Metabolism, nutrient cycling and denitrification in Boston Harbor sediments in 1998

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FINAL REPORT

METABOLISM, NUTRIENT CYCLING AND DENITRIFICATION IN BOSTON HARBOR SEDIMENTS IN 1998

for

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EXECUTIVE SUMMARY

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

1) Sediment oxygen uptake in the Harbor ranged over the seasonal cycle from approximately 18 mmol $m^{-2}d^{-1}$at the shallow Quincy Bay Station (QB01) in May to 96 mmol $m^{-2}d^{-1}$ at the Hingham Bay Station (BH08A). Average rates for the May to October season were highest at Station BH08A, which was heavily colonized by the mat-building amphipod community.

2) Dissolved inorganic nitrogen fluxes in Boston Harbor ranged from 0.5 mmol N $m^{-2}d^{-1}$ at Station QB01 in May to 11 mmol N $m^{-2}d^{-1}$ at Station BH02 in July. This range was narrower than in some previous years. The relative proportions of NH_4 and NO_3 in the DIN flux continue to correlate with benthic infaunal abundances, with NO_3 comprising a large fraction of the flux at those sites heavily colonized by the amphipod community.

3) Directly measured rates of denitrification in Boston Harbor ranged from 0.5 mmol N m^{-2} d^{-1} at Station BH02 to 5.4 mmol N m^{-2} d^{-1} at Station BH03. The rates at BH02 fell in the middle of the range of values observed at that station since 1993, whereas those from BH03 fell in the lower part of its range. Direct measurements were on average 55% of stoichiometric estimates, similar to observations made during 1992-1994. Highest rates continued to occur with large numbers of amphipods, with highest overall rates for 1998, as estimated by stoichiometry, measured at Station BH08A.

4) Respiration at depositional sites in the harbor was equivalent to 63% (based upon oxygen and 1991 production estimates) to 85% (based upon DIC) of the production in the overlying water. Benthic nutrient release could supply 34% of the N and 58% of the P required for primary production.

5) Porewater constituents are important indicators of sediment processes. Porewater sulfide and Eh results indicated that the sediments at BH02 and BH03 are more oxidizing than when the studies began in 1992.

6) Although stations continue to exhibit year to year variability, the very high rates of 1993 and 1995 have not been repeated for three years, even though amphipods continue to be present. This suggests that some “mining” of sediment stores may have taken place. Rates are now typical of productive coastal sediments.

1. INTRODUCTION

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 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). We examined sediment-water exchanges of oxygen, total carbon dioxide (DIC), nitrogen (ammonium, nitrate, urea), silicate, and phosphorus at stations in Boston Harbor four times in 1998. 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, and (2) better characterize the variability in conditions in Boston Harbor prior to wastewater diversion in 1999, and (3) provide data for the water quality model developed by HydroQual.

We have discussed the importance of benthic fluxes from an ecological perspective at length in our previous reports. Briefly, sediments of coastal environments play an important role in nutrient recycling and organic matter decomposition. The breakdown of organic material on the bottom releases nutrients to the overlying water and consumes oxygen. The nutrients which are released can be reused by the phytoplankton to support primary production.

In addition to serving as a source of inorganic 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).

2. SAMPLING DESIGN

The sampling sites are shown in Figure 1. Two of the Harbor sites sampled in 1998, BH02 and BH03, have been sampled every year since 1992. The other two, BH08A and QB01 have been sampled since 1995. Surveys were carried out during mid-May, early July, mid-August, and late October. All survey cruises were completed in one day. The sampling locations, water depths, and sediment classifications are given in Table 1. The sampling dates, water temperatures, bottom water oxygen concentrations, and salinities of the sites are shown in Table 2.

Fig. 1. **Boston Harbor Benthic Nutrient Flux Stations 1998.**

Table 1. Station locations, water depth, and sedimentary classification for Boston Harbor stations visited in 1998.

Station	Location	N Latitude	W Longitude	Water depth range(m)[1]	Sedimentary Classification [2]
BH02	Central Outer Harbor	42° 20.62’	71° 00.13’	9.1 - 13.3	reworking
BH03	Off Long Island, Former sludge Disposal area	42° 19.82’	70° 57.72’	6.2 – 9.7	depositional
BH08A	Hingham Bay, Southern Harbor	42° 17.46’	70° 55.33’	7.3 - 9.6	depositional
QB01	Quincy Bay, Southern Harbor	42° 17.61’	70° 59.27’	2.9 - 5.1	depositional

[1.] Depth varied depending on tide.

[2.] According to Knebel and Circe, 1995

Table 2. Boston Harbor Stations, Survey ID, Date of Survey, and bottom water temperature, dissolved oxygen (D.O.) and salinity.

Station	Survey ID	Date	Temp (°C)	DO (mg/L)	Salinity (ppt)
BH02	NC981	05/18/98	10.0	9.3	29.7
	NC982	07/07/98	15.7	8.4	29.3
	NC983	08/11/98	13.3	8.7	32.6
	NC984	10/29/98	11.6	8.8	31.5
BH03	NC981	05/18/98	11.1	9.2	28.6
	NC982	07/07/98	15.0	8.3	29.3
	NC983	08/11/98	14.7	8.0	32.0
	NC984	10/29/98	11.2	9.3	31.9
BH08A	NC981	05/18/98	11.7	9.4	28.4
	NC982	07/07/98	15.3	7.7	29.5
	NC983	08/11/98	14.4	7.9	32.5
	NC984	10/29/98	11.1	9.4	32.4
QB01	NC981	05/18/98	13.1	9.5	27.4
	NC982	07/07/98	17.4	6.7	29.0
	NC983	08/11/98	16.0	8.3	32.1
	NC984	10/29/98	11.3	10.8	32.2

2.1 Location and Rational for Stations

Four Harbor stations were sampled during 1998. Two of these stations, BH02 and BH03, have been monitored since 1992, although the location of BH03 has varied slightly. During 1995-1997 Station BH03A, located about 200m west of BH03, was sampled; however these two stations are comparable and for the purpose of discussing long term trends will be considered the same. The other two, Stations BH08A and QB01 have been monitored since 1995.

Station BH03, off Long Island and near the old sludge disposal site, has been sampled 4 to 5 times annually since 1992. This site has been undergoing dramatic changes over this time period, as sludge dumping ceased at the end of 1991 and large numbers of mat-building amphipods have colonized the area. Station BH02 has been monitored because it is considered more typical of the muddy sediments influenced by the extant sewage outfall and has experienced less dramatic changes in loading over the monitoring period. Stations BH08A in Hingham Bay and QB01 in Quincy Bay represent depositional areas in the southern harbor.

All four stations were sampled four times in 1998, from spring to fall, concentrated on the time of the year when the sediments are most active. The first survey of the year was in mid-May, a time chosen both because temperatures are low and we expect that organic matter from the spring bloom has recently been deposited on the sediments. The following two surveys were in July and August, summer months often characterized by the highest flux rates. The last survey was in

October, when water temperature begins to fall and rates of benthic processes generally decline as organic matter is depleted.

3. METHODS

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

3.1 Field Sampling

All stations in Boston Harbor were sampled by SCUBA divers. Two large, 15-cm. diameter core tubes were used to obtain sediment for flux measurements. 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 and BH03, two to three additional cores, approximately 10.1-cm. in diameter, were taken for direct measurements of N_2 flux. Bottom water temperature, O_2, and salinity were measured in situ with a water quality monitoring probe (Hydrolab Scout 2 Multiparamenter Water Quality Data System).

At each station 15 liters of water were collected with a diaphragm pump from just above the bottom and immediately filtered through a series of cartridge filters (nominally 20 and 1.0 µm). This water, which was held at in situ temperatures, was used to replace the overlying water in the 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 that the headspaces of the cores were completely filled with water. This prevents sediment disturbance during handling. Upon arrival cores were placed in a dark incubator where they were held uncapped, overnight, at the in situ temperature of the station. Flux measurements were begun within 12-24 hours of sampling. Prior to initiating flux measurements, the overlying water of each core was replaced with the filtered seawater collected at each station. Two BOD bottles filled with the filtered water obtained from each station were used to correct for respiration in the water overlying the sediments.

Cores were sealed with core 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 over time.

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

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

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

3.3 Porewater Sampling and Analysis

Sediment samples for porewater extraction were taken from all 4 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 and phaeopigments were collected from all four stations at the beginning and end of the season (May and October) with the idea of capturing inputs from the spring and fall phytoplankton blooms. 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 Direct Measurements of Denitrification

Sediment denitrification was measured as the direct flux of N_2 gas from sediment cores in gas-tight N_2-free chambers. 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, and the field 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.

3.7 Denitrification Using 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.

3.8 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 previous studies on benthic metabolism and sediment nutrient cycling in the harbor. In particular, comparisons of sediment respiration, nutrient fluxes, and porewater constituents come largely from annual reports to the MWRA from two groups of researchers. Rather than cite the extensive list at every data comparison, we present the list here: A) For data from 1991-1994: Giblin et al, 1992; Giblin et al, 1993 ; Giblin et al, 1994; Giblin et al, 1995; Giblin et al, 1997; B) For data from 1995-1997: Howes, 1998a; Howes, 1998b; Howes, 1998c.

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 Benthic Respiration and Nutrient Fluxes

4.1.1 Oxygen Uptake

Boston Harbor sediment oxygen uptake ranged from approximately 18 to 96 mmol O_2 m^{-2} d^{-1} between May and October 1998 (Figure 2). There was no clear difference between northern and southern harbor stations; in fact, both the highest and lowest rates were measured in the southern harbor. At all stations except BH03, highest respiration rates were measured in July. These high rates co-occurred with the highest bottom water temperatures of the four times we sampled, although it was atypical for temperatures to be warmer in July than in August. Summer bottom water temperatures in Boston Harbor as well as in Massachusetts Bay in1998 were cooler than the 1993-1997 average (Libby et al., 1998 annual water column report, in prep.).

The highest respiration rate we measured in 1998, 96 mmol O_2 m^{-2} d^{-1}, was measured in July at Station BH08A. BH08A had the highest annual rate of all four stations, 77 mmol O_2 m^{-2} d^{-1}, and the highest rates at each sampling time with the exception of the October rates measured at

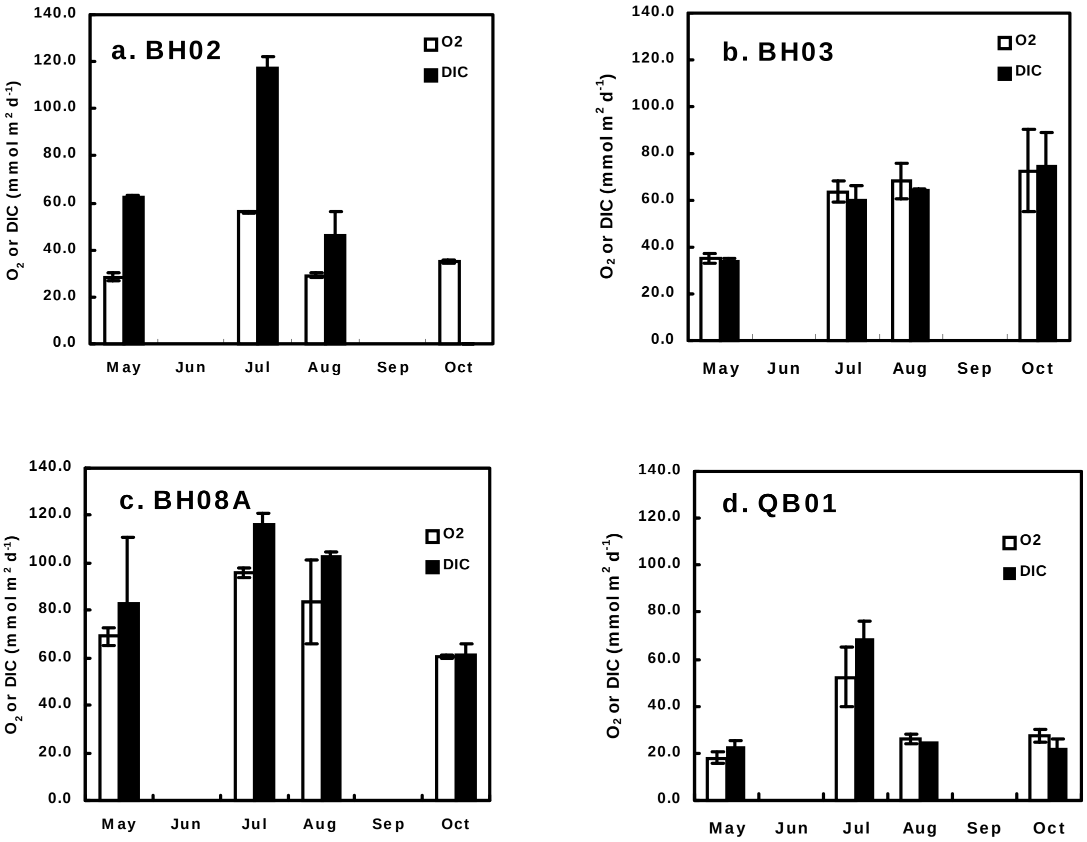

Figure 2. Sediment Respiration as measured by O_2 uptake or CO_2 flux at a.) BH02, b.) BH03, c.) BH08A, d.) QB01. Error bars represent the standard error of the mean of two cores.

BH03. Respiration at BH03 followed a different seasonal pattern than the other stations, peaking in October at 73 mmol O_2 m^{2}d$^{-1,}$ but with similarly high rates occurring in July and August (64 and 68 mmol O_2 m^{-2} d^{-1}, respectively). Sediments at both BH03 and BH08A were heavily colonized by the amphipod community. However, at Station BH08A, highest respiration rates seemed to correspond to temperature.

Respiration rates at BH02 peaked at 57 mmol O_2 m^{-2} d^{-1}. Sediments at Station BH02 were, typically, more reducing than the other stations, and the amphipod mat was absent. There were also few animals present in the sediments of Station QB01. Station QB01 was characterized by lower rates of respiration than the other three sites, although rates measured here this year were not very different from those at BH02. The highest rate measured at this station was 53 mmol O_2 m^{-2} d^{-1}.

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

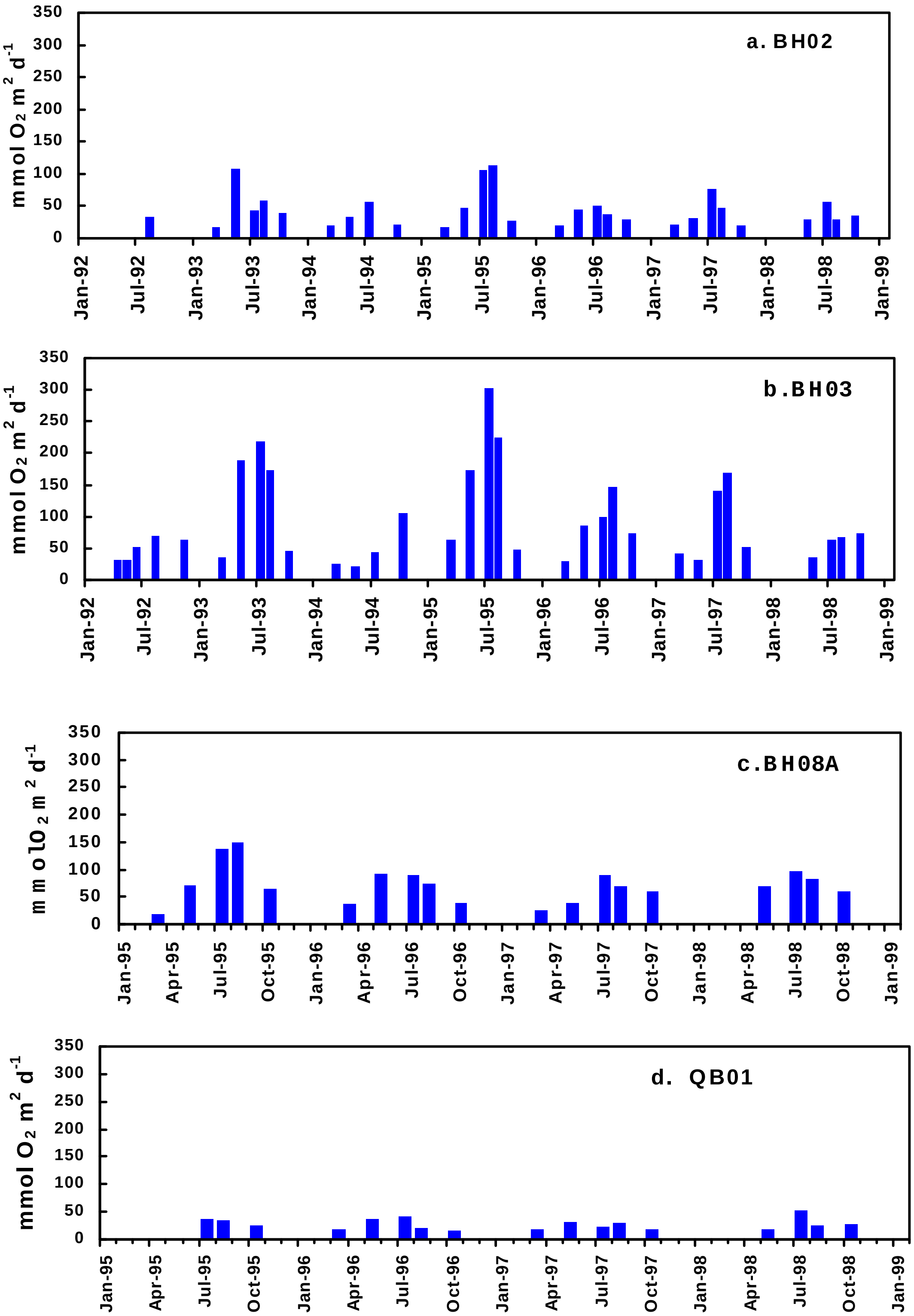

Figure 3. O2 flux from 1992-1998 at a) BH02 and b) BH03 and from 1995-1998 at c) BH08A and d) QB01. Note differences in time line on the x-axis.

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 1998 were very similar to the previous two years, but were lower than those measured in 1995 (Fig 3c). In general, respiration rates at QB01 have remained relatively constant since 1995 (Fig 3d).

4.1.2 Total CO_2 Measurements

Total CO_2 (DIC) fluxes at harbor stations ranged from approximately 22 to 117 mmol CO_2 m $^{-2}$d^{-1} between May and October 1998 (Figure 2). The seasonal pattern of CO_2 fluxes was similar to that of oxygen uptake. Fluxes at Station BH08A were as high or higher than at the other stations at all times except for October, when a higher rate was measured at BH03. Peak fluxes of 117, 116, and 68 mmol CO_2 m $^{-2}$d^{-1} occurred at Stations BH02, BH08A, and QB01, respectively, in July, while the peak flux at BH03 was 74 mmol CO_2 m $^{-2}$d^{-1} and occurred in October. Unfortunately, CO_2 fluxes for BH02 in October were lost.

CO_2 fluxes at Station BH02 and BH03 measured in 1998 showed similar trends to those measured in 1992-1994 (data for CO_2 flux from 1995-1997 are unavailable). At both stations, patterns of CO_2 release generally follow those of O_2 consumption. At BH03, the two fluxes have also usually been similar in magnitude, although in 1993 we observed the more unusual circumstance of O_2 flux rates exceeding CO_2 flux rates (Giblin et al, 1997). At BH02, the typical pattern has been that CO_2 release exceeds that of O_2. Implications of the differences in these trends are discussed in Section 4.2.

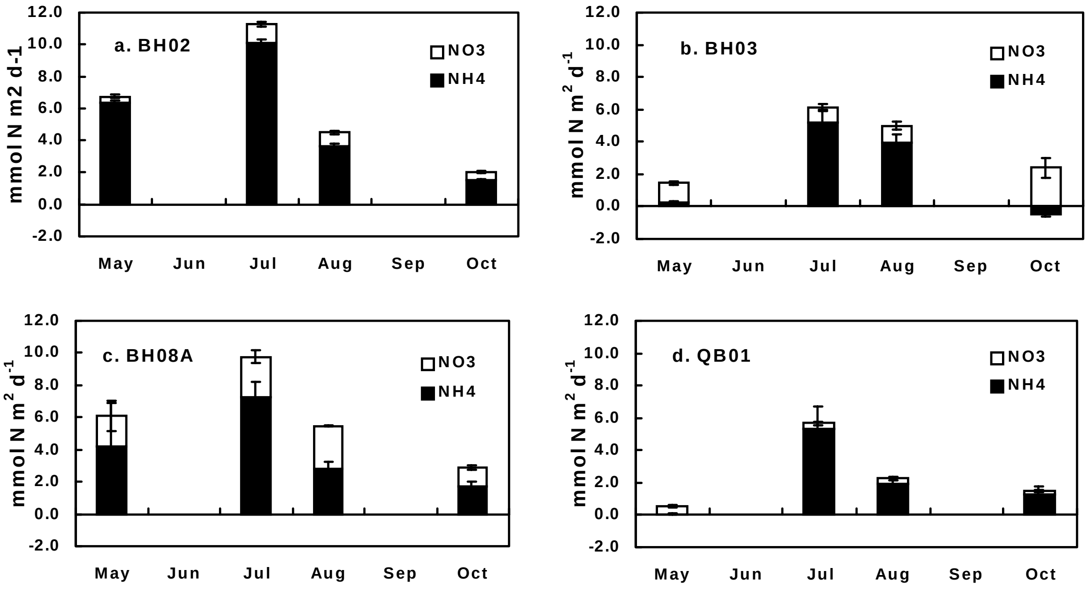

Figure 4. DIN flux, showing relative contributions of NO3 and NH4, at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the means of two cores.

4.1.3 DIN Release from Sediments

The combined flux of ammonium plus nitrate and nitrite (DIN) to the overlying water ranged from of 0.5 mmol N $m^{-2}d^{-1}$ at Station QB01 in May to a release of more than 11 mmol N $m^{-2}d^{-1}$ at Station BH02 in July (Figure 4). The pattern of release was similar to that of O_2 consumption, with all stations having peak fluxes in July. Highest annual fluxes were from Stations BH02 and BH08A, which had very similar annual averages of 6.2 and 6.1 mmol N $m^{-2}d^{-1}$.

At the two stations where large abundances of amphipods were noted, a significant portion of the DIN flux was comprised of nitrate at all sampling times. At Station BH08A (Fig. 4c), 25 to 50 % of the flux was nitrate with the highest percentage occurring in August. At Station BH03 (Fig. 4b) in May, when ammonium flux was quite small, 80% of the DIN flux was comprised of nitrate. In October, 100% of the nitrogen flux out of the sediments of BH03 was nitrate; at this same time, ammonium was taken up by sediments at this station. During July and August, nitrate was between 16 and 24% of the DIN flux at BH03.

At Stations BH02 (Fig. 4a) and QB01 (Fig 4c), DIN fluxes were dominated by ammonium. The exception occurred at Station QB01 in May, when there was no measurable ammonium flux into or out of the sediments, and the nitrate flux was quite small. More typically, nitrate comprised less than 30% of the DIN flux at these two stations.

A comparison in the long term trends of DIN release from the two northern harbor stations, BH02 and BH03, show striking differences between these two stations in the relative contributions of ammonium and nitrate to DIN fluxes (Fig 5a). DIN fluxes from Station BH02 have been dominated by NH_4, except in 1995 when nitrate did contribute a large proportion. In contrast, DIN fluxes from BH03, the old sludge disposal site, have been dominated by nitrate, especially from 1993-1997. This pattern coincides with observations of high numbers of benthic infauna during these years. Rates of DIN flux at BH02 were similar in 1998 to previous years. In contrast, DIN release at BH03 seems to have continued the decline observed in the previous two years (Howes, 1998c) as sediments at this site are “mined out”.

DIN flux at Station BH08A has remained fairly constant since 1995, with NO_3 comprising a significant portion of the flux in all years. Fluxes at Station QB01 were higher in 1998 than in the previous two years, but similar to those measured in 1995.

4.1.4 Urea Fluxes

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

Urea fluxes in the harbor were small and variable. Calculated rates indicated that urea was taken up by sediments as often as it was released. Although some flux rates calculated from individual cores had r^2s greater than 0.5, at no time did duplicate cores both yield rates with significant r^2s. The highest r^2 for any rate measurement was 0.77. These results combined with

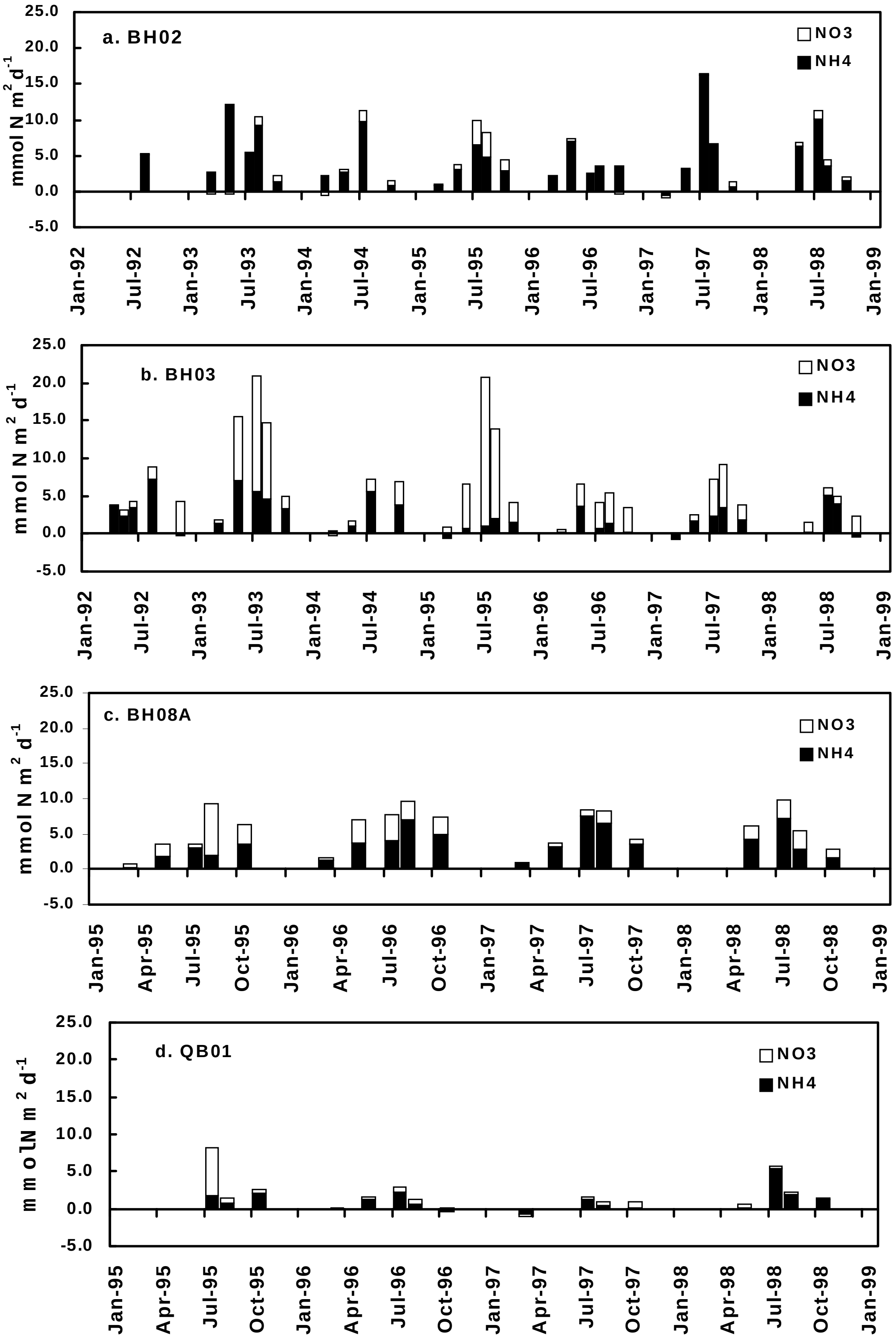

Figure 5. DIN flux, showing relative contributions of NO3 and NH4, from 1992-1998 at a)BH02 and b) BH03, and from 1995-1998 at c) BH08A and d) QB01. Note differences in time line on x-axis.

large standard errors around the means of duplicate cores demonstrate the irregularity of these fluxes. Although calculated urea fluxes in 1998 were larger than in previous years, the variability in the data continue to suggest that urea fluxes, to date, do not account for a significant part of the total nitrogen flux.

4.1.5 Silica Fluxes

Silica fluxes were higher in July at all stations except BH03 (Fig 6), with highest rates, 19 mmol Si $m^{-1}d^{-1}$, observed at Station BH08A. The annual silica flux at BH08A, 12 mmol Si $m^{-1}d^{-1}$, was also the highest of all other stations. Similar to the patterns observed for other fluxes, rates of silica release from sediments at BH03 seem to be declining, whereas they seem to be increasing at BH08A. Silica flux at Station BH03 peaked at 9 mmol Si $m^{-1}d^{-1}$, occurring in October rather than in July. The extremely high and sustained silica fluxes observed during 1993 at Station BH03 (Giblin et al, 1994) have not recurred there or at any of the other stations. Lowest silica fluxes were measured at Station QB01 in May, a time when the presence of benthic diatoms was noted in the field and in the laboratory. The presence of these diatoms at Station QB01 is understandable given the shallowness of the station (only 3m). Benthic diatoms, positioned to intercept Si fluxes out of the sediments, may have been responsible for the lower fluxes.

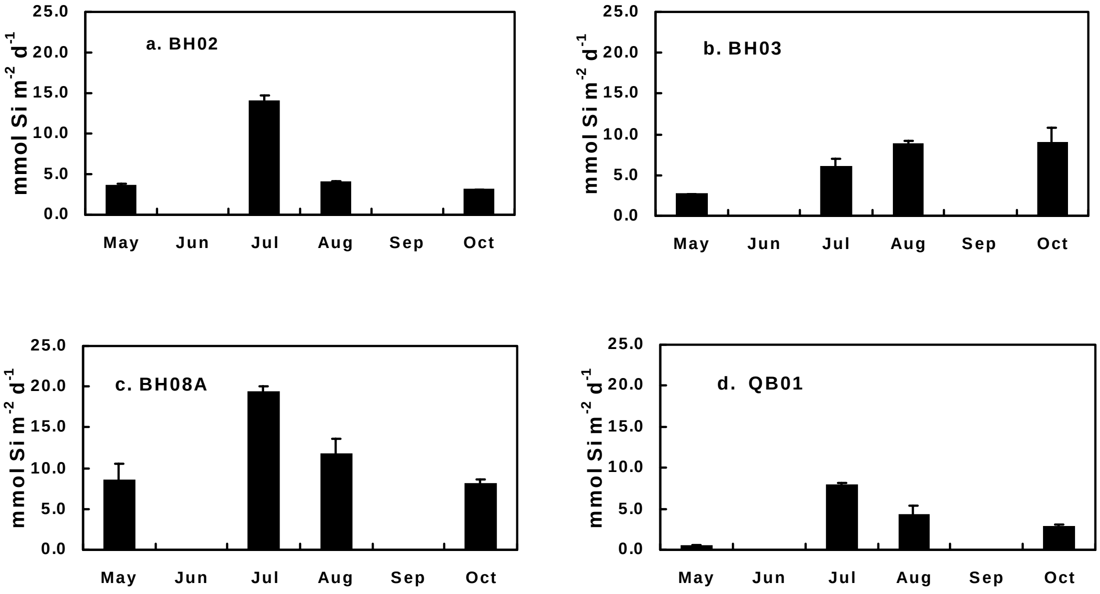

Figure 6. Silicate flux at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the mean of two cores.

4.1.6 Phosphate Flux

Phosphate fluxes from the Harbor stations ranged from -0.2 mmol P $m^{-2}d^{-1}$ at Station QB01 to over 2 mmol P $m^{-2}d^{-1}$ at Station BH02 (Figure 7). Again, three of the four stations sampled, with BH03 being the exception, exhibited peak rates in July, when temperatures were the warmest. Maximal rates at BH03 occurred in August. The maximum phosphate flux we observed at BH02 was the highest since an extremely high rate, 7.8 mmol P $m^{-2}d^{-1}$, was measured in May 1993 (Fig.

8a). Rates at BH08A were somewhat higher than had been reported for the previous three years (Fig. 8c) (Howes, 1998c). At QB01, flux rates of phosphate out of the sediments in July and August appeared quite high compared to the previous three years, although these rates were still low at 0.5 mmol P $m^{-2}d^{-1}$ or less (Fig. 8d). Sediments took up phosphate in October at Stations BH02 and QB01, as well as in May at QB01.

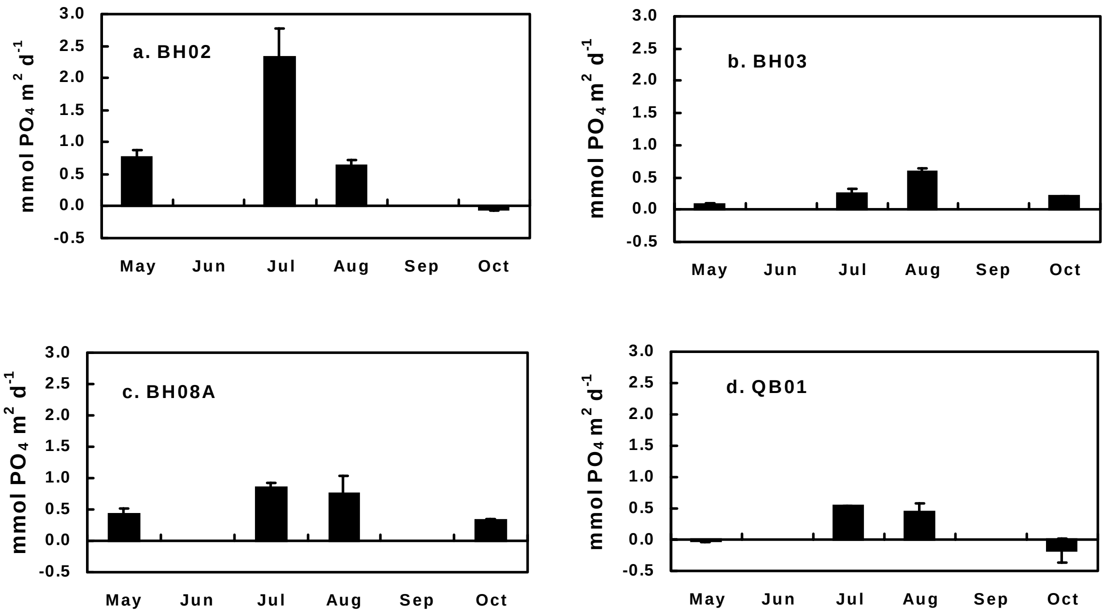

Figure 7. Phosphate flux at a) BH02, b) BH03, c) BH08A, and d) QB01. Error bars represent the standard error of the mean of two cores.

4.2 Flux Ratios

4.2.1 CO_2/O_2 (DIC/O_2)

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

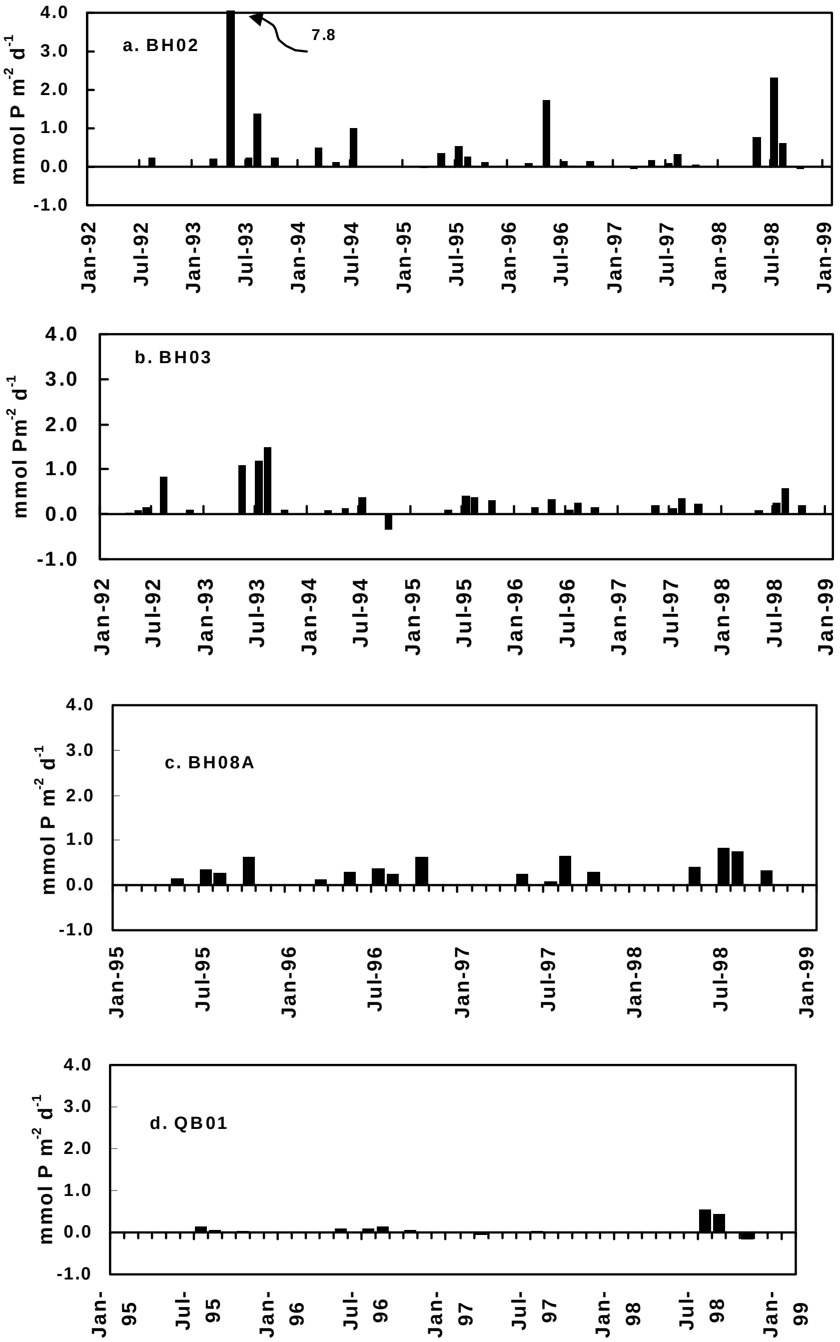

Figure 8. Phosphate flux from 1992-1998 at a) BH02 and b)BH03 and from 1995-1998 at c) BH08A and d) QB01.

In 1998, the annual average RQ was very close to 1.0 at all stations except BH02 (Fig. 9a). For May through August , the average RQ at this station was 2.0, similar to what we measured in 1994. This value suggests a large amount of sulfur storage and that sulfur storage in 1998 was similar to that in 1994. DIC fluxes collected in 1995-1997 were not available as this report was being prepared, so observations on trends between years cannot be made.

Station BH03 had an RQ just under 1.0, with O_2 uptake rates indistinguishable from CO_2 release rates. Our results suggests that RQ values at this station approximate 1.0 when amphipod activity is high, such as in 1993 and this year. The annual average RQ at BH08A was 1.2, with CO_2 release always at least slightly higher than O_2 uptake. At QB01, the RQ was 1.1, with O_2 uptake just exceeding CO_2 release in August.

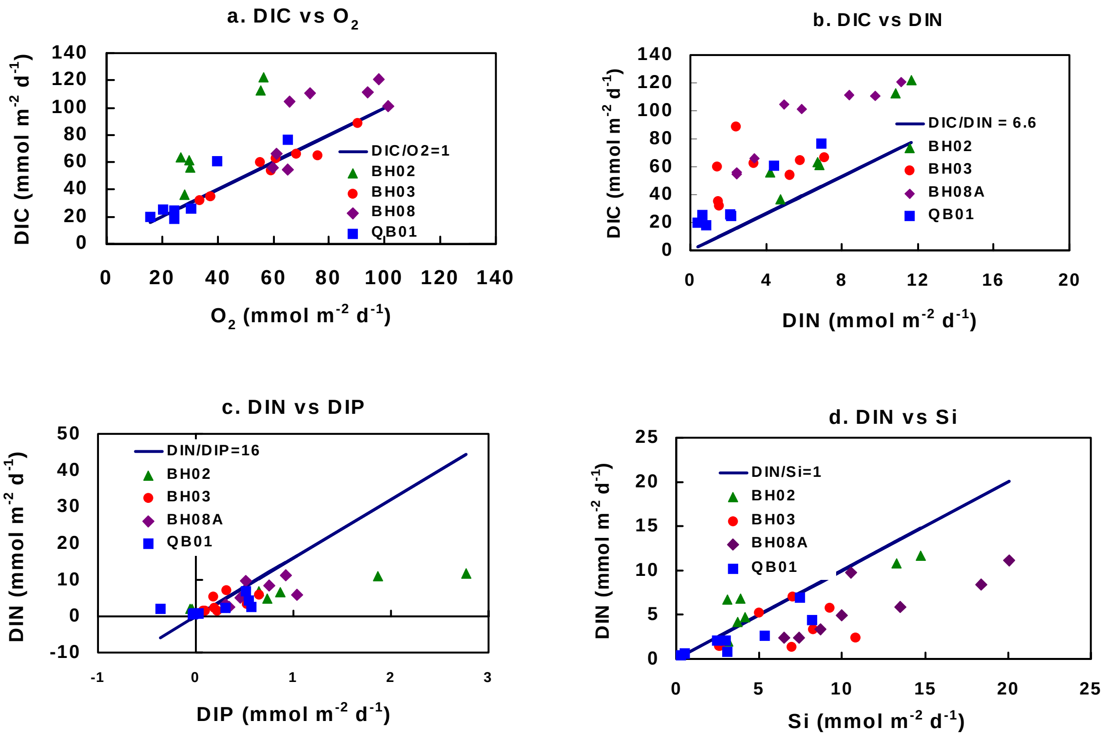

Figure 9. Ratios of element fluxes at all stations (symbols) relative to theoretical ratios (solid lines). a) DIC/O_2, b) DIC/DIN, c) DIN/DIP, d) DIN/Si.

4.2.2 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 6.625. Ratios higher than expected indicate that less DIN flux was measured than expected from respiration measurements, and it is assumed that the missing nitrogen has been denitrified.

In 1998, CO_2/DIN flux ratios were always higher than 6.6, ranging from 9.2 at BH02 to 43 at QB01, both results from May. A seasonal pattern was not apparent. Annual averages were lowest at Station BH02 (10.0) and highest at BH03 (16.5) (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 4.3.

4.2.3 DIN/DIP

Following the Redfield proportions, the expected ratio of DIN flux to DIP flux is 16. Denitrification decreases this ratio while strong P binding in oxidized sediments tends to increase the ratio. DIN/DIP flux ratios exceeded 16 only twice in 1998, in May (17.2) and July (24.7) at Station BH03. Annual averages were all less than 16, ranging from 6.7 to 12.9 (Fig 9c). These low ratios are typical of marine sediments and indicate that sediment processing would tend to push Boston Harbor toward N limitation rather than P limitation.

4.2.4 DIN/Si

Silica is required by phytoplankton in about the same amounts as is nitrogen. The flux ratio observed from sediments is influenced by the proportion of the organic matter derived from siliceous phytoplankton (see discussion in Giblin et al. 1994). Another factor that may affect the DIN to Si ratio is denitrification. We calculated annual average DIN/Si flux ratios of 0.5, 0.5, and 0.7 at Stations BH03, BH08A, and QB01, respectively, all of which are depositional sites (Fig 9d). At BH02 , the only sediment “reworking” site, the ratio was 1.0. 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 from fluxes at Station QB01 in May, concurrent with the lowest Si flux measured and the presence of benthic diatoms.

4.3 SEDIMENT DENITRIFICATION RATES

4.3.1 Direct Measurement of Denitrification

In 1998, direct measurements of denitrification were made at Stations BH02 and BH03, but not at BH08A or QB01. Rates ranged from 0.9 mmol N $m^{-2}d^{-}1$ at Station BH02 to 10.7 mmol N $m^{-2}d^{-1}$ at BH03, with both of these rates occurring in October (Fig 10). Overall, rates were higher at Station BH03, but the temporal patterns of the two stations were in opposite directions. At Station BH02, highest rates occurred in May, and rates declined over the season. At BH03, low rates for this station were observed in May and July, after which rates increased through October.

The trends in denitrification at these two stations illustrate different mechanisms operating within the harbor. Station BH02 has low abundances of benthic infauna and is often characterized by highly reducing sediments. At this site, “classic biogeochemistry” (without macrofauna) prevails; hence rates are more directly related to temperature. Station BH03, on the other hand, has been colonized by a dense mat community of benthic infauna (primarily by amphipods, *Ampelisca* and *Leptocheirus*) since the cessation of sludge dumping in 1992. The bio-irrigation and sediment “mining” activities of these animals have become the primary mechanisms determining benthic fluxes at this site.

In the past extremely high rates of denitrification at Station BH03 have been measured when there were large numbers of amphipods present (August, 1993, and July and August of 1995, 1996, and 1997). Although large numbers of amphipods were still present at this site, denitrification rates were somewhat lower in 1998 than in the previous years (Fig. 11). However, as DIN flux rates were also low, denitrification accounted for a large proportion of the total benthic N flux at BH03, averaging 54% over the year, and as much as 85% in October. Denitrification rates at BH02 in 1998 were similar to those of the previous year, and were about average for this site.

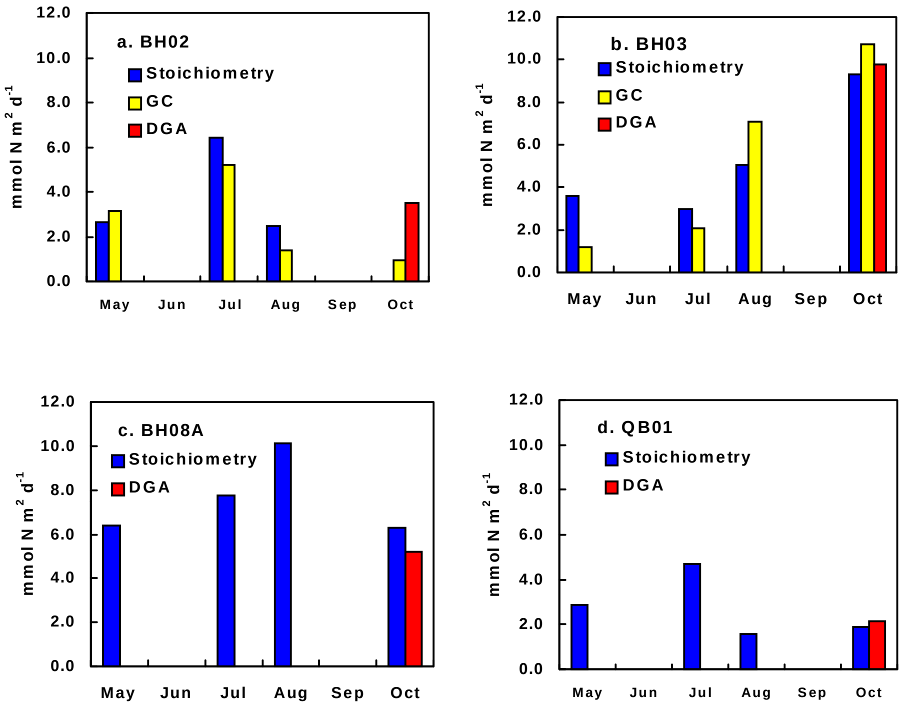

Figure 10. Denitrification as measured by stoichiometry (solid bar), the direct method using gas chromatography (GC, at BH02 and BH03 only; empty bar) and by dissolved gas analysis (DGA, October only; grey bar) for a)BH02, b)BH03, c) BH08A, and d) QB01.

The direct method uses the difference in rates of N_2 flux from the sediments of differently treated cores to calculate that attributable to denitrification. Both cores must be pre-incubated. One core is flushed with a He:O_2 (80:20) mixture to maintain it in oxic conditions but to lower the background of ambient N_2 in the water overlying the core as much as possible. The other is flushed with pure helium in order to drive the core anoxic and lower the N_2. Thus held under anoxic conditions, denitrification is inhibited and the remaining N_2 flux measurable in the core is attributed to diffusion out of the sediments. This value is then subtracted from the rate measured in the oxic core, and the difference is attributed to denitrification.

One limitation of the method is that this preincubation period lasts 36-48 hours, potentially long enough for the sediment processes in the cores to change significantly from ambient, especially under the pre-incubation conditions. Another is that results from these cores are compared to measurements made on the larger nutrient flux cores that are not held for this time and are not manipulated in any way. A third consideration relates primarily to Station BH03, or any site where there are high numbers of benthic infauna. The amphipods in cores from BH03 are all killed in the anoxic treatment, which of course terminates active ventilation of sediments in these cores. At this point, fluxes of N_2 from these cores may no longer be representative of *in situ* diffusive, non-denitrification, fluxes.

4.3.2. Stoichiometric Measurements of Denitrification

As in the past, we estimated denitrification from all the sites by calculating stoichiometric relationships between fluxes and comparing them to expected Redfield relationships (see Section 3.7). Using this technique, we observed rates and seasonal patterns similar to those of the direct measurements. Using this technique, we observed peak rates at BH02 of 6.4 mmol N $m^{-2}d^{-1}$ occurring in July and peak rates of 9.3 mmol N $m^{-2}d^{-1}$ occurring at BH03 in October. These numbers compare to directly measured rates of 5.2 and 10.7 mmol N $m^{-2}d^{-1}$, respectively.

We also calculated denitrification rates stoichiometrically for Stations BH08A and QB01. Rates at BH08A were very high, ranging from 6.3 mmol N $m^{-2}d^{-1}$ in October to 10.1 mmol N $m^{-2}d^{-1}$ in August. In contrast, rates at Station QB01 were the lowest of the four stations, peaking in July at 4.7 mmol N $m^{-2}d^{-1}$.

The limitations of this method have been thoroughly discussed in previous reports (see Gblin et al, 1993; Giblin et al 1994). Our ability to accurately measure CO_2 fluxes has allowed us to avoid many of the problems inherent in other measures of decomposition (e.g., O_2 uptake) needed in this method. The remaining issue is in the assumption of Redfield ratios for fresh phytoplankton being appropriate for the organic matter being decomposed. Bulk sediments typically have a C/N much higher than do phytoplankton, however bulk sediment ratios are not necessarily representative of the organic matter pool being decomposed. We believe the Redfield ratio more closely approximates that of the labile carbon pool. Seasonal deviation may also occur if there is a lag between carbon mineralization and nitrogen mineralization.

4.3.3 Comparison of Stoichiometric and Direct Method of Measuring Denitrification

We compared the direct measurements of denitrification to the estimates calculated using the stoichiometric method for Stations BH02 and BH03. In the past we have observed that there can be considerable scatter in the relationship between the two methods when individual dates are compared but that annual averages show better agreement (Giblin et al. 1993; 1994). For 1998, the annual average rate for the harbor stations was indistinguishable between the two methods (4.4 vs 4.7 mmol N $m^{-2}d^{-1}$, direct vs stoichiometry).

At BH03, both methods resulted in an annual average of approximately 5.2 mmol N $m^{-2}d^{-1}$. The difference in the harbor annual average stated above came largely from a small difference in the annual average at Station BH02, which was 3.9 mmol N $m^{-2}d^{-1}$ as measured by stoichiometry, and 3.3 measured directly. However, these averages for BH02 covered only the period from May to August because the stoichiometric estimate could not be calculated for BH02 in October.

In October, a third estimate of denitrification was made. Samples taken from the nutrient flux cores were analyzed by mass spectrometry (courtesy of Jeff Cornwell) to determine N_2/Ar ratios of the samples over the same time course as was used for the respiration and nutrient fluxes (Kana et al, 1994). This technique measures the change in N_2 gas against that of argon, which behaves conservatively. Results from these analyses closely match our stoichiometric estimates made on the same cores (Fig 9). We will continue to compare this technique to both the stoichiometric and GC methods.

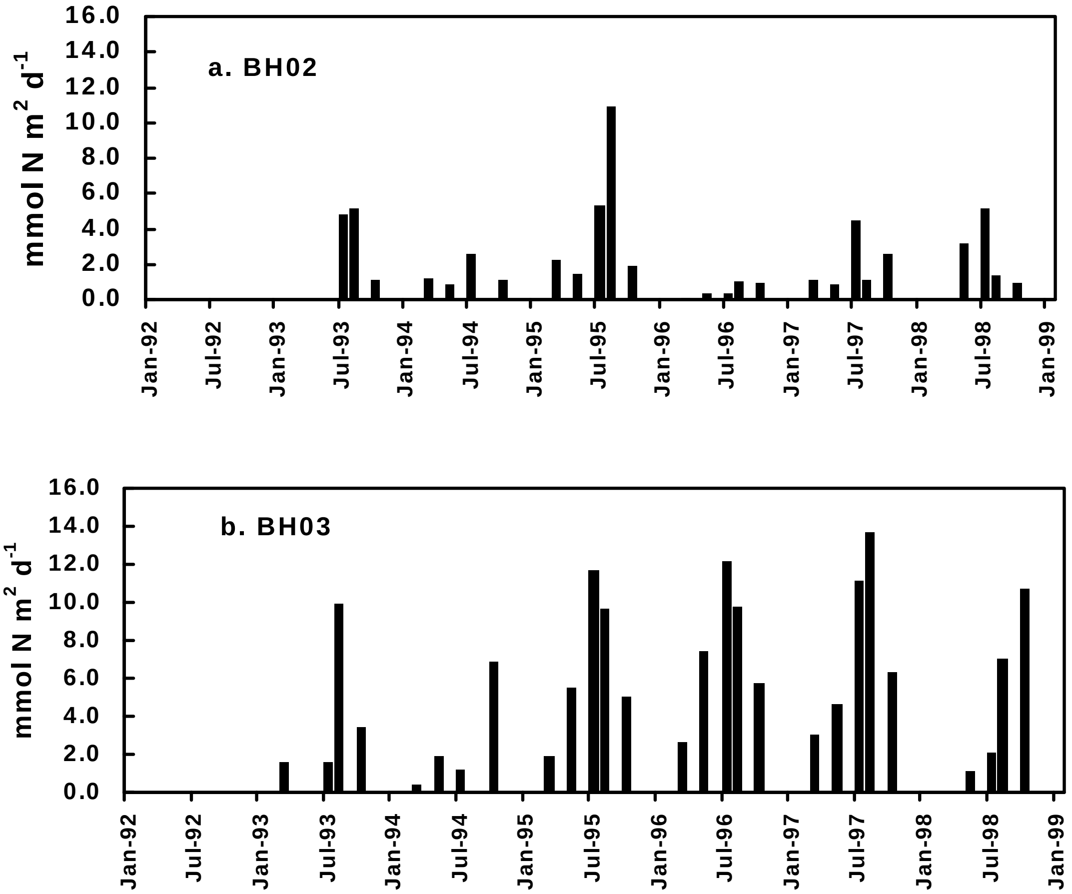

Figure 11. Denitrification (direct measurement) from 1993-1998 at a) BH02 and b) BH03.

4.4 SEDIMENT CHARACTERISTICS

4.4.1 Nitrogen and Carbon

Average carbon and nitrogen content of surface sediments at Stations BH02, BH03, and BH08A were quite similar in 1998 (Table 3). Sediments at Station QB01 were lower in C and N content. The widest range in values was measured at BH02: carbon ranged from 4.1% in May to 1.8% in August, while nitrogen ranged from 0.54% to 0.23% in the same months. At the three other stations, highest carbon and nitrogen content occurred in July. These values were similar to those we measured in the harbor throughout 1991-1994 (Giblin et al, 1997), although the May values at BH02 were among the highest. It has also been a consistent pattern that sediments at BH02 experience the widest range in values. This station is the only one of the four in an area classified as reworking rather than depositional. It is adjacent to Governor's Island Flats, also a reworking environment, but a much shallower one where benthic production may be important. Suspension and redeposition of sediments carrying variable loads of labile carbon may explain the range in C and N we observed at this station.

4.4.2 Pigments

Chlorophyll *a*, which is the active pigment present in living or recently dead plants, showed no seasonal pattern at BH02 or BH03, but there was some indication of a pattern at the other two stations. At BH08A, there was more chlorophyll *a* in the top 3 cm of sediment in October than there was in May. At QB01, the opposite was true. In May, the surface 2 cm of sediment at this stations had large concentrations of chlorophyll *a* , averaging 13.7 µg cm^{-3} over that interval. We recorded field and laboratory observations of benthic diatoms on surface sediments from this site. At all four stations, there was a trend of increasing phaeopigment concentrations in the sediments as the season progressed. The largest increase in phaeopigments occurred at BH03, where concentrations nearly doubled over the season. Total pigment inventories summed over the top 5 cm ranged from 103 µg cm^{-2} at QB01 in May to 216 µg cm^{-2} at BH03 in October.

The inventories we measured in 1998 in May and October at BH02 were similar to those we measured in 1994, but had increased by over 50% at BH03. Harborwide, it appeared the average for total pigment inventories for the top 5 cm of sediment in 1998 (~160 µg cm^{-2}) was somewhat higher than that from the same stations averaged over the years 1995-1997 (~125µg cm^{-2}) (Howes, 1998c). Apart from real increases in sediment chlorophyll *a* and phaeopigments, higher estimates from 1998 may be partially explained by having only spring and fall measurements, whereas all previous years (1992-1997) included winter and summer measurements. Also, our method for extracting pigments from sediments includes a freezing step which facilitates the extraction of pigments bound in sediment matrices such as fecal pellets or detritus (Sun et al, 1991). Therefore, some of the difference in measurements between 1998 and 1995-1997 may reflect a difference in "free" and "bound" pigments.

Table 3. %Carbon, %Nitrogen, and Pigment Concentrations from Boston Harbor sediments in 1998.

Station	Date	%C[1]	%N[1]	Chlorophyll *a*[2] µg/cm^2	Total Pigments[2] µg/cm^2
BH02	May	4.1	0.54	42.2	161.3
	July	2.3	0.29		
	August	2.0	0.26		
	October	1.8	0.23	32.4	177.0
BH03	May	2.3	0.26	13.2	134.6
	July	3.5	0.37		
	August	2.5	0.26		
	October	2.8	0.34	16.2	215.8
BH08A	May	2.6	0.35	15.0	149.0
	July	2.7	0.37		
	August	2.5	0.33		
	October	2.5	0.33	18.1	203.8
QB01	May	2.2	0.25	34.2	103.1
	July	2.2	0.25		
	August	1.6	0.18		
	October	2.4	0.25	9.1	128.6

[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.

4.5 POREWATER CONSTITUENTS

Oxidation-reduction potential (Eh) was measured at all stations and at all four sampling times (Fig 12 a-d). Patterns in Eh were similar to those of previous years. Station BH02 had the most reducing sediments overall, but showed a seasonal progression towards more oxidized conditions, with highest Eh values occurring in October. At Stations BH03 and BH08A, where sediments are actively irrigated by infauna, conditions were most highly oxidized in October and August, respectively. These Eh maxima coincided with peak times of nitrate flux and denitrification at these sites.

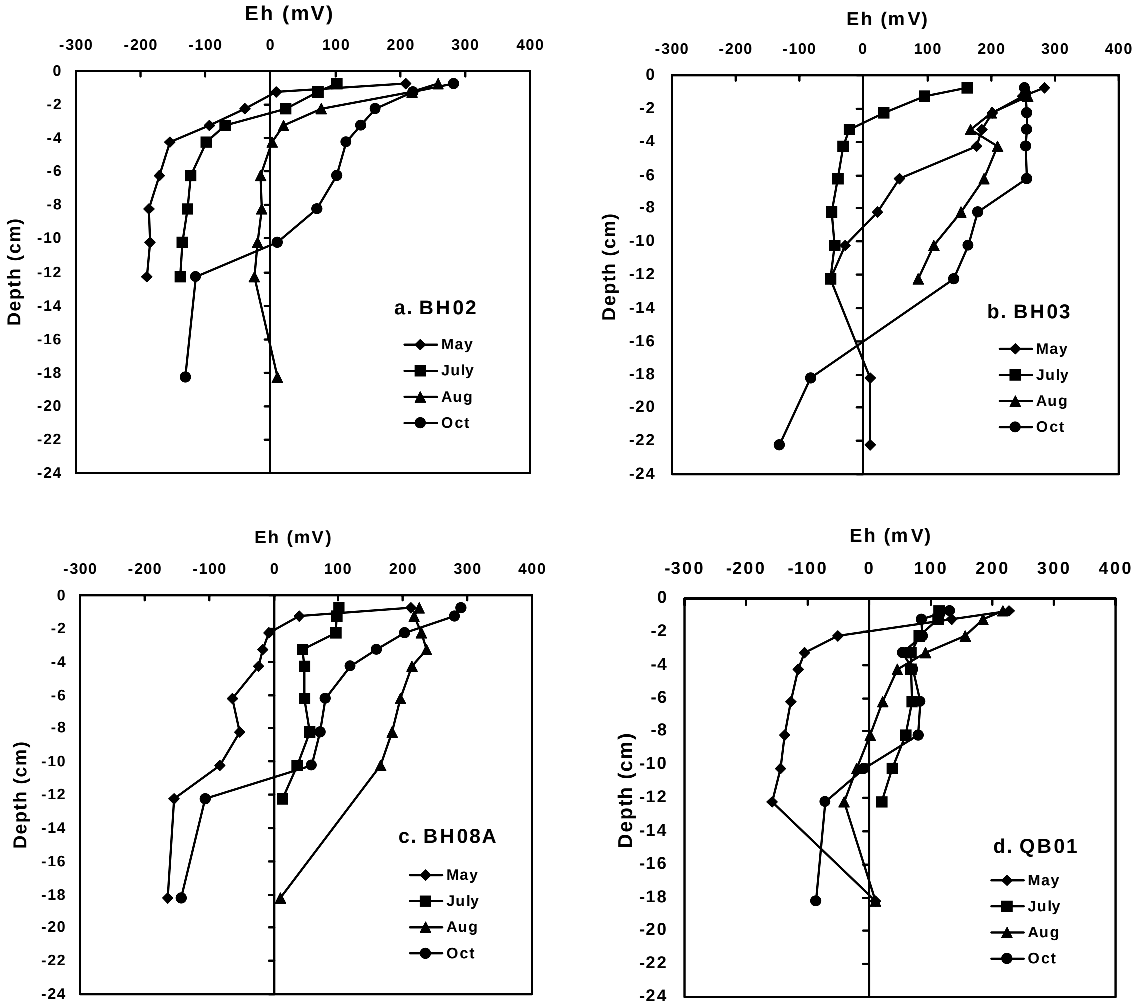

Figure 12. Oxidation-reduction potential (Eh) from sediment cores from each survey for a) BH02, b) BH03, c) BH08A, and d) QB01.

Other porewater constituents were measured in July and August only. Porewater profiles suggested that sediments were slightly more oxidized than in previous years. The only station where sulfide concentrations were appreciable was Station BH02 (Fig. 13 a-d). Station BH02 had a shallow layer of a few cm near the surface where sulfide was not detected and then sulfide concentrations increased rapidly with depth (Figure 13a). Sulfide concentrations at this station were quite high at depth reaching 4.8 mM at 12cm in July. At the same depth in August, sulfide concentrations had decreased to 2.6 mM.

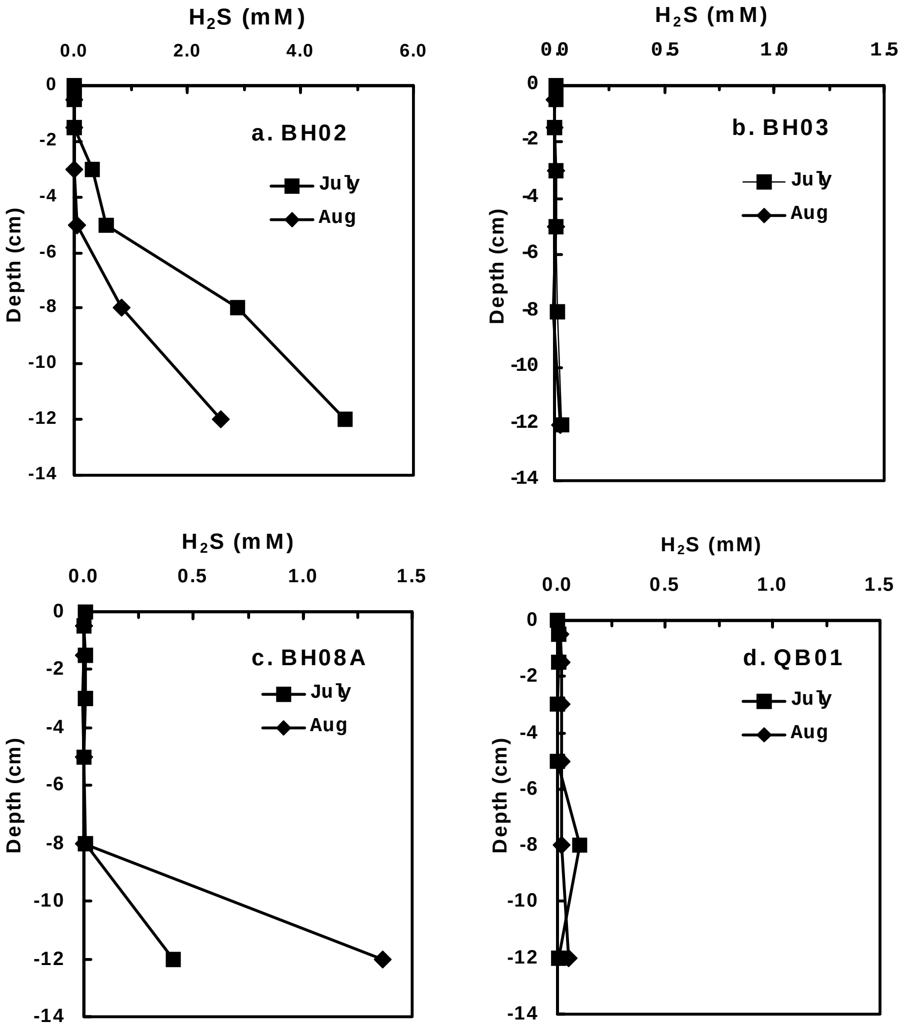

Figure 13. Hydrogen sulfide concentrations in porewaters in July and August at a) BH02, b) BH03, c) BH08A, and d) QB01. Note differences in scale.

5. IMPORTANCE OF SEDIMENT FLUXES TO NUTRIENT BUDGETS IN THE HARBOR

One way to put benthic fluxes in perspective is to relate rates of metabolism and nutrient recycling to primary production in the overlying water column. However, as we currently do not have sites representative of all sediment types within the harbor, we must be careful in extrapolating these rates to the whole harbor. Also, our measurements in 1998 spanned the active season from May to October, but did not include a winter measurement. For the following reasons, our annual averages are likely overestimates: 1) the stations do not include sandy, typically lower-activity sediments, 2) the averages do not include a winter rate, and 3) the averages are not area-weighted.

Even with the caveats above in mind, we believe our previous conclusions about the limited contribution of benthic fluxes to nutrient cycling in Boston Harbor are still valid because trends in fluxes in 1998 were similar to those measured in the past and nutrient inputs to the harbor have not changed significantly. As stated before, benthic regeneration of nutrients in Boston Harbor could account for a significant portion of phytoplankton requirements; however, external inputs to the system are an order of magnitude larger, well in excess of phytoplankton requirements. If we include winter rates based on previous years measurements in our annual estimates for 1998 and assume a similar rate of primary production as was used in our earlier comparisons (74 mmol C m^{-2} d^{-1} (1991)), rates of remineralized nitrogen for the four depostional sites sampled in 1998 could account for almost 35% of phytoplankton N requirements, while remineralized phosphorus could account for nearly 58%. (Note: The relative areal extent of depositional sediments in Boston Harbor is about 51% (Knebel and Circe, 1995).)

Similarly, the effect of denitrification on removing N from the system has not significantly changed. The area- weighted average of 4 mmol N $m^{-2}d^{-1}$ calculated for 1992-1994 (based on stoichiometry) accounted for 17% of N inputs into the harbor (Giblin et al, 1997). Using simple averages from our four stations, and including an estimated winter rate, our 1998 average for denitrification was 5.1 mmol N $m^{-2}d^{-1}$ or roughly 22% of inputs. The average of the direct measurements was about half that measured by stoichiometry, consequently indicating that denitrification could be responsible for removing only about 10% of N inputs. These two percentages approximate the range of estimates reported previously (Nowicki, 1997 ; Howes, 1998c).

6. SUMMARY AND MONITORING ISSUES

1. In general, nutrient fluxes in the harbor measured between May and October, 1998, were maximal in July at Stations BH02, BH08A, and QB01, coinciding with warmest temperatures. At Station BH03, maximal rates occurred in October.

2. Sediment oxygen uptake in the Harbor ranged over the seasonal cycle from approximately 18 mmol $m^{-2}d^{-1}$ at the shallow Quincy Bay Station (QB01) in May to 96 mmol $m^{-2}d^{-1}$ at the Hingham Bay Station (BH08A). Average rates for the May to October season were highest at Station BH08A, which like Station BH03, the former sludge disposal site near Long Island, was heavily colonized by the mat-building amphipod community.

3. Dissolved inorganic nitrogen fluxes in Boston Harbor ranged from 0.5 mmol N $m^{-2}d^{-1}$ at Station QB01 in May to 11 mmol N $m^{-2}d^{-1}$ at Station BH02 in July. This range was narrower than in some previous years, and did not include very high values as observed at Station BH03 in 1993 and 1995. The relative proportions of NH_4 and NO_3 in the DIN flux continue to correlate with benthic infaunal abundances, with NO_3 comprising a large fraction of the flux at those sites heavily colonized by the amphipod community.

4. Phosphate fluxes were somewhat higher overall in 1998 than in the previous four years of monitoring at BH02 and BH03, and than the previous three years at BH08A and QB01. Higher rates had been measured at BH02 and BH03 in 1993.

5. Directly meaasured rates of denitrification in Boston Harbor ranged from 0.5 mmol N m^{-2} d^{-1} at Station BH02 to 5.4 mmol N m^{-2} d^{-1} at Station BH03. The rates at BH02 fell in the middle of the range of values observed at that station since 1993, whereas those from BH03 fell in the lower part of its range. Direct measurements were on average 55% of stoichiometric estimates, similar to observations made during 1992-1994. Highest rates continued to occur with large numbers of amphipods, with highest overall rates for 1998, as estimated by stoichiometry, measured at Station BH08A.

6. In 1998, the release of carbon dioxide averaged over the season was similar to oxygen uptake for three out of the four harbor stations. In particular, at Station BH03 the CO_2/O_2 (respiratory quotient) was just under 1.0, with CO_2 release rates indistinguishable from O_2 uptake rates. Similar results were observed in 1993; at both times, amphipod activity was high. At Station BH02, the RQ was 2.0, suggesting a large amount of sulfur storage occurring at this site.

7. Respiration at depositional sites in the harbor was equivalent to 63% (based upon oxygen and 1991 production estimates) to 85% (based upon DIC) of the production in the overlying water. Benthic nutrient release could supply 35% of the N and 58% of the P required for primary production.

8. Porewater constituents are important indicators of sediment processes. Porewater sulfide and Eh results indicated that the sediments at BH02 and BH03 are more oxidizing than when the studies began in 1992.

9. Although stations continue to exhibit year to year variability, the very high rates of 1993 and 1995 have not been repeated for three years, even though amphipods continue to be present, suggesting that some “mining” of sediment stores may have taken place. Rates are now typical of productive coastal sediments.

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