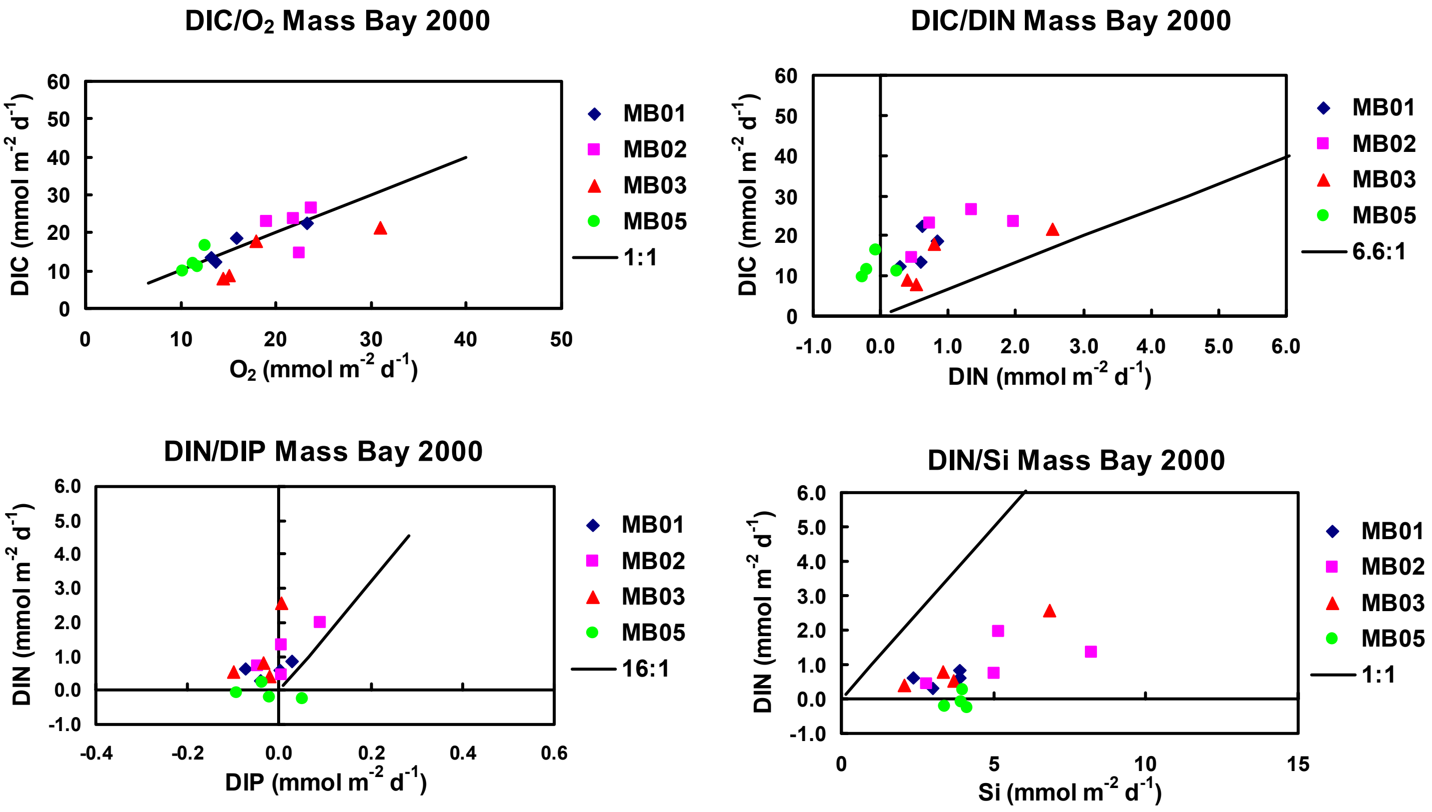

Fig. 19 Ratios of element fluxes at all Bay stations (symbols) relative to theoretical ratios (solid lines). a) DIC/O$_2$, b) DIC/DIN, c) DIN/DIP, d) DIN/Si.

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, about 0.38, occurred at Station MB02 in October and MB03 in July, driven by peak DIN fluxes at these times. At the Nearfield stations, DIN/Si flux ratios seem to show a decadal pattern. They 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 been less similar and have increased (Fig. 20b). Very low ratios have been characteristic for Station MB05 sediments. From 1994 to 1999, the annual average DIN/Si ratio at Station MB05 fell in a very narrow range of 0.05 (1999) to 0.08 (1994 and 1997). In 2000, flux ratios at this station were negative from May to August due to DIN uptake by sediments. In October, the DIN/Si ratio was very similar to previous years at 0.06.

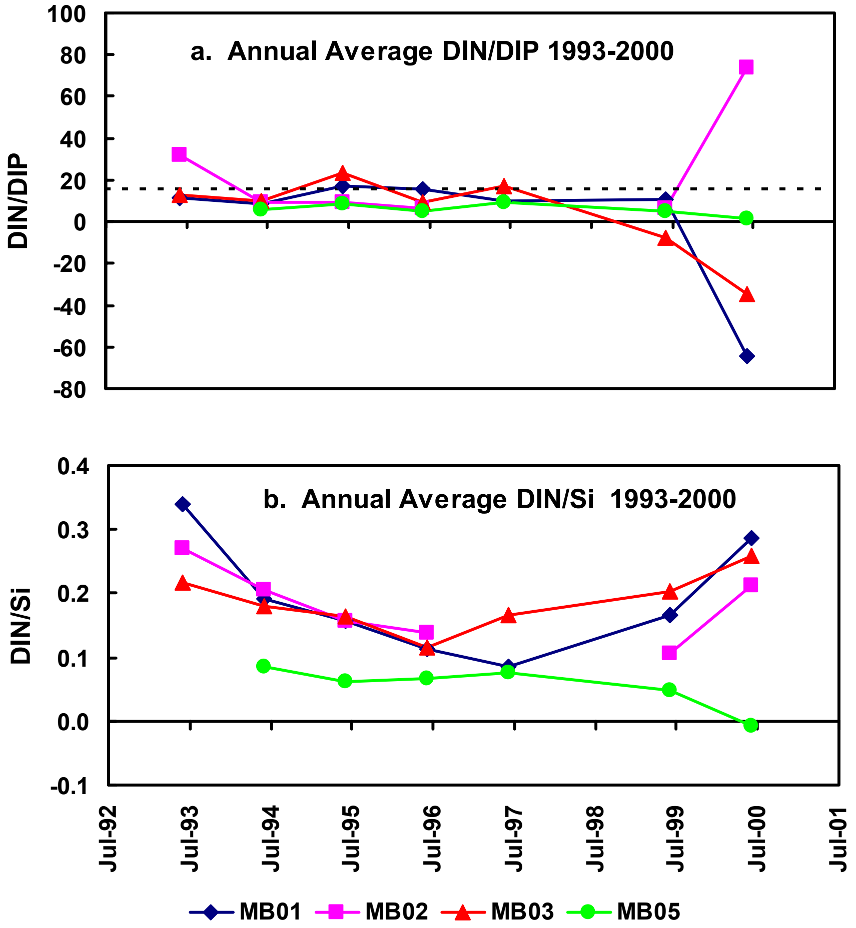

Fig. 20. Changes in annual average sediment flux ratios of a. DIN/DIP and b. DIN/Si at Massachusetts Bay stations, 1993-2000. The dotted line in (a.) is at 16:1.

4.2.3 SEDIMENT DENITRIFICATION RATES

4.2.3.1 Direct Measurement of Denitrification

Denitrification rates were directly measured by gas chromatography on sediment cores from Stations MB02 and MB03 in May and October. 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 October to 4.1 mmol N m^{-2}d^{-1} at the same station in May; in the previous year, the high rates at this station were in October and the low in May, opposite of this year (Fig. 21b). Although the highest rates were measured in sediments from MB02, Station MB03 sediments had quite high and very similar rates in both months, 3.8 mmol N m^{-2}d^{-}1 in May and 3.9 mmol N m^{-2}d^{-}1 in October (Fig 21d). These rates are among the highest recorded during the monitoring program (Fig 21). By these measurements and for May and October only, denitrification accounted for between 40% and 90% of the total dissolved nitrogen flux at MB02, and about 87% 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 (Fig. 21). Denitrification rates estimated by stoichiometry for Station MB02 in

May were 1.7 mmol N $m^{-2}d^{-1}$ as estimated by stoichiometry, compared to 4.1 mmol N $m^{-2}d^{-1}$ measured directly. In October, the two methods compared more favorably 1.6 mmol N $m^{-2}d^{-1}$ from stoichiometry and 1.3 mmol N $m^{-2}d^{-1}$ by direct measure. At Station MB03, stoichiometric rates were much lower than direct measures: 0.95 mmol N $m^{-2}d^{-1}$ and 1.9 mmol N $m^{-2}d^{-1}$ for May and October (compare to 3.8 and 3.9 mmol N $m^{-2}d^{-1}$, respectively). These rates, however, and the difference between them, are very similar to those from 1999.

Stoichiometric estimates of denitrification were made for all four sampling months and for all four stations in the Bay. Of the Nearfield stations, MB02 had the highest seasonal average of 2.2 mmol N $m^{-2}d^{-1}$, and MB03 had the lowest average of 1.0 mmol N $m^{-2}d^{-1}$. Peak rates occurred in August at MB01 and MB02, but in October at MB03. At Station MB05, peak rates (2.5 mmol N $m^{-2}d^{-1}$) also occurred in August; the low rate (1.4 mmol N $m^{-2}d^{-1}$)at this site occurred in October. The seasonal average was 1.7 mmol N $m^{-2}d^{-1}$.

These stoichiometric estimates imply that a very large percentage of the total DIN flux in Massachusetts Bay is accounted for by denitrification, ranging from 46% in August at MB03 to nearly 85% at Station MB01 in July. Results from Stellwagen station MB05 suggest that denitrification accounted for essentially the entire N flux from these sediments in May through August, and 85% in October. These percentages are quite high. Annual estimates from other coastal sediments range from 15 to 70% (Seitzinger, 1988).

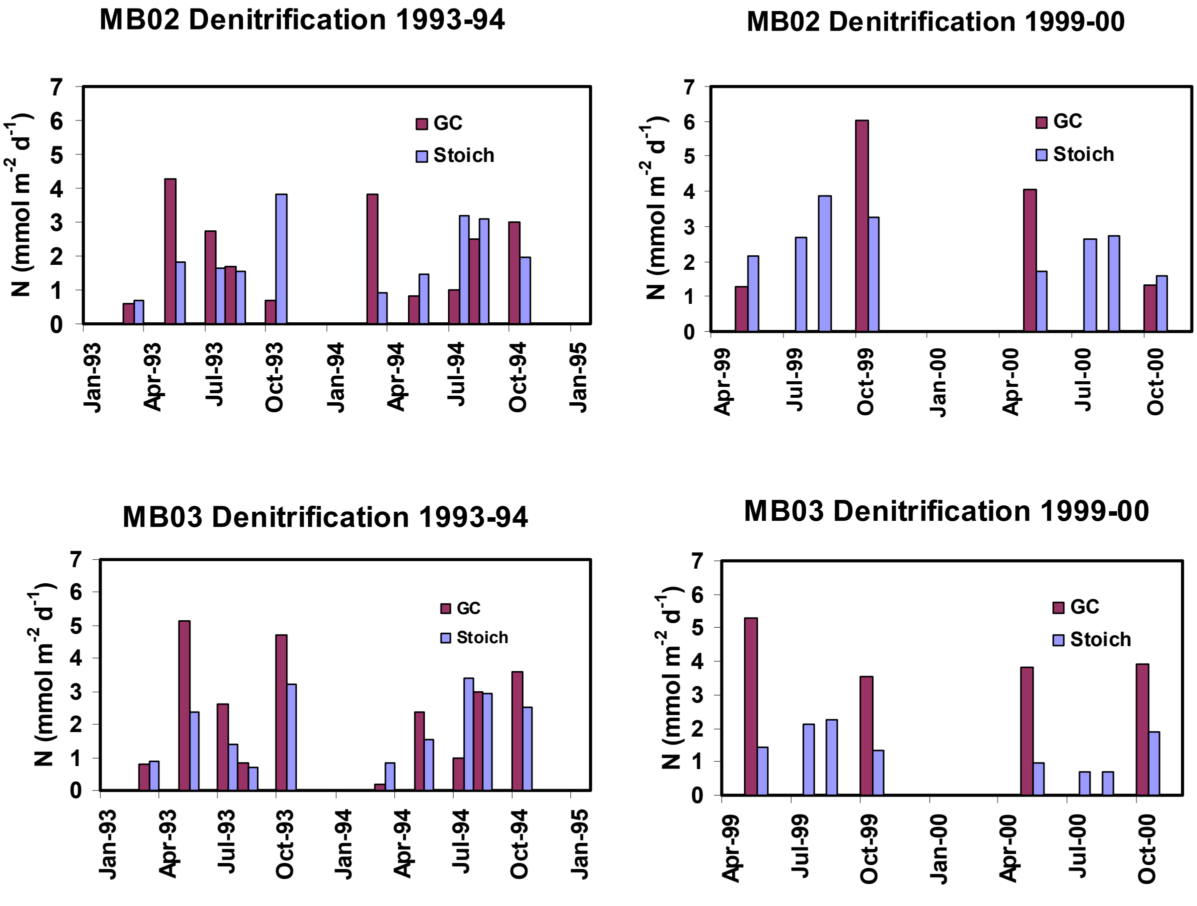

Fig. 21. Denitrification rates measured directly by GC and as estimated by stoichiometry for Station MBO2 in a.) 1993-1994 and b.) 1999-2000 and for Station MB03 in c.)1993-1994 and d.) 1999-2000.

4.2.4 SEDIMENT CHARACTERISTICS

4.2.4.1 Nitrogen and Carbon

For the second year in a row, organic nitrogen and carbon content of surface sediments was higher in Stellwagen Basin sediments than in Massachusetts Bay Nearfield sediments (Fig. 22, Table 4), At Station MB05 in the Basin, sediment %TOC and %TON were quite similar at all sampling times, averaging 1.4%TOC and 0.15% TON, very similar to the previous year. Sediments from the Nearfield showed more variability, with concentrations peaking in October at MB02 and MB03, but in July at MB01. Of the three Nearfield stations, the highest average TOC was 1.2% (MB02) and the lowest was 0.9% (MB03). Nitrogen content was similar across the three stations, averaging about 0.1%. C/N ratios were lowest and showed least seasonal variability at Station MB05, ranging only from 10.1 to 10.6, whereas they changed over the season at the Nearfield stations. Ratios at MB02 and MB03 followed similar seasonal patterns, with the lowest ratio in July and higher ratios at the end of the season. Although the pattern was similar between these two stations, ratios at MB03 were lower than at MB02. At MB01, C/N was the same as for MB02 in May and October, but exhibited a different seasonal pattern compared to the other two staions, with a peak of 14.5 in July.

Organic nitrogen and carbon content of Nearfield sediments at Stations MB01 and MB03 were lower than in earlier years (1993-1995) of the monitoring program but nearly the same as in 1999 (Fig. 23). This appears to be the case also at MB02, however organic matter concentrations at this station were much lower in the earlier years than at MB01 and MB03 so the decrease is much less. In contrast, there has been no change in the Stellwagen Basin sediments over the same period.

If C/N is an indication of the quality of organic matter input to these sediments, then in recent years it appears the benthos in Massachusetts Bay has been receiving lower quality inputs than has the deeper water Station MB05 in Stellwagen Basin. Within the Bay, there seem to be clear differences in organic matter input to the three stations, at least in terms of timing.

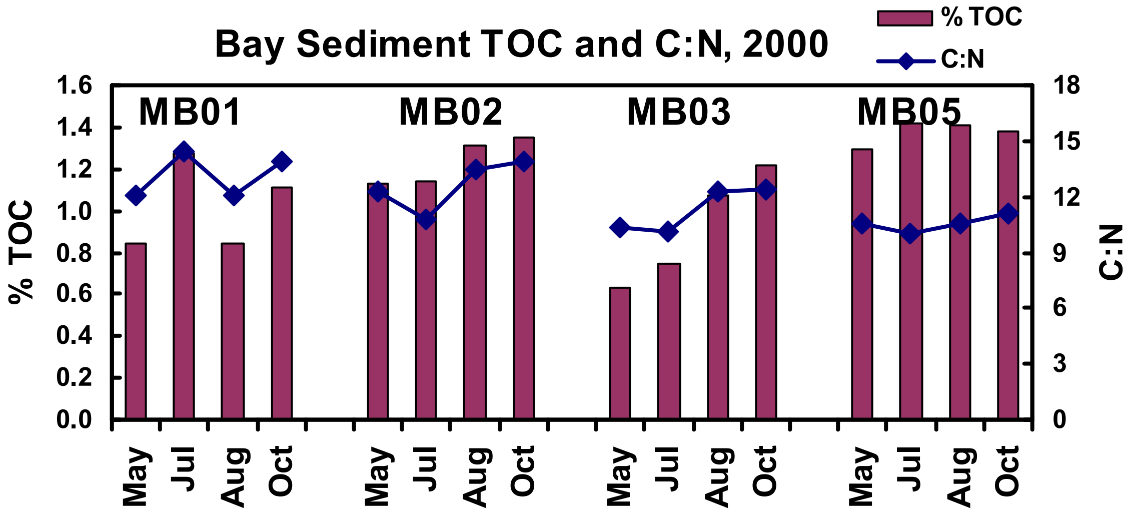

Figure 22. Sediment % organic carbon and molar C:N ratios for Bay sediments, 2000.

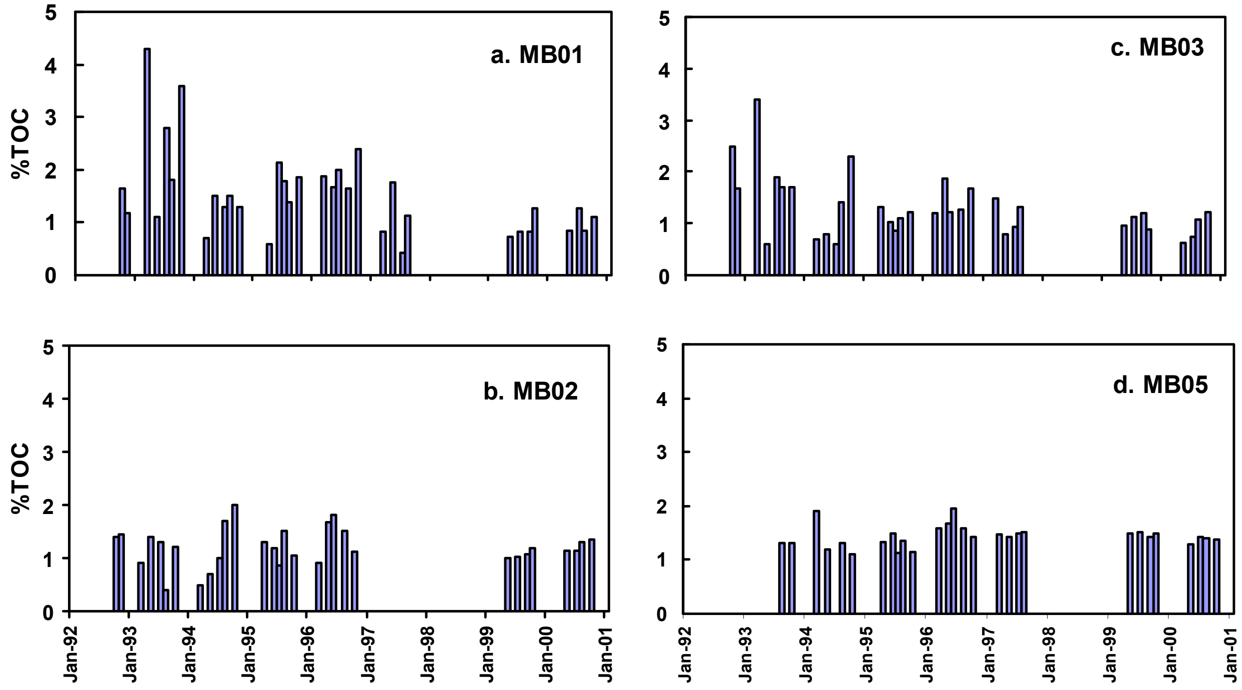

Figure 23. Changes in %TOC in the top 2 cm of sediments at Massachusetts Bay stations since late 1992: a.)MB01, b.) MB02, c.) MB03, d.) MB05.

4.2.4.2 Pigments

In 2000, inventories of pigments, chlorophyll *a* + phaeopigments, summed over the top 5 cm of sediment were somewhat higher than they had been in 1999 at Station MB01 and MB05, but somewhat lower at MB02 and MB03 (Fig. 24). However, as in 1999, the inventories of total chlorophyll pigments were higher than most other years. As was the case for Boston Harbor results, the increase appeared to be in the phaeopigment fraction, as chlorophyll *a* inventories were in general lower than in previous years. As noted in Section 4.1.4.2, our protocol may extract more phaeopigments than methods used in other years.

Total pigment inventories were in general highest in October for the Nearfield stations (Table 4), in contrast to the previous year when highest levels were recorded in May, possibly reflecting differences in spring and fall phytoplankton blooms in the two years. At two of the Nearfield stations, MB02 and MB03, the peak in chlorophyll *a* also occurred in the fall. Station MB03 in particular had quite high chlorophyll levels in October, one of the highest recorded during the baseline monitoring; the inventory for the top 5 cm was 12.6 µg/cm^{-2}. These levels became present in the fall after a depletion of chlorophyll *a* in sediments of all three stations in early summer; chlorophyll concentrations were below detection in July.

At the Stellwagen Basin station, chlorophyll *a* as well as total pigments, peaked in May, were drawn down sharply by July, and then increased until October (Fig. 24, Table 4). The May chlorophyll peak, at 9.7 µg/cm^{-2}, was among the highest recorded at this station. Overall, chlorophyll inventories at this station in 2000 were similar to those of previous years.

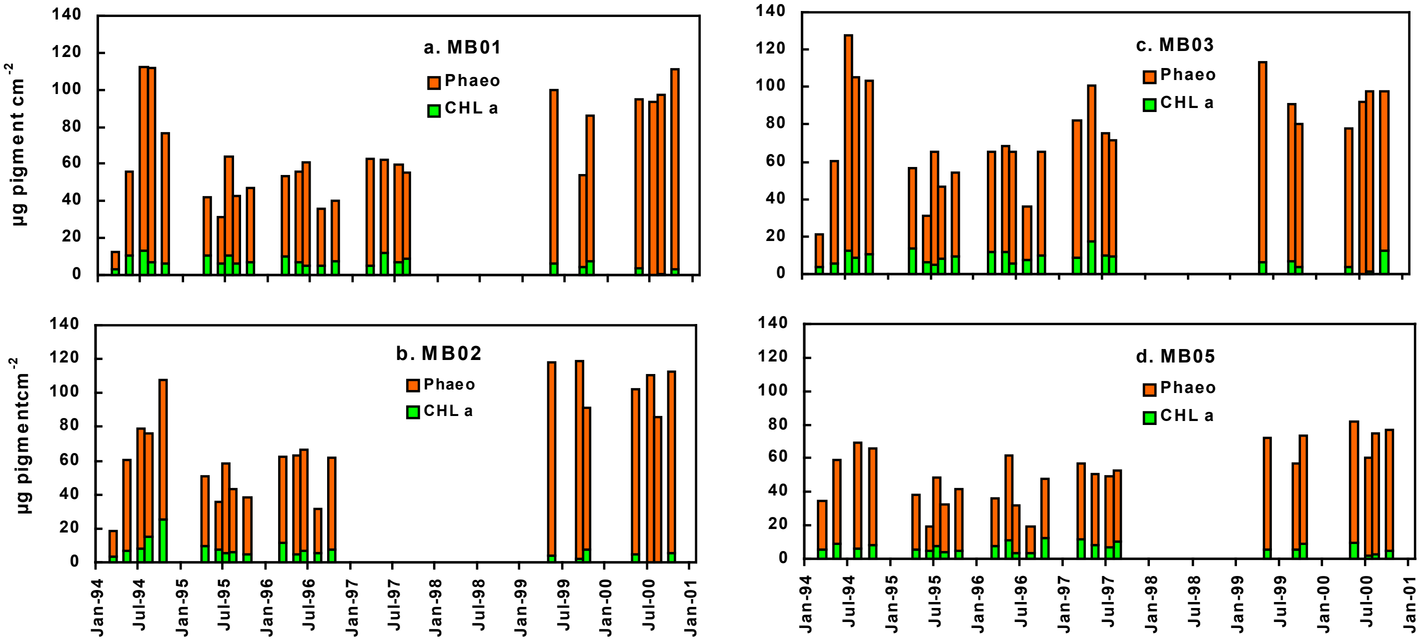

Figure. 24 Inventories of chlorophyll *a* and phaeopigments in the top 5 cm. of sediments at Bay stations a.) MB01, B.) MB02, c.) MB03, and d.) MB05.

Table 3. % Organic Carbon, % Organic Nitrogen, and Pigment Inventories from Bay sediments in 2000.

Station	Date	%TOC[1]	%TON[1]	Chlorophyll *a*[2] µg/cm^2	Total Pigments[2] µg/cm^2
MB01	May	0.8	0.08	3.9	95.0
	July	1.3	0.10	bd	93.4
	August	0.8	0.08	0.74.5	97.0
	October	1.1	0.09	3.37.5	110.9
MB02	May	1.1	0.11	4.6	102.6
	July	1.1	0.12	bd	107.6
	August	1.3	0.11	0.3	86.0
	October	1.4	0.11	5.7	112.6
MB03	May	0.6	0.07	4.0	77.6
	July	0.8	0.09	bd	91.4
	August	1.1	0.10	1.3	97.8
	October	1.2	0.11	12.6	97.6
MB05	May	1.3	0.14	9.7	81.7
	July	1.4	0.16	1.9	60.3
	August	1.4	0.16	2.7	75.1
	October	1.4	0.15	4.5	77.2

[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.
bd= below detection

4.2.5 POREWATER CONSTITUENTS

Oxidation-reduction potential (Eh) was measured at all Bay stations and at all four sampling times (Fig 25 a-d). In the Nearfield, overall patterns in Eh were similar to those of previous years (Howes, 1998a) in that these sediments are typically very oxidized. However there is year to year variability. Last year, 1999, all four stations followed a similar progression of Eh values through the season: sediments were most reduced in May, most oxidized in July and were returning to winter conditions through early September and October. In 2000, seasonal patterns in Eh were different from 1999 and from station to station. MB01 and MB05 followed a similar progression of Eh changes, with conditions in sediments most oxidizing early in the season (May) and least so at the end of the season (October). At MB03, lowest Eh values were also measured in October, but the most highly oxidized conditions were measured mid- season, in July. At MB02, in contrast to the other stations, there was little change between the May and July profiles, but then a larger decrease resulted in lowest values at this station being measured in August.

The similarities between 1999 and 2000 were that the Eh profiles changed very little with depth after about 4 or 5 cm in both years, with the result that the RPD was not encountered by 18 cm, the total depth of the core sample, at any station. In previous years, the RPD had been noted at much shallower depths. 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. At Station MB05, the RPD was at about 5cm in 1994 but as deep as 20 cm in 1995-1997 (rough extrapolation from data; Howes, 1998a-c).

We have yet to detect sulfides in the porewaters of Massachusetts Bay sediments. This observation is consistent with highly oxidized sediments, and high Eh values. Sulfides are generally present only after Eh values reach –200 mV or below (Stumm and Morgan, 1966). The detection of sulfides would signal a notewothy change in these sediments towards more reducing conditions.

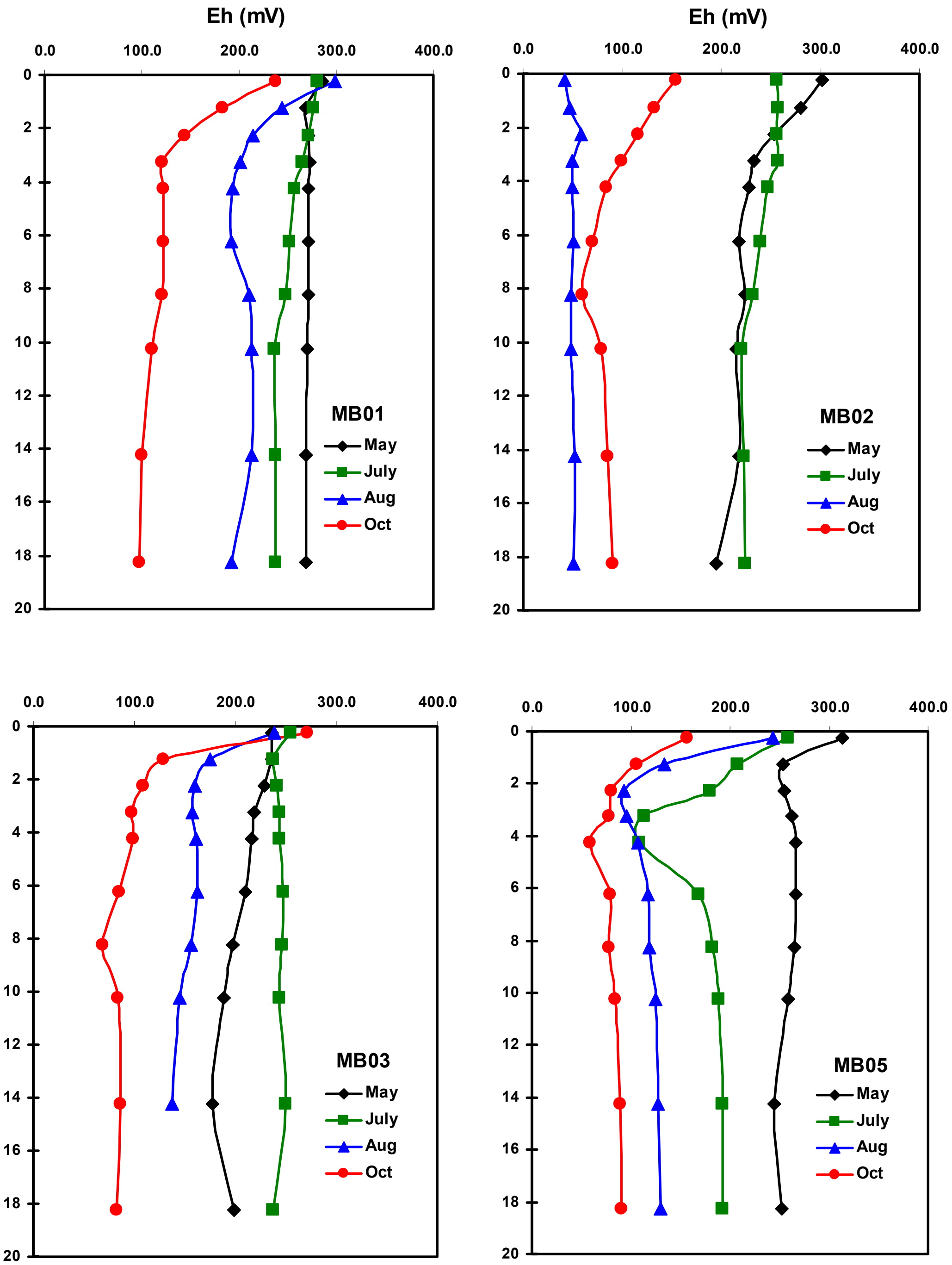

Figure 25. Oxidation-reduction potential (Eh) from sediment cores from each survey in 2000 for a) MB01, b) MB02, c) MB03, and d) MB05.

4.2.6. SUMMARY OF TRENDS IN BAY NUTRIENT FLUXES

2000 marked the final year of baseline monitoring in Massachusetts Bay. The Bay outfall came on line September 6. We conducted only one set of benthic flux measurements soon after the diversion, in late October. None of our measurements made at that time indicated a change in benthic processes, so we have not distinguished the October results from the rest of the 2000 data (see Section 4.3 below).

Sediment respiration rates in the Nearfield of Massachusetts Bay in 2000 were very similar to high rates reported for 1999. In particular, the very high rates observed at MB02 were observed again in 2000. Oddly, there was no seasonal pattern in respiration at this station, as had been typical in earlier years, and little at the other two Nearfield stations. The seasonal pattern was damped even at Station MB05, in Stellwagen Basin. Although bottom water temperatures were warmer earlier in the season than normal, temperature did not explain high rates observed in May.

Both 1999 and 2000 were notable for sustained and large phytoplankton blooms. It is tempting to speculate that increased deposition of high quality organic matter fueled the higher and sustained sediment respiration rates. However, direct evidence of increased deposition was lacking. In fact, sediment carbon content appears to have decreased in the last two years, especially at MB01 and MB03. There was little change in average organic matter content at MB02, where respiration has increased the most, but like respiration, sediment carbon did not show seasonal variability. Also, sediment chlorophyll *a* content has not increased at these stations, although total chlorophyll pigments may have. An interaction between temperature and substrate availability may be creating the patterns we observe. In addition, changes in benthic fauna may be playing a role not explicitly examined in these studies.

DIN release from Nearfield sediments was higher in 1999 and 2000 than it had been in 1995 to 1997, but similar or lower (MB01) than in 1993 and 1994. In contrast to respiration, however, a seasonal pattern in DIN fluxes was apparent in 1999 and 2000. Silica fluxes paralleled DIN fluxes in seasonal pattern, but not in magnitude in relation to previous years. In that regard, Si fluxes were more like respiration: higher at MB02 the past two years than previously, and about average at MB01 and MB02. Nutrient fluxes from sediments at our Farfield station, Station MB05, have shown little variability since the somewhat higher rates observed in 1993-1994.

Phosphate fluxes in 2000 were very small, among the lowest rates measured during baseline monitoring of the Nearfield, and often were directed into the sediment. However, the large PO_4 uptake rates observed at Station MB03 in 1999 were not repeated. Ratios of DIN to DIP fluxes were either negative due to PO_4 uptake, or were greater than the expected ratio of 16.0. This suggests that nutrient release by sediments would push the Bay towards phosphorus limitation, an unusual circumstance for marine systems.

Several measures indicate that Nearfield sediment redox conditions were more oxidizing than at the beginning of baseline monitoring. In both 1999 and 2000, sediment respiration quotients were closer to 1.0 than in the early 1990s. Sediment redox values have been quite high, with the apparent redox potential discontinuity (ARPD) very weak or absent in most cores. Phosphate uptake is also consistent with oxidized sediments.

Denitrification rates in Bay sediments have not shown a long-term trend. As a percent of total nitrogen flux, however, denitrification is very important in the Bay, often accounting for the majority of total remineralization.

4.3 OBSERVATIONS AFTER INITIATION OF BAY DISCHARGE

As mentioned earlier in this report, we have conducted only one set of flux measurements since the Bay outfall became operational on September 6, 2000. These measurements were made just seven weeks later, during the week of October 23. We observed no anomalies in the parameters measured at this time compared to August, 2000, or to patterns observed in previous years. In fact, we did not expect to observe a change after so short a time. Sediment processes are integrative, and typically have a slow response time.

Projections made by the Bays Eutrophication Model (BEM) of POC flux to the sediments, including effluent and algal-derived POC, indicated that an increase would occur only in a very localized area around the outfall, and the increase would be less than a doubling (HydroQual, 1995). Our nutrient flux stations are outside the area projected to see an increase. The model projections required five years to achieve a new equilibrium response representative of the full effect of the outfall, a length of time derived from time constants of decay and delivery of particulates to the sediments. The limited impact projected by the model was largely attributable to secondary treatment, which produces effluent with low solids and carbonaceous biological oxygen demand (cBOD). For 2000, monthly average total suspended solids (TSS) and cBOD were around 15 and 10 mg/L, respectively, well under the limits set by the 1999 NPDES permit. (Werme and Hunt, 2001).

Prior to 1999, we postulated that a change in benthic nutrient fluxes of as little as 20% of the annual average would be detectable. Rates measured over the first six years of monitoring fell within a relatively narrow range, and seasonal patterns were consistent. In 1999 and 2000, however, we observed rates and seasonal patterns well outside previous observations. In hindsight, it was fortuitous that the baseline period lasted longer than originally intended; otherwise, higher sediment respiration rates in 1999 and 2000 at Station MB02, for example, might have been considered anomalous and incorrectly attributed to the outfall. We now have a better understanding of the natural high variability in Massachusetts Bay; it is unlikely that we will observe any effect of the Bay outfall on sediment nutrient cycling until after many months of operation.

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