# 2003 Annual benthic nutrient flux monitoring report

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# 2003 Annual
# Benthic Nutrient Flux
# Monitoring Report

**Submitted to**

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# EXECUTIVE SUMMARY

The Benthic Nutrient Flux Studies were initiated in 1990 to examine spatial and temporal trends of benthic processing of organic matter at selected stations in Boston Harbor and Massachusetts Bay. The overall objectives of the studies have been to quantify sediment-water exchanges of oxygen, total carbon dioxide, and nutrients in order to define benthic-pelagic coupling in the harbor and bay. In addition, sediment indicators of organic matter loading and processing, such as organic carbon and pigment concentrations and redox conditions, have also been monitored. Until late in 2000, the focus of these studies was on monitoring the recovery of the harbor as sewage treatment was improved, and in providing baseline information about all of these processes in Massachusetts Bay before the ocean outfall became operational. In 2001, monitoring of the harbor recovery continued, but baseline monitoring of the bay ended. The emphasis changed to monitoring the response of the bay ecosystem to the relocation of the outfall.

We are now examining the baseline and post-relocation data in terms of the Outfall Monitoring Plan that was written in 1991 to guide the monitoring efforts in Massachusetts Bay before and after the harbor outfall was relocated (MWRA 1991). The two questions that were posed for the benthic flux monitoring of the Massachusetts Bay Nearfield were:

I. How do the sediment oxygen demand, the flux of nutrients from the sediment to the water column, and denitrification influence the levels of oxygen and nitrogen in the water near the outfall?

II. Have the rates of these processes changed?

## MASSACHUSETTS BAY

At the heart of the questions for benthic flux monitoring was the concern that the diversion of effluent from Boston Harbor to Massachusetts Bay might increase organic matter loading to the nearfield area, thereby enhancing benthic respiration and nutrient fluxes. Higher rates of benthic respiration (or sediment oxygen demand) might lead to lower oxygen levels in the sediments and water column. Various changes in nutrient fluxes might occur, including shifts in the quantity and form of nitrogen released to the overlying water and in the ratio of nutrients released.

To date, we have observed little or no indication of changes related to the ocean outfall. For the third year since the outfall became operational, we have seen only inconsistent and small changes in measures of sediment organic matter, and rates of benthic respiration and nutrient fluxes have been well within or lower than typical baseline observations.

Any increase in organic matter content of surface sediments in the nearfield that was noted in 2001 and 2002 did not continue in 2003. At Station MB03, where the largest apparent increase had occurred in 2001, organic carbon content dropped slightly from 2002 levels of 1.4% to 1.1% in 2003. A similar decrease was observed at MB02, while at MB01 there was no change. Similarly, there was little or no change at Stellwagen Station MB05. Nearfield C/N ratios of sediment organic matter were typical of baseline in 2003 after apparently aberrant low and high values in 2001 and 2002, respectively.

Sediment chlorophyll at nearfield stations in 2003 was typical of baseline and similar to the previous year. The inventory over the top 5 cm of sediment averaged over the season and across the three stations was

5.4 ug $cm^{-2}$. Ratios of carbon to nitrogen were also typical, averaging about 11.7. Neither parameter suggested atypical deposition of fresh phytoplankton material to the benthos.

In 2003, there was no indication of increased S.O.D. or increased nutrient fluxes from nearfield sediments. Fluxes were generally in the mid to low end of baseline observations. There was little relationship to temperature in any of these fluxes, and in fact nutrient fluxes tended to decline over the season rather than increase with temperature. Other controls on these fluxes most likely include carbon deposition and infaunal abundance, although simple linear relationships are weak. Fluxes at station MB05 were quite typical, and at this station, where the range in temperature is small, sediment chlorophyll may play a relatively more important role in regulating fluxes.

Although the rates of sediment oxygen demand would be high enough to affect the seasonal drawdown of oxygen in the water column in the nearfield if the water column were stagnant, the rate of water renewal from the Gulf of Maine is sufficient to nearly completely override the effect of local benthic metabolism. The renewal rate of the bottom water, which is determined by wind and other climatological factors, determine the timing and strength of the seasonal oxygen drawdown.

Fluxes of DIN in 2003 were in the mid to low end of the range observed during baseline monitoring. Fluxes were at times characterized as uptake rather than release. For the second year, at Station MB03 we observed very low or negative (uptake) fluxes of $NH_4^+$, such that the seasonal average DIN efflux was comprised entirely of $NO_3^-$. At MB01 and MB02 the seasonal average efflux was comprised of 45% and 70% $NO_3^-$, respectively. These low DIN fluxes result in a contribution of nitrogen amounting to less than 6% of the requirements for nearfield primary production. At station MB05, we observed moderate effluxes of $NO_3^-$ from and small uptake of $NH_4^+$ into the sediments in 2003.

In 2003, $PO_4^-$ fluxes were low compared to the baseline range and often negative, particularly in October in the nearfield and in August and October at Station MB05. Silica fluxes were moderate compared to baseline in the nearfield during most of the season, but very low in October. At MB05, Si fluxes were variable, with moderate to high rates in May and July, very weak and atypical fluxes in August, and low fluxes in October.

Denitrification rates in the nearfield were typical of baseline observations. Due to the low DIN flux, denitrification accounted for between about 80% and 100% of the total nitrogen (DIN + $N_2$) flux at these stations.

There was no indication of decreased sediment oxidation in any of our measurements. Respiratory quotients were very close to 1.0, Eh profiles indicated oxidizing sediment conditions, and dissolved sulfides were not detected.

## BOSTON HARBOR

Although the monitoring questions were written to address concerns in the nearfield of Massachusetts Bay, they may also be used to guide our evaluation of changes observed in Boston Harbor. For the harbor, however, we must think of the questions in terms of the effects of reductions in organic matter loading. Certainly the diversion of sewage effluent away from the harbor has had noticeable effects on nutrient loading. Reductions in organic matter loading have been more subtle, however, because the most significant reductions in organic matter loading began much earlier with the cessation of sludge disposal and subsequent treatment improvements.

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring, and including the three years since diversion. Decreases in TOC have been most pronounced at Stations BH03, BH08A, and QB01 whereas TOC content at station BH02 has varied. The large range of values observed across the four stations early in the monitoring program has narrowed in the past four years (2000-2003).

Another measure of organic matter, sediment chlorophyll, was about average for two of the stations in 2003, BH03 and BH08A, but higher than usual at two others, BH02 and QB01. Observations of benthic diatoms and sediment profiles of chlorophyll suggest that *in situ* production is important at these sites.

Sediment oxygen demand in 2003 was within baseline observations. There was little variability across stations in seasonal averages, which had increased somewhat from the low rates observed in 2002. Fluxes of DIN and $PO_4^-$ were also within baseline ranges, but increased somewhat over 2002 rates at BH02 and BH08A while staying the same or decreasing slightly at BH03 and QB01. Fluxes of dissolved silica were much more variable across stations in 2003, and Station BH08A had fluxes greater than observed during baseline for most of the sampling period. With the exception of the DSi fluxes, it appears that the large variability in oxygen and nutrient fluxes between stations and years that was observed early in the monitoring program has largely disappeared.

Using post-relocation rates of primary production at the mouth of the harbor and seasonal averages of DIN and $PO_4^-$ fluxes, we calculate that these fluxes could each contribute about 35% of phytoplankton N and P requirements. Silica fluxes from the sediment were large enough in 2003 to support nearly all primary production. With the reduction in nutrient inputs to the harbor after the relocation of the outfall, these contributions may become significant, however oceanic and remaining terrestrial inputs still exceed the needs of primary production.

Similarly, the decrease in nitrogen loading to the harbor may shift the role of denitrification in the overall N budget. Although denitrification rates are equivalent to the remaining terrestrial loading, oceanic inputs remain the overwhelming source to the system, and decrease the N sink provided by denitrification to less than 10% of total inputs.

Patterns in redox measurements varied across stations. At BH02, respiratory quotients were somewhat elevated, and further evidence of reducing conditions was supplied by Eh measurements and high concentrations of dissolved sulfides at depth in sediment cores. Conditions at Station BH08A were less reducing than in the previous year. Respiratory quotients averaged the theoretical 1.0 at this station this year. The reappearance of amphipods at this site probably contributed to the return to more oxic sediment conditions that are typical for this station. At BH03 and QB01, RQs were less than 1.0. Eh profiles were generally more positive than at the other two stations, and sulfides were detected only at very low levels.

The decrease in the magnitude of benthic fluxes, of oxygen as well as nutrients, in addition to the dramatic decrease in variability in fluxes across stations suggests that the harbor benthic environment has progressed significantly along the path of "recovery". The role that infauna has played has been significant in areas like BH08A and BH03, and the status of those benthic communities will no doubt continue to mediate changes in benthic nutrient cycling. However we are beginning to see responses related to region wide forcing such as climate patterns.

## LINKAGES ACROSS MONITORING DATASETS

The existence and availability of a long term and comprehensive dataset for Boston Harbor and Massachusetts Bay has enabled us to begin to look for linkages across datasets. We have begun to see such links between the nearfield benthic flux dataset and the water column, benthic infauna, and USGS sediment trap datasets.

We find connections between winter-spring water column temperatures and water column chlorophyll and S.O.D. that help explain the loss of a seasonal pattern in the S.O.D. data. Warmer than normal early season temperatures are related to the failure of the spring phytoplankton bloom which in turn reduces organic matter input to the benthos. Warmer than normal temperatures also may induce larger than expected early season fluxes.

We also find connections between increased infaunal abundance and more oxidizing conditions in nearfield sediments. There is also a suggestion that increasing numbers are related to larger fluxes, mush as we have observed in Boston Harbor. In addition, trends in the USGS dataset of changes in clay content in a nearfield station correspond to trends we have seen in organic matter content, and may help discern the origin of this material.

## CROSS SYSTEMS COMPARISONS

Comparisons among the benthic flux datasets for Boston Harbor, the nearfield of Massachusetts Bay, and Stellwagen Basin yield three main observations: 1.) Fluxes in Boston Harbor are always larger than in Massachusetts Bay and Stellwagen Basin; 2.) Inter- and intra-annual variability in fluxes in Boston Harbor is much greater than in Massachusetts Bay and Stellwagen Basin; 3.) Fluxes in Boston harbor have decreased dramatically over the period of the monitoring program, and in some cases now approach fluxes more typical of Massachusetts Bay.

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# 1.0 INTRODUCTION

Boston Harbor and the Massachusetts Bays have experienced major shifts and reductions in sewage inputs over the last ten to twelve years as the Massachusetts Water Resources Authority (MWRA) has implemented improvements to the sewage treatment plant servicing the greater Boston metropolitan area. As part of an extensive monitoring effort mandated by the NPDES permit and directed by MWRA, we have been conducting studies on benthic metabolism and nutrient cycling in depositional sediments of these two systems.

A series of upgrades to the treatment process has occurred since 1989, when increases to pumping capacity were begun (Taylor, 2001a). In September, 1991, disposal of sludge within the harbor was discontinued, resulting in reduction of solids loads to the system by about 25%, from over 150 tons per day to about 110 tons/day. Further reductions in solids loading occurred with the completion of a new primary treatment plant in 1995, and the beginning of secondary treatment in 1997. By the end of 2000, solids discharge had dropped to about 32 tons/day (Werme and Hunt, 2001). Concurrent with these decreases have been decreases in biological oxygen demand (BOD) and metals and other toxic compounds. Concentrations of particulate and organic nitrogen in the effluent stream have also decreased, but total nitrogen concentrations have been reduced only a small amount, as inorganic nitrogen (primarily ammonium), produced from organic nitrogen during secondary treatment, is not removed. The final phase in the MWRA's Deer Island project occurred in September 2000, when all sewage effluent was diverted out of Boston Harbor to a new deepwater outfall in Massachusetts Bay.

The Benthic Nutrient Flux Studies were initiated in 1990 to examine spatial and temporal trends of benthic processing of organic matter at selected stations in Boston Harbor and Massachusetts Bay. The overall objectives of the studies have been to quantify sediment-water exchanges of oxygen, total carbon dioxide, and nutrients in order to define benthic-pelagic coupling in the harbor and bay. In addition, sediment indicators of organic matter loading and processing, such as organic carbon and pigment concentrations and redox conditions, have also been monitored. Until late in 2000, the focus of these studies was on monitoring the recovery of the harbor as sewage treatment was improved, and in providing baseline information about all of these processes in Massachusetts Bay before the ocean outfall became operational. In 2001, monitoring of the harbor recovery continued, but baseline monitoring of the bay ended. The emphasis changed to monitoring the response of the bay ecosystem to the relocation of the outfall.

We are now examining the baseline and post-relocation data in terms of the Outfall Monitoring Plan that was written in 1991 to guide the monitoring efforts in Massachusetts Bay before and after the harbor outfall was relocated (MWRA, 1991). The plan was designed using recommendations from the National Research Council, experience from previous monitoring plans and peer review from the scientific community and the public. Possible environmental responses to the outfall discharge were listed as questions (R-n), from which were derived overall testable questions. The two questions that were posed for the benthic flux monitoring of the Massachusetts Bay nearfield and the possible response questions from which there were derived were:

I. **How do the sediment oxygen demand, the flux of nutrients from the sediment to the water column, and denitrification influence the levels of oxygen and nitrogen in the water near the outfall?**

   *(R5. Will increased water-column and benthic respiration contribute to depressed oxygen levels in the water?*

R.6. Will increased water-column and benthic respiration contribute to depressed oxygen levels in the sediment?)

**II. Have the rates of these processes changed?**

(R4. Will enrichment of organic mater contribute to an increase in benthic respiration and nutrient flux to the water column?)

The annual report written for the year 2001 (Tucker *et al*. 2002) provides a thorough review of our understanding of both the Boston Harbor and Massachusetts Bay systems during baseline monitoring, and our observations during that first year after the outfall was relocated. In this report we compare the results from 2001 and 2002 to those baseline studies to address the monitoring questions. We also review data from Boston Harbor and address the monitoring questions in terms of reductions rather than enrichments in organic matter loading.

The work described below has been accomplished by two groups of researchers. We performed the benthic nutrient cycling studies during 1991-1994 (with colleagues from Battelle and the University of Rhode Island) and 1998-2003 (Giblin *et al*., 1992; Kelly and Nowicki 1992; Giblin *et al*., 1993; Kelly and Nowicki, 1993; Giblin *et al*., 1994; Giblin *et al*., 1995; Tucker *et al*., 1999; Tucker *et al*, 2000; Tucker *et al*, 2001; Tucker *et al.*, 2002; Tucker *et al*., 2003). Dr. Brian Howes and his colleagues were responsible for the data collected during 1995-1997 (Howes, 1998a; Howes, 1998b; Howes, 1998c). A detailed description of current field and laboratory methods used may be found in Tucker *et al.*, 2002b.

## 2.0 MASSACHUSETTS BAY

Massachusetts Bay is part of the larger Gulf of Maine (GOM) system, which dominates the dynamics and ecological conditions for the bay. The general circulation pattern is that GOM water flowing to the south may enter Massachusetts Bay near Cape Ann, setting up a weak counterclockwise circulation that exits off the tip of Cape Cod. The temperature and salinity of this water, together with wind and climatological factors, determine the timing and strength of seasonal (summer) stratification patterns within Massachusetts Bay. Data gathered during baseline monitoring demonstrated that concentrations of dissolved oxygen present in GOM water at the onset of stratification in the spring contributed directly to the degree of seasonal $O_2$ depletion in the bottom waters of the bay (Geyer *et al*., 2002). In addition, nutrients are delivered to the bay in GOM water. Discharge from the bay outfall represents a perturbation to this system, the significance of which is still in question.

We have monitored three stations, MB01, MB02, MB03, in the nearfield region of Massachusetts Bay and one station, MB05, in the farfield (Stellwagen Basin) (Fig. 1). Stations MB01, MB02, and MB03 have been monitored nearly every year since fall of 1992, and Station MB05 has been monitored since fall of 1993. Station MB02 was not visited in 1997, and no stations in Massachusetts Bay were sampled in 1998. The three nearfield stations are located in depositional areas in about 33 meters of water. Two of these, MB01 and MB02, are located approximately 4 and 3.6 km, respectively, northwest of the center of the bay outfall array, and the third, MB03, is 4.6 km southwest of the site. The Stellwagen station, MB05, is 12 km northeast of the site, in a depositional area about 75 meters deep.

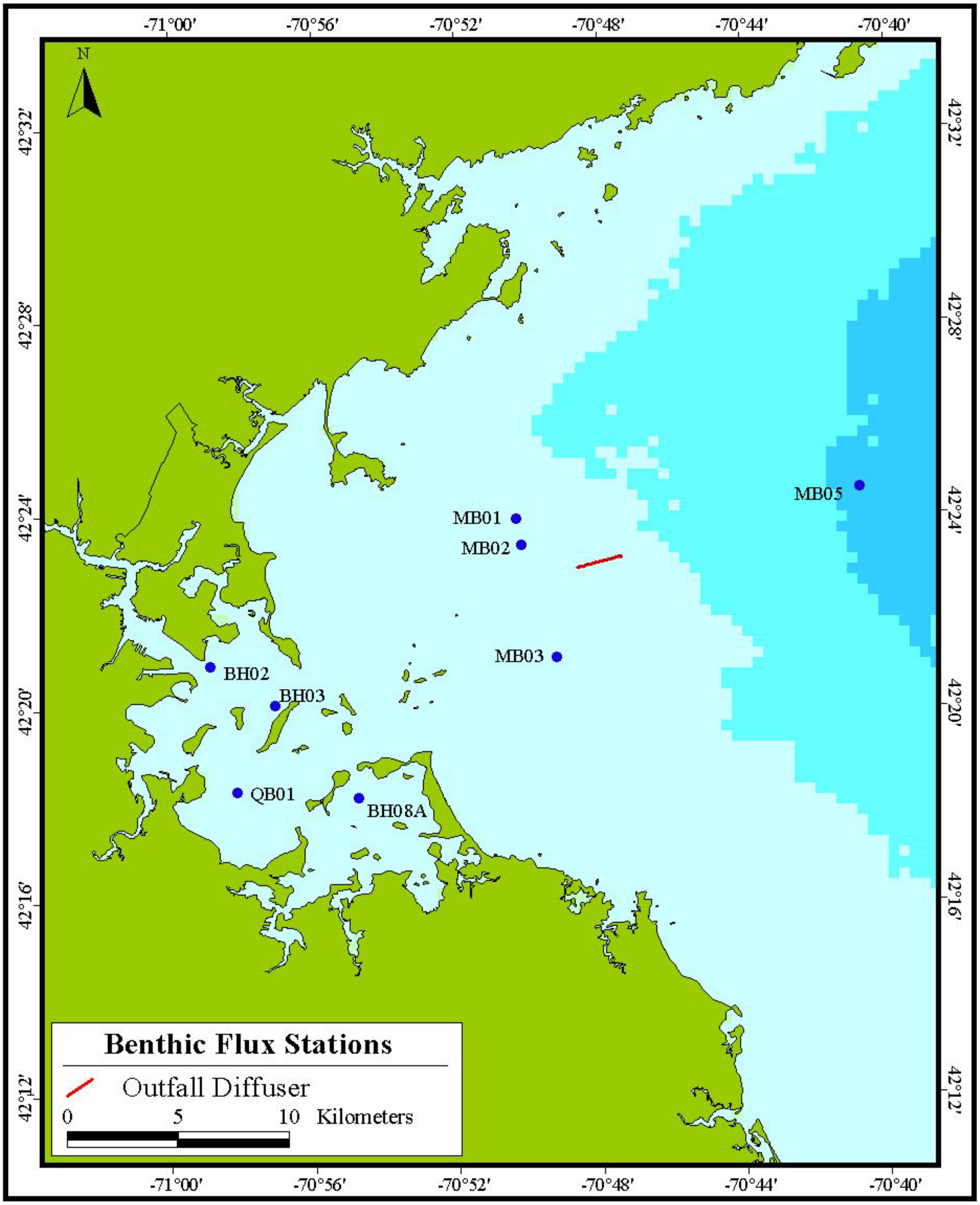



**Figure 1. Benthic nutrient cycling stations in Massachusetts Bay and Boston Harbor.**

## 2.1 Organic Matter Loading

Organic matter fuels benthic metabolism, so changes in either the supply of organic matter to the sea floor and/or to the quality of the organic matter can lead to changes in benthic respiration and nutrient fluxes. With the relocation of the outfall to Massachusetts Bay, there was concern that there would be an enrichment effect in the organic matter loading to the benthos. This enrichment might be derived from effluent particulates or it might be derived from enhanced phytoplankton productivity.

We have monitored organic matter content in the sediments two ways. We have measured organic carbon and nitrogen content in surface sediment, and we have measured chlorophyll pigments.

### 2.1.1 Total Organic Carbon

During baseline monitoring, organic carbon (OC) content in the sediments of the four Massachusetts Bay stations ranged from 0.4% to 4.3%, but with values more typically between 1.0% and 2.9%. Peaks in organic carbon content did not usually correspond to periods of phytoplankton blooms, but very high values observed in 1993 did seem to correspond to the effects of a late 1992 storm that redistributed sediments in the Bay (Bothner, 2002). In 2003, seasonal (May-October) average sediment TOC from the three Nearfield stations ranged from 1.1% to 1.4% (Fig. 2). These averages included a high value of 2.3% at MB01 and a low of 0.6% at MB02, both in July. Otherwise, TOC levels did not show much seasonal variability, with remaining values ranging only from 0.9% to 1.4% TOC. We previously noted a reversal in 2001 of what had been a decreasing trend in seasonal average TOC at two of the nearfield stations (MB01 and MB03) (Tucker et al, 2003). No further upward trend was observed in 2003, and in fact TOC was somewhat lower at Stations MB02 and MB03 than in the previous two years.

The seasonal average at Farfield station MB05 was higher, 1.6%, and varied very little over the sampling period. This is the same average value as the previous year, which ends a trend of slowly increasing carbon content in sediments at this deepwater site. However it continues the pattern observed since 1997 that average TOC content at MB05 has been greater than that at the nearfield stations.

Insight into the quality of organic matter may be gained from ratios of organic carbon to nitrogen. Higher ratios reflect organic mater that is relatively depleted in nitrogen, and therefore considered to be of lower quality or lability. At the three nearfield stations, carbon to nitrogen ratios (C/N) in surface sediments returned to values typical of baseline, following high (poorer quality) values observed in 2002. In 2003, ratios fell within a narrow range of 11.4 to 12.2. At MB05, there was little change in C/N, and the ratio at this station continued to be lower than that of the Nearfield stations (Fig. 3).

### 2.1.2 Sediment Pigments

In 2003, chlorophyll *a* content, measured as inventories over the top 5 cm of sediment, was well within the monitoring baseline (Fig 4.). At the three nearfield stations, there was some tendency for higher concentrations in May and July than in August and October, ranging from a high of 8.9 $\mu g\ cm^{-2}$ at MB02 in May to a low of 2.4 $\mu g\ cm^{-2}$ at the same station. When averaged over the May to October season, inventories across the three nearfield stations as well as at MB05 were similar. The lowest inventory of 4.4 $\mu g\ cm^{-2}$ was observed at MB02, and the highest, 6.0 $\mu g\ cm^{-2}$, at MB03. At MB05 there was little change across the season, and the seasonal average was 6.2 $\mu g\ cm^{-2}$. These seasonal averages were also remarkably similar to those of the previous year. The high inventories noted at some stations during 2001 have not been repeated.

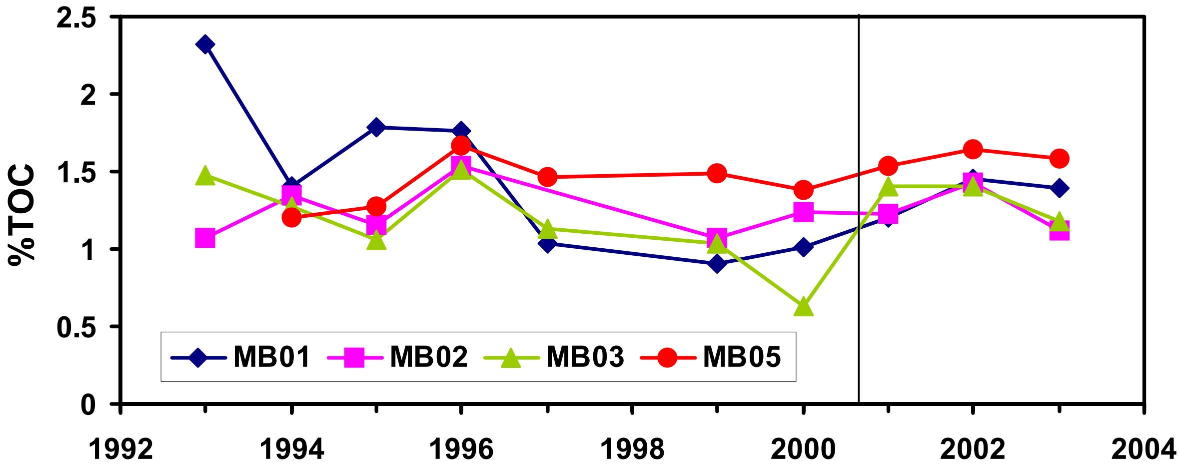



**Figure 2. Organic carbon content of top 2 cm of sediment at Nearfield stations MB01, MB02, and MB03 and Farfield station MB05. The vertical line marks the transition from baseline to post-relocation observations.**

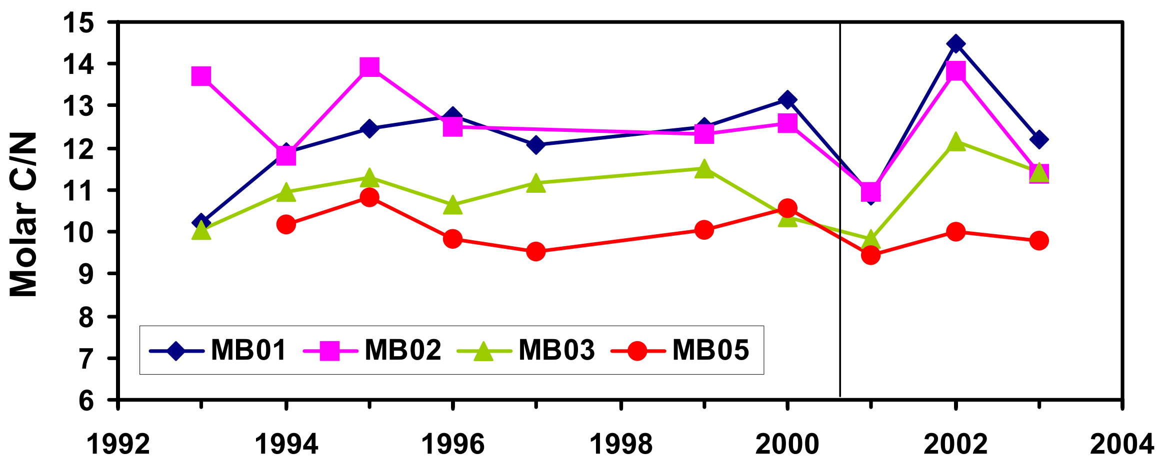



**Figure 3. Molar TOC/TON for top 2 cm of sediment. The vertical line marks the transition from baseline to post-relocation observations.**

Profiles of sediment chlorophyll provide more detail on seasonal changes. Profiles at all four stations showed elevated concentrations in May, especially at Stations MB02 and MB03. At Station MB02 the May profile was elevated through the top 4 cm as compared to low and flat profiles from the rest of the season. These concentrations were reflected in the high inventory mentioned above. At Station MB01, a surface peak was also observed in October, and a subsurface (3-4 cm) peak in July .The surface profiles probably reflect recent phytoplankton deposition, whereas the subsurface peaks may reflect mixing into

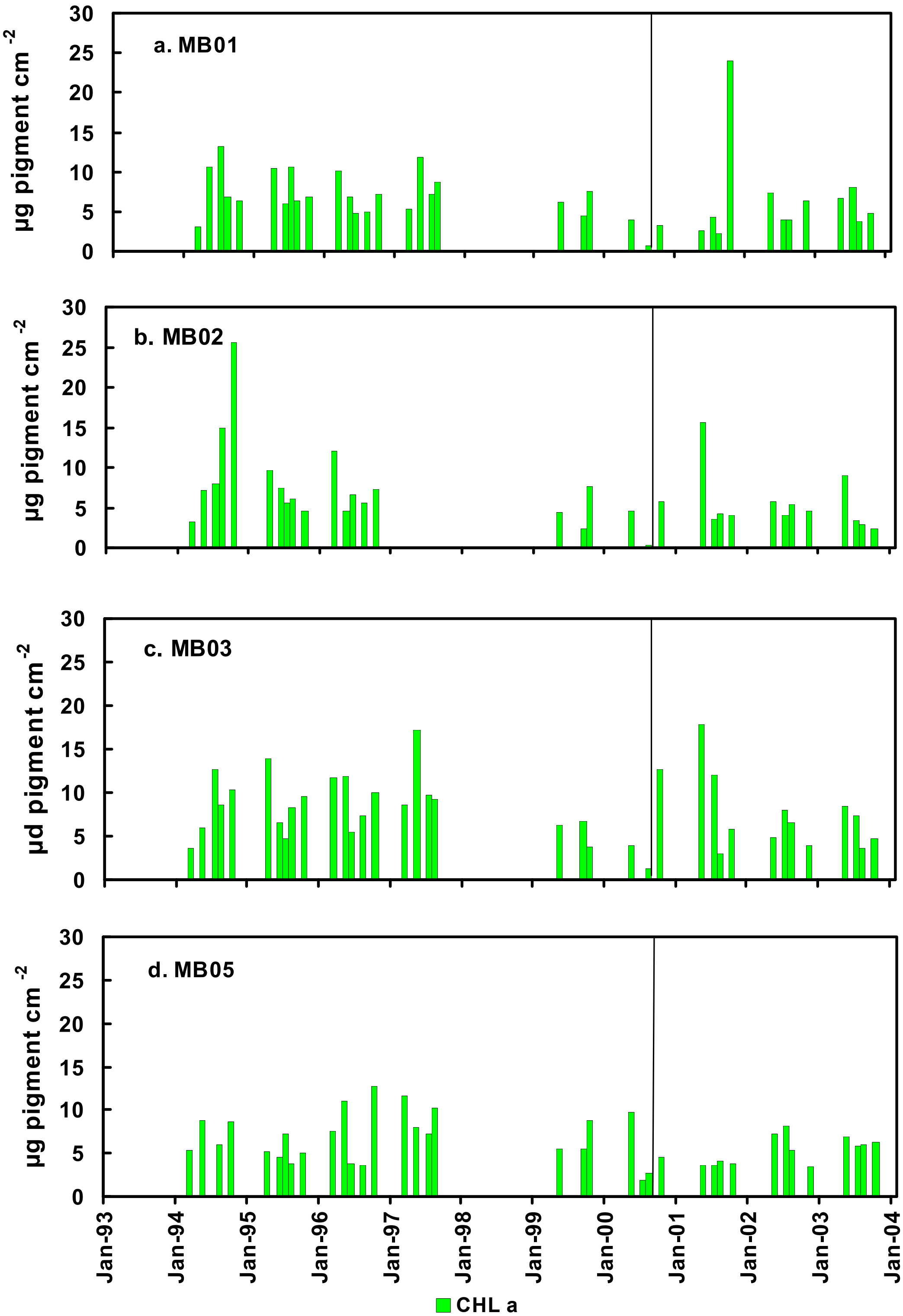



**Figure 4. Chlorophyll *a* inventory for top 5 cm of sediment at Nearfield stations a.) MB01, b.) MB02, and c). MB03, and Farfield station c). MB05. Vertical lines mark the transition from baseline to post-relocation observations.**

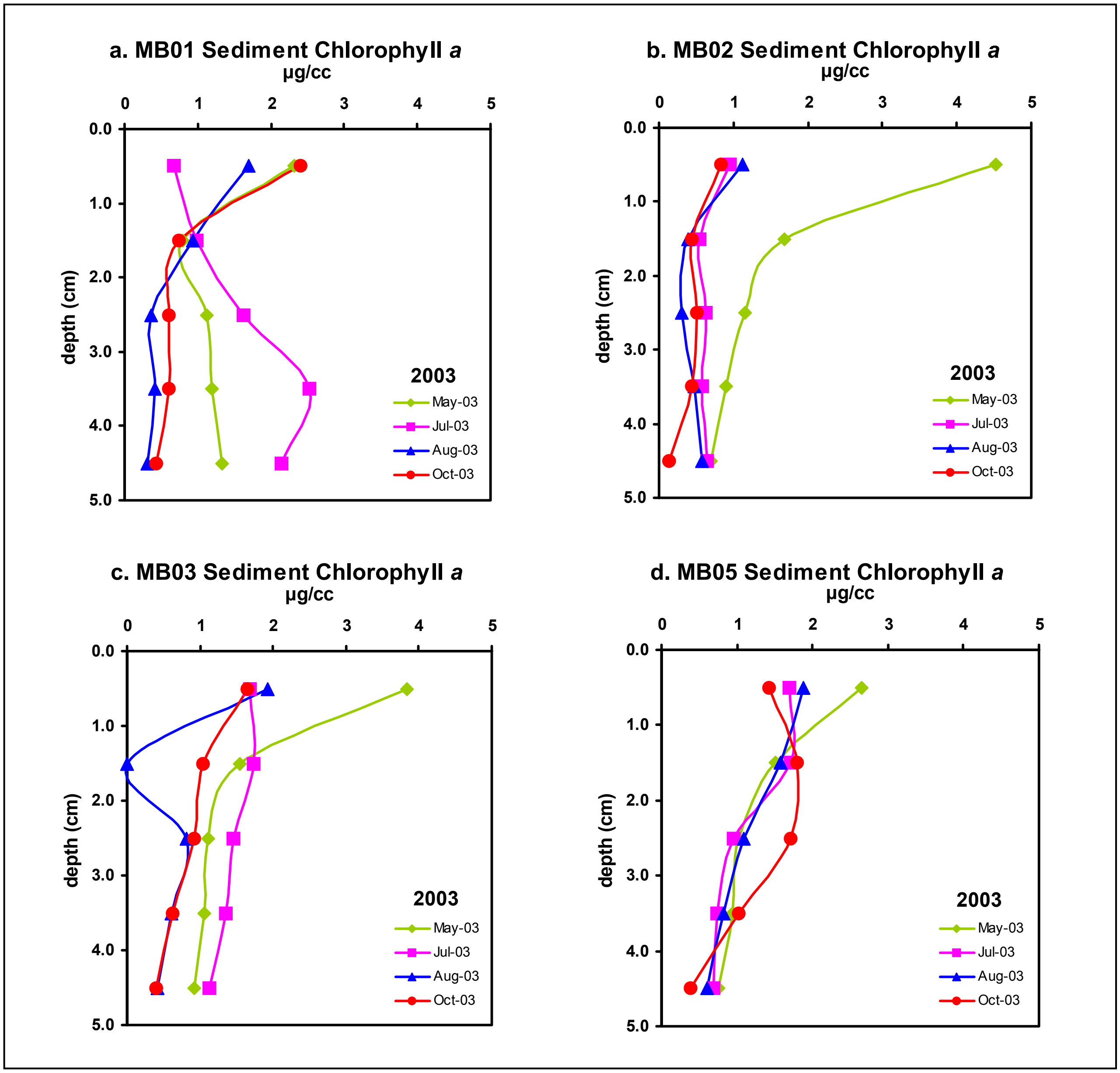



**Figure 5. Profiles of chlorophyll a concentration (µg/cc) in top 5 cm of sediment in 2003 from Massachusetts Bay Stations a.) MB01, b.) MB02, c.) MB03, and d.) MB05.**

the sediments by infauna. Chlorophyll *a* measurements provide a much more sensitive indicator of recent phytoplankton deposition (or in some cases, in situ production) than do measures of organic carbon. Normally chlorophyll *a* contributes a very small amount to the total carbon and therefore the two do not necessarily correspond to each other. For example, the surface peak in chlorophyll *a* at MB02 in May was not accompanied by any noticeable peak in the %TOC. In this particular case, the carbon contained in the total pigment (chlorophyll *a* plus phaeophytin *a*) constituted only 0.05% of the total carbon, which is below the detection limit of the method for TOC, and would not make a measurable change in the TOC. Clearly the two measures are indicators of different sources of carbon to the benthos.

Although there were some elevated values of chlorophyll and possibly in TOC in the first year after the outfall came on-line, three additional years of data have shown no other indication of an increase in organic matter deposition in the Nearfield. Organic carbon and chlorophyll concentrations have remained fairly constant, well within baseline, and the unusually high chlorophyll and low C/N ratios of 2001 have not been repeated. These observations strengthen our earlier arguments that those high levels resulted from deposition of the large phytoplankton bloom of 1999-2000 rather than from any outfall effect. In 2002 and 2003, sediment chlorophyll concentrations were lower and more typical of baseline, and did not indicate unusual inputs of fresh material, which corresponds to typical levels of water column chlorophyll during this period. In addition, sediment chlorophyll was similar across the region from the nearfield to Stellwagen, belying a local, outfall effect on this parameter.

## 2.2 Sediment Oxygen Demand

The baseline range for the seasonal average sediment oxygen demand for our three nearfield stations was 12.4 to 24.7 mmol $m^{-2}$ $d^{-1}$ with a grand mean across stations and years of 17.0 mmol $m^{-2}$ $d^{-1}$ (Fig. 6a). In 2003, seasonal average SOD ranged from 15.6 mmol $m^{-2}$ $d^{-1}$ at MB03 to 18.3 at MB01, and the average across the three stations was 17.3 mmol $m^{-2}$ $d^{-1}$( Fig. 7 a-c). Clearly observations in 2003 were well within baseline.

Highest rates for 2003 were observed in May at Stations MB01 and MB02 at 21.2 and 22.7 mmol $m^{-2}$ $d^{-1}$ respectively. In fact, at Station MB01, this was the second year in a row that May rates slightly exceeded the baseline range for that month at that station; however these rates did not exceed the entire range observed during monitoring. The only other measurement that fell outside the baseline range was a low rate of 12.8 mmol $m^{-2}$ $d^{-1}$ at MB03 in August. Most measurements for 2003 fell in the mid to low end of the baseline range.

At farfield station MB05, seasonal average SOD was very typical of baseline (Fig 6a). We have seen little variability in fluxes at this station, with the seasonal average during baseline ranging only from 7.8 to 15.3 mmol $m^{-2}$ $d^{-1}$. In 2003, the seasonal average was 12.2 mmol $m^{-2}$ $d^{-1}$., with rates ranging from 8.5 mmol $m^{-2}$ $d^{-1}$ in August to 16.7 mmol $m^{-2}$ $d^{-1}$in July (Fig. 7d).

Multiple factors influence SOD. Over all years and including colder March data (which are available from 1992 to 1997), the primary control in the nearfield was temperature, which explained about 30% of the variability in rates of sediment respiration we observed. However, an interesting shift in this relationship seemed to occur after 1995. Using only May through October data, which is available for all years, we found that temperature explained on average 45% of the variability in S.O.D. that we observed from 1993 through 1995. From 1996 on, however, that relationship failed ($r^2$ of only 0.02). We cannot explain this shift, but it may be related to early season differences in bottom water temperature (see Section 4.0) that narrow the temperature range over which we make these measurements. In a similar fashion, in Stellwagen basin where bottom water temperatures vary little over the season, temperature explains only about 10% of the variability in SOD. At this station, correlations between seasonal average sediment chlorophyll inventory over the top 5 cm of sediment and seasonal average SOD accounts for over 30% of the variability, whereas this correlation is insignificant for the nearfield stations.

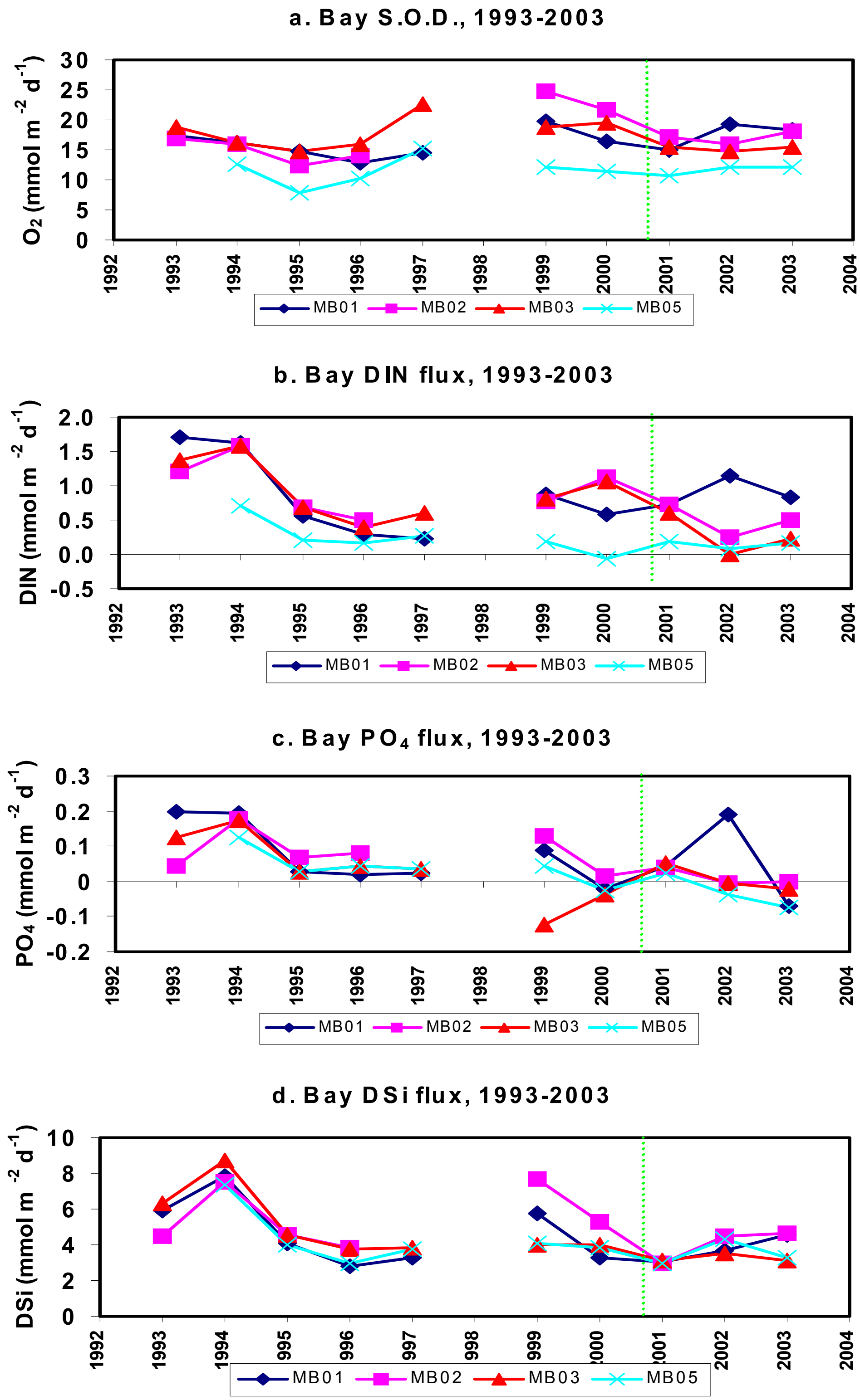



**Figure 6. Seasonal (May-October) averages of a.) sediment oxygen demand (S.O.D.), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Massachusetts Bay stations in 1993-2003. The vertical lines mark the transition between baseline and post-relocation observations.**

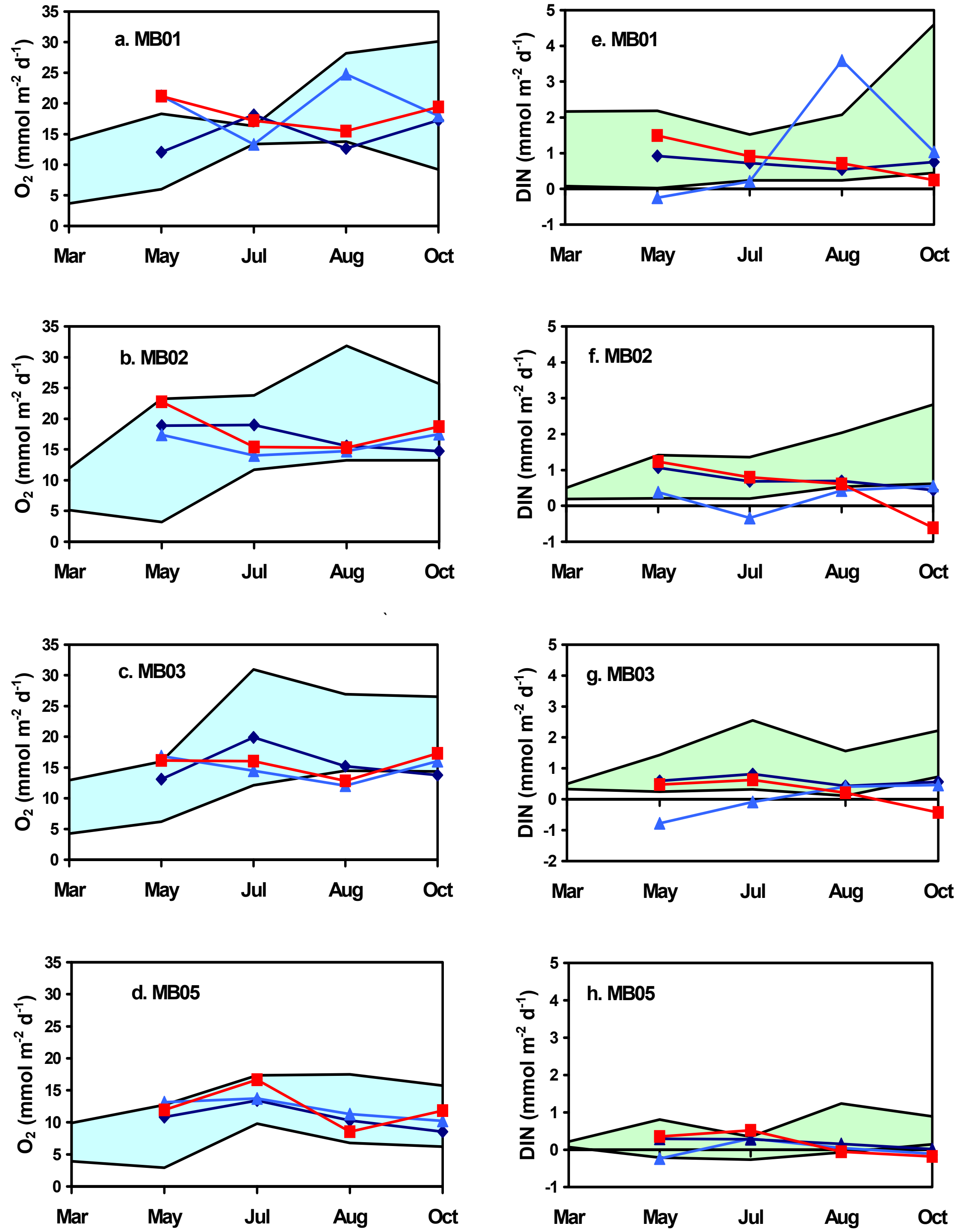



**Figure 7. Sediment oxygen demand ($O_2$ flux) and DIN flux for 2001 (♦), 2002 (▲) and 2003 (■) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations MB01, MB02, MB03, and MB05, respectively.**

### 2.2.1 Contribution to Oxygen Drawdown in Bottom Water

Several lines of evidence indicate that the seasonal drawdown of oxygen in the nearfield is regionally rather than locally controlled. Geyer, Libby, and Giblin (2002) concluded that seasonal patterns observed in the Nearfield are largely created by advection of water from the Gulf of Maine, reporting a strong correlation between deep water dissolved oxygen concentrations at the boundary between the Gulf of Maine and Massachusetts Bay and the deep water oxygen concentration in the Nearfield ($r^2$=0.92). Variations in DO were well but independently correlated with temperature and salinity, such that a statistical model using both of these variables explained nearly 80% of the variance in fall DO concentrations. These analyses indicated that physical factors rather than biological consumption control the seasonal drawdown of $O_2$ in waters near the outfall.

However, the contribution of the biological consumption should not be discounted. The temperature effect noted above acts partly through the fact that oxygen consumption (respiration) in both the bottom water and the sediments is temperature-sensitive. Also, the magnitude of sediment oxygen demand in the muddy sediments of the Nearfield typically equals or exceeds that of the annual drawdown, which is about 0.04 mg $L^{-1}$ $d^{-1}$ (Geyer et al., 2002). For example, in 2002 and 2003, the May to October average S.O.D. was 16.7 and 17.3 mmol $m^{-2}$ $d^{-1}$, respectively, which translates to about 0.05-0.1 mg $L^{-1}$ $d^{-1}$, depending on the depth of the stratified layer used (5-10 meters).

## 2.3 Nutrient Flux

The regeneration of inorganic nutrients by sediment decomposition of organic matter is an important part of nutrient cycling in coastal systems, and may play a large role in supporting primary production. The monitoring program recognized the role of sediment regeneration of nutrients and questioned whether nutrient flux to the water column might be enhanced by any organic matter enrichment, particularly in the area near the outfall.

In the three years that the bay outfall has been operational, we have seen no evidence of increased nutrient regeneration from the sediments. In fact, fluxes of dissolved inorganic nitrogen (DIN = $NH_4^+$ + $NO_3^-$ + $NO_2^-$), phosphate, silica, and urea have in general been at the low end of the range of fluxes observed during baseline monitoring.

### 2.3.1 DIN

In 2003, rates of dissolved inorganic nitrogen (DIN) flux from nearfield sediments were in the mid to low end of the baseline range (Fig 6b and 7e-g), ranging from 0.6 to 1.6 mmol $m^{-2}$ $d^{-1}$. Fluxes this year were highest early in the season (May) and lowest at the end of the season (Oct.). Low rates towards the end of the season included occurrences of $NH_4^+$ uptake at Stations MB02 and MB03. In the case of MB02 in October, these uptake rates were substantial, nearing 1 mmol $m^{-2}$ $d^{-1}$ As was noted for 2002, these observations of $NH_4^+$ uptake were not typical of the baseline period.

Nitrate comprised a major portion of the DIN efflux in the nearfield, ranging from 43% of the seasonal average flux at Station MB01 (Fig. 8a) to 100% (for the second year running) at Station MB03 (Fig. 8c), and resulting in an overall average for the three nearfield stations of 71%. More typically, the larger component of the DIN flux is $NH_4^+$. Although nitrate contribution to the DIN flux had been as high as 64% on occasion during baseline (at MB01 in 1996), it had not comprised the whole of the flux until 2002 and 2003 at MB03. Averaging over the three nearfield stations and from May to October, nitrate accounted for 57% and 71% of the DIN efflux in 2002 and 2003, respectively. This change is driven by variability in the $NH_4^+$ flux, however, rather than changes in $NO_3^-$ flux. Over all the nearfield data, $NH_4^+$

flux has ranged from –0.9 to 4.0 mmol $m^{-2}$ $d^{-1}$, for a total range of about 5 mmol $m^{-2}$ $d^{-1}$ , whereas $NO_3^-$ flux has ranged only from –0.5 to 0.7 mmol $m^{-2}$ $d^{-1}$, for a total of less than 1.0 mmol $m^{-2}$ $d^{-1}$

At MB05, DIN fluxes were about average those observed during baseline (Fig. 7h), ranging from -0.05 mmol $m^{-2}$ $d^{-1}$ to 0.52 mmol $m^{-2}$ $d^{-1}$ (the overall range at this station is -0.26 to 1.24 mmol $m^{-2}$ $d^{-1}$ ). Higher rates occurred in May and July followed by very low or negative rates (influx) in August and October. As was the case for the nearfield, influxes were of $NH_4^+$ rather than $NO_3^-$. These rates were in general lower than rates in the nearfield, as has been typical, however very similar to rates at one of the three nearfield Stations, MB03, which has exhibited very low DIN fluxes in the last two years.

### 2.3.2 Phosphorus, Silica, and Urea

Like DIN fluxes, phosphorus and silica fluxes in the nearfield from 2003 were typical or lower than observed during baseline monitoring (Fig 8a-c for $PO_4^-$, e-g for DSi). Urea fluxes continued to be quite low and variable (data not shown).

For most of the season, phosphate fluxes in the Nearfield were negligible or directed into the sediments. Only at MB01 in May did we observed significant (replicate fluxes with $r^2$>0.5) $PO_4^-$ flux out of sediments, however the flux was very small (0.08 mmol $m^{-2}$ $d^{-1}$ )(Fig. 9a). Significant uptake of -0.8 mmol $m^{-2}$ $d^{-1}$ was observed at MB02 in October and MB05 in August (Fig. 9b and 9c, respectively). This pattern of very low or negative fluxes was similar to that observed in the previous year. Seasonal averages for both years were low compared to much of the baseline, but not unprecedented (Fig 6c). The other year we observed negative fluxes of phosphate at the majority of our stations was in 2000, before the bay outfall became operational.

Phosphate fluxes at the farfield station MB05 were also low compared to baseline (Fig. 9d). Fluxes were essentially negligible in May and July, and negative (uptake) in August and October. The only period with significant fluxes was in August, when the rate was -0.15 mmol $m^{-2}$ $d^{-1}$. Although an overall negative flux was observed in 2001 and 2002, the seasonal average for 2003 of -0.07 mmol $m^{-2}$ $d^{-1}$ was the lowest yet observed at this station.

Nearfield dissolved silica fluxes in 2003 were intermediate to low as compared to baseline, with rates falling below that of the baseline range for October at two of the three stations. A high rate of 6.0 mmol $m^{-2}$ $d^{-1}$ was observed at MB01 in August (Fig 9e) and a low of 1.68 mmol $m^{-2}$ $d^{-1}$ at MB03 in October (Fig. 9g). Seasonal averages ranged from 3.1 mmol $m^{-2}$ $d^{-1}$ at MB03 to 4.6 mmol $m^{-2}$ $d^{-1}$ at both MB01 and MB02 (Fig. 6d) and were well within baseline observations. Silica fluxes at Station MB05 were variable over the 2003 season: they were typical of the station in May, on the high end of baseline values for July, essentially nonexistent in August, and low for baseline in October (Fig. 9h). The seasonal average of 3.2 mmol $m^{-2}$ $d^{-1}$ was, however, quite typical. The negligible fluxes in August were quite unusual as silica fluxes at all of these Massachusetts Bay stations are usually easily measurable.

### 2.3.3 Nutrient Flux Contribution to Primary Productivity

Average annual primary production in the nearfield area in 2003 at 272 g C $m^{-2}$ $y^{-1}$ (or 62 mmol C $m^{-2}$ $d^{-1)}$ was low compared to the previous two years (Libby *et al*., 2004). Following Redfield considerations, this amount of production would require 9.4 mmol $m^{-2}$ $d^{-1}$ of N or Si, and 0.6 mmol $m^{-2}$ $d^{-1}$ of P . Using the seasonal average DIN flux from our three nearfield stations of 0.52 mmol $m^{-2}$ $d^{-1}$, which would be an overestimate of the DIN flux because it does not include winter rates nor fluxes from other, less active sediment types, we find that benthic DIN flux represented less than 6% of phytoplankton requirements, which although small, was twice as much as the previous year. Similar calculations revealed no contribution from $PO_4^-$ fluxes in 2003, as the seasonal average flux was negative. Fluxes of dissolved

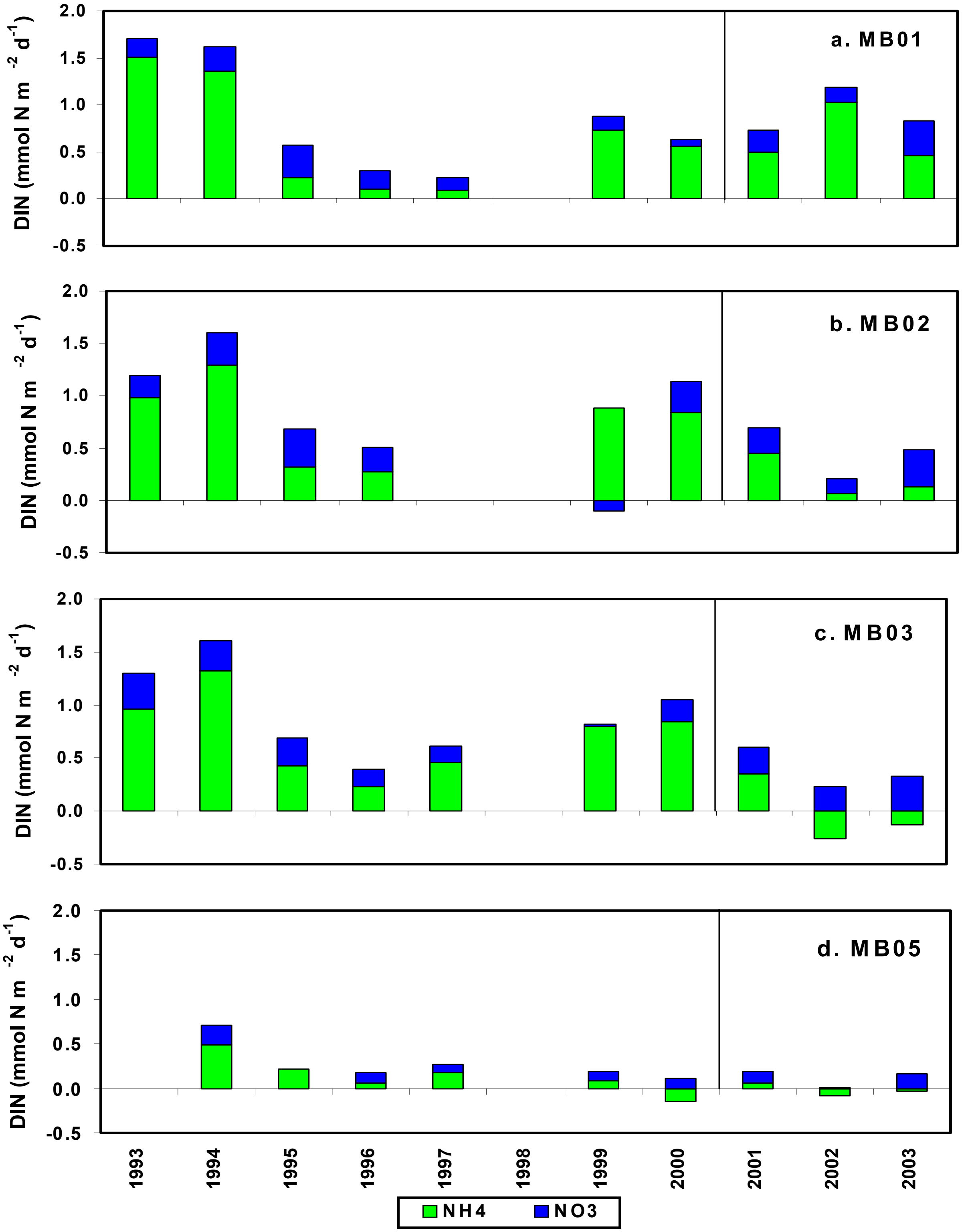



**Figure 8. May-October seasonal average DIN flux from 1993-2003 at bay stations a.) MB01, b.) MB02, c.) MB03, d.) MB05. The vertical line marks the transition from baseline to post-relocation observations.**

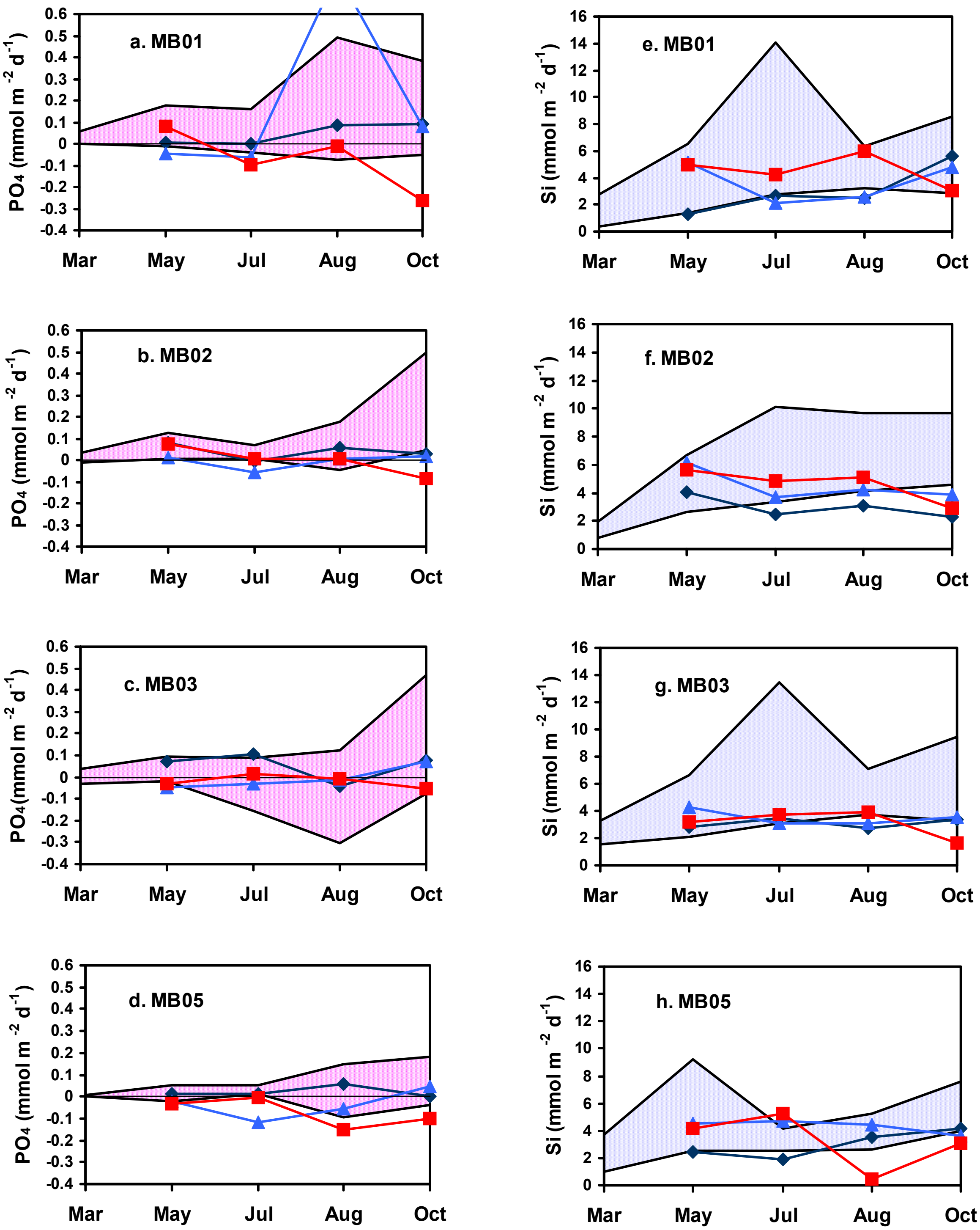



**Figure 9. Phosphate and dissolved silica flux 2001 (♦), 2002 (▲) and 2003 (■) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO4 flux and panels e-h depict DSi flux for stations MB01, MB02, MB03, and MB05, respectively.**

silica, however, could account for about 44% of requirements, assuming a 1:1 relationship between silica and nitrogen. There are several caveats on this calculation, including the fact that we used annual rates for primary productivity compared to seasonal (May through October only) rates for benthic fluxes, which would cause an overestimation of the contribution of benthic fluxes. Another reason this may be an overestimation is that our sampling sites are biased to the muddy, and presumably more active sediments of the bay.

## 2.4 Denitrification

Direct measurements of denitrification have been made periodically at two nearfield stations, MB02 and MB03. Since 1999, denitrification has been measured during the first and last surveys of the season only, in May and October. In 1993 and 1994, there was more thorough seasonal coverage in the data, as measurements were made during each survey. These measurements have revealed considerable variability in the rates of denitrification, and no discernable seasonal pattern.

Denitrification rates in 2003 were within baseline ranges (Fig. 10). A high rate of 4.3 mmol N $m^{-2}$ $d^{-1}$ was observed at MB02 in May, and the low rate for this year was 2.2 mmol N $m^{-2}$ $d^{-1}$, at MB03 in October. We have previously noted that denitrification rates at these two nearfield stations are often of similar and sometimes greater magnitude than the DIN fluxes. For the baseline period, we calculated that denitrification accounted for about 65% of the total N flux in the soft sediments of Massachusetts Bay. In 2001, that percentage was higher, about 80% of total N flux. In 2002 denitrification rates, were considerably higher than DIN fluxes, accounting for between 83% and 100% of total nitrogen flux from the sediments. In 2003 the pattern was similar, with denitrification accounting for between 78% and 87% of the flux in May, and 100% in October, when DIN flux was directed into the sediments.
The increase in the relative importance in denitrification as compared to DIN flux that we have observed recently is driven by decreases in DIN flux rather than any change in denitrification.

## 2.5 Redox

One of the concerns of the monitoring effort is whether any increased organic matter loading will lead to higher sediment respiration, and subsequently to depressed oxygen levels in the sediments. Although we have not seen evidence of increased sediment respiration, further insight into this question may be gained by examining other indicators of sediment redox conditions; e.g. respiratory quotients, Eh, and presence of dissolved sulfides in sediment porewater.

### 2.5.1 Respiratory Quotient

In aerobic respiration, carbon dioxide is produced at a rate equal to that at which oxygen is consumed, therefore the ratio of $CO_2$ production to $O_2$ consumption, called the respiratory quotient (RQ) is equal to 1.0. In sediments, where both aerobic and anaerobic respiration may occur, instantaneous RQs may differ from 1.0. They may exceed 1.0 if the end products of anaerobic process are stored in the sediments and not reoxidized. However, when these end products are reoxidized, a process that may be enhanced by bioturbation or other physical disturbance of the sediment, the resulting RQ may be less than 1.0. Integration of RQs over a seasonal or annual cycle may therefore provide a better assessment of the oxidation state of the sediments.

Respiratory quotients appear to have decreased over time since monitoring began (note that $CO_2$ data are not available for 1995-1998). In the early years of monitoring (1992-1994), respiratory quotients measured during core incubations of sediments from the three nearfield stations as well as from the farfield station were often greater than 1.0. Seasonal averages (omitting winter) were also greater than

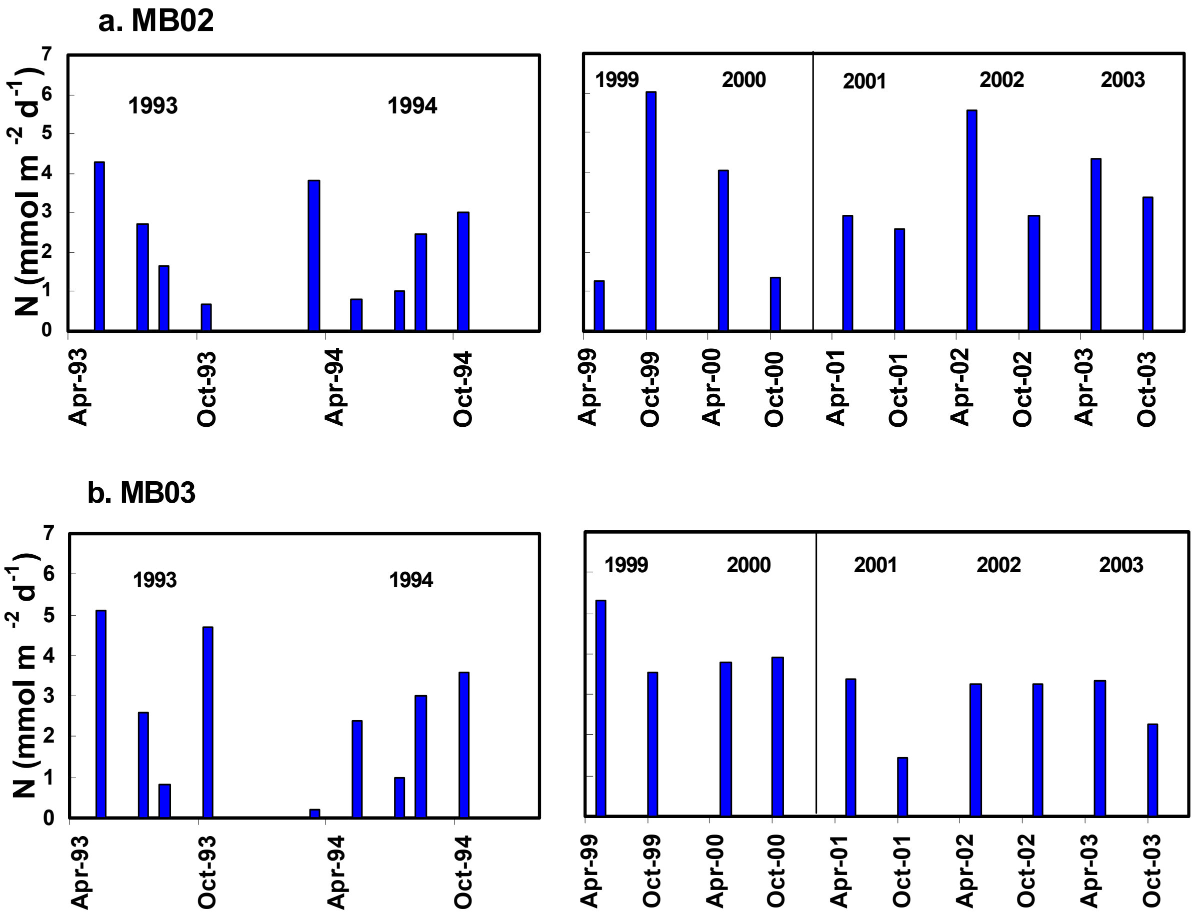



**Figure 10. Denitrification at two nearfield stations, a.) MB02, and b.) MB03. Denitrification measurements were not conducted in Massachusetts Bay in 1995-1998. The vertical line marks the transition between baseline and post-relocation of the outfall.**

1.0, indicating that anaerobic processes were important (Fig 11). Since 1999, RQs at these stations have been lower, in fact sometimes substantially less than 1.0, but seasonal averages have been very close to 1.0.

In 2003, seasonal averages at all four stations were very close to 1.0, typical of the period that began in 1999. In the Nearfield, RQs were a little above 1.0 in May and July, below 1.0 in August, and very nearly 1.0 in October. At MB05, a different pattern was observed, with high RQs in May, low in July, nearly 1.0 in August and a bit high again in October (data not shown).

### 2.5.2 Eh profiles

Oxidation-reduction potential measured as Eh in 2003 continued to be indicative of highly oxic conditions in sediment cores from Massachusetts Bay (Fig. 12). We have not observed any tendency towards decreased oxygen levels in these sediments in the three years post-relocation of the outfall. Values continue to be well above those that would indicate the presence of dissolved sulfides (-100 to – 200 mV), and in fact we did not detect sulfides in these cores in July or August during our porewater measurements.

Profiles of Eh in 2003 were in general similar to those observed in recent years, although we have not observed any consistent seasonal pattern from year to year or among stations. This is not surprising given the highly oxic and therefore "poorly poised (buffered)" state of the sediments.

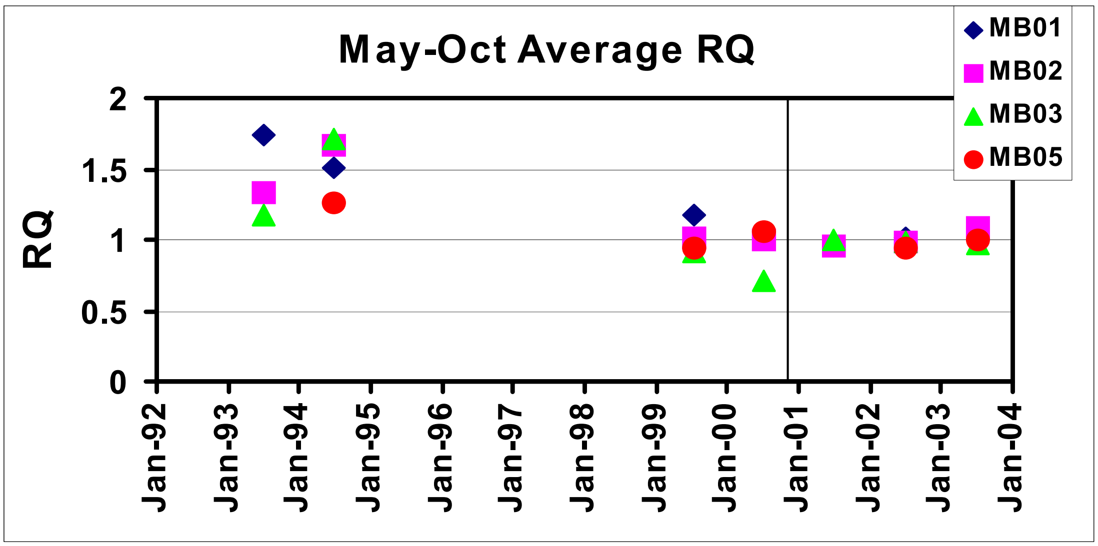



**Figure 11. Seasonal (May-October) average respiratory quotients for Nearfield stations MB01, BM02, MB03, and Farfield station MB05 from 1993-2003. The vertical line marks the transition from baseline to post-relocation observations.**

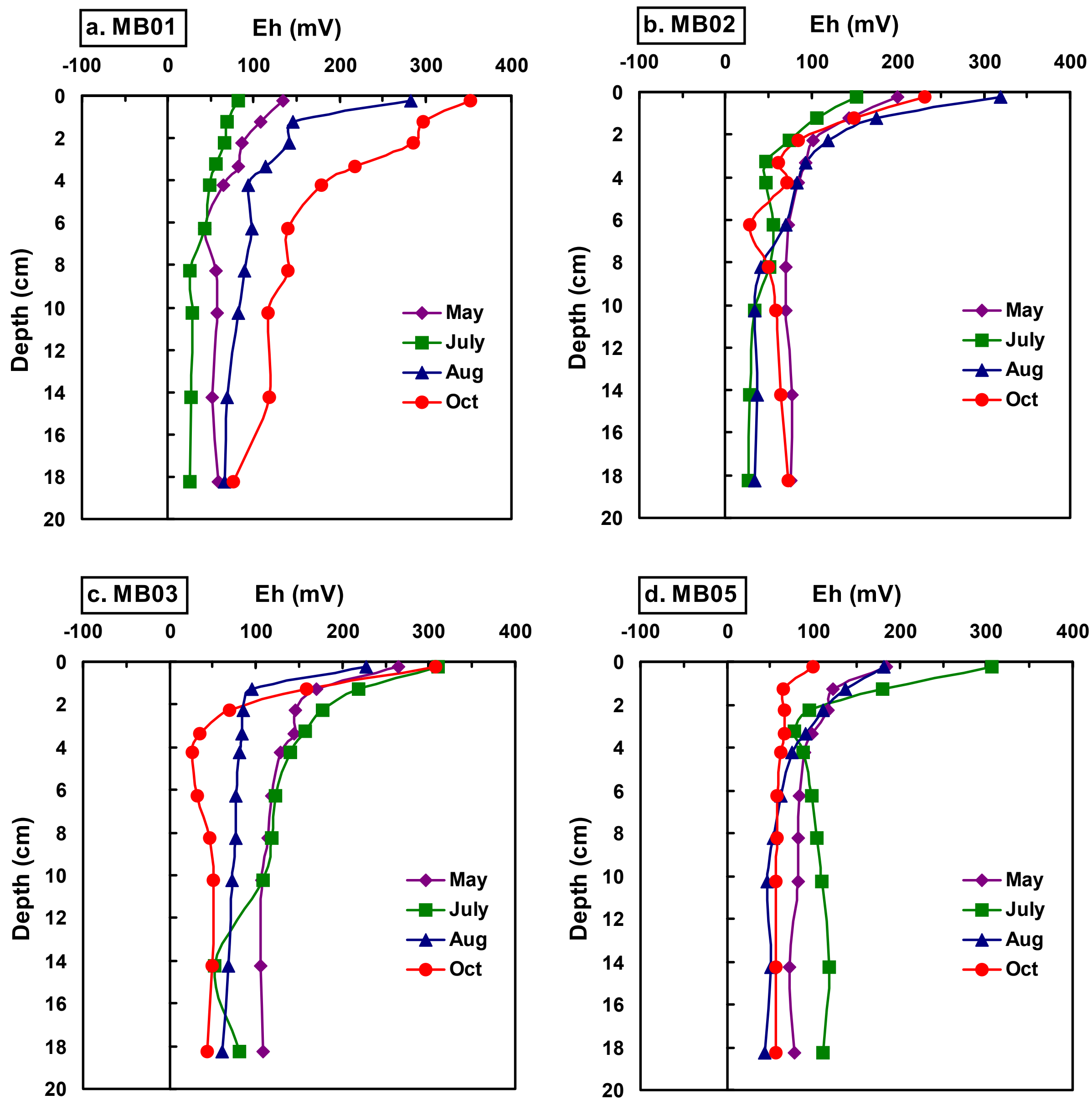



**Figure 12. Eh profiles for May through October, 2003, from Nearfield stations a.) MB01, b.) MB02, c.) MB03, and Farfield station d.) MB05.**

# 3.0 BOSTON HARBOR

Boston Harbor is a tidally dominated coastal embayment within the larger Massachusetts Bay system. It is broadly divided into northern and southern portions by Long Island, with tidal exchange occurring through President Roads for the northern portion and Nantasket Roads for the southern portion. Tidal flushing results in a short water residence time in the harbor, ranging from about 2 days near the inlets to about 17 days in some areas around the periphery of the harbor where tidal currents are weaker (Signell and Butman, 1992). Such active flushing serves to dilute and remove freshwater inputs of nutrients and contaminants from the harbor, but also delivers saltier water, and "ocean-side" nutrients and other materials to the harbor. In fact, a model run for the year 1994 emphasized the importance of oceanic loading to Boston Harbor (Kelly, 1998).

Large point sources of nutrients and contaminants, derived from land, however, have long been implicated as the cause of severe degradation of the harbor. Sources have included municipal wastes delivered through outfalls as sewage plant effluent and sludge/effluent mixtures or directly through combined sewer overflows (CSOs), as well as industrial wastes delivered through rivers. Although both northern and southern sections of the harbor have suffered from long-term wastewater inputs, some areas have been more severely affected than others, depending on their proximity to these sources.

The reduction of solids loading to the harbor, initially by the cessation of sludge disposal at the end of 1991 and subsequently by treatment improvements at Deer Island and the diversion of the Nut Island influent to the Deer Island Plant in the summer of 1998 (Taylor, 2001b), was the primary agent of change in Boston Harbor until offshore diversion occurred in September, 2000. Benthic habitats in the north harbor that were directly affected by sludge disposal, in particular Station BH03, have undergone large changes in their biology and chemistry. In contrast, areas in the south harbor exhibited little change during this time.

The diversion of all MWRA effluent offshore marked the final phase in MWRA's Deer Island project, and resulted in dramatic improvements in water quality in the first 12 months after outfall relocation. Taylor (2002) reported that in the first year after diversion, average DIN concentrations in the harbor were 55% lower than the baseline average. After three years, similar reductions were reported, resulting in an overall reduction of 59% for the post diversion period (Taylor, 2004). Within the DIN pool, a large and persistent decrease in the proportion contributed by $NH_4^+$ has been observed; during baseline, NH4+ accounted for over 50% of the DIN as compared to an average of 23% during the three years post diversion. Sustained reductions were also observed in phosphorus concentrations (38% in DIP for the three year period). For some parameters, large changes in the first year did not persist at all locations in the harbor in the second and third years. In the first year, water column chlorophyll *a* decreased by nearly 50%, particulate carbon decreased by nearly 40%, and water clarity increased by about 15%. For the following two years, the decrease in chlorophyll *a* was 19%, in particulate carbon was 28%, and the increase in water clarity (as determined by the extinction coefficient) was 2%.

Four harbor stations have been repeatedly sampled in the benthic nutrient cycling program throughout the monitoring period (Fig. 1). Two stations, BH02 and BH03, are located in the northern section of Boston Harbor and have been sampled routinely since September, 1991. The other stations, BH08A and QB01, are in the southern harbor, and have been visited since 1995. Through 1997, these stations were visited in March, May, July, August, and October. After that time, the March surveys were discontinued.

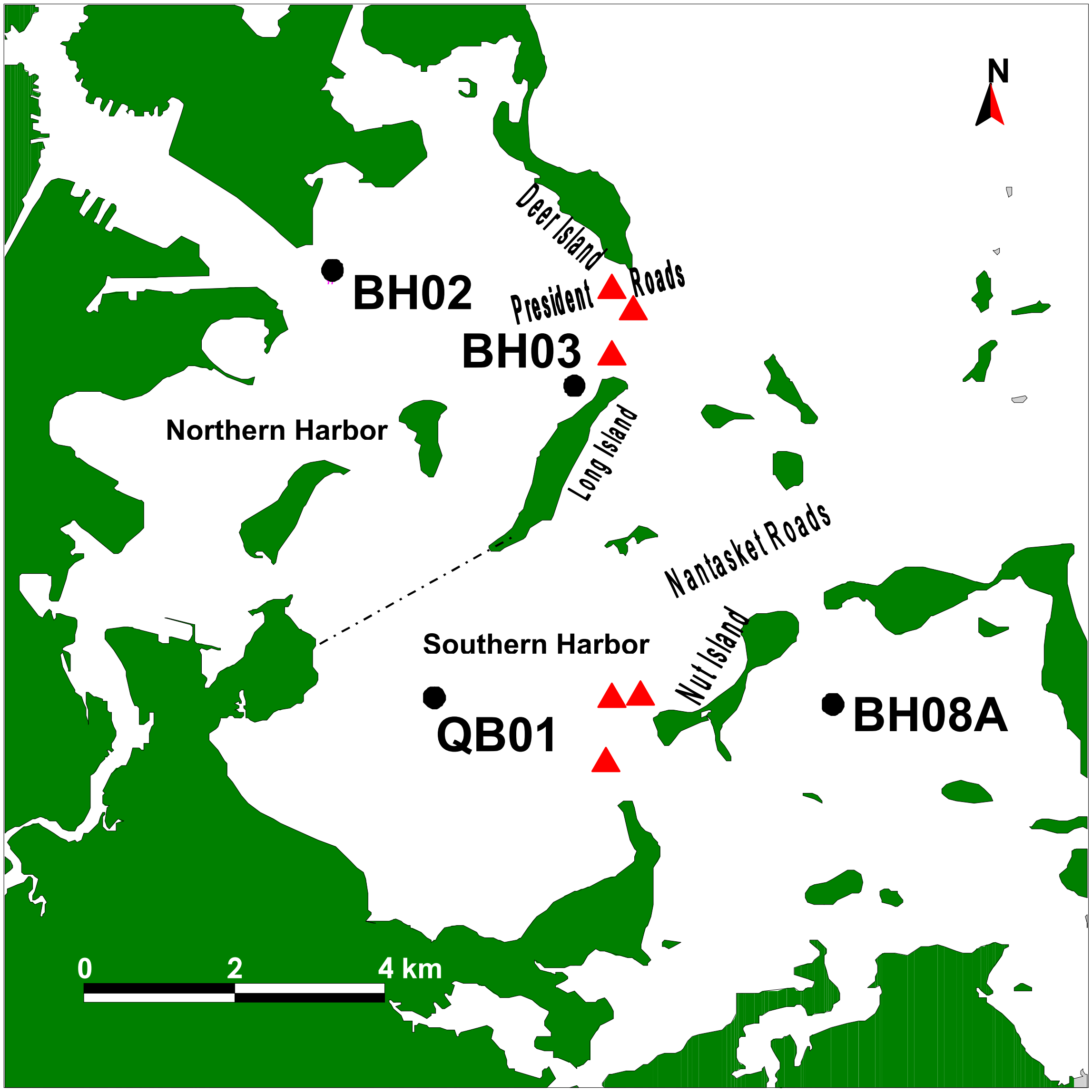



**Figure 13. Locations of four Boston Harbor stations. Harbor outfalls, no longer in use, are marked by triangles (▲).**

## 3.1 Organic Matter Loading

### 3.1.1 Total Organic Carbon

Organic matter loading to Boston Harbor decreased significantly over the baseline monitoring period due to the cessation in late 1991 of sludge disposal in the harbor and with subsequent improvements in sewage treatment. Accordingly, we observed a decrease in the organic matter content of sediments in the Harbor over the baseline period as these direct inputs decreased and carbon stores were metabolized. Beginning in 1999, reductions in sediment TOC from year to year continued but became smaller, and the variability across stations decreased. There was no observable change in this pattern after the MWRA outfall was relocated offshore in September 2000. However, there is potential to see further reductions if the relocation results in any reductions in primary productivity and thereby decreases in organic matter deposition to the benthos.

In 2003, seasonal averages of total organic carbon (TOC) were similar to those observed in 2002, and ranged from 2.0% to 2.6% (Fig. 14). Only Station QB01 showed a decrease this year compared to the previous year. At this station average TOC decreased from 2.5% in 2002 to 2.0% in 2003. Otherwise, organic content of sediments at these stations has been relatively constant since 2000. The very high percentages (over 4%) that were observed at these stations at various times before 1999 have not recurred. Although there remain some small areas of sediment focusing within Boston Harbor where TOC sometimes still exceeds 4% (eg. Station T04 in Savin Hill Cove; Maciolek *et al.*, 2003), it appears that sediments in most of the harbor are "winding down".

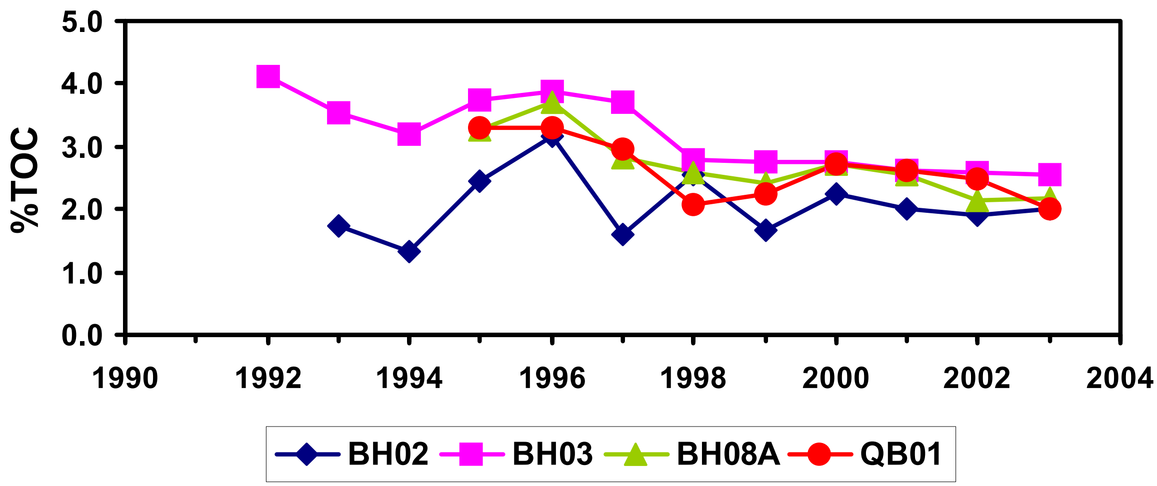



**Figure 14. Seasonal average TOC (% dry weight) for top 2 cm of sediment.**

### 3.1.2 Sediment Pigments

Concentrations of photosynthetic pigments in the surface layers of sediment may be used as another indicator of organic matter content. Concentrations of chlorophyll *a* alone may also provide an indication of recent input, resulting from either deposition from the water column or, in the shallow waters of the harbor, from *in situ* production.

Through 2002, the only changes we had observed in sediment pigment concentrations occurred between 1997 and 1998, and may have been related to slight differences in methodologies used by two groups of investigators. (This difference was reflected in the phaeopigment fraction only and would have resulted from differing extraction efficiencies for phaeopigments). There was no apparent change in the two years after relocation of the MWRA outfall

In 2003, total sediment pigment inventories (integrated over the top 5 cm of sediment; Fig. 15) seemed to increase somewhat, especially in the two stations in the south harbor. The largest chlorophyll *a* inventory yet observed, 49.5 ug chl *a* $cm^{-2}$ was found at Station QB01 in May (Fig. 15d). Benthic diatoms were noted at this time. High levels of sediment chlorophyll were also observed at Station BH08A and BH02 early in the season (Fig. 15a and 15c). At BH02, large inventories over the entire season were consistent with observations of recent years. Since 1998, this station has had the highest seasonal average chlorophyll *a* inventories of the four harbor stations. Otherwise, chlorophyll *a* levels were typical of previous observations. The increase in total pigments, then, was largely comprised by the phaeopigment fraction. At three out of the four stations, seasonal average phaeopigment inventories were the highest yet recorded. The exception was Station BH03, where although the levels were not *the* highest, they were among the highest (data not shown).

It is unclear how much of these elevated concentrations was derived from phytoplankton deposition and how much from *in situ* production. Sediment profiles of chlorophyll *a* provide some insight (Fig. 16). For example, at Station QB01 in May, when chlorophyll *a* inventories were very high, the profile revealed extremely high concentrations of chlorophyll *a* at the surface and down to two cm (Fig 16d). In this case, since we did observe benthic diatoms at this time, it was clear that the elevated chlorophyll levels were derived in large part from *in situ* production. A profile of similar shape but lower concentrations was observed at the same time at BH08A (Fig. 16c), when chlorophyll levels were high but the presence of diatoms was not noted. By inference, however, we could reasonably assume they were present. Diatoms are not always easily visible at the surface since they are able to migrate within the sediments and may also be transported downward by bioturbation. At BH02, when inventories were high, a subsurface (at about 2 cm) peak was observed (Fig. 16a). This occurred in May, July and October. Highest chlorophyll inventories were observed in July at this station, and the profile revealed elevated concentrations throughout the top 5 cm. It is likely that these subsurface peaks in chlorophyll *a* represent diatom biomass rather than deposition. In contrast, at Station BH03 where the lowest inventories of the four stations occurred, profiles did not show surface or subsurface peaks (Fig 16b). With the exception of the May profile noted above, at BH08A profiles were similarly featureless. These two stations typically support large numbers of benthic amphipods and other infauna that presumably graze down diatom production.

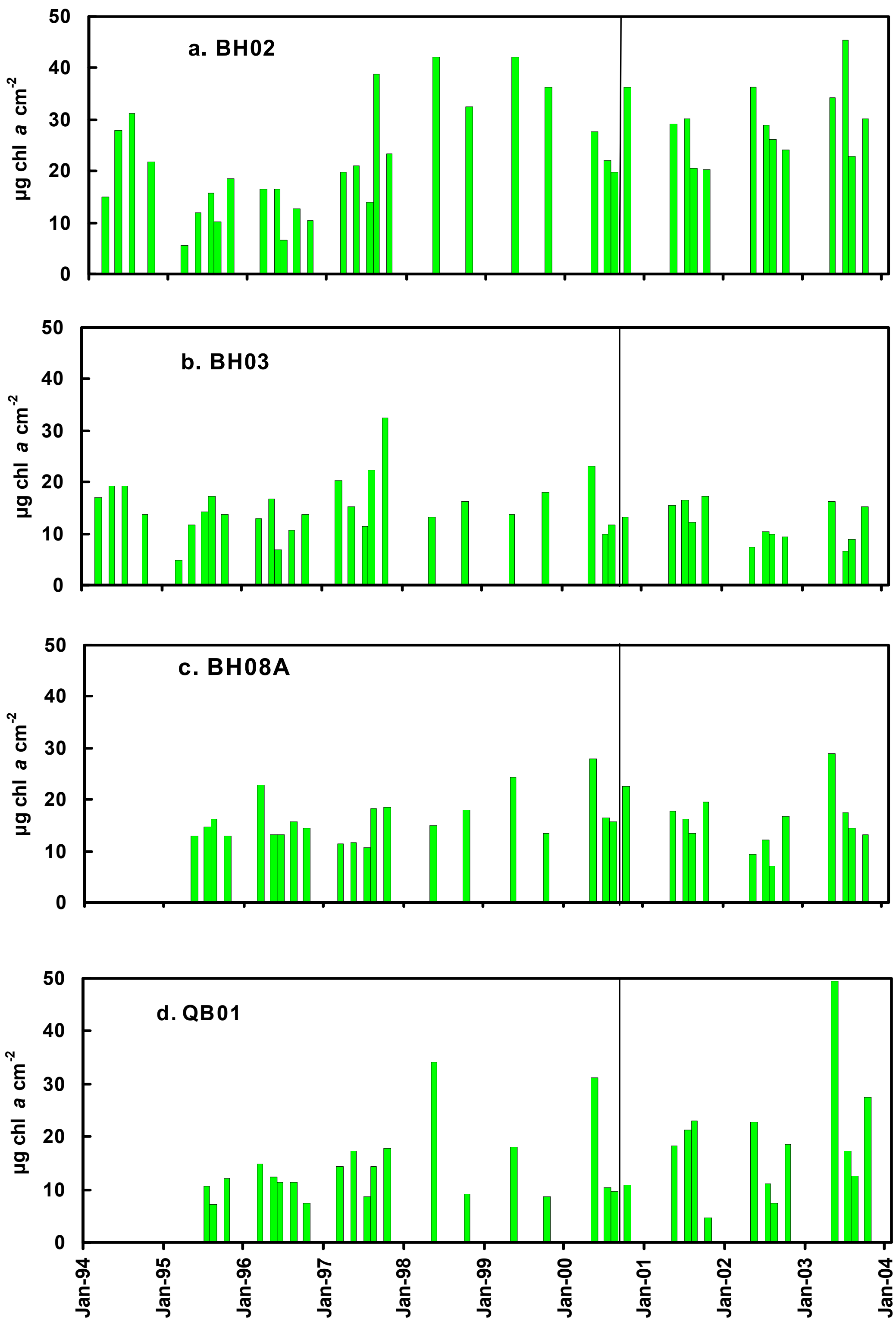



**Figure 15. Chlorophyll a inventory for top 5 cm of sediment at northern harbor stations a.) BH02, b.) BH03, and southern harbor stations c.) BH08A, d.) QB01. The vertical line marks the transition from baseline to post -relocation observations.**

## 3.2 Sediment Oxygen Demand

Sediment oxygen demand in Boston Harbor in 2003 returned to rates more typical of the period since 1998, following all-time low rates in 2002. For three of the four stations, BH02, BH03, and BH08A, rates remained in the mid to lower end of the baseline range and seasonal averages were consistent with rates measured previously (Fig. 17a). At Station QB01, however, the seasonal average was the highest yet observed at this station, and was essentially the same as rates at BH02 and BH03, about 50 mmol $m^{-2}$ $d^{-1}$. At Station BH08A, rates were higher, although well within the baseline range for the station, averaging 70 mmol $m^{-2}$ $d^{-1}$.

In the northern harbor, at Stations BH02 and BH03, S.O.D. was fairly constant from May through August, and then decreased in October (Fig. 18a, b). The same decrease during October was observed at the two southern harbor stations, but rates were more variable in the earlier part of the season. At BH08A, peak rates for all the stations of 102.1 mmol $m^{-2}d^{-1}$ occurred in July (Fig. 18c). This was nearly twice the rate observed at the other three stations at this time. The high seasonal average rate at QB01 was derived from an anomalously high rate for this station of 79.1 mmol $m^{-2}$ $d^{-1}$ measured in May, followed by continued high rates, as compared to baseline, for the rest of the season (Fig. 18d). Low October rates ranged from 16.2 at BH02 to 36.2 at BH08A.

In 2002, at BH02 and QB01 where physical processes dominate, an unusually strong relationship (as determined by the coefficient of determination, $r^2$) between temperature and S.O.D. was observed. Temperature explained 67% and 77% of the observed variability at Stations BH02 and QB01, respectively. In 2003, the relationship was weaker at BH02, where temperature explained 42%, but still higher than the 28% effect observed with all years combined. At QB01, however, there was no relationship between temperature and S.O.D. in 2003 ($r^2$= 0.002). At this station, combining all years yields an $r^2$ of only 0.15, so the strong relationship in 2002 was unusual. The very high respiration rates observed in May were responsible for the collapse of the temperature relationship. At BH03 and BH08A, where biology is the dominant process, the importance of temperature was strong, ranging between 47% and 59%, which was higher than the effect for all years combined.

With the return to typical S.O.D. in 2003, it is beginning to appear that 2002 was an anomalous year. In fact, 2002 has now been characterized as one of the droughtiest years in recent history. Discharge from the Charles River was the lowest yet observed during the monitoring program, at an annual average of only 6.5 $m^3$ $sec^{-1}$ (Libby *et al*., 2004). In contrast, average discharge of 11.25 $m^3$ $sec^{-1}$ in 2003 was among the higher observation. We think the drought of 2002 resulted in less land-derived inputs to the harbor (including nutrients and organic matter), which caused a reduction in S.O.D. and nutrient fluxes. In addition, we noticed a general absence of the amphipod mat. In 2003 river discharge was more typical, the amphipods were present, and rates returned to typical. It is clear that factors other than temperature interact to determine S.O.D. at these stations, and that these factors may vary annually and across stations.

Except in restricted embayments, the harbor is well flushed by tidal mixing, such that even during years that experienced extremely high levels of S.O.D. (i.e. 1993 or 1995), we did not observe hypoxia at any of our stations. The decreasing rates of sediment respiration we have observed would result in even less contribution to any water column drawdown of oxygen by the benthos.

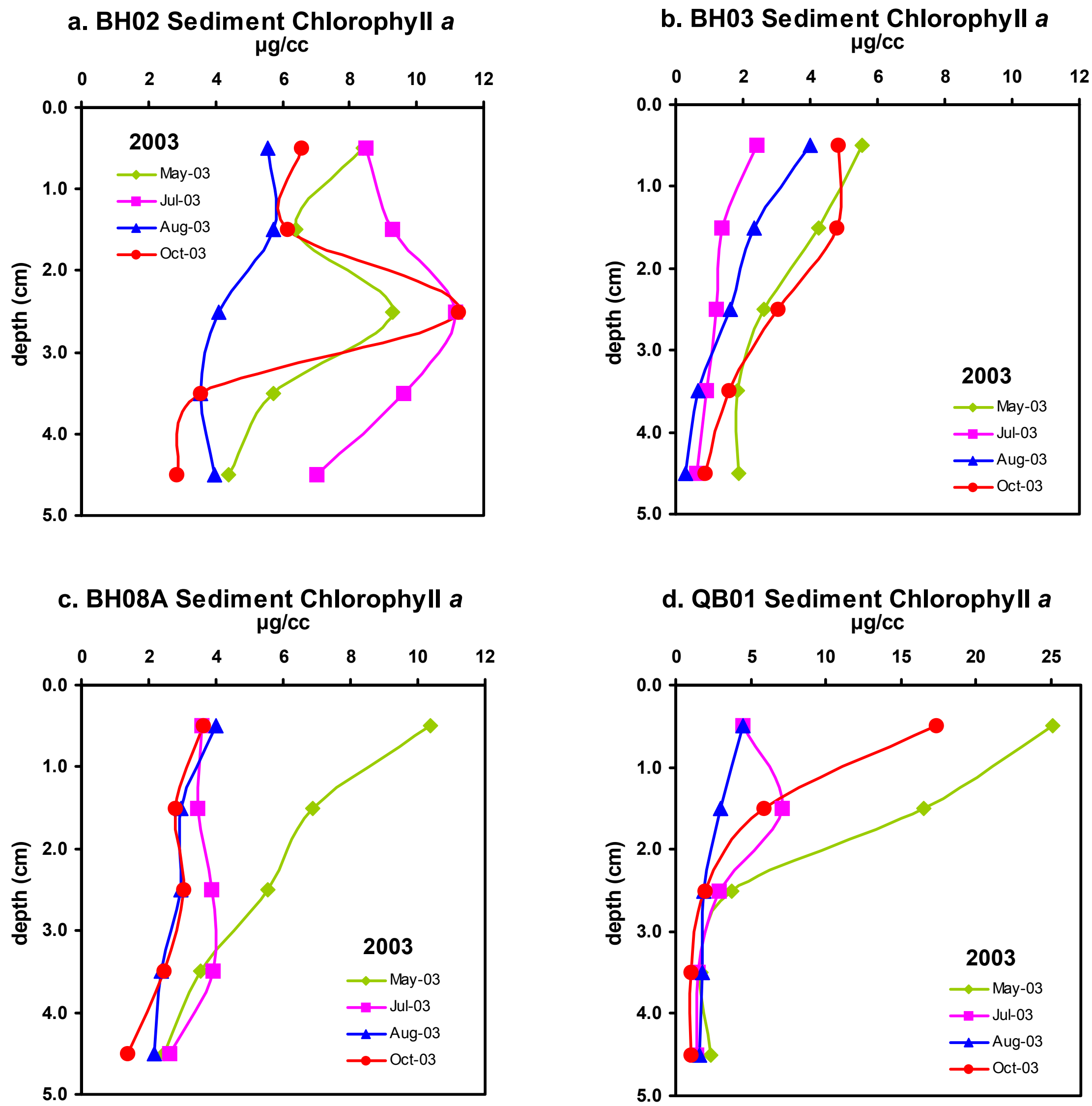



**Figure 16. Profiles of chlorophyll a in top 5 cm of sediment at Boston Harbor stations a.) BH02, b.) BH03, C.) BH08A, and d.) QB01.**

## 3.3 Nutrient Fluxes

Like sediment respiration, benthic fluxes of DIN, phosphate and silica (Fig. 17b-d) have all decreased since the beginning of the monitoring program at stations BH02, BH03, and BH08A. In contrast, there has been little change at Station QB01. The large variability we observed from station to station and year to year early in the monitoring program has abated, such that flux rates across all four harbor stations are now very similar. It appears that conditions in the harbor are entering a new equilibrium.

### 3.3.1 DIN

DIN fluxes in 2003 continued to be low to moderate as compared to baseline ranges. As compared to the previous two post-relocation years, seasonal average rates at three of the four stations were intermediate, ranging from 1.7 mmol $m^{-2}$ $d^{-1}$ at QB01 to 4.1 mmol $m^{-2}$ $d^{-1}$ at BH08A (Fig. 17b). At BH02, rates were slightly higher than in the previous two years, and the seasonal average was 5.0 mmol $m^{-2}$ $d^{-1}$. Similar to the pattern we saw for SOD, daily rates at all four stations declined in October; at BH03, in fact, the flux became negative (Fig. 18b). Highest daily rates of 7.6 mmol $m^{-2}$ $d^{-1}$ were observed in July at BH02 (Fig. 18e). There was no anomalously high DIN flux at QB01 in May to correspond to the high SOD observed at that time (Fig. 18h).

Strong seasonal patterns that were observed in 2002 occurred in 2003 at only two of the stations, BH02 and QB01, where, as noted before, physical processes are more important than biological processes. At these two stations, temperature explained over 90% of the observed variability. At the other two stations, where biology dominates, the relationship was weaker, as well as weak compared to the effect with all years combined. At Station BH03, temperature explained only 18% of the variability, as compared to nearly 30% for all years and in stark contrast to 2002, when it explained nearly 100%. At BH08A, the relationship had an $r^2$ of 0.43, whereas for all years it was 0.52, and for 2002, was 0.85.

Harborwide, the major component of the DIN flux in 2003 was $NH_4^+$. At BH02 and QB01, $NH_4^+$ accounted for 80% and 62% of the DIN flux. At BH03 and BH08A, where biological activity increases oxidation of the sediments, $NO_3^-$ was slightly more important, accounting for 56% and 52% respectively. We have not observed very large percentages of the flux comprised by $NO_3^-$ since the early 1990s at Station BH03, when the amphipod mat was at its peak at that station.

### 3.3.2 Phosphate and Silica

Fluxes of phosphate in 2003 fell mostly in the middle of the baseline range, but were variable from station to station (Fig. 19 a-d). Seasonal averages were higher than the previous year at two stations, BH02 and BH08A, but lower at the other two, BH03 and QB01 (Fig. 17c). Average rates ranged from essentially no flux at stations BH03 and QB01, to 0.51 mmol m-2 d-1 at Station BH02. Most of the stations followed a seasonal pattern, with higher daily rates in July and August, and low and often negative rates in May and October. Fluxes peaked in July, when highest rates of 1.5 mmol m-2 d-1 were observed at Station BH02. Lowest rates were found in October at Station BH03, where an uptake of 0.33 mmol m-2 d-1 was observed.

$PO_4$ fluxes are controlled by a combination of biological and chemical factors, and therefore do not always correlate well with temperature. For example, at BH02, which often has quite reducing sediments, the regression with temperature for all years yields an $r^2$ of only 0.01. In 2003, however, a much stronger seasonal pattern was apparent such that temperature explained about 75% of the variability at all stations except Station BH03. We observed a similarly strong relationship with temperature in 2002 across all four stations. At BH03, the relationship was weaker, yielding an $r^2$ of 0.19, curiously very similar to the relationship between temperature and DIN flux at this station (which was also weaker than for the other three stations). In general, we seem to be seeing a stronger connection between temperature and $PO_4^-$ flux than was typical for these stations. For all years combined, the $r^2$s ranged from 0.01 to 0.36

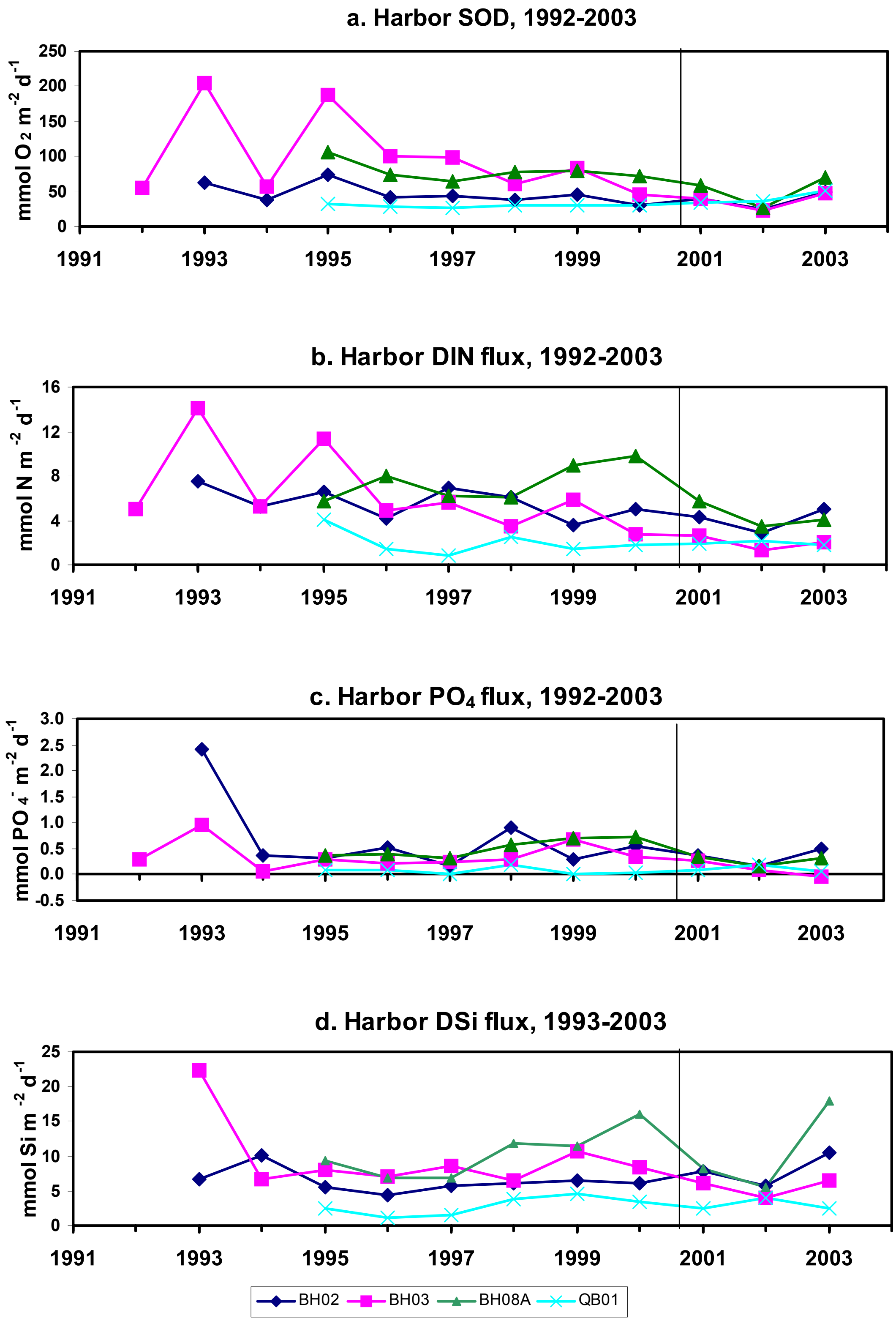



**Figure 17. Seasonal (May-October) averages of a.) sediment oxygen demand (SOD), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Boston Harbor stations in 1993-2002. The vertical lines mark the transition between baseline and post-relocation observations.**

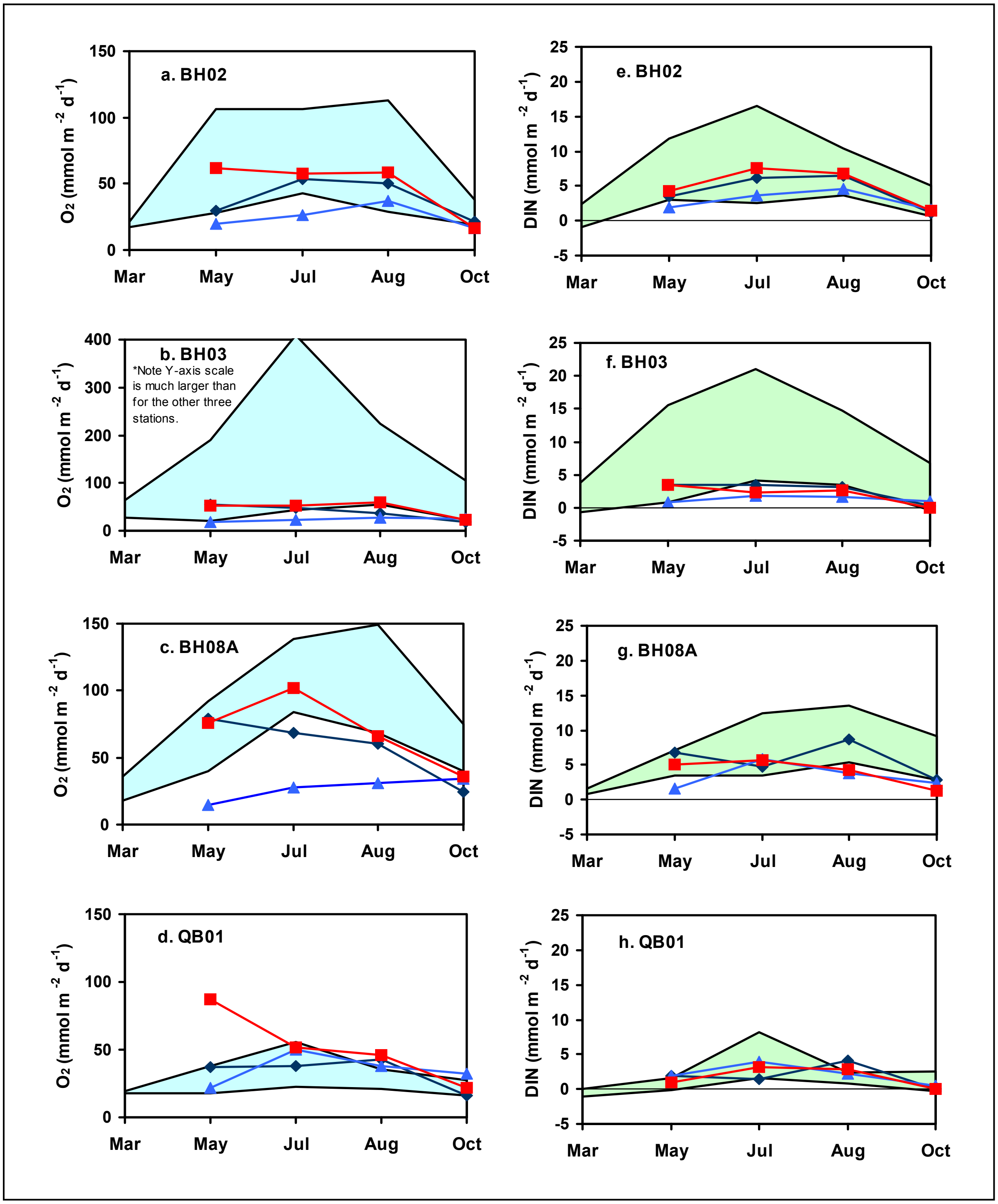



**Figure 18. Sediment oxygen demand ($O_2$ flux) and DIN flux for 2001 (♦), 2002 (▲) and 2003 (■) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations BH02, BH03, BH08A, and QB01, respectively.**

Silica fluxes varied widely from station to station in 2003, with seasonal averages ranging from 2.4 mmol $m^{-2}$ $d^{-1}$ at QB01 to 17.9 mmol $m^{-2}$ $d^{-1}$ at Station BH08A (Fig. 17d). The large flux at BH08A was the highest yet observed at his station, and daily rates were higher than the baseline maxima in May through August (Fig. 19g). Fluxes peaked in July with a daily rate of nearly 28 mmol $m^{-2}$ $d^{-1}$; by October, fluxes had fallen to a rate at the low end of the baseline range. Similarly high fluxes had been seen once before at this station when a seasonal average flux of 16.1 was measured in 2000. The only larger flux occurred at BH03 in 1993 (seasonal average 22.3 mmol $m^{-2}$ $d^{-1}$). A high daily rate of 23.6 mmol m-2 d-1 at Station BH02 in August led to the highest ever seasonal average flux of 10.5 mmol m-2 d-1 at this station as well (Fig. 19e). A similarly high seasonal rate of 10.0 had been observed in 1994, but the more typical flux has been about 6 mmol $m^{2}d^{-1}$ at Station BH02.

At the other two stations, Si fluxes were typical of baseline. The seasonal average of 6.5 mmolm-2d-1 at BH03 was a bit higher than the previous low year, but well within the baseline range (Fig. 17d). In fact, daily rates were generally in the low end of that range. At QB01, fluxes were in the middle of the range in July and October, but a bit high in May and low in August (Fig. 19h). The August flux, in fact, was directed into the sediment; however these fluxes were not linear and should essentially be considered as "no flux'. In 2002, Si fluxes showed a strong seasonal pattern, with temperature explaining between 70% and 95% of the variability observed. In 2003, only one of the stations, BH08A, showed such a strong relationship. At that station, the $r^2$ for the relationship was 0.89. At BH02 and BH03, the relationship was weaker and more typical of that seen when all years are combined, or around 35-40%. At QB01, there was no relationship with temperature in this year.

### 3.3.3 Benthic Flux Contribution to Primary Production

The relocation of the sewage outfall has ended the direct input of a large source of nutrients to the Harbor. With this change, the relative contribution of nutrients supplied to the water column by benthic recycling may have increased. We can make a rough estimate of this contribution using post relocation rates of primary production and benthic fluxes. Annual average primary production rate from water column station F23 at the mouth of the harbor was 274 g C $m^{-2}$ $yr^{-1}$, lower than the previous two years and about the same as for Massachusetts Bay (Libby *et al.*, 2004). Using Redfield relationships, 9.4 mmol $m^{-2}$ $d^{-1}$ of nitrogen would be needed to support this production. Benthic fluxes in 2003 supplied on average 3.2 mmol DIN $m^{-2}$ $d^{-1}$ or about 34% or phytoplankton requirements. A similar calculation shows that about 36% of P requirements would also be met by benthic recycling. Benthic fluxes of dissolved silica in 2003, however, were sufficient to meet nearly all of phytoplankton requirements (98%), based on a 1:1 ratio with nitrogen requirements. As noted for similar estimates made for our bay sites (Section 2.3.3) there are caveats on this calculation regarding annual averages for primary production versus seasonal averages for the nutrient fluxes, and a bias towards depositional and presumably more active sites, both of which would lead to overestimates of the potential flux contribution. In addition, we have no information on how much of this regenerated N and P is intercepted by benthic primary producers, which may be considerable. Also, model estimates of inputs from other sources, including terrestrial and oceanic (which would include some contribution from the ocean outfall; Kelly, 1998), still exceed phytoplankton requirements and may render benthic fluxes less important. A post-relocation nutrient budget for the harbor is needed in order to better assess the current contribution of benthic fluxes.

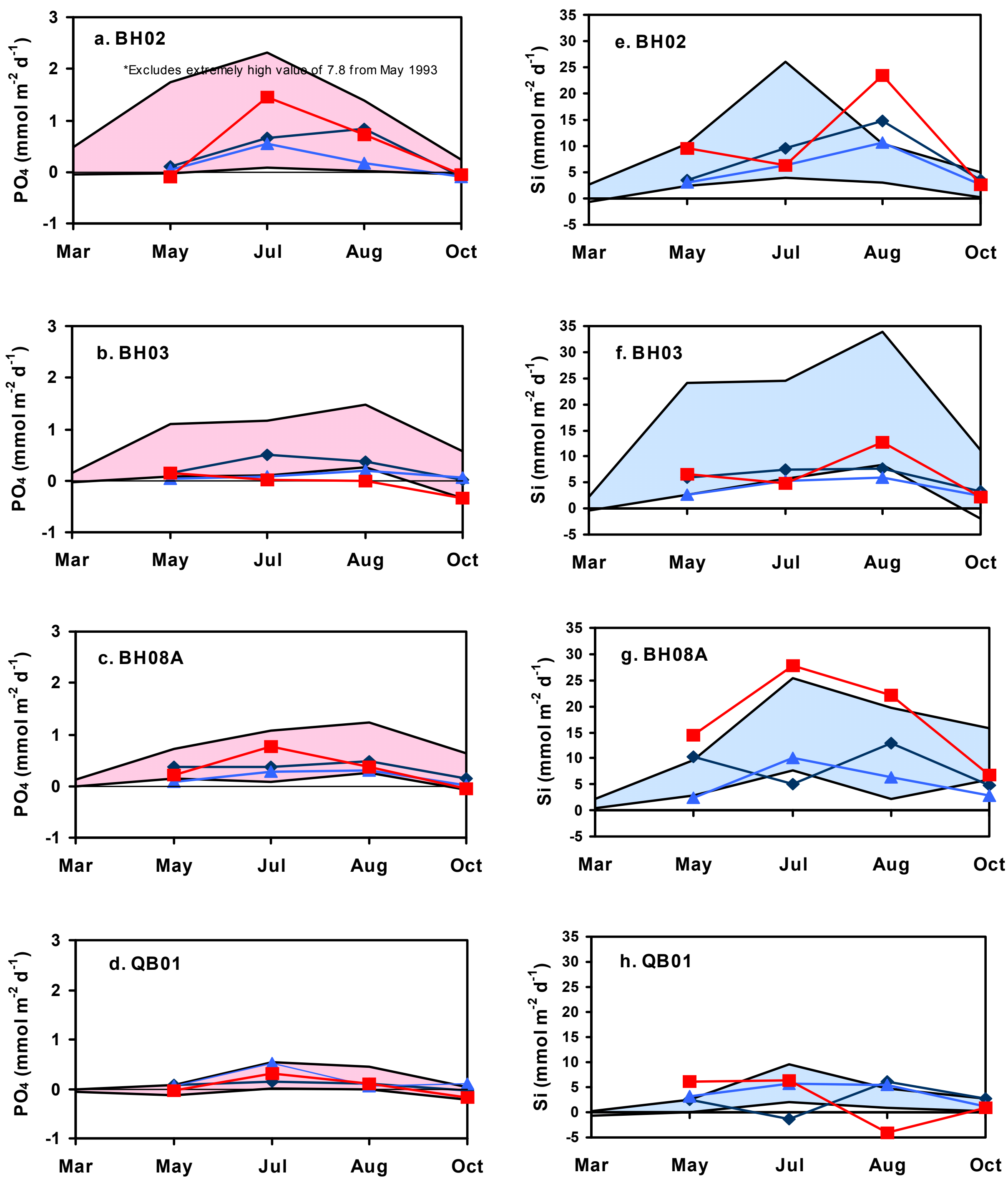



**Figure 19. Phosphate ($PO_4$) and dissolved silica (DSi) flux for2001 (♦), 2002 (▲) and 2003 (■) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict $PO_4$ and panels e-h depict DSi flux for stations BH02, BH03, BH08A, and QB01, respectively.**

## 3.4 Denitrification

In 2003, rates of denitrification at the two harbor stations where it is measured, BH02 and BH03, were within the ranges observed during baseline monitoring and very similar to each other (Fig. 20a). At Station BH02, seasonal average rates of 5.7 mmol N m-2 d-1 were about the same as they had been for the previous four years. At BH03, the seasonal average was 5.1 mmol N $m^{-2}$ $d^{-1}$, up somewhat from the previous two years and ending a four-year steady decline in denitrification rates at this station. Denitrification rates at BH02 showed a strong relationship to temperature ( $r^2$ = 0.86), which we don't often see, with rates ranging from 2.7 mmol N m-2 d-1 in May to 8.6 in July (Fig. 20 b). Rates at BH03, however, did not follow a seasonal pattern in 2003, because rates were relatively high in May (Fig. 20c). Peak rates for the station of 7.0 mmol m-2 d-1 occurred in August, followed by low rates for the year of 3.4 mmol N $m^{-2}$ $d^{-1}$ in October.

As discussed in a previous report (Tucker et al, 2002), the decrease in N loading to the harbor caused by the relocation of the sewage outfall may shift the role of denitrification in the overall N budget. In the cited report, estimates of harborwide denitrification rates were in excess of 1000 mmol $m^{-2}$ $y^{-1}$; including the 2003 observations did not significantly change this estimate. Estimates of the remaining terrestrial inputs of N were also on the order of 1000 mmol $m^{-2}$ $y^{-1}$, suggesting that denitrification might act as a sink equivalent to inputs. However, model estimates suggest that oceanic inputs remain the overwhelming input to the system (Kelly, 1998), and decrease the N sink provided by denitrification to less than 10% of total nitrogen inputs.

## 3.5 Redox

Indicators of redox conditions in harbor sediments have varied with year and station, but in general that variability has decreased with time. The reduction in organic matter loading to the harbor is the most likely explanation for decreases in S.O.D. and therefore more oxic conditions in the sediments. At some sites in the harbor, e.g. BH03 and BH08A, the process of "burning off" all the organic matter has been accelerated by the presence of a dense infaunal population (the amphipod mat) that helped reoxidize the sediments through bioturbation. The effects of the infaunal community included deeper oxidized layers at these sites, and changes in RQs from values well over 1.0 early in the monitoring program to values close to or somewhat lower than 1.0 in recent years. High concentrations of dissolved sulfides (> 0.5mM) are no longer detected in the porewaters at Station BH03. At Station BH02, where the amphipod community was typically not present, change has been more gradual. Early in the monitoring program, the oxic layer in sediments at this site was typically quite shallow, and RQs and sulfide concentrations were quite high. There were signs of improvement in recent years, especially 1999 and 2001, when the oxic layer appeared to have deepened and RQs were much closer to 1.0. Dissolved sulfides continued to be present at high concentrations at this site, but were encountered at deeper depths in the porewater profiles. At QB01, a site whose somewhat sandier sediments facilitate porewater irrigation, redox conditions have traditionally been less variable, with RQs consistently close to 1.0.

### 3.5.1 Respiratory Quotients

In 2003, respiratory quotients (RQs) were consistent with trends we have observed over the past several years (Fig. 21). At Stations BH02 and BH08A RQs averaged about 1.0 over the May to October period. At BH02, RQs were a little less than one at the start of the season, but increased through October, reaching a high for all stations for the year of 1.6. These values are not atypical for this station, but they indicate that the relative importance of anaerobic processes at this site continues to vary from year to year. At BH08A, values hovered near 1.0 throughout the season. At the other two stations, BH03 and QB01,

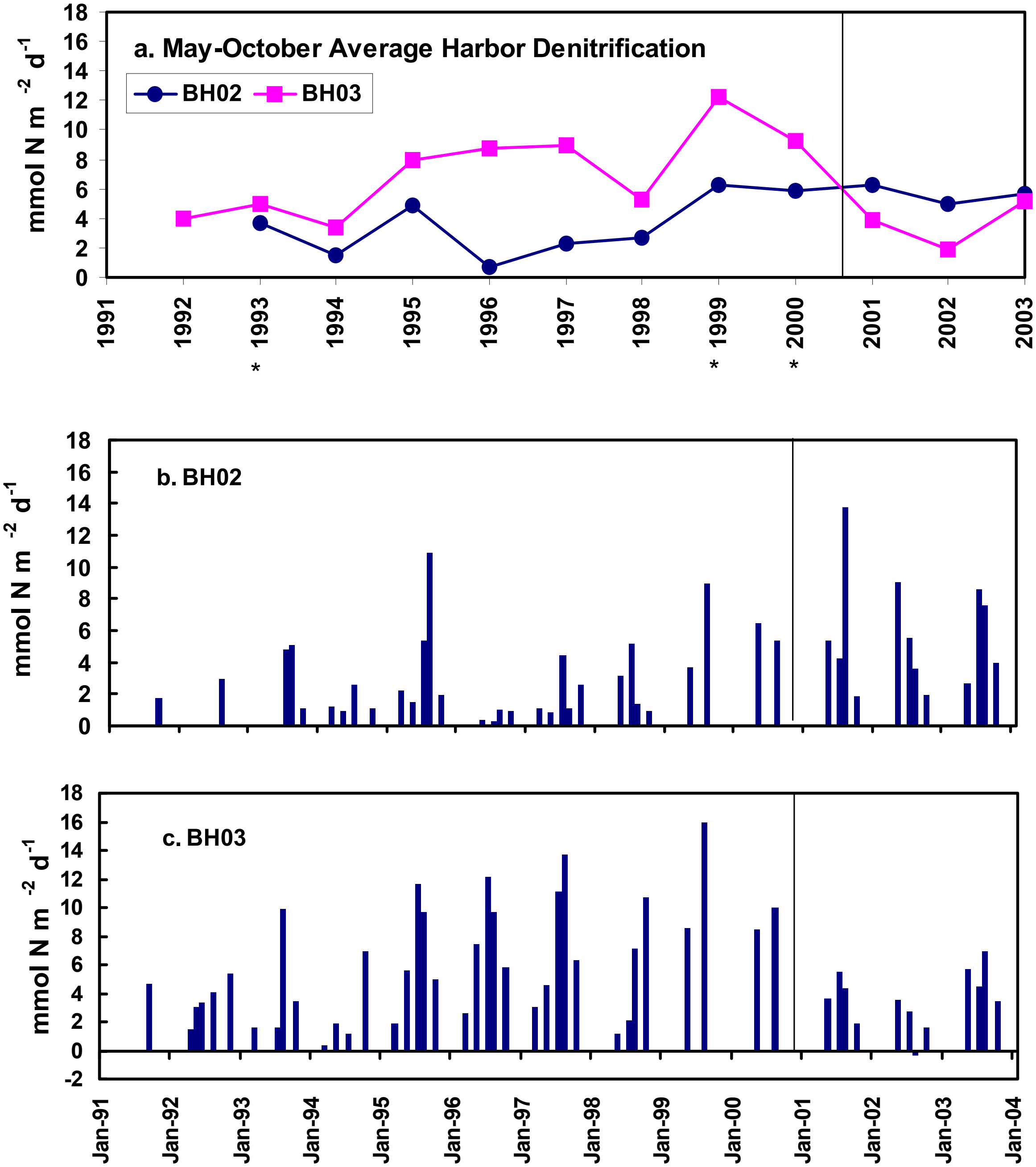



**Figure 20. Denitrification in Boston Harbor: a.) May-October seasonal averages for Station BH02 and BH03 from 1992-2003; * marks years when averages were of three rather than four surveys; b.) survey means for BH02 and c.) BH03 from 1991-2003. Vertical lines mark the transition between baseline and post-relocation measurements.**

RQs were less than 1.0 throughout out the season with the exception of May values just at 1.0 at BH03. RQs at these two stations averaged about 0.8 for the period, the lowest observed at these two stations. These low values would suggest that reoxidation of anaerobic end products was occurring throughout the season; however we did not measure large concentrations of such end products (i.e. sulfides) in the porewater. This pattern is somewhat counter-intuitive, as one would expect more reducing conditions to occur in these warmer months when S.O.D. is higher, with reoxidation occurring in the winter, and at present we have no clear explanation for it.

### 3.5.2 Eh Profiles and Porewater Sulfide

Profiles of reduction potential (Eh) (Fig. 22) taken from within sediment cores during 2003 did not show a consistent seasonal pattern across the four stations as had been the case in 2002. However profiles were not atypical for these stations. In general, Station BH02 had the most reducing sediments, which has been a consistent pattern throughout the monitoring program. The other three stations tend to have more oxidizing sediment due either to bioturbation (BH03 and BH08A) or physical mixing of sediments.

The two southern harbor stations had similar patterns (Fig. 22 c and 22d) in that sediments there were well oxidized through the top 10 cm throughout the sampling period, however high and low values occurred at different times. Below 10 cm, values at times decreased to the point (~ -150mV) where sulfate reduction should occur. In fact, sulfide concentrations of 0.2 mM and 0.6 mM were measured at Station BH08A in July and August, respectively, below 10 cm depth. (July and August are the two months when porewater measurements are made.) Eh measurements in May and October suggested that sulfides should have also been present at depth at this station during those months. At QB01, Eh values also reached levels that would suggest the presence of sulfides in May, July, and October. Measurements made in July confirmed the presence of sulfides below 10 cm depth at a concentration of 0.1mM.

In the northern harbor, Eh profiles varied more across the sampling period (Fig 22a and 22b). At Station BH02, profiles in the top 8-10 cm were quite different from month to month, with the most oxidizing sediments present in May, and most reducing in July. In July, Eh dropped to less than -150mV at a shallow depth of 2-3 cm. Below 10 cm, profiles looked the same across the whole season, leveling out around -150 to -175 mV. In July, sulfides were detected within the top two cm, and reached high concentrations of 3.5 mM below 10 cm. In August, sulfide concentrations were first detected slightly deeper (~4 cm) but reached similar high concentrations of 3.2 mM below 10 cm. Although porewater measurements were not made in May and October, Eh profiles suggested that high concentrations of sulfide would have been present below 10cm in May, and by about 6-8 cm in October. At Station BH03, sulfides were only detected once and at low concentrations, at depth in August. At this time Eh profiles did approach -150. Similar Eh values were reached in May and October. The July profile, however, revealed the most oxidizing sediments of the season for this station, in direct contrast to Station BH02. It should be noted, however that profiles at this station often do not reach the same sediment depth as for the other stations. There is a gravel layer that we often encounter at around 10-12 cm at this station that our probes cannot penetrate.

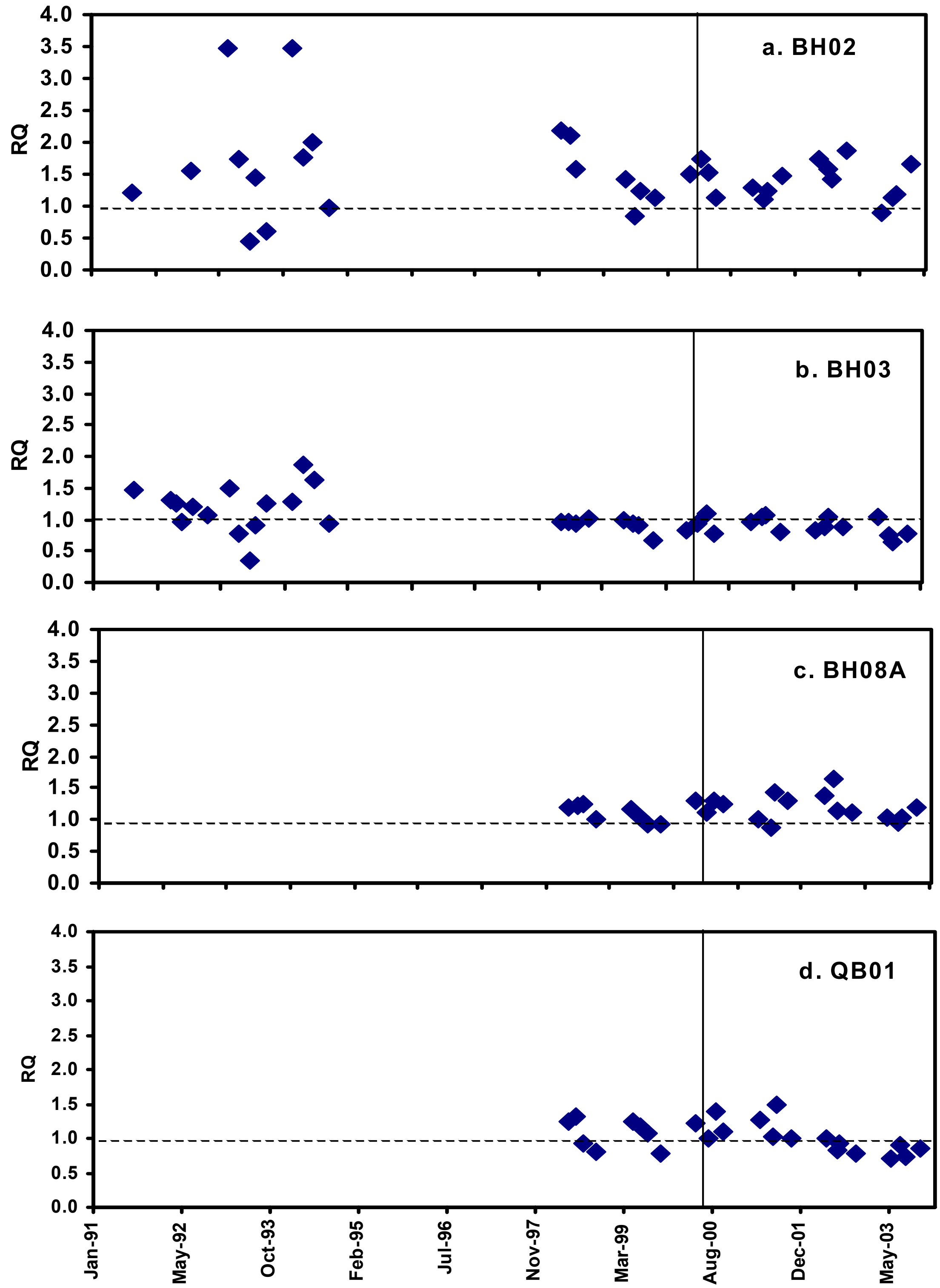



**Figure 21. Changes in respiratory quotient over time at Boston Harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01. The horizontal dashed line marks the ratio at 1:1. The vertical solid line marks the transition from baseline to post-relocation observations.**

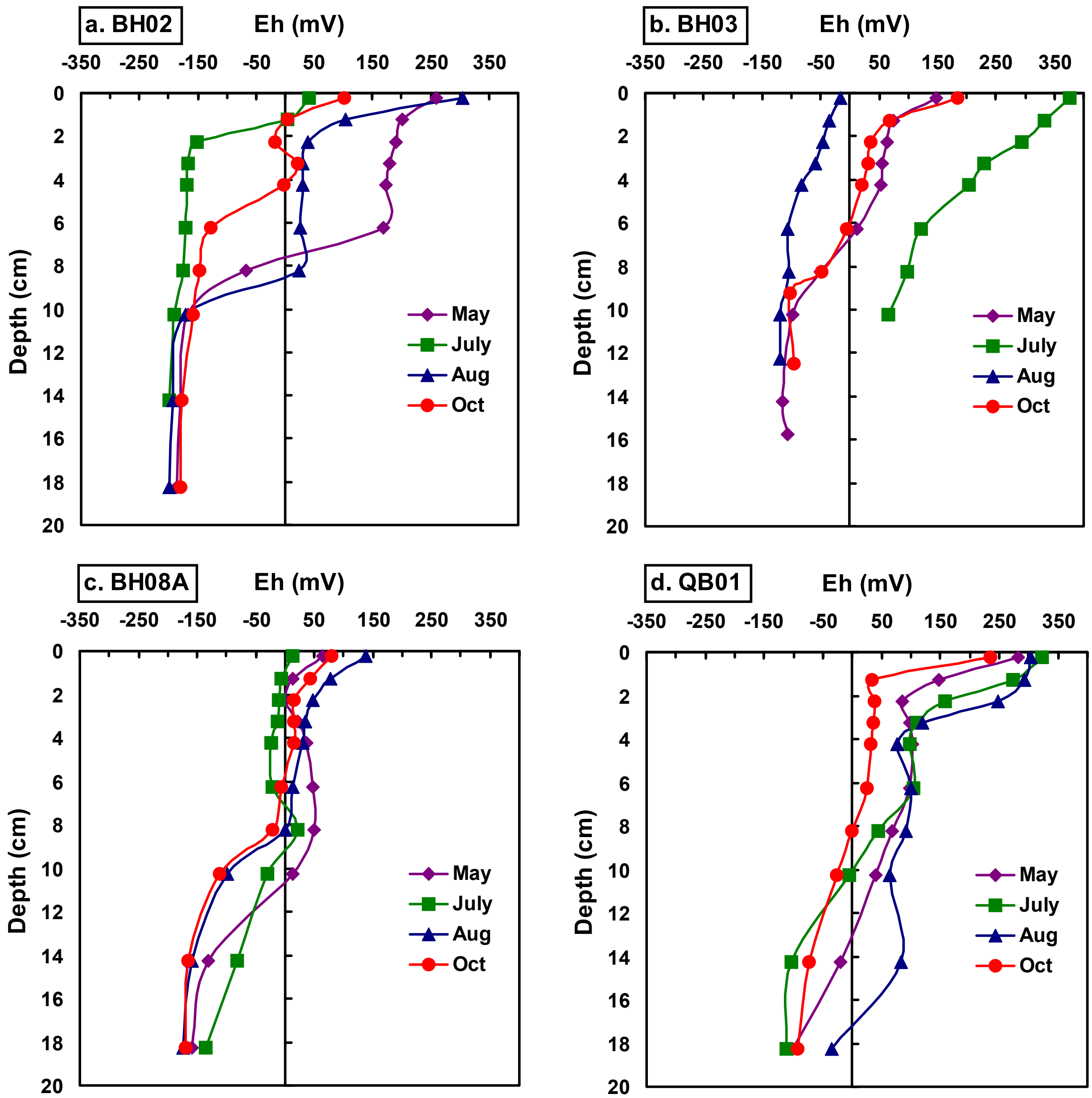
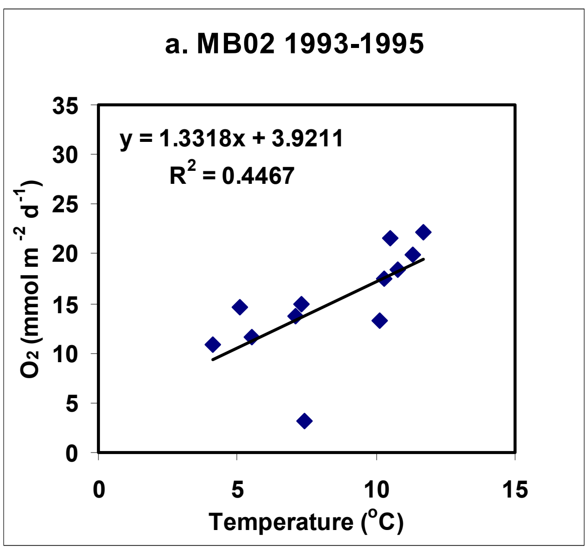



**Figure 22. Eh profiles for May through October, 2003, from Harbor stations a.) BH02, b.)BH03, c.) BH08A, and d.) QB01.**

# 4.0 LINKAGES ACROSS MONITORING DATASETS

We are fortunate and unique among coastal researchers to have this long-term, comprehensive dataset for Boston Harbor and Massachusetts Bay. Equipped with this dataset, we have been better able to assess the annual variability in these systems, which in many cases is larger than our *a priori* assumptions led us to expect. What drives this variability? In the harbor, it is clear that it has been driven by changes in sewage inputs, which had for so long overwhelmed all other influences. With the relocation of the outfall, however, we are beginning to see responses to factors such as local climatology (refer to Section 3.2), and we expect to more clearly discern the influence of Massachusetts Bay. But what drives the patterns we have seen in Massachusetts Bay? By comparing trends across datasets within the monitoring program, we hope to find linkages that will help create a better and more comprehensive understanding of the system. We have begun to try to interpret our benthic flux dataset in terms of trends that have been reported in other parts of the monitoring program.

For example, we have reported a loss of seasonal pattern in the S.O.D. in our three nearfield stations (Section 2.2 and Fig. 23). In investigating this observation, we noticed that early season (May) incubation (bottom water) temperatures seemed to have warmed over the period of the monitoring program. There are at least two reasons that this might reduce the seasonal pattern. Warmer temperatures may have been responsible for larger than usual benthic fluxes through direct stimulation of microbial activity at the time of year when low rates would be expected. Also, the difference between early and late season temperature decreased, likely damping any temperature effect and therefore seasonal pattern. We turned to the water column monitoring dataset (Libby et al, 2004) to look for a trend in bottom water temperatures for Massachusetts Bay. In these data we did, in fact, notice a pattern of warming in winter bottom water temperatures from about 1993 through 2002 (Fig. 24). So here we may have an example of patterns in benthic fluxes being regulated by a region -wide trend in water temperature, which then may also make a link to large-scale climate patterns such as the North Atlantic Oscillation (NAO).



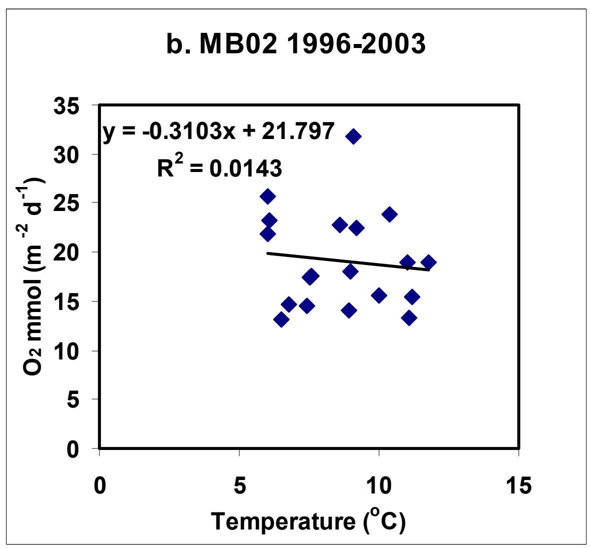




**Figure 23. Representative regressions of oxygen uptake versus temperature at Station MB02 for a. 1993-1995, when temperature explained 45% of variability at this station and b. 1996-2003, when temperature explained less than 2% of variability.**

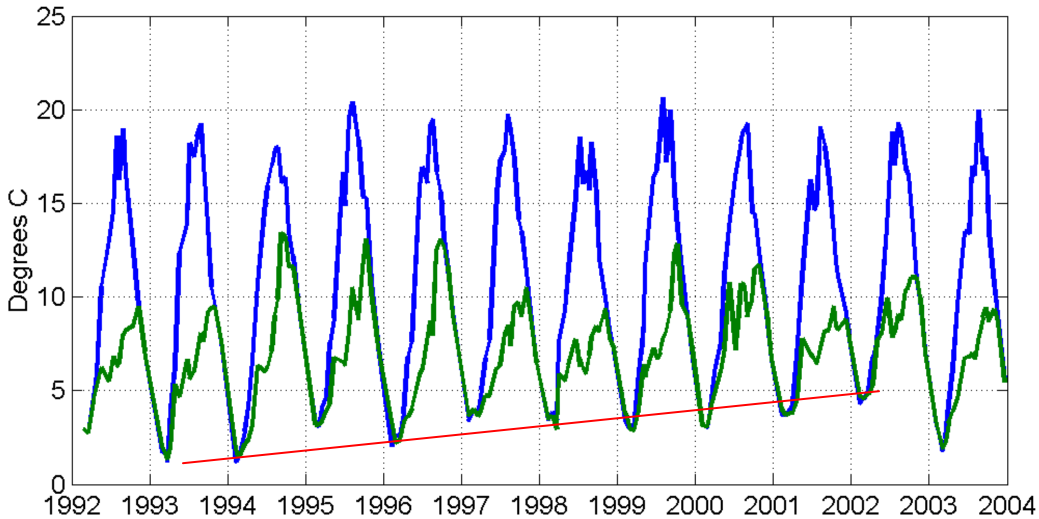



**Figure 24. Near-surface (blue) and near bottom (green) temperature observed in the vicinity of the outfall (taken from *Libby et al.,* 2004). The red line was hand drawn.**

Changes in temperature patterns may have other, system wide effects that would also affect benthic fluxes. In another part of the water column monitoring, a relationship between winter-early spring water temperatures and chlorophyll concentrations during the spring bloom was found. Warm spring temperatures appeared to lead to lower bloom chlorophyll concentrations in Massachusetts Bay (Fig. 25). This pattern was similar to that observed in Narragansett Bay, where 25 years of data have been used to show that warm spring temperatures lead to a weakening or failure of the spring bloom, possibly through the stimulation of grazing (Oviatt et al., 2002). Presumably, a reduction in water column primary production would affect organic matter delivery to the sediments, and therefore benthic fluxes. In fact, annual average water column chlorophyll is correlated with seasonal average sediment pigment inventories (chlorophyll plus phaeophytin)($r^2$ = 0.46). Accordingly, we found that for data through 2002, annual average water column chlorophyll could explain nearly 50% of the variation in the seasonal average nearfield S.O.D. (Fig. 26).

Trends observed in still other parts of the monitoring program may also help explain additional parameters that have been monitored in the benthic flux program. For instance, researchers at USGS observed two large peaks in the percent clay in surface sediments at a station near our Stations MB01 and MB02 during the period from 1990 to 2002 (Bothner, 2002). The larger of the two peaks was observed after a major storm that occurred in December 1992, which resuspended and redeposited sediments from inshore areas to depositional areas offshore. Some of the highest organic carbon content that we have observed at Station MB01 also occurred at this time. We can assume that the source of the organic carbon was the same as for the clay, which was the inshore areas including Boston Harbor.

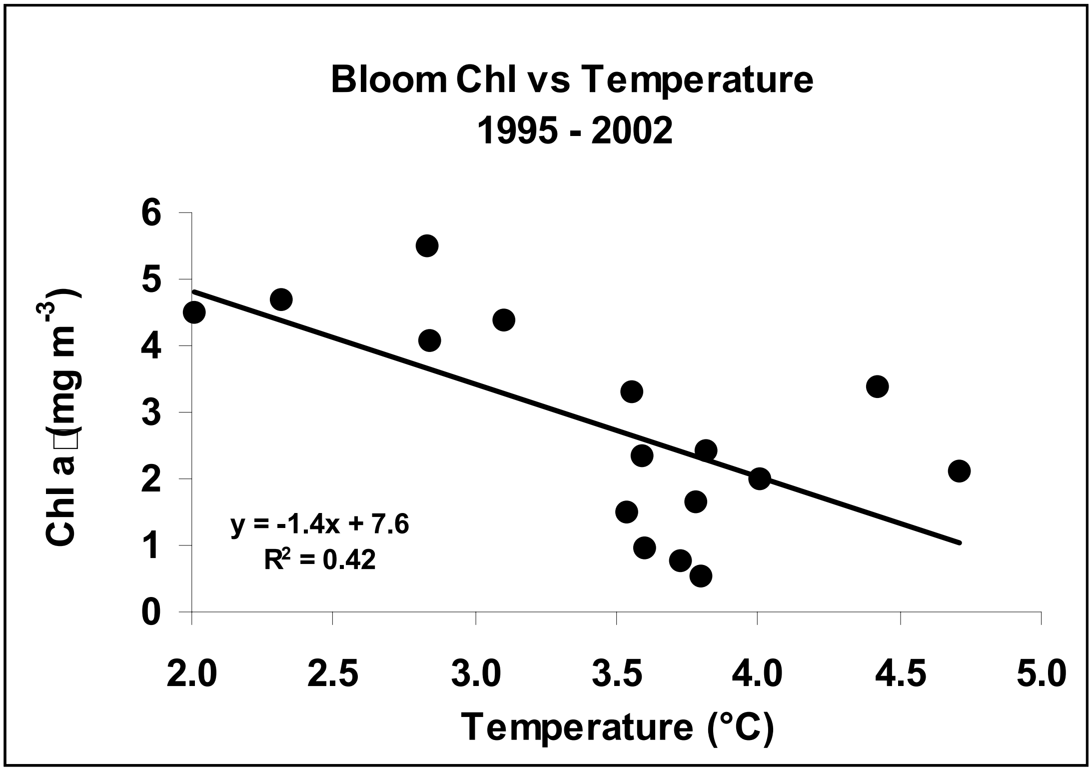



**Figure 25. Relationship between winter-early spring water temperatures and chlorophyll concentrations during the spring bloom (modified from Fig. 4-26A in Libby *et al*. 2003).**

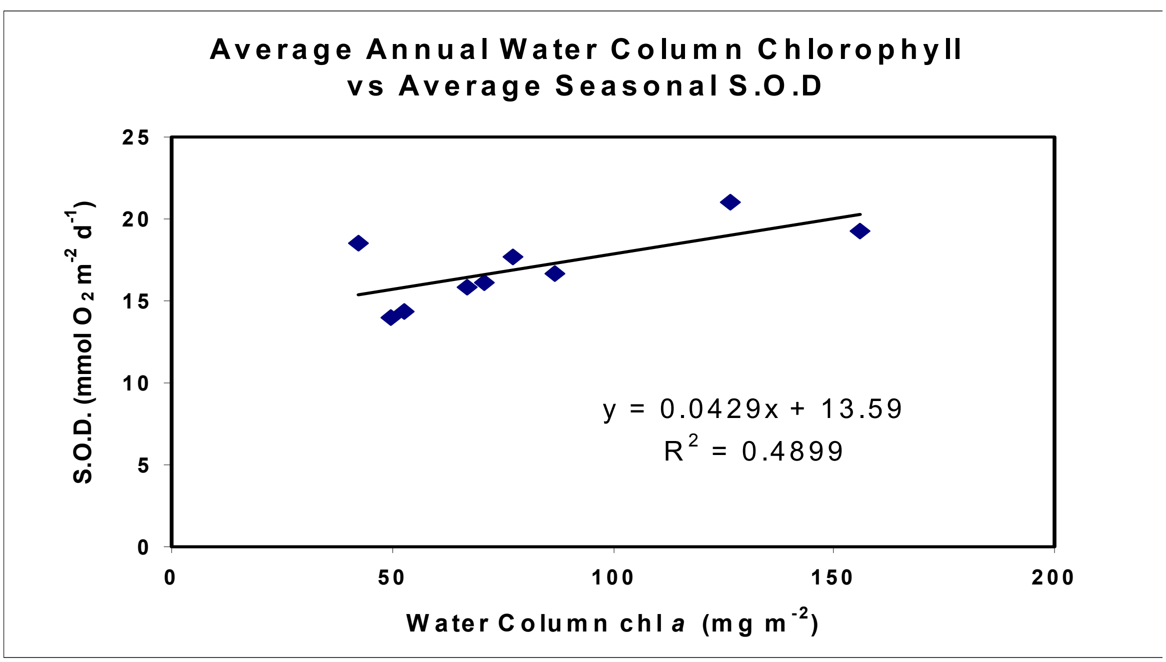



**Figure 26. Relationship between Nearfield water column chlorophyll and S.O.D.**

Some of the higher DIN fluxes we have observed at this site were also observed during this time, presumably fueled by this "new" carbon. The second peak in percent clay was observed during 2001, the year after the ocean outfall became operational. However the origin of this material is unclear and at this time we did not observe any sustained increase in organic carbon content at any station, nor did we observe elevated fluxes.

The 1992 storm also had an effect of infaunal populations. There was a decrease in infaunal abundance during 1993, which seemed to rebound through the 1990s and into the 2000s (Maciolek *et al.,* 2003). The reflection of this pattern in our data may be seen in sediment redox characteristics. In later years, corresponding to increasing abundances, Eh profiles became more positive, indicating more oxic conditions than had been present in earlier years when infauna were less abundant. As evidenced dramatically in Boston Harbor, bioturbation can play a major role in setting redox conditions, and we think that is what is happening in Massachusetts Bay as well. Sediment profile images (Kropp et al, 2002) that show numerous tube dwelling organisms and relatively thick surface oxidized layers support this link. We have also seen some evidence of a direct link between infaunal numbers and S.O.D. At Station MB01, we found a strong correlation ($r^2 = 0.78$) when August abundance, as number of individuals per grab, was compared to August rates of S.O.D. (Tucker *et al.,* 2003).

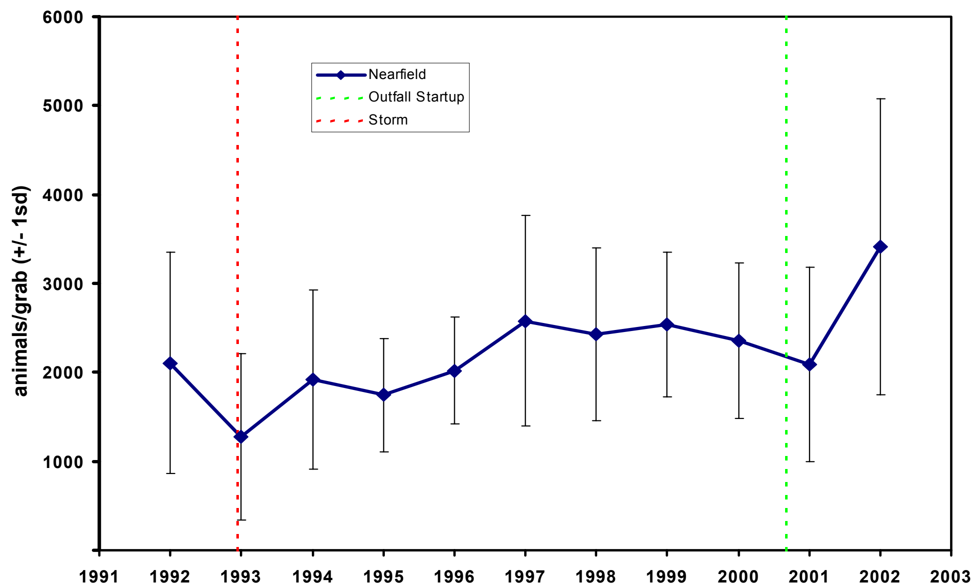



**Figure 27. Long term trend in infaunal abundance (adapted from Maciolek *et al.,* 2003)**

These linkages between data sets are intriguing, and we hope to further explore them and uncover others as the monitoring program continues.

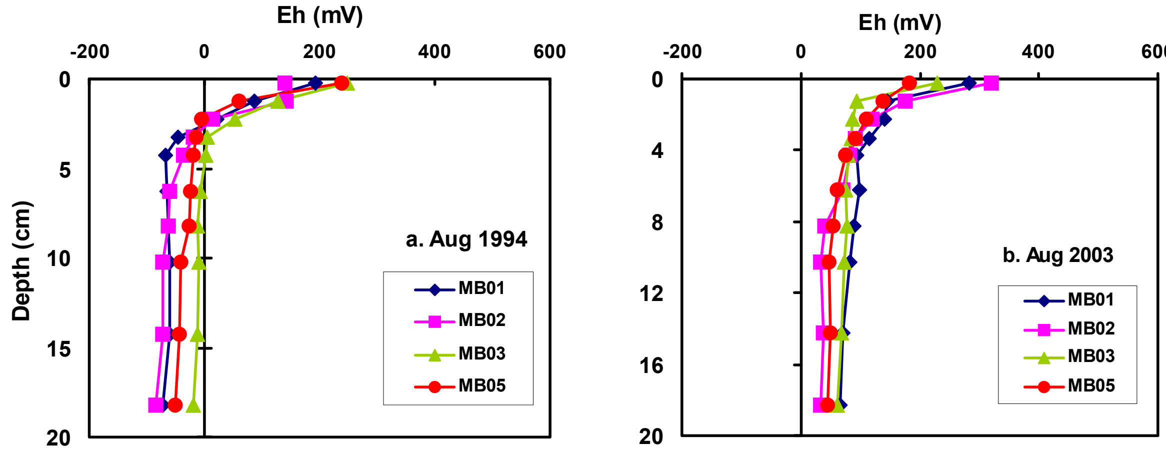



**Figure 28. Eh profiles in nearfield sediments from a.) August, 1994 and b.) August, 2003.**

# 5.0 SUMMARY

## 5.1 Massachusetts Bay

At the heart of the questions for benthic flux monitoring was the concern that the diversion of effluent from Boston Harbor to Massachusetts Bay might increase organic matter loading to the nearfield area, thereby enhancing benthic respiration and nutrient fluxes. Higher rates of benthic respiration (or sediment oxygen demand) might lead to lower oxygen levels in the sediments and water column. Various changes in nutrient fluxes might occur, including shifts in the quantity and form of nitrogen released to the overlying water and in the ratio of nutrients released.

To date, we have observed little or no indication of changes related to the ocean outfall. For the third year since the outfall became operational, we have seen inconsistent and small changes in measures of sediment organic matter, and rates of benthic respiration and nutrient fluxes have been well within or lower than typical baseline observations.

Any increase in organic matter content of surface sediments in the nearfield that was noted in 2001 and 2002 did not continue in 2003. At Station MB03, where the largest apparent increase had occurred in 2001, organic carbon content dropped slightly from 2002 levels of 1.4% to 1.1% in 2003. A similar decrease was observed at MB02, while at MB01 there was no change. Similarly, there was little or no change at Stellwagen Station MB05. Nearfield C/N ratios of sediment organic matter were typical of baseline in 2003 after apparently aberrant low and high values in 2001 and 2002, respectively.

Sediment chlorophyll at nearfield stations in 2003 was typical of baseline and similar to the previous year. The inventory over the top 5 cm of sediment averaged over the season and across the three stations was 5.4 ug $cm^{-2}$. Ratios of carbon to nitrogen were also typical, averaging about 11.7. Neither parameter suggested atypical deposition of fresh phytoplankton material to the benthos.

In 2003, there was no indication of increased SOD or increased nutrient fluxes from nearfield sediments. Fluxes were generally in the mid to low end of baseline observations. There was little relationship to temperature in any of these fluxes, and in fact nutrient fluxes tended to decline over the season rather than increase with temperature. Other controls on these fluxes most likely include carbon deposition and infaunal abundance, although simple linear relationships are weak. Fluxes at station MB05 were quite typical, and at this station, where the range in temperature is small, sediment chlorophyll may play a relatively more important role in regulating fluxes.

Although the rates of sediment oxygen demand would be high enough to affect the seasonal drawdown of oxygen in the water column in the nearfield if the water column were stagnant, the rate of water renewal from the Gulf of Maine is sufficient to nearly completely override the effect of local benthic metabolism. The renewal rate of the bottom water, which is determined by wind and other climatological factors, determine the timing and strength of the seasonal oxygen drawdown.

Fluxes of DIN in 2003 were in the mid to low end of the range observed during baseline monitoring. Rates were at times characterized as uptake rather than release. For the second year, at Station MB03 we observed very low or negative (uptake) fluxes of $NH_4^+$, such that the seasonal average DIN efflux was comprised entirely of $NO_3^-$. This was also the case in 2002; however the $NH_4^+$, uptake was nearly twice as large in that year. At MB01 and MB02 the seasonal average efflux was comprised of 45% and 70% $NO_3^-$, respectively. These low DIN fluxes result in a contribution of nitrogen amounting to less than 6% of the requirements for Nearfield primary production. At station MB05, we observed moderate effluxes of $NO_3^-$ from and small uptake of $NH_4^+$ into the sediments in 2003.

In 2003, $PO_4^-$ fluxes were low compared to the baseline range and often negative, particularly in October in the Nearfield and in August and October at Station MB05. Silica fluxes were moderate compared to baseline in the Nearfield during most of the season, but very low in October. At MB05, Si fluxes were variable, with moderate to high rates in May and July, very weak and atypical fluxes in August, and low fluxes in October.

Denitrification rates in the nearfield were typical of baseline observations. Due to the low DIN flux, denitrification accounted for between about 80% and 100% of the total nitrogen (DIN + $N_2$) flux at these stations.

There was no indication of decreased sediment oxidation in any of our measurements. Respiratory quotients were very close to 1.0, Eh profiles indicated oxidizing sediment conditions, and dissolved sulfides were not detected.

## 5.2 Boston Harbor

Although the monitoring questions were written to address concerns in the nearfield of Massachusetts Bay, they may also be used to guide our evaluation of changes observed in Boston Harbor. For the harbor, however, we must think of the questions in terms of the effects of reductions in organic matter loading. Certainly the diversion of sewage effluent away from the harbor has had noticeable effects on nutrient loading. Reductions in organic matter loading have been more subtle, however, because the most significant reductions in organic matter loading began much earlier with the cessation of sludge disposal and subsequent treatment improvements.

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring, including the three years since diversion. Decreases in TOC have been most pronounced at Stations BH03, BH08A, and QB01 whereas TOC content at station BH02 has varied. The large range of values observed across the four stations early in the monitoring program has narrowed in the past four years (2000-2003).

Another measure of organic matter, sediment chlorophyll, was about average for two of the stations in 2003, BH03 and BH08A, but higher than usual at two others, BH02 and QB01. Observations of benthic diatoms and sediment profiles of chlorophyll suggest that *in situ* production is important at these sites.

Sediment oxygen demand in 2003 was within baseline observations. There was little variability across stations in seasonal averages, which had increased somewhat from the low rates observed in 2002. Fluxes of DIN and PO4 were also within baseline, but increased somewhat over 2002 rates at BH02 and BH08A while staying the same or decreasing slightly at BH03 and QB01. Fluxes of dissolved silica were much more variable across stations in 2003, and Station BH08A had fluxes greater than observed during baseline for most of the sampling period. For most of these parameters, Station BH03, which in the early days of the program had by far the largest fluxes, now most closely resembles Station QB01, which has traditionally had the smallest fluxes. Except for the DSi fluxes, we continue to note that the large variability between stations and years that was observed early in the monitoring program has largely disappeared.

We do not know whether the large DSi fluxes were related to water column deposition of diatom tests or whether they were derived from benthic forms. Benthic diatoms were noted in Harbor sediments during the year; however, our casual observations do not always match periods and sites of large DSi fluxes. More concerted effort to detect the abundance of these organisms would be needed to make the connection.

Using post-relocation rates of primary production at the mouth of the harbor and seasonal averages of DIN and $PO_4^-$ fluxes, we calculate that these fluxes could each contribute about 35% of phytoplankton N and P requirements. Silica fluxes from the sediment were large enough in 2003 to support nearly all primary production. With the reduction in nutrient inputs to the harbor after the relocation of the outfall, these contributions may become significant, however oceanic and remaining terrestrial inputs still exceed the needs of primary production.

Similarly, the decrease in nitrogen loading to the harbor may shift the role of denitrification in the overall N budget. Although denitrification rates are equivalent to the remaining terrestrial loading, oceanic inputs remain the overwhelming source to the system, and decrease the N sink provided by denitrification to less than 10% of total inputs.

Patterns in redox measurements varied across stations. At BH02, respiratory quotients were somewhat elevated, and further evidence of reducing conditions was supplied by Eh measurements and high concentrations of dissolved sulfides at depth in sediment cores. These conditions are not atypical for this station, but they indicate the relative importance of anaerobic process at this site continues to vary from year to year. Conditions at Station BH08A were less reducing than in the previous year, and sulfides were detected only in the deepest sections of cores. Respiratory quotients averaged the theoretical 1.0 at this station this year. The reappearance of amphipods at this site probably contributed to the return to more oxic sediment conditions that are typical for this station. At BH03 and QB01, RQs were less than 1.0. Eh profiles were generally more positive than at the other two stations, and sulfides were detected only at very low levels.

The decrease in the magnitude of benthic fluxes, of oxygen as well as nutrients, in addition to the dramatic decrease in variability in fluxes across stations suggests that the harbor benthic environment has progressed significantly along the path of "recovery". However, we still see variability in redox parameters, especially at station BH02 but now also at station BH08A. The role that infauna has played has been significant in areas like BH08A and BH03, and the status of those benthic communities will no doubt continue to mediate changes in benthic nutrient cycling.

## 5.3 Cross-System Overview

At this point in the monitoring program, it is interesting to take a step back from the details of a given year or system, and look at what we have observed in a broad sense across the entire Boston Harbor-Massachusetts Bay system. In the following four graphs, we have shown station averages of oxygen (Fig. 29a) and nutrient fluxes (Fig. 29 b-d) for Boston Harbor, (4 stations), Massachusetts Bay (3 stations) and Stellwagen Basin (1 station) for all years sampled. In these graphs, several patterns are obvious.

First, in all cases, all fluxes in Boston Harbor are much larger than those in Massachusetts Bay and Stellwagen Basin, and often those from Massachusetts Bay are larger than those in Stellwagen. This pattern follows that of increasing water column depth, which is often used as a proxy for organic matter content. Indeed, organic matter content is nearly twice as high in Boston Harbor as in Massachusetts Bay (2.6% TOC, n=41, range 1.3%-4.1%, and 1.3%, n=29, range 0.6-2.3% for the harbor and bay, respectively). However, our Stellwagen Basin station typically has a slightly higher organic carbon content (1.5%, n=9, range (1.2-1.7) than do those in Massachusetts Bay. It may be that the carbon in Stellwagen Basin is of poorer quality than that in the shallower bay stations, having been exposed to water column processing during a longer settling time. Alternately, year-round lower temperatures in the deeper bottom waters of Stellwagen Basin may simply slow biological processes. In the cases where fluxes in Mass Bay and Stellwagen are equivalent (i.e. $PO_4^-$ and DSi), chemical and physical processes may be as important as biological processes in determining fluxes, and therefore not as sensitive to temperature.

It is also obvious that inter-annual variability in the harbor fluxes has been much greater than in the bay and basin Intra-year variability has also been larger in the harbor as compared to the bay (cannot assess this for Stellwagen given the single station). This variability in the harbor is not surprising given that station characteristics have been much more variable than for bay stations. These characteristics include 1.) organic carbon content, which varied across stations and time, especially in the early years of monitoring, and resulted in wide ranges in fluxes and redox conditions; 2.) presence or absence of infauna, especially the amphipod mats, which in 1993 resulted in some of the highest S.O.D. ever reported; 3.) and proximity to various types of sewage inputs. Of course, all of these are inter-related.

Rates and variability in the harbor have decreased over time, in some cases nearing bay rates. We attribute this decrease to reductions in sewage inputs to the harbor. Now that effluent discharge has been relocated offshore, we are beginning to see variability in the harbor driven by other, large scale processes such as climatology. For example the very low fluxes observed during 2002 may be attributable to an anomalously dry year that caused low freshwater (and therefore land-derived nutrient) discharge to the harbor. In contrast, we have observed no indication of increased fluxes or variability in the bay since the relocation of the effluent discharge.

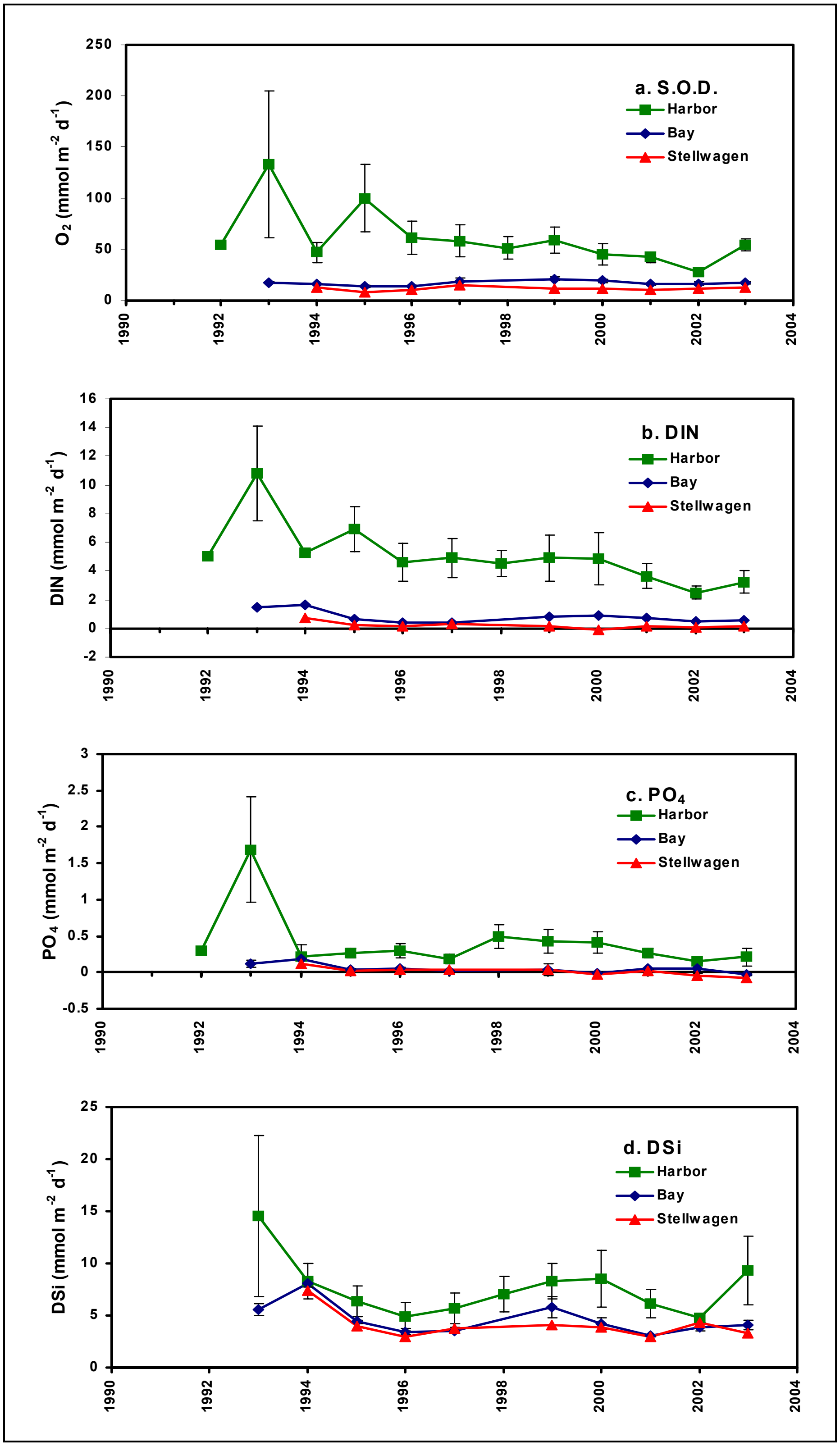



**Figure 29. Survey averages of a.) S.O.D., b.) DIN flux, c.) PO4 flux, and DSi flux for Boston Harbor (■), Massachusetts Bay (♦), and Stellwagen Basin (▲). Error bars represent the standard error of the mean.**

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# Appendix A

**Station names, survey IDs, date of survey, station locations, near-bottom water sampling depth, temperature, dissolved oxygen (D.O.) and salinity for Boston Harbor and Massachusetts Bay stations visited in 2003.**

# Appendix A

*Station names, survey IDs, date of survey, station locations, near-bottom water sampling depth, temperature, dissolved oxygen (D.O.) and salinity for Boston Harbor and Massachusetts Bay stations visited in 2003.*

| Station | Survey ID | Date | Latitude | Longitude | Depth (m) | Temp (oC) | D.O. (mg.L$^{-1}$) | Salinity (psu) |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| BH02 | NC031 | 05/20/03 | 42.34370 | -71.00217 | 8.1 | 11.4 | 8.92 | 30.2 |
| | NC032 | 07/14/03 | 42.34417 | -71.00252 | 8.2 | 15.8 | 8.11 | 31.1 |
| | NC033 | 08/11/03 | 42.34375 | -71.00232 | 9.9 | 15.2 | 7.98 | 32.0 |
| | NC034 | 10/29/03 | 42.34373 | -71.00224 | 9.0 | 10.7 | 8.34 | 31.8 |
| | | | | | | | | |
| BH03 | NC031 | 05/20/03 | 42.33022 | -70.96169 | 6.1 | 11.8 | 9.01 | 29.7 |
| | NC032 | 07/14/03 | 42.33118 | -70.96167 | 8.2 | 16.2 | 8.15 | 31.0 |
| | NC033 | 08/11/03 | 42.33062 | -70.96175 | 9.3 | 14.2 | 8.25 | 32.4 |
| | NC034 | 10/29/03 | 42.33058 | -70.96194 | 7.5 | 10.6 | 8.29 | 32.5 |
| | | | | | | | | |
| BH08A | NC031 | 05/20/03 | 42.29108 | -70.92216 | 6.5 | 11.5 | 9.06 | 30.4 |
| | NC032 | 07/14/03 | 42.29100 | -70.92185 | 8.5 | 15.9 | 8.40 | 31.8 |
| | NC033 | 08/11/03 | 42.29103 | -70.92190 | 10.1 | 13.9 | 8.31 | 32.7 |
| | NC034 | 10/29/03 | 42.29110 | -70.92208 | 7.0 | 10.9 | 8.54 | 32.0 |
| | | | | | | | | |
| QB01 | NC031 | 05/20/03 | 42.29352 | -70.98785 | 2.8 | 12.8 | 8.70 | 29.2 |
| | NC032 | 07/14/03 | 42.29340 | -70.98797 | 4.6 | 16.5 | 7.91 | 31.3 |
| | NC033 | 08/11/03 | 42.29337 | -70.98777 | 5.7 | 16.6 | 7.83 | 32.2 |
| | NC034 | 10/29/03 | 42.29357 | -70.98783 | 2.0 | 11.3 | 8.61 | 30.6 |
| | | | | | | | | |
| MB01 | NC031 | 05/19/03 | 42.40295 | -70.83730 | 31.6 | 5.8 | 7.70 | 31.2 |
| | NC032 | 07/15/03 | 42.40253 | -70.83712 | 33.0 | 7.4 | 9.01 | 32.3 |
| | NC033 | 08/12/03 | 42.40305 | -70.83746 | 31.4 | 7.3 | 7.70 | 33.4 |
| | NC034 | 10/28/03 | 42.40325 | -70.83735 | 33.0 | 9.5 | 7.38 | 32.6 |
| | | | | | | | | |
| MB02 | NC031 | 05/19/03 | 42.39253 | -70.83448 | 32.6 | 5.8 | 8.88 | 31.5 |
| | NC032 | 07/15/03 | 42.39247 | -70.83455 | 33.4 | 7.8 | 8.84 | 33.0 |
| | NC033 | 08/12/03 | 42.39240 | -70.83477 | 32.7 | 7.4 | 8.28 | 32.8 |
| | NC034 | 10/28/03 | 42.39238 | -70.83450 | 34.4 | 9.6 | 7.46 | 32.3 |
| | | | | | | | | |
| MB03 | NC031 | 05/19/03 | 42.34787 | -70.81618 | 32.0 | 5.8 | 9.52 | 32.2 |
| | NC032 | 07/15/03 | 42.34790 | -70.81641 | 32.2 | 7.8 | 8.70 | 33.8 |
| | NC033 | 08/12/03 | 42.34832 | -70.81713 | 32.3 | 7.8 | 8.82 | 33.5 |
| | NC034 | 10/28/03 | 42.34798 | -70.81618 | 31.3 | 9.3 | 7.09 | 32.8 |
| | | | | | | | | |
| MB05 | NC031 | 05/19/03 | 42.41640 | -70.65199 | 47.5 | 4.6 | 10.89 | 32.2 |
| | NC032 | 07/15/03 | 42.41620 | -70.65401 | 34.9 | 6.5 | 9.40 | 33.3 |
| | NC033 | 08/12/03 | 42.41643 | -70.65215 | 44.3 | 6.4 | 8.57 | 33.4 |
| | NC034 | 10/28/03 | 42.41648 | -70.65213 | 46.2 | 8.1 | 7.15 | 32.8 |

# Appendix B

## Comparison of Two Denitrification Methods

From 1992 through 2003, a method developed by Barbara Nowicki at the University of Rhode Island was used to measure denitrification. A detailed description of sampling and measurement methods for this technique is given in Nowicki *et al*. (1997) and in the CW/QAPP (Tucker and Giblin, 1998).

Briefly, for each estimate of $N_2$ flux, two sediment cores are incubated at ambient temperature. Prior to the flux incubation, the overlying water and headspace in one core (the oxic core) is sparged with a mixture of 80% Helium (He):20% $O_2$ in order to maintain an oxic environment while lowering the background level of $N_2$ within the core. The overlying water and headspace in the other core (the anoxic core) is sparged with 100% He to remove both $O_2$ and $N_2$. The anoxic core provides an abiotic control for $N_2$ diffusing from the porewater and conditions under which coupled nitrification/denitrification is prevented. During the incubation, $N_2$ gas within the headspace of both cores is monitored by drawing off samples of the headspace and analyzing it on a gas chromatograph with a thermal conductivity detector. Denitrification is calculated as the difference in $N_2$ production in the oxic and anoxic cores.

A newer technique for measuring denitrification uses a quadrupole mass spectrometer equipped with a membrane inlet (membrane inlet mass spectrometer or MIMS) to precisely measure $N_2$/Argon (Ar) ratios of dissolved gases in water samples (Kana *et al*., 1998). Dinitrogen gas concentrations are affected by both biological and physical processes, whereas Ar is affected only by physical processes. Deviations from equilibrium ratios of these two gases therefore reflect biological processes acting on the $N_2$. The mass spectrometer is capable of measuring very small deviations in this ratio, thereby providing a very sensitive and precise method for measuring denitrification. Whereas gas chromatography offers a precision of measurement for gas concentrations on the order of 0.3-1%, the mass spectrometer yields a precision of 0.05% for gas ratios.

Importantly for our benthic flux studies in Boston Harbor and Massachusetts Bay, samples for dissolved gas analysis (DGA) are taken from the same cores as are used for flux measurements, allowing for direct comparison of fluxes from a given core. Four to five samples are taken over the incubation time course, simultaneously with the nutrient flux samples.

In 2003, we used both techniques. Results indicate that the two techniques are not directly comparable. (Fig. B1). Most of the GC results are higher than MIMS. Other GC results are lower, perhaps reflecting variation in one or both techniques.

For a number of reasons, the GC technique may be expected to have higher or more variable results than the MIMS technique. One reason is that bio-irrigation by benthic invertebrates leads to faster abiotic degassing of $N_2$ from sediments in the oxic core than in the anoxic core (in which the animals would have been killed). Another reason is that during the long incubations used for the GC technique (typically 5 days), $NH_4^+$ builds up in both the porewater and the overlying water. Higher porewater ammonium leads to higher nitrification, which in turn leads to higher coupled nitrification/denitrification (Giblin, unpublished data). The MIMS method has a shorter incubation time of 1-2 days (the same as the nutrient flux cores), which results in less build-up of $NH_4^+$ over the course of the incubation.

The GC technique is also very labor intensive. It takes about 7 person hours for each denitrification rate result. Time constraints limit the number of measurements, which limits spatial and temporal coverage and our ability to do replicate measurements. The MIMS technique, in comparison, takes under one fourth of the time for each denitrification result. The MIMS technique does require greater care in sample handling and has stricter tolerances for changes in temperature and pressure. Nevertheless, its benefits out-weigh these difficulties enough for this technique to have become the preferred technique in the wider scientific community.

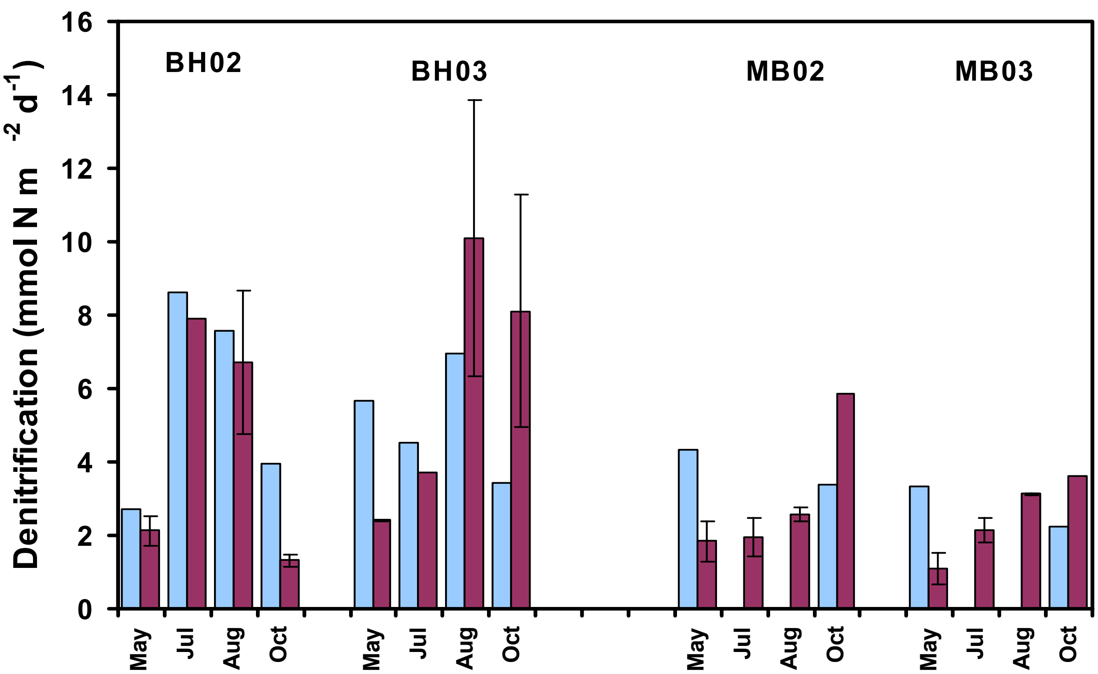


**Fig. B1. Denitrification rates as measured by the GC technique (light blue bars) and the MIMS technique (dark red bars) for Boston Harbor Stations BH02 and BH03 and Massachusetts Bay Stations MB02 and MB03. GC data are not available for the Massachusetts Bay Stations in July and August. Error bars on the MIMS data represent the standard error of the mean of duplicate cores; where error bars are not present, results from only one core were used. There is no error estimate for the GC data.**

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