# 2006 Annual benthic nutrient flux monitoring report

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# 2006 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.

In 2006, physical/climatological factors that affected Massachusetts Bay were not as dramatic as the storms of the previous year, but they were important. The relatively quiet conditions were favorable for the development of a large winter/spring (largely diatom) bloom. It was also a very wet year, with record-high river discharge in May, along with overall high discharge for the year, which presumably carried significant load of terrestrially derived nutrients, organic matter, and fresh water to the system. In July, strongly upwelling-favorable conditions likely contributed to the unusual subsurface summer chlorophyll bloom that was observed south of the outfall.

As a nearfield average, organic matter measured as TOC in 2006 was typical at 1.1%. Although two of the stations (MB02 and MB03) seem to have been varying up and down together since 2002, the third station, MB01, has been slowly declining over the same period. Average TOC at this station was only 1.0%, and was only lower in 1999 (0.9%). In contrast, there has been little change in TOC at our deeper, Stellwagen Basin station. Here the TOC averaged 1.6% for the season, very similar to the previous five years. We have detected no change in TOC between the pre- and post-diversion periods at any of the stations.

Inventories of chlorophyll *a* in nearfield sediments in 2006 were among the highest observed during the monitoring period. Highest inventories occurred in May, reaching 13.5µg $cm^{-2}$ at Station MB03. These high inventories included very high concentrations present at the sediment surface in May at all stations, averaging 10.5 µg $cc^{-1}$ (about twice the usual concentration), and presumably resulting from the deposition of the large winter/spring diatom bloom. Similarly, an elevated signal in July at Station MB03 originated from the summer, subsurface bloom that was present in the water column above this station. At the Stellwagen station, chlorophyll *a* inventories were much lower than in the nearfield, averaging about 2.5 µg $cm^{-2}$ but typical for this station. Even so, some expression of the two phytoplankton blooms was suggested by slightly elevated surface concentrations in May and July. There has been no change in average sediment chlorophyll content since the relocation of the outfall.

Rates of SOD in 2006 were typical. The average for the May to November sampling period for the nearfield stations was 15.6 mmol $m^{-2}$ $d^{-1}$, whereas the baseline mean is 17.2 mmol $m^{-2}$ $d^{-1}$. Rates varied only narrowly over the season, ranging from 12.2 to 20.7 mmol $m^{-2}$ $d^{-1}$. At Stellwagen Station MB05, seasonal average SOD was 12.2 mmol $m^{-2}$ $d^{-1}$, lower than the nearfield average but nearly identical to the previous year. The baseline average for this station is 11.6 mmol $m^{-2}$ $d^{-1}$.

Fluxes of DIN in 2006 were also quite typical. The seasonal average across the nearfield stations was 0.5 mmol $m^{-2}$ $d^{-1}$ as compared to a baseline average of 0.9 mmol $m^{-2}$ $d^{-1}$. The seasonal average for each station was very similar, but included uptake of DIN (primarily $NH_4^+$) at Station MB03 in July and MB02 in October. $NO_3^-$ comprised on average 36% flux, much less than in the previous year, but more consistent with typical conditions. At station MB05, average DIN flux for 2005 was 0.25 mmol $m^{-2}$ $d^{-1,}$ the same as the baseline mean. At this station, $NO_3^-$ comprised 57% of the seasonal average efflux.

In 2006, $PO_4^-$ fluxes at the nearfield stations were characteristically small and/or negative, resulting in a small seasonal average uptake of 0.02 mmol $m^{-2}$ $d^{-1}$ compared to a baseline mean efflux of 0.06 mmol $m^{-2}$ $d^{-1}$. At Station MB05, the seasonal average flux was negligible (< 0.01 mmol $m^{-2}$ $d^{-1}$).

Average nearfield Si flux were 3.5 mmol $m^{-2}d^{-1}$ compared to the baseline average of 5.1 mmol $m^{-2}d^{-1}$ , and varied little across stations. At MB05, Si fluxes in 2006 were 4.6 mmol $m^{-2}d^{-1}$ , quite typical as compared to the baseline average of 4.3 mmol $m^{-2}d^{-1}$.

The potential contribution of nutrients recycled in the benthos to water column primary production remained small in 2006. Seasonal average nutrient fluxes compared to annual average primary production indicated that the DIN flux could account for less than 5% of primary production, and since there was average uptake of $PO_4^-$, there was no contribution of this nutrient. Dissolved silica could contribute about 34% of phytoplankton requirements. There has been no change in the potential contributions between pre-relocation (1995-1998) and post-relocation periods (2001-2006). Those comparisons are (pre- vs. post-) 3.7% vs. 4.3% for nitrogen, and 24% vs. 26% for silica. For the years with average efflux of PO4-, the potential contribution was 0.04% for both periods.

The average denitrification rate for 2006 at the two nearfield stations where it has traditionally been measured was 2.2 mmol N $m^{-2}d^{-1}$ , very similar to the baseline mean of 2.7 mmol N $m^{-2}d^{-1}$ . At the third nearfield station, the seasonal average was lower 1.4 mmol N $m^{-2}d^{-1}$. At the Stellwagen station the rate was also 1.4 mmol N $m^{-2}d^{-1}$. In 2006, denitrification accounted for 78% of the average total inorganic nitrogen (DIN + $N_2$) flux at the nearfield stations, and 86% at the Stellwagen station.

There was no indication of decreased sediment oxidation in any of our measurements. Respiratory quotients ranged from 1.0 to 1.2 in the nearfield and at the Stellwagen station was 0.85. Eh profiles indicated oxidizing sediment conditions.

There has been no indication of increased SOD or increased nutrient fluxes from nearfield sediments. Table 2 shows a summary of pre- (1993-2000) and post- (2001-2006) relocation fluxes. Instead, these data trend towards decreases especially for $NH_4^+$ (and therefore DIN) and Si fluxes. Decreases in the other data have been small compared to the variability, and we would suggest there has been no real change in SOD, $NO_3^-$ fluxes, $PO_4^-$ fluxes or denitrification.

**BOSTON HARBOR**

The diversion of wastewater disposal from the mouth of Boston Harbor to the offshore location was the final step in minimizing the impacts of the Deer Island Treatment Facility on the harbor, but recovery in the harbor began before this event as various stages of treatment improvements were initiated. In particular, reductions in solids loading to the harbor were very significant to the benthic community, contributing to decreases in sediment organic carbon that were observed well before outfall relocation. Very high rates of benthic respiration "burned off" much of the carbon stores within the sediments, and were enhanced by the bioturbating effects of the *Ampeliscid* amphipod community that bloomed in the harbor during this period. With the diversion, a large source of nutrients to the water column was removed, leading to decreases in primary production, and thereby further decreases in inputs to the sediments. The cumulative effects are that now, six years after outfall relocation, organic carbon content of the sediments, benthic respiration, and other nutrients have seemingly stabilized at a level quite typical of many coastal marine environments.

In 2006, the total organic carbon content (TOC) at our four stations was very similar, ranging only from 1.7% to 2.3%. At two stations, BH02 and BH03, these values represented slight increases from the previous year, and marked the first year that the trend at these stations has not continued to decline. AT Station BH03, coarse sediments and the absence of amphipods had been noted for 2004-2005. In August and October 2006, field observations recorded a return to muddier sediments, and amphipods, though not mats, were present. Decreases in TOC from the very high values in the early 1990s seem to reflect the step-wise reductions in solids loadings that resulted from treatment improvements. This pattern was followed most closely at Station BH03, followed by BH08A and QB01, whereas TOC content at station BH02 has varied. Along with reductions in TOC, the large range of values observed across the four stations early in the monitoring program has narrowed in the past several years (2000-2006).

Sediment chlorophyll *a* inventories in 2006 were typical for the trends observed at each station for the previous three years at Station QB01, and for essentially the entire monitoring period for the other three stations. It has been characteristic at Station BH02 and has become so at Station QB01 to have higher chlorophyll levels than the other two stations. In 2006, the average seasonal inventory for these two stations was 31.1 µg $cm^{-2}$ compared to 11.7 µg $cm^{-2}$ at BH03 and BH08A. Much of this chlorophyll may be attributed to benthic diatoms that are commonly observed at these stations, but we are unable to differentiate benthic from water column origins. Smaller inventories of chlorophyll at Stations BH03 and BH08A may be related to higher grazing pressure at these sites.

Sediment oxygen demand in 2006 was typical of the post-relocation period, but slightly higher than in 2005, which had the lowest SOD yet observed. SOD was lower than the baseline range at all stations except Station QB01, which was generally within the baseline range. This station never exhibited the extremely high rates of the other stations, so it has been typical for pre-and post- relocation rates to be

similar. The harbor-wide average was 29.1 mmol $m^{-2}d^{-1}$, compared to a post-relocation average of 34 mmol $m^{-2}d^{-1}$, whereas the baseline mean was 69.4 mmol $m^{-2}d^{-1}$.

Fluxes of DIN, $PO_4^-$ , and dissolved Si in 2006 were also typical of the post-relocation period, averaging 2.5, 0.2, and 4.3 mmol $m^{-2}d^{-1}$, respectively, as compared to the averages for the period of 2.7, 0.2 and 5.2 mmol $m^{-2}d^{-1}$. In contrast the averages for the baseline period were 5.8, 0.5, and 8.0 mmol $m^{-2}d^{-1}$. We continue to note that the large variability between stations and years that was observed early in the monitoring program has largely disappeared for DIN and $PO_4^-$ fluxes. Si fluxes have shown larger variability within the post-relocation period (2003), but in 2006, average fluxes were quite consistent across all stations.

Since outfall diversion, water column primary production has also decreased in the harbor. We expected that benthic remineralization might provide a relatively more important source of nutrients to the phytoplankton after outfall diversion, but in fact fluxes have decreased so much that these potential contributions have decreased. Using rates of primary production from a station at the mouth of the harbor and seasonal averages of fluxes, we calculate that these fluxes could have supplied about 23% and 22% of phytoplankton N and P requirements, respectively, for the post-relocation period. Before relocation, the potential contributions were 30% for DIN and 41% for $PO_4^-$. The potential contribution of silica fluxes has not changed, being about 41% for both periods.

In 2006, rates of denitrification at the two harbor stations where it has traditionally been measured, BH02 and BH03, were within baseline measurements but among the lowest of both baseline and post-relocation measurements. The average for the two stations in 2006 was 1.6 mmol N $m^{-2}d^{-1}$ as compared 3.2 mmol N $m^{-2}d^{-1}$ for the post-relocation period and to 5.5 mmol N $m^{-2}d^{-1}$for the baseline period. Low rates may have been partly due to the new analytical method. This method enables us to measure denitrification at the other two harbor stations, BH08A and QB01. Including all four stations, the harborwide average for 2006 becomes 1.4 mmol N $m^{-2}d^{-1}$, which is very similar to the average of 1.8 mmol N $m^{-2}d^{-1}$ for the three years for which we have data for all stations. As a percentage of the combined DIN + denitrification flux of N from the sediments, denitrification can vary widely; in 2006 it represented on average 47% of the combined flux. Due to the large change in loading to the harbor, denitrification is now the major sink of nitrogen, accounting for about 60% of the total inputs, whereas before relocation it accounted for 14%.

Patterns in redox measurements varied across stations. At three of the stations, average respiratory quotients (RQs) for the season were greater than 1.0, ranging from 1.1 to 1.6 in a pattern not atypical for the harbor. RQs at one of these stations, Station BH02, were greater than 1.0 throughout the season and the highest of all four stations, as is also typical. At this station evidence of anaerobic respiration is often found in Eh profiles. At the other two stations, RQs were more variable through the season, and exhibited values both above and below 1.0. In contrast, at the fourth station, BH03, RQs were always less than 1.0, averaging 0.8 for the season and suggesting ongoing reoxidation of sediments at this site.

Consistent with the RQs, oxidation-reduction potential measured as Eh profiles in the top 10 –20 cm of sediment cores revealed most highly oxidized sediments at Station BH03 and most reduced at Station BH02. Eh values low enough to suggest sulfate reduction were encountered one or more times during the season at all stations except BH03, but only at relatively deep positions (8 cm or more) in the profile. These profiles are not atypical of those observed in muddy coastal sediments.

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. The role that infauna has played has been significant in areas like

BH08A and BH03, and the presence or absence of those benthic communities will no doubt continue to impact benthic nutrient cycling.

Table 3 is a summary of the flux data for the pre- (1992-1995 through 2000) and post- (2001 through 2006) diversion years. We have observed between a 35% and 67% reduction between the two time periods, depending on the flux. Much of this decrease actually happened during the pre-diversion period and was related to the first phases of sewage disposal improvements. However, the relocation of the outfall marked a final phase to this part of the Boston Harbor project, so the pre-diversion years integrate all of the changes. Insofar as our four sampling stations are representative, we have witnessed a remarkable change in rates of metabolism and nutrient cycling in the sediments of Boston Harbor.

## CROSS SYSTEMS COMPARISONS

If we compare the long-term datasets for Boston Harbor, the nearfield of Massachusetts Bay, and Stellwagen Basin, most notable is the decreases in SOD and nutrient fluxes that have been observed at the harbor stations. At the beginning of the monitoring program, these fluxes were quite large, and much greater than those in Massachusetts Bay. Currently, fluxes have decreased nearly to the level of those in Massachusetts Bay. As the magnitude of the fluxes has decreased, so has the temporal and spatial variability.

Fluxes of SOD and DIN from the Massachusetts Bay nearfield stations are typically slightly higher than those from the Stellwagen station, but $PO_4^-$ and Si fluxes have been similar. Importantly, there have been no increases observed in bay fluxes since the bay outfall became operational in September, 2000.

It is also interesting to look at these changes in the context of other, similar coastal systems. We have compared Boston Harbor and Massachusetts Bay SOD, both pre- and post-diversion, to a range of other estuaries (Nixon, 1981). The comparison shows there has been little change in Massachusetts Bay between the two periods. In Boston Harbor, however, there has been a remarkable change. The 1995 data for the harbor exceeded the range of the other estuaries presented. Since then, however, SOD in Boston Harbor has decreased dramatically, reaching its lowest point to date in 2005, when the only two systems that had lower SOD were Kaneohe Bay, HI, and our own Massachusetts Bay. (2005 was also the lowest year to date for Massachusetts Bay.) In 2006, summer SOD was higher than in 2005 and was similar to that measured in 2004. We may find that 2004 and 2006 are the more typical years in a system that seems to be stabilizing at a new equilibrium.

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# 1.0 INTRODUCTION

Boston Harbor and the Massachusetts Bays have experienced changes in wastewater inputs as the Massachusetts Water Resources Authority (MWRA) has implemented improvements to the sewage treatment plant servicing the greater Boston metropolitan area. A series of upgrades to the treatment process began in 1989, when increases to pumping capacity were made (Taylor, 2001a). In December, 1991, disposal of sludge within the harbor was discontinued, resulting in reduction of solids discharge 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 were decreases in biological oxygen demand (BOD) in the effluent, as well as metals and other toxic compounds. Concentrations of particulate and organic nitrogen in the effluent stream also decreased, but total nitrogen concentrations were reduced less, as inorganic nitrogen is not removed by secondary treatment. 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.

As part of an extensive monitoring effort mandated by the outfall permit and directed by MWRA, we have been conducting studies on benthic metabolism and nutrient cycling in depositional sediments of these two systems. 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, 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?**

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

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

- *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 the current report we compare the results from 2006 to those baseline studies and to the previous five years of post-relocation observations 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 1998-2005 (Giblin et al., 1992; Kelly and Nowicki 1992; Giblin et al., 1993-1995; Kelly and Nowicki, 1993; Tucker et al., 1999-2006). 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, including the following changes that occurred in 2004, may be found in Tucker and Giblin (2005). These changes were made after a review of the entire monitoring program and were approved by the Outfall Monitoring Science Advisory Panel (OMSAP) ( MWRA, 2003). The changes made to the benthic nutrient flux studies were:

1. Urea measurements were discontinued. Previous years' observations had found that urea flux was always a very minor part of the sediment nitrogen flux.
2. Porewater measurements of nutrients, alkalinity, and sulfides were discontinued. Although useful for better understanding of fluxes from the sediments, these measurements were not critical for monitoring. Measurements of Eh and pH were retained as important indicators of overall sediment conditions. Should significant changes in Eh occur, the more extensive measurements could be reinstated.
3. Denitrification measurements were made using an improved method. The new method enabled us to obtain measurements at all of our stations for the first time; however, it tends to produce lower flux estimates. This caveat has been noted throughout the report.

# 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. GOM water flowing south from the GOM 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 the object of these studies.

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. Through 1997, all stations were sampled in March, May, July, August, and October. After 1997, the March surveys were discontinued.

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.

In Massachusetts Bay, physical and climatological factors set the stage for the biology and chemistry of the system. In 2005, two large northeasterly storms in May played a critical role for benthic processes, both in Massachusetts Bay and Boston Harbor. They lasted long enough and generated waves of sufficient height to resuspend bottom sediments in the nearfield, resulting in an increase in sediment grain size and a decrease in biogenic structures. Another strong northeaster in October also impacted the nearfield benthos.

In contrast, 2006 was a quiet year, with no major storms, and no major disturbances to the benthos. A large diatom bloom was present in March, followed by a *Phaeocystis* bloom in April. Even though it was mild in terms of storminess, 2006 was a very wet year, with flows from the Merrimack and Charles Rivers in May the highest since the 1938 hurricane (Libby et al, 2007). Annual average flows were second only to those observed in 2005. Heavy river flows, especially from the Merrimack may carry large loads of terrestrially derived organic matter, nutrients, and other materials, as well as fresh water, into Massachusetts Bay. 2006 was also notable as being tied for having the most upwelling-favorable period (July) documented in the monitoring program. These conditions led to an unusual summer, subsurface phytoplankton bloom to the south of the outfall.

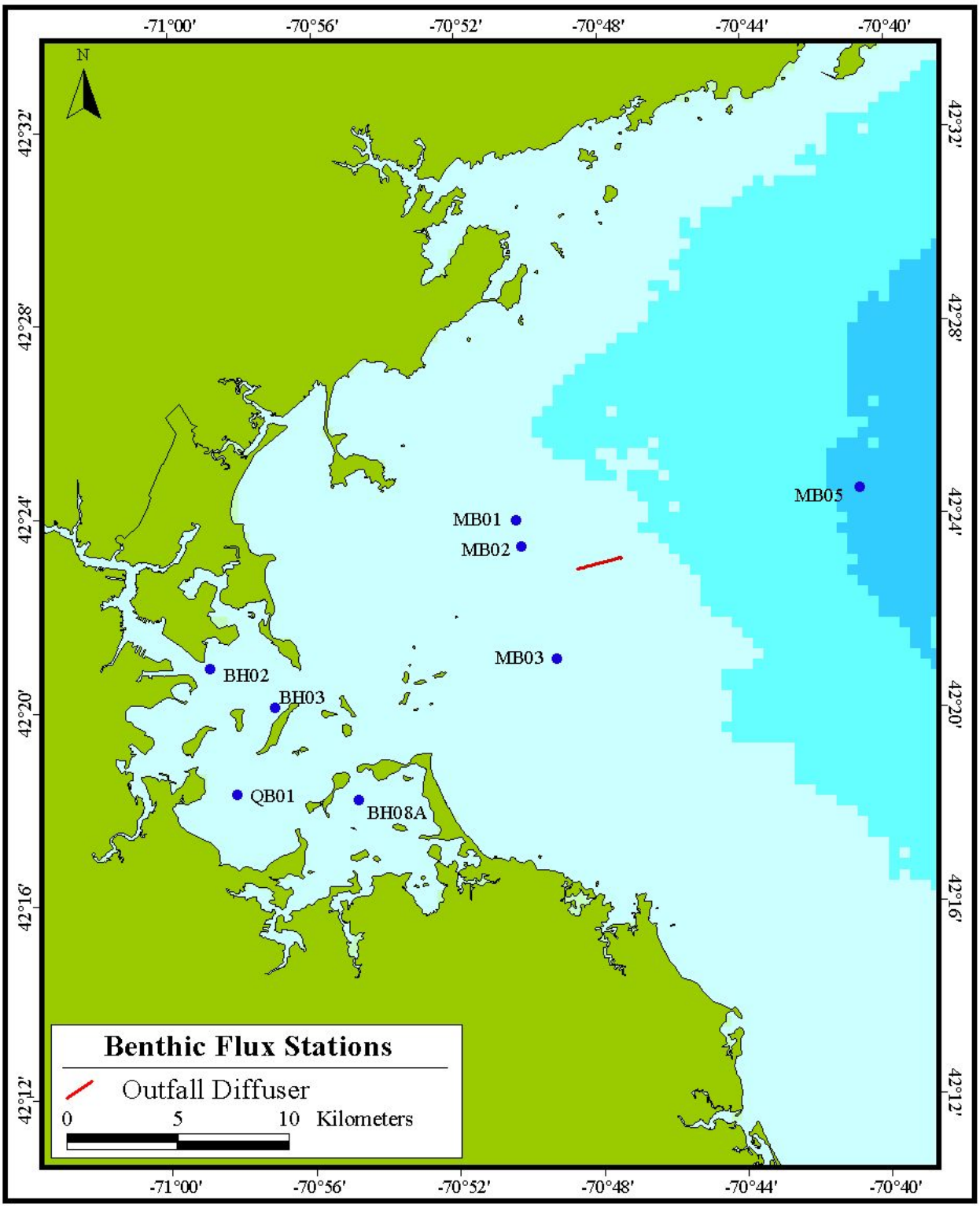


**Figure 1. Benthic nutrient cycling stations in Massachusetts Bay and Boston Harbor.**

## 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%. The very high values, which occurred in 1993, seemed to correspond to the effects of a late 1992 storm that redistributed sediments in the Bay (Bothner, 2002). Other peaks in organic carbon content typically have not corresponded well with other storms or with other potential causes such as phytoplankton blooms.

In 2006, seasonal average TOC (Fig 2) at the three nearfield stations ranged from 1.0% at Station MB01 to 1.2% at Station MB03. These values represented a small decrease from the previous year at Station MB01, but an increase at Station MB03. At the third nearfield station, MB02, there was also a small increase in TOC from the previous year. These values continue the pattern we have observed between stations in recent years. That is, Station MB02 and MB03 seem to be responding similarly in terms of interannual variability, increasing and decreasing together since 2002, whereas MB01 is exhibiting a different pattern, slowly decreasing in TOC over the same period. At the Stellwagen station, the 2006 average TOC was 1.6 %, similar to the previous year, and quite typical for this station.

Within the season, TOC content varied from station to station and survey to survey, ranging from 0.8 to 1.5 % across all four stations. The three nearfield stations did not display similar seasonal patterns nor did they seem to correlate well with events in the water column. Although the large spring diatom bloom was evident in surface chlorophyll *a* concentrations (see Section 2.1.2), this event was not apparent in the TOC. In fact, highest TOC, 1.7 %, was observed in August at Station MB05. A small increase in TOC from 1.2% to 1.5 % between May and July at Station MB03 may have been related to the unusual subsurface summer bloom; certainly there was evidence of this bloom in the surface chlorophyll *a* at this station (Section 2.1.2). However, the increase in TOC was not outside normal variability. After July, TOC at Station MB03 decreased. A similar pattern, albeit with lower values, was observed at Station MB01, with the high value for this station being a typical 1.1% in July and the low being the lowest for all stations this season at 0.8% in October. At Station MB02 and the farfield station MB05, TOC increased over the season, whereas chlorophyll decreased.

Ratios of TOC to total N (C/N: Fig. 3) in 2006 were elevated at MB01 and MB03, reaching values of 15.0 and 13.0 (averaged over the May to October period), respectively, which were higher than previously observed at these two nearfield stations. AT MB02, C/N was also high, but not as high as it had been in 2005. At these three nearfield stations, there seems to have been an upward trend in C/N since 2003 or 2004. However, this very short term trend follows low and high observations in 2001 and 2002, respectively, all of which may simply be natural variability at these sites.

These high C/Ns seem counterintuitive given the high chlorophyll *a* levels observed this year, so we are left to speculate about other sources of organic matter. One might be POC from the outfall, which would be expected to have a high C/N. However, solids in the Deer Island effluent have been decreasing over

this time (MWRA, 2006). Another might be terrestrial-derived POC, which also would have high C/N. Given the fact that 2005 and 2006 had the highest river discharge from the Merrimack River of the monitoring program (Libby et al, 2007), this second source seems plausible. In fact, an unprecedented high C/N of 17.1 was found at Station MB01, nearest the Merrimack, in May, the time of spring runoff. At farfield station MB05, C/N was lower than in the nearfield at 10.2 and typical for this station. It has been a consistent pattern over the entire monitoring program that C/N has been lower and much less variable at this deeper station than at the nearfield stations.

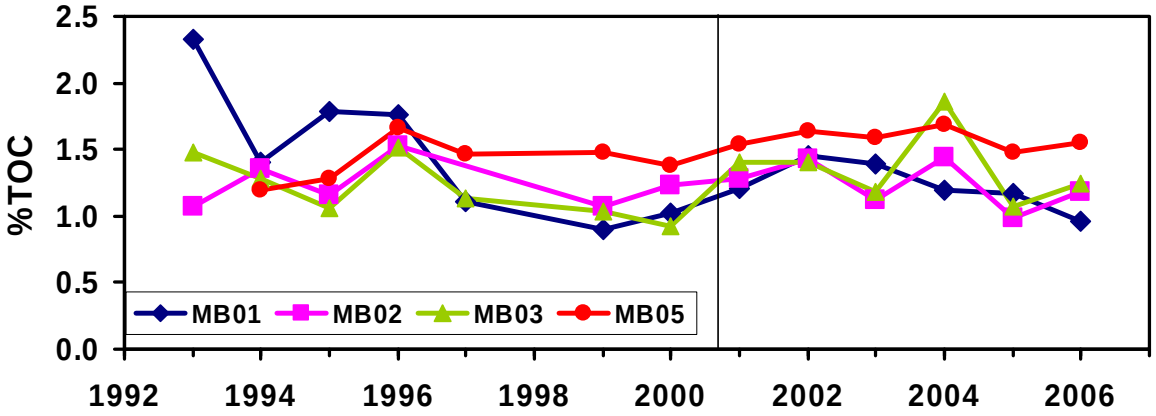


**Figure 2. Organic carbon content of top 2 cm of sediment at Nearfield stations MB01, MB02, and MB03 and Farfield station MB05. The vertical line marks the transition from baseline to post-relocation observations.**

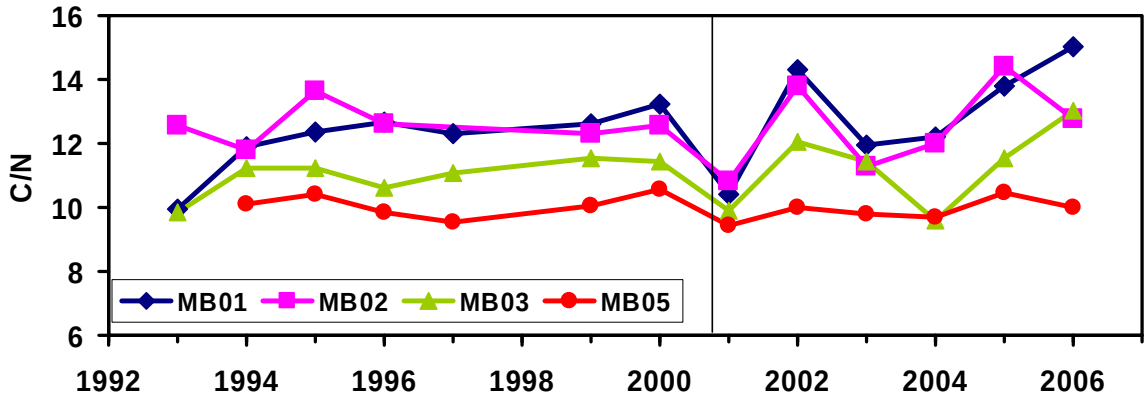


**Figure 3. Molar TOC/TON for top 2 cm of sediment. The vertical line marks the transition from baseline to post-relocation observations.**

### 2.1.2 Sediment Pigments

In 2006, chlorophyll *a* inventories for the top 5 cm of sediment at the nearfield stations were among the highest observed during the monitoring program. Seasonal averages ranged from 8.5 µg $cm^{-2}$ at Station MB01 to 13.5 µg $cm^{-2}$ at Station MB03. Peak inventories occurred in May at Stations MB01 (15.1µg $cm^{-2}$) and MB02 (18.2 µg $cm^{-2}$). Similarly high inventories were observed at MB03 in May, but slightly higher levels for this station occurred in July (17.4 µg $cm^{-2}$). Lowest inventories occurred, in August for all three stations and ranged from 4.2 µg $cm^{-2}$ at MB01 to 8.5 µg $cm^{-2}$ at MB03. At the Stellwagen station MB05, the chlorophyll *a* inventory was much lower than in the nearfield and typical for this station. Here, inventories ranged from a high of 9.0 µg $cm^{-2}$ in May to a low of 4.0µg $cm^{-2}$ in October.

Profiles through the top 5 cm of sediment revealed elevated surface concentrations of chlorophyll *a* at all three nearfield stations in May. These surface concentrations ranged from 8.2µg $cc^{-1}$ at MB03 to 13 µg $cc^{-1}$ at MB02 (Fig. 5), in contrast to typical concentrations of less than 5 µg $cc^{-1}$. A small surface signal was also apparent in the farfield. These profiles were repeated in July at Stations MB03 and MB05, but the surface expression of chlorophyll had disappeared from the profiles at Stations MB01 and MB02. We normally interpret such profiles as evidence of recent deposition of a phytoplankton bloom, and in fact there was a sizable winter/spring bloom in the nearfield in 2006 that could account for the May profiles. A second bloom occurred in July; this bloom was unusual in its timing, and because it was a subsurface bloom that only occurred in the southwest corner of the nearfield. This timing and location is consistent with the surface chlorophyll signature noted in July at Station MB03 and possibly at MB05 if the general current flow patterns are invoked. In previous years, we have been frustrated in the lack of evidence of the spring bloom in the sediment pigments. The difference in 2006 was that a large component of these blooms was diatoms, which sink readily when they senesce, whereas in many recent years the blooms have been largely *Phaeocystis*, which tends to remain buoyant longer and may be advected out of the system.

In spite of the strong chlorophyll signal observed in the surface sediments of the nearfield in 2006, we did not find a correlation with C/N. Although it is common to use C/N as an indicator of carbon quality, in bulk sediments it is not a sensitive enough measure to pick up small, by comparison, chlorophyll inputs to the total organic carbon pool. For example, assuming a carbon/chlorophyll ratio of 50, the inventory of 14.9 µg of chlorophyll *a* for the top 2 centimeters of sediment observed at MB02 in May 2006 would contribute about 97 µg TOC per g dry weight of sediment, only 0.9% of the total 10300 µg/g measured.

### 2.1.3 Pre- and Post- Relocation Comparison

In spite of the apparent deposition of chlorophyll to nearfield sediments in 2006, there is still no discernible pre- versus post- relocation difference in this measure of organic matter input. Mean values of chlorophyll *a* inventories were accompanied by high variability during both periods. Similarly, there has been no change in organic carbon content at these sites. Our measures of TOC and pigment inventories suggest that 2006 was a very typical year in terms of organic matter loading to the benthos of Massachusetts Bay. These data add to the previous five years' observations that there has been no change in organic matter content of nearfield sediments since the bay outfall became operational at the end of 2000. The mean seasonal average for each station over the pre-relocation (baseline) years compared to the post-relocation years for TOC and total pigments are shown in Figures 6 and 7, respectively. There is no statistical difference between the pre- and post- years for either measure given the variability around each of these means**.**

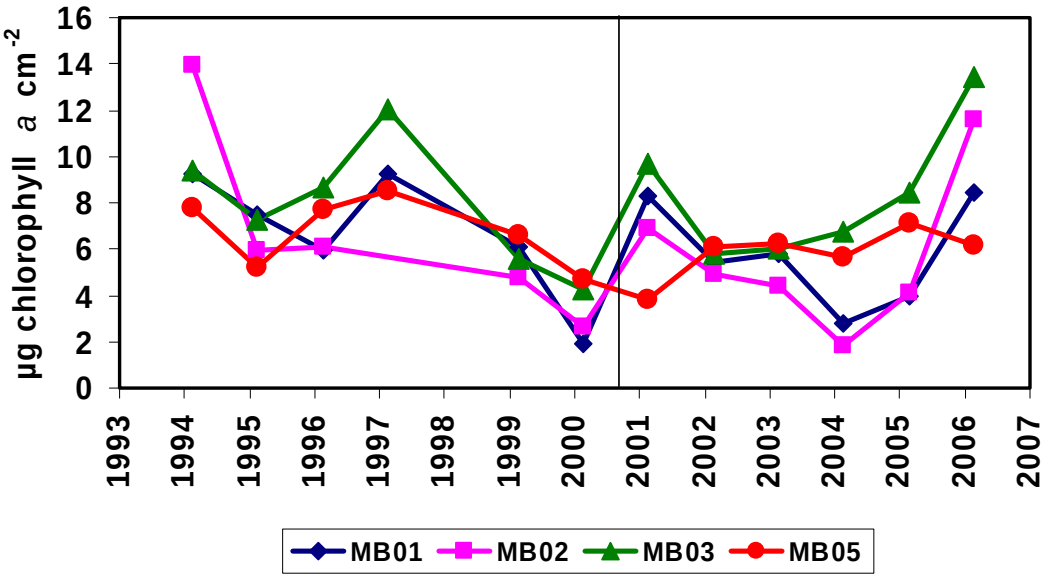


**Figure 4. Chlorophyll *a* inventory for top 5 cm of sediment at Nearfield stations a.) MB01, b.) MB02, and c). MB03, and Farfield station c). MB05. The vertical line marks the transition from baseline to post-relocation observations.**

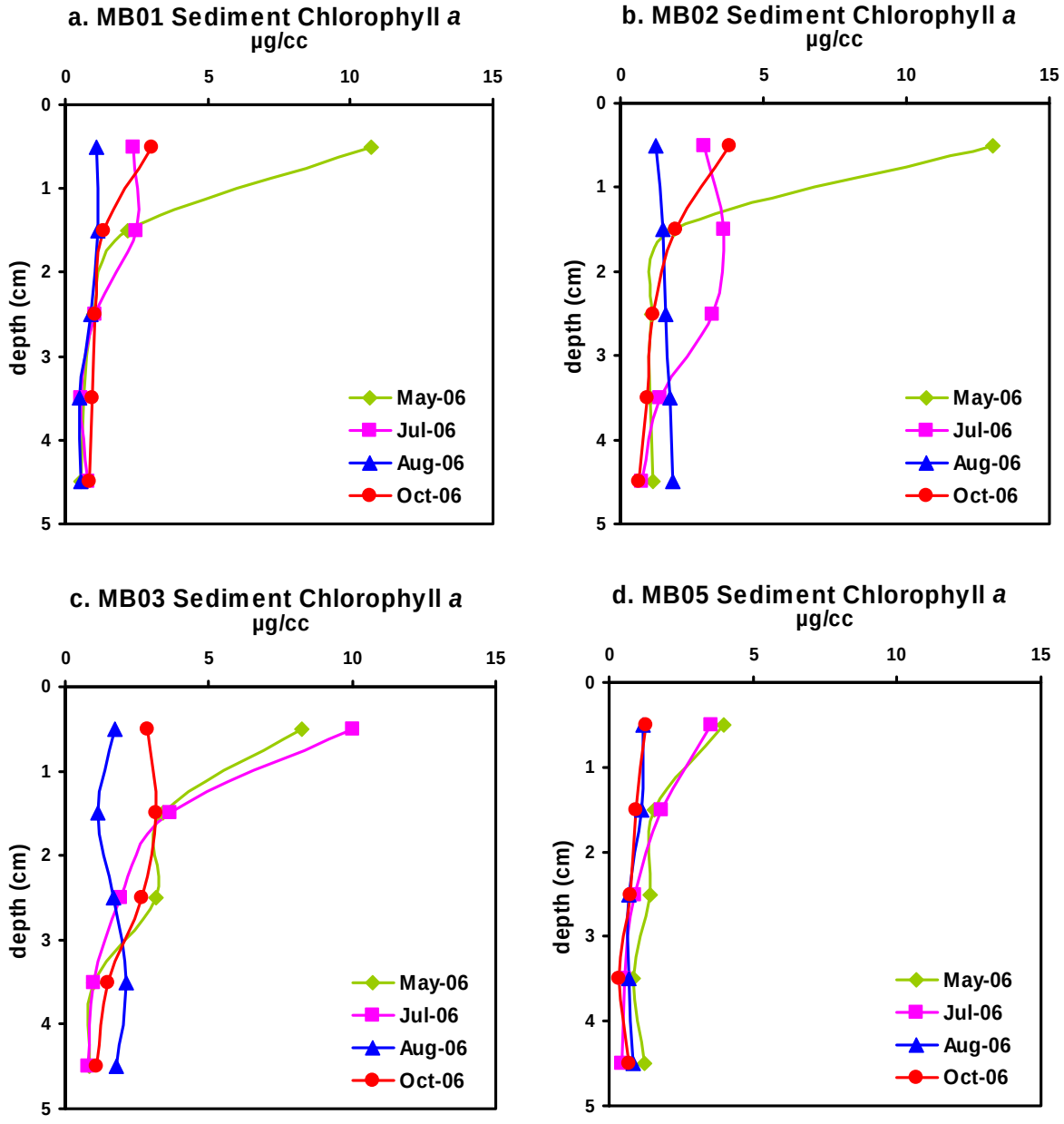


**Figure 5. Profiles of chlorophyll *a* concentration (µg/cc) in top 5 cm of sediment in 2006 from Massachusetts Bay Stations a.) MB01, b.) MB02, c.) MB03, and d.) MB05.**

## 2.2 Sediment Oxygen Demand

The baseline range for the seasonal average sediment oxygen demand (SOD) for our three nearfield stations was 12.4 to 24.7 mmol $m^{-2}$ $d^{-1}$ (Fig. 8a and 9a-c), with a grand mean across stations and years of 17.2 mmol $m^{-2}$ $d^{-1}$. In 2006, seasonal average SOD ranged from 13.9 mmol $m^{-2}$ $d^{-1}$ at MB01 to 18.1 at MB03, and the average across the three stations was 15.6 mmol $m^{-2}$ $d^{-1}$(Fig. 8 a). Observations in 2006 were well within baseline, but higher than in 2005 (nearfield average was 12.6 mmol $m^{-2}$ $d^{-1}$).

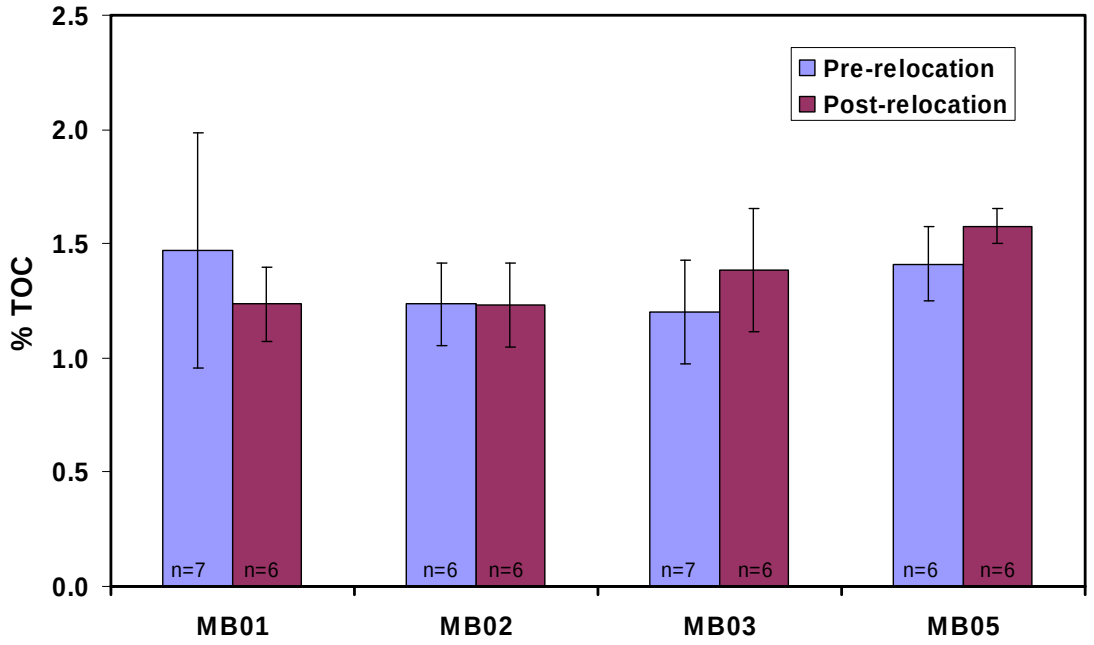


**Figure 6. Sediment TOC pre- and post- relocation of the outfall. Data are seasonal averages over all available years for each station. Error bars represent one standard deviation of the mean.**

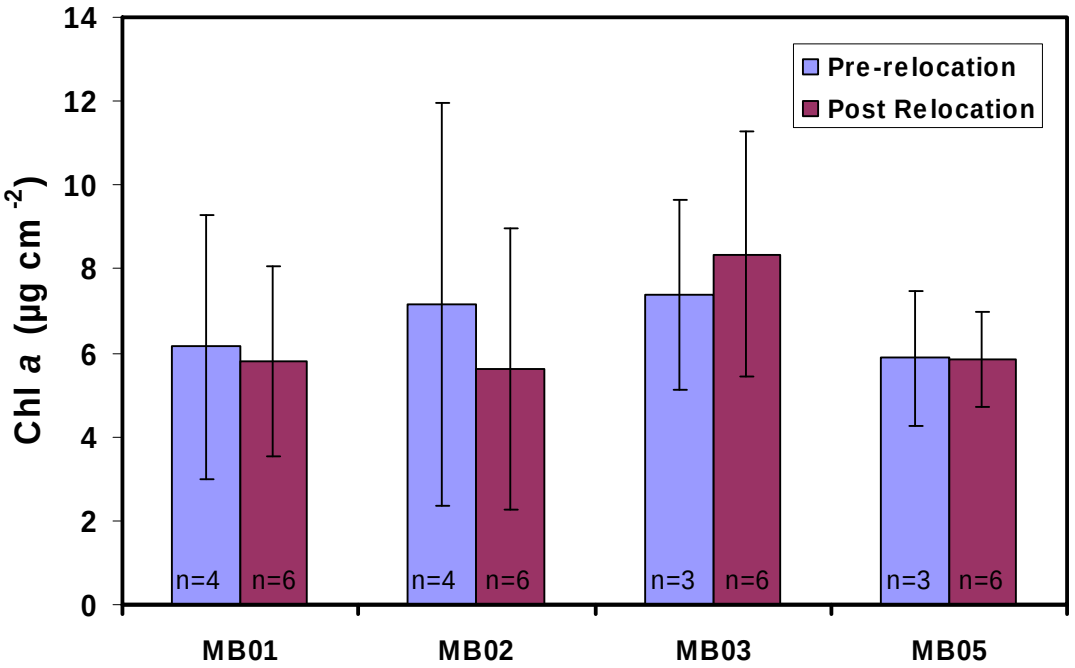


**Figure 7. Sediment total chlorophyll pre- and post- relocation of the outfall. Data are seasonal averages over all available years for each station (data from 1995-1997 are omitted due to possible differenced in phaeopigment measurements). Error bars represent one standard deviation of the mean.**

The narrow range of SOD in 2006 was reflected in a weak seasonal pattern. Rates at MB01 and MB02 tracked each other unusually closely, starting in the middle of the baseline range (12.2 and 14.1 mmol $m^{-2}$ d-1, respectively) for these stations in May. SOD increased from May to July to a point near the middle of the range, decreased sharply by August to a level at the bottom of the baseline range, and then increased again from August to October, ending near the bottom of the range for these two stations (15.2 and 15.4 mmol $m^{-2}$ $d^{-1}$, respectively). At MB03, SOD began near the top of its range for May (14.8 mmol $m^{-2}$ $d^{-1}$), increased between May and July, but stayed nearly the same into August before increasing to the high rate of the year for all nearfield stations of 20.7 mmol $m^{-2}$ $d^{-1}$ in October. Rates observed between July and October stayed near the middle of the range for this station.

At farfield station MB05, seasonal average SOD was very typical of baseline observations (Fig 8a). We have seen little variability in fluxes at this station, with the "extremes" in seasonal average during the baseline period being 7.8 mmol $m^{-2}$ $d^{-1}$ in 1995 and 15.3 mmol $m^{-2}$ $d^{-1}$ in 1997. All other values fell between 10 and 13 mmol $m^{-2}$ $d^{-1}$. In 2006, the seasonal average was a very typical 12.2 mmol $m^{-2}$ $d^{-1}$. SOD at this station ranged narrowly, with the high of 13.8 mmol $m^{-2}$ $d^{-1}$ occurring in August and the low of 10.9 mmol $m^{-2}$ $d^{-1}$ occurring in October (Fig. 9d).

After the first three years of monitoring (1993-1995) we reported a strong correlation between temperature and SOD. From 1995-2005, however, this relationship was inconsistent, and sometimes even negative. In 2006, we once again have observed good, positive correlations between SOD and temperature at the nearfield stations. A particularly strong correlation was found at Station MB03, with temperature explaining 83% of the variability in SOD. At MB01 and MB02 temperature could explain 59% and 22%, respectively.

We continue to analyze the data to look for correlations between SOD and expected controls on SOD. We would expect that benthic respiration would respond to fresh inputs of carbon from the spring phytoplankton bloom. Simple linear regression of SOD on pigment inventories or carbon content has yielded mixed results over the monitoring period, and that was still the case in 2006. For two of the three stations, MB02 and MB03, we found good correlations between SOD and total sediment chlorophyll (chlorophyll *a* + phaeophytin *a*), with the $r^2$s for the regressions 0.44 and 0.53, respectively. At the third station, MB01, this regression was very strong ($r^2 = 0.97$), but the relationship was negative (respiration decreased with increasing pigments). When chlorophyll *a* alone was used as the independent variable, the relationship observed at MB03 became stronger ($r^2 = 0.61$). At MB01, the relationship switched from negative to positive with an $r^2$ of 0.48. Curiously, at Station MB02, there was no relationship at all with chlorophyll *a* alone ($r^2 = 0.07$). When SOD was regressed on TOC, all of the results from the nearfield stations yielded inverse relationships. In contrast, there was some positive relationship between SOD and TOC at the farfield station ($r^2 = 0.32$), but none whatsoever with total pigments or chlorophyll *a*.

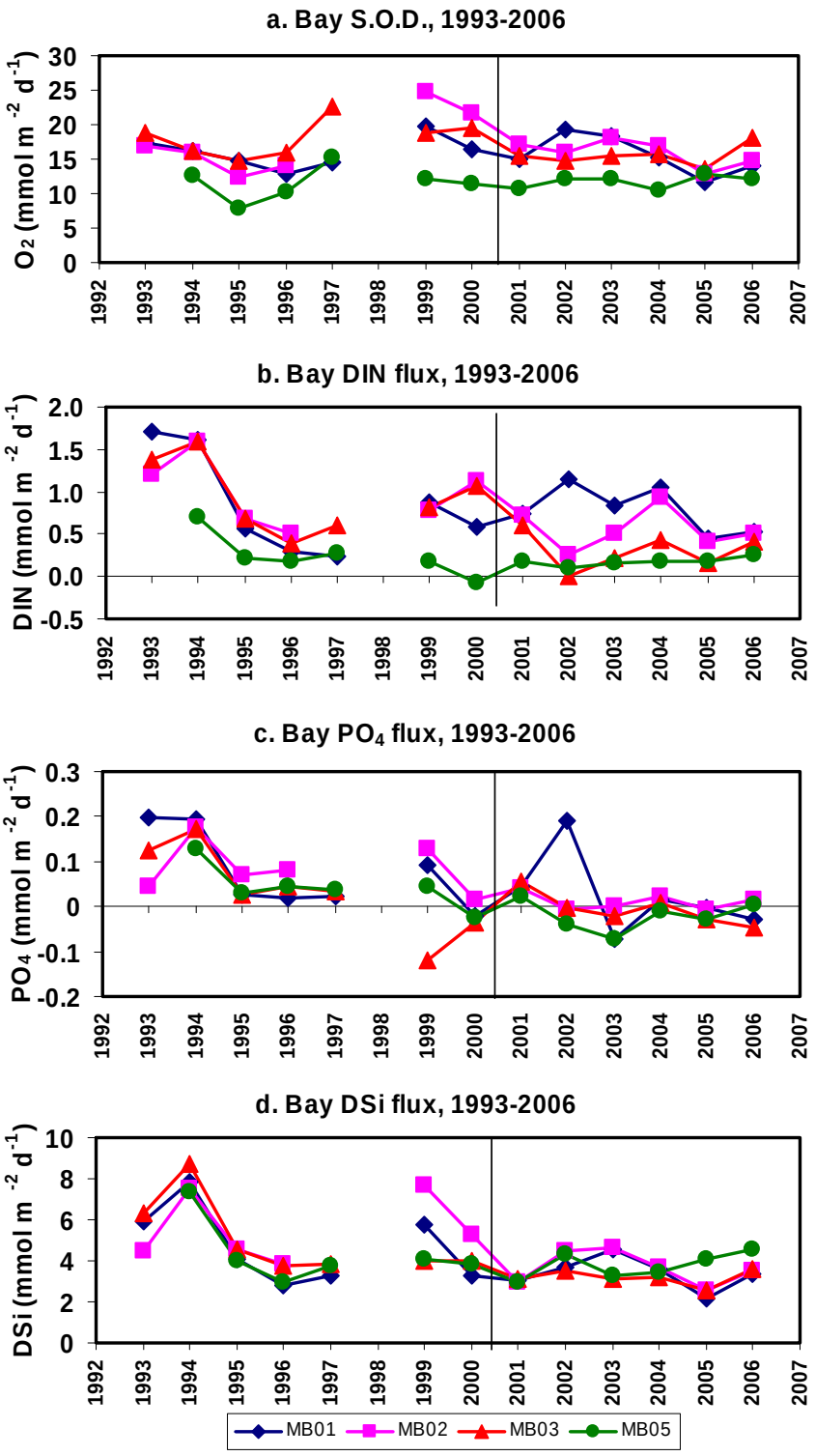


**Figure 8. Seasonal (May-October) averages of a.) sediment oxygen demand (S.O.D.), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Massachusetts Bay stations in 1993-2006. The vertical lines mark the transition between baseline and post-relocation observations.**

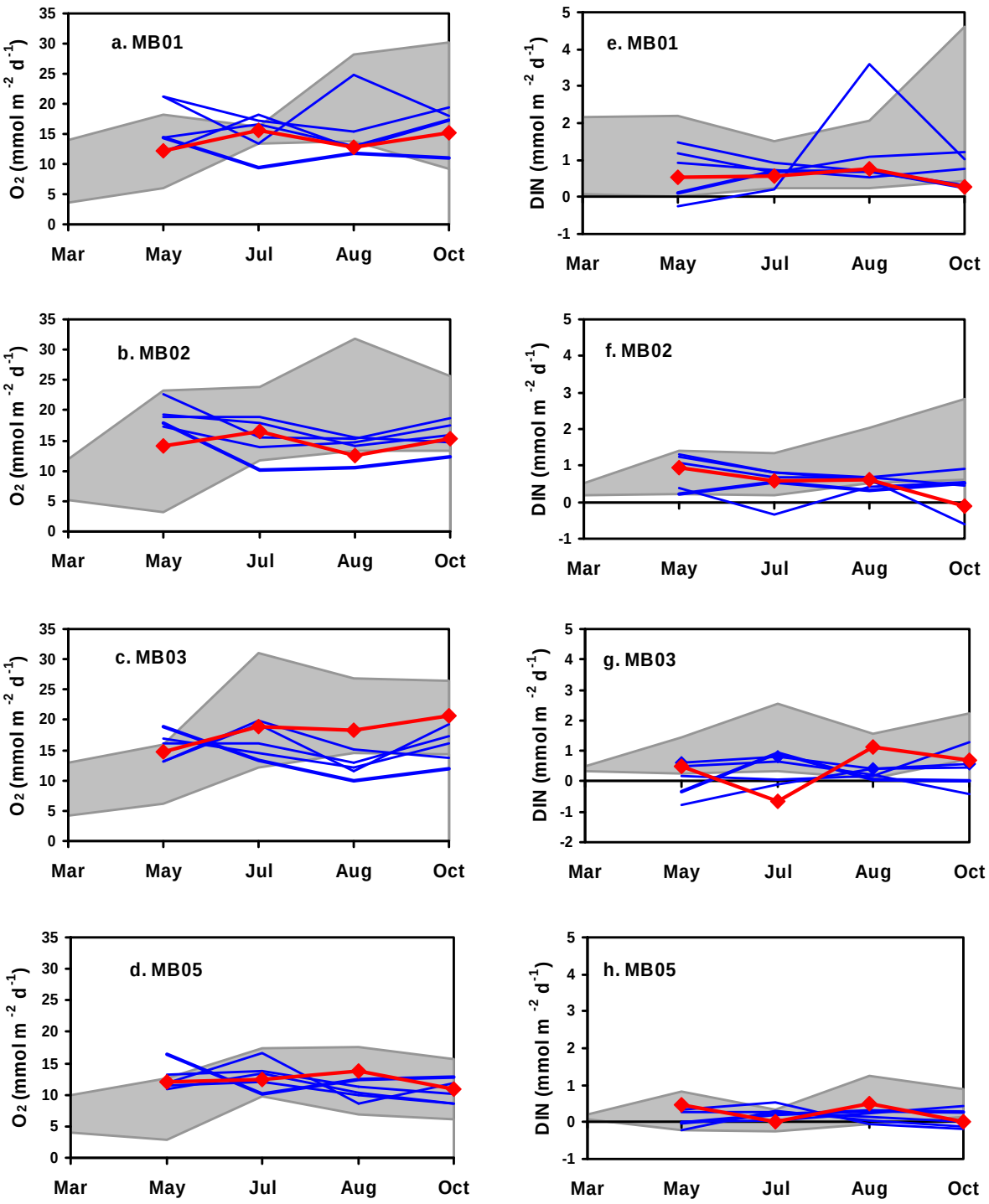


**Figure 9. Sediment oxygen demand ($O_2$ flux) and DIN flux for 2006 (-♦-),compared to other post-relocation years (2001-2005, solid lines) and to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations MB01, MB02, MB03, and MB05, respectively.**

## 2.3 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 six 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 (data for urea not shown) have in general been at the low end of the range of fluxes observed during baseline monitoring.

### 2.3.1 DIN

In 2006, DIN fluxes from nearfield sediments were in the mid to low end of the baseline range (Fig 8b and 9e-g), and varied from uptake of 0.67 mmol $m^{-2}$ $d^{-1}$ at Station MB03 in July followed by an efflux of 1.1 mmol $m^{-2}$ $d^{-1}$ at the same station in August. At MB01, DIN flux increased slowly through the first part of the season to a high of 0.75 mmol $m^{-2}$ $d^{-1}$ in August and then fell to 0.27 mmol $m^{-2}$ $d^{-1}$ in October, the low for the station. At MB02, highest rates, 0.93 mmol $m^{-2}$ $d^{-1}$, occurred early in the season, falling slowing thereafter and ending with an uptake of 0.12 mmol $m^{-2}$ $d^{-1.}$ Seasonal average DIN flux, however, was similar across the three stations ranging only from 0.41 mmol $m^{-2}$ $d^{-1}$ at MB03 to 0.53 mmol $m^{-2}$ $d^{-1}$ at MB01.

Nitrate (used throughout text as shorthand for $NO_3^- + NO_2^-$) comprised between 30% (MB02) and 41% (MB03) of the seasonal average DIN flux in 2006 (Fig 10a-c). This is in contrast to 2005, when it comprised nearly all of the seasonal flux. The 2006 pattern, however, is consistent with the more typical condition, in which $NH_4^-$ is the largest component of the flux. The proportionally very high nitrate fluxes in 2005 were attributed to physical disturbance of the sediments caused by an unusually stormy year.

At MB05, DIN fluxes fell near the middle of the overall range of values observed at this station, but were on the high end of the range as a seasonal average (0.25 mmol $m^{-2}$ $d^{-1}$). The seasonal pattern was similar to that described for MB03, although the fluctuations were smaller. It was an atypical pattern for this station, with highest and equivalent fluxes (0.48 and 0.49 mmol $m^{-2}$ $d^{-1}$) occurring in May and August, and essentially no flux in July and October (0.02 and 0.01 mmol $m^{-2}$ $d^{-1}$). Nitrate made up 57% of the average DIN flux (Fig. 10d).

The "seesaw" pattern observed in the DIN flux over the season at station MB03 (Fig. 9g) was of interest because it occurred in both the $NH_4^+$ and $NO_3^-$ components of the flux, was repeated in the $PO_4^-$ (Fig. 11c) and DIC fluxes, but was not found at the other two stations. The relatively large uptake of DIN at MB03 might be attributed to typical spatial variation among these sites. However, it was the simultaneous uptake in both components of the DIN ($NH_4^+$ and $NO_3^- + NO_2^-$) as well as in $PO_4^-$ and DIC (see sections 2.3.2 and 2.5.1) that was curious. An unusual, for the time of year, subsurface phytoplankton bloom was present in the water column at this time (Libby et al, 2007), and we measured large concentrations of chlorophyll *a* in surface sediments. We are tempted to suggest there might have been uptake of nutrients and $CO_2$ by still-active phytoplankton cells in the water or that had sunk to the sediment surface, but this interpretation seems unreasonable given that our core incubations are carried out in the dark. We are left without an explanation beyond typical variability.

### 2.3.2 Phosphorus and Silica

In the nearfield, phosphate fluxes were characteristically small and/or negative in 2006 (Fig. 8c), with the one exception, referred to above, of a relatively large uptake of $PO_4^-$, 0.25 mmol $m^{-2}$ $d^{-1}$, at Station MB03 in July (Fig 11c). There was also small uptake of $PO_4^-$ at this station in May. The largest efflux, 0.07 mmol $m^{-2}$ $d^{-1,}$ occurred in August at MB03. There was also efflux in October. The large uptake in July followed by release in August produced the same seasonal "seesaw" pattern in the $PO_4^-$ fluxes at MB03 that were noted for the DIN fluxes. A hint of this pattern existed at Station MB01 and MB05, however the periods of uptake of $PO_4^-$ versus efflux were not consistent across stations (Fig. 11 a and d). At MB01, sediments took up $PO_4^-$ at all times except August, whereas at MB05 the pattern alternated between efflux and uptake. At MB02 we measured uptake in May and October and efflux in July and August (Fig. 11b). The only similarity across all four stations was that they all experienced peak $PO_4^-$ effluxes in August. Although these differences in patterns are interesting, the magnitude of the fluxes is small. Seasonal averages ranged from weak uptake at MB01 and MB03 ( 0.03 and 0.05 mmol $m^{-2}$ $d^{-1}$ , respectively) to release at MB02 and MB05 (0.02 and < 0.01 mmol $m^{-2}$ $d^{-1}$ , respectively).

Dissolved silica fluxes at the nearfield stations in 2006 were mostly within the lower end of the baseline range (Fig. 8d). Largest fluxes of the season, 5.5 mmol $m^{-2}$ $d^{-1}$, occurred at Station MB02 in July and were followed by the smallest, 1.6 mmol $m^{-2}$ $d^{-1}$, at the same station in August (Fig. 11f). Largest fluxes were observed at all stations in July (Fig. 11 e-g). Otherwise, the three stations each followed their own seasonal pattern. Largest variability was observed at MB02, and the least at MB03. Seasonal averages, however, were quite similar, ranging only from 3.4 mmol $m^{-2}$ $d^{-1}$ at MB01 to 3.6 mmol $m^{-2}$ $d^{-1}$ at MB03. At Station MB05, the seasonal average Si flux, 4.6 mmol $m^{-2}$ $d^{-1}$, was larger than in the nearfield, driven mostly by higher rates in May and August (Fig. 8d). Similar to the nearfield, Si fluxes peaked in July at this station (Fig. 11h).

### 2.3.3 Nutrient Flux Contribution to Primary Productivity

Average annual primary production in the nearfield area in 2006 was 298.5 g C $m^{-2}$ $y^{-1}$ (or 68.2 mmol C $m^{2}$ $d^{-1}$) (average production from Stations N04 and N18; Oviatt, pers. com; Note: previous reports have included data from Station F23, at the mouth of Boston Harbor, in this nearfield average. However, to be consistent with the Water Column Monitoring program, in this report we have omitted the data from F23 in the averages.). Following Redfield considerations, this amount of production would require 10.3 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 0.48 mmol $m^{-2}$ $d^{-1}$, we find that benthic DIN flux represented only 4.7% of phytoplankton requirements. Because there was seasonal average *uptake* of $PO_4^-$ by the benthos in 2006, there was no contribution to the water column. Fluxes of dissolved silica, however, could account for 34% of requirements, assuming a 1:1 relationship between silica and nitrogen. If we look at these relationships for the years we have data before and after outfall relocation, we see that there has been little change. From 1995-2000 (excluding 1998 because there are no benthic flux data) we calculate that benthic recycling could account for 3.7% of the nitrogen and 24% of the silica needed to fuel primary production. For the years that there was an overall efflux of PO4- from the sediments (4 out of 5 years), it could account for only 0.04%. From 2001-2006, we calculate a potential contribution of 4.3% of nitrogen and 26 % of silica. For years with $PO_4^-$ efflux (3 out of 6), that potential contribution was 0.04%, the same as the pre-diversion years.

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 depositional, and presumably more active sediments of the bay.

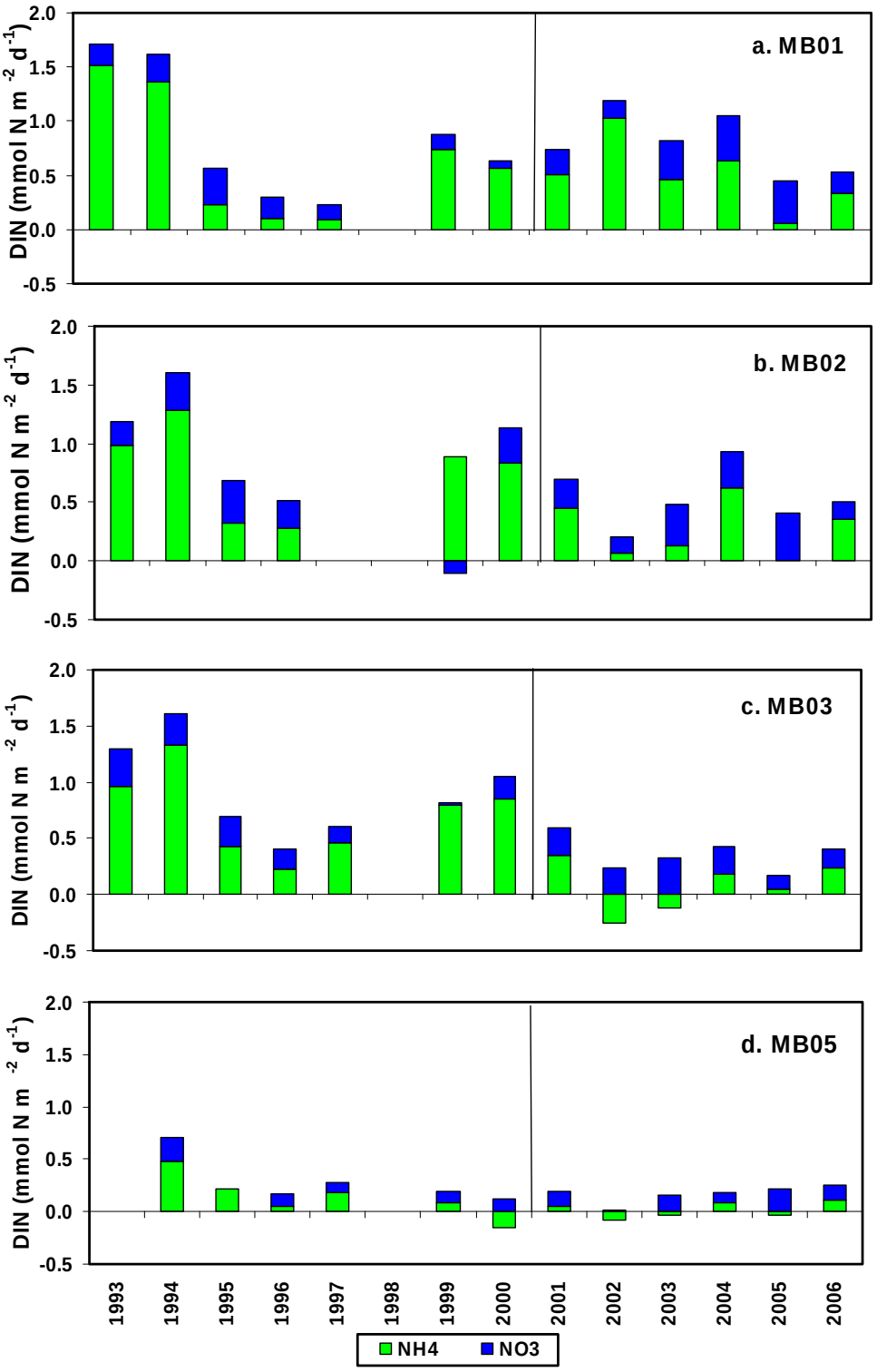


**Figure 10. May-October seasonal average DIN flux from 1993-2006 at bay stations, partitioned into $NH_4^+$ and $NO_3^-$+$NO_2^-$ a.) MB01, b.) MB02, c.) MB03, d.) MB05. The vertical line marks the transition from baseline to post-relocation observations.**

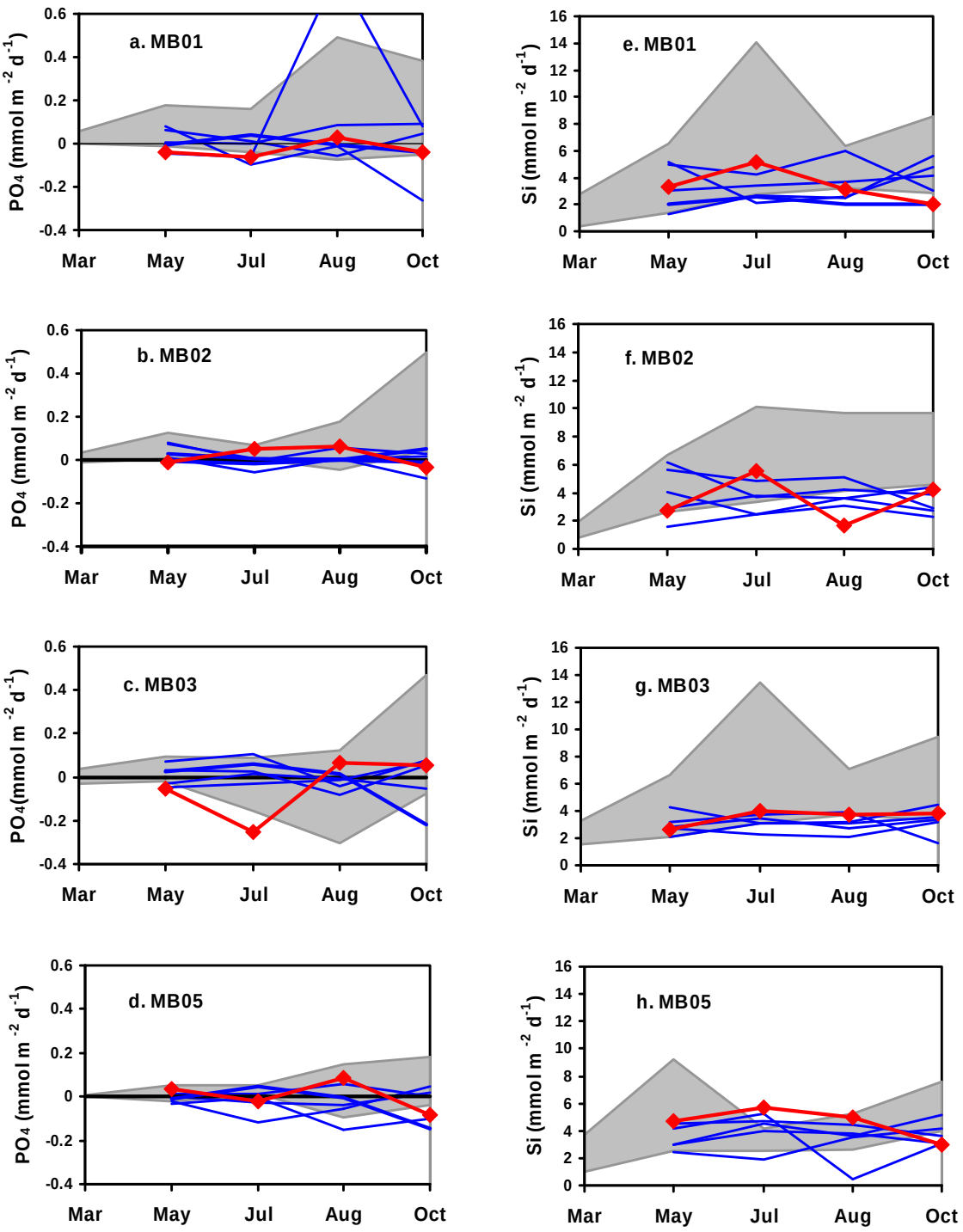


**Figure 11. Phosphate and dissolved silica for 2006 (-♦-),compared to other post-relocation years (2001-2005, solid lines) and to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict $PO_4^-$ flux and panels e-h depict DSi flux for stations MB01, MB02, MB03, and MB05, respectively.**

## 2.4 Denitrification

Over the course of the monitoring program, direct measurements of denitrification have been made routinely at two nearfield stations, MB02 and MB03, but the frequency of measurement has varied. In 1993 and 1994, measurements were made during each of five annual surveys: March, May, July, August, and October. Denitrification measurements were not made from 1995 through 1998. They resumed in 1999, but were only conducted at the beginning and end of the season, May and October (also in 1999 the March surveys were discontinued). Beginning in 2004, a change in analytical method allowed us to once again measure denitrification during all (four) annual surveys: May, July, August, October. In addition, for the first time, we made measurements at Station MB01 and farfield station MB05. These measurements have revealed considerable variability in the rates of denitrification, and no discernable seasonal pattern.

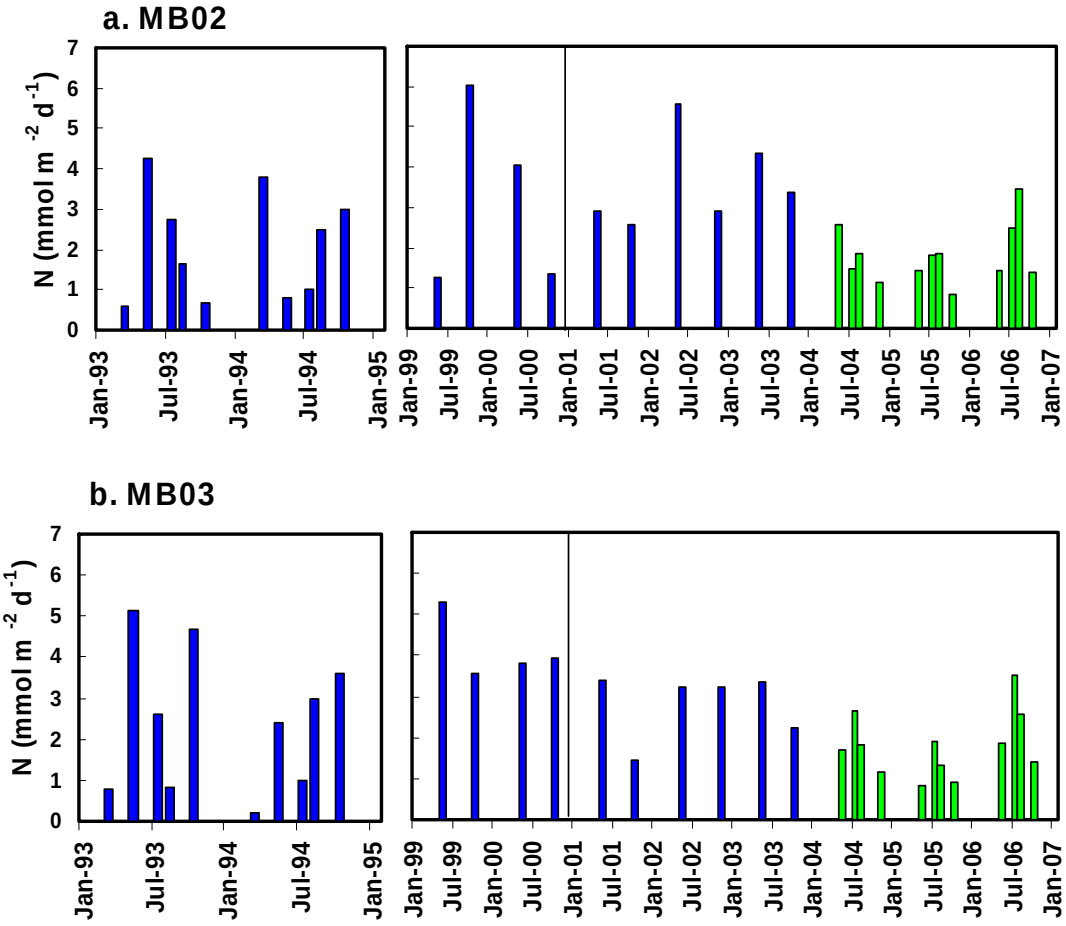


**Figure 12. Denitrification at two nearfield stations, a.) MB02, and b.) MB03. Denitrification measurements were not conducted in Massachusetts Bay in 1995-1998. Data from 2004-2006 were produced using the new analytical method and are highlighted in green. The vertical line marks the transition between baseline and post-relocation of the outfall.**

Denitrification rates at our long-term nearfield stations MB02 and MB03 in 2006 were within the overall baseline ranges (Fig. 12), but higher than in 2005. Seasonal averages at these two stations were very similar, 2.2 and 2.3 mmol N $m^{-2}$ $d^{-1}$, respectively. A similar seasonal pattern was observed at both of these stations, with higher rates in the summer and lower rates in spring and fall. The highest rates for both stations was 3.5 mmol N $m^{-2}$ $d^{-1}$, but occurred in August at MB02 and July at MB03. Denitrification rates at the third nearfield station, MB01, were similar to those at MB02 and MB03 in May and October, but much lower than these two stations in July and August, reaching only 1.7 and 1.0 mmol N $m^{-2}$ $d^{-1}$. The seasonal average for MB01 was 1.4 mmol N $m^{-2}$ $d^{-1}$. At MB05, the seasonal average was also 1.4 mmol N $m^{-2}$ $d^{-1}$, and rates did not fluctuate very much within the season.

We have previously noted that denitrification rates at the two long-term nearfield stations were 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 inorganic N flux (DIN + denitrified N) from the sediments of these two stations. From 2001 through 2003, that percentage was higher, ranging from about 80% to 100% of the total flux. The increase in the relative importance of denitrification was attributed to decreases in DIN flux rather than to increases in denitrification. We continue to see this pattern. In 2006, denitrification accounted for between 61% and 100% of the combined efflux in the nearfield. At Station MB05 it comprised 75% to 98% of the flux. For 2004-2006, for which we have data for all stations and all surveys, denitrification accounted for about 73 % of the average efflux at the nearfield stations and 85% at the farfield station.

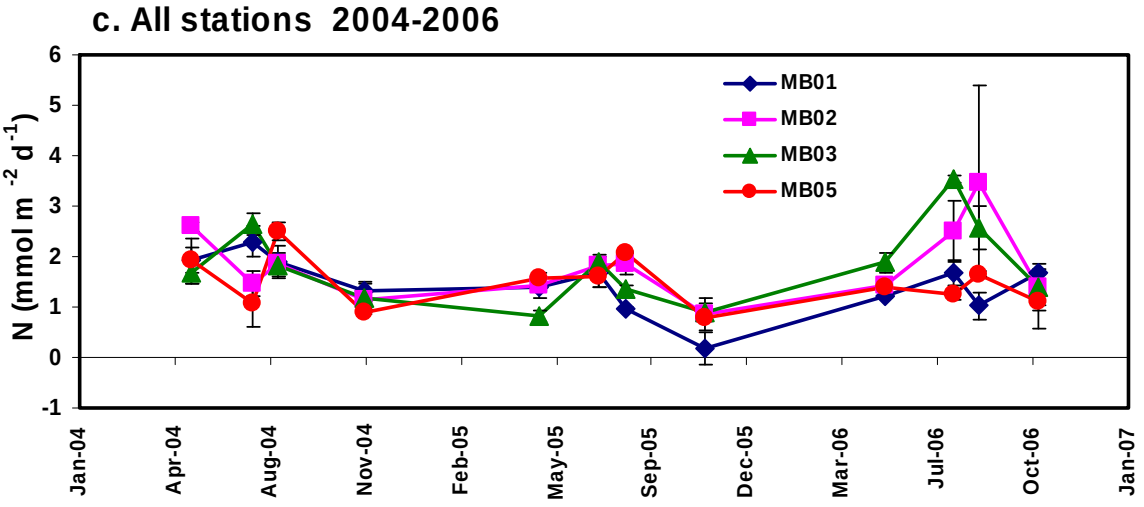


**Figure 13. Denitrification at all four Massachusetts Bay Stations in 2004, 2005, and 2006.**

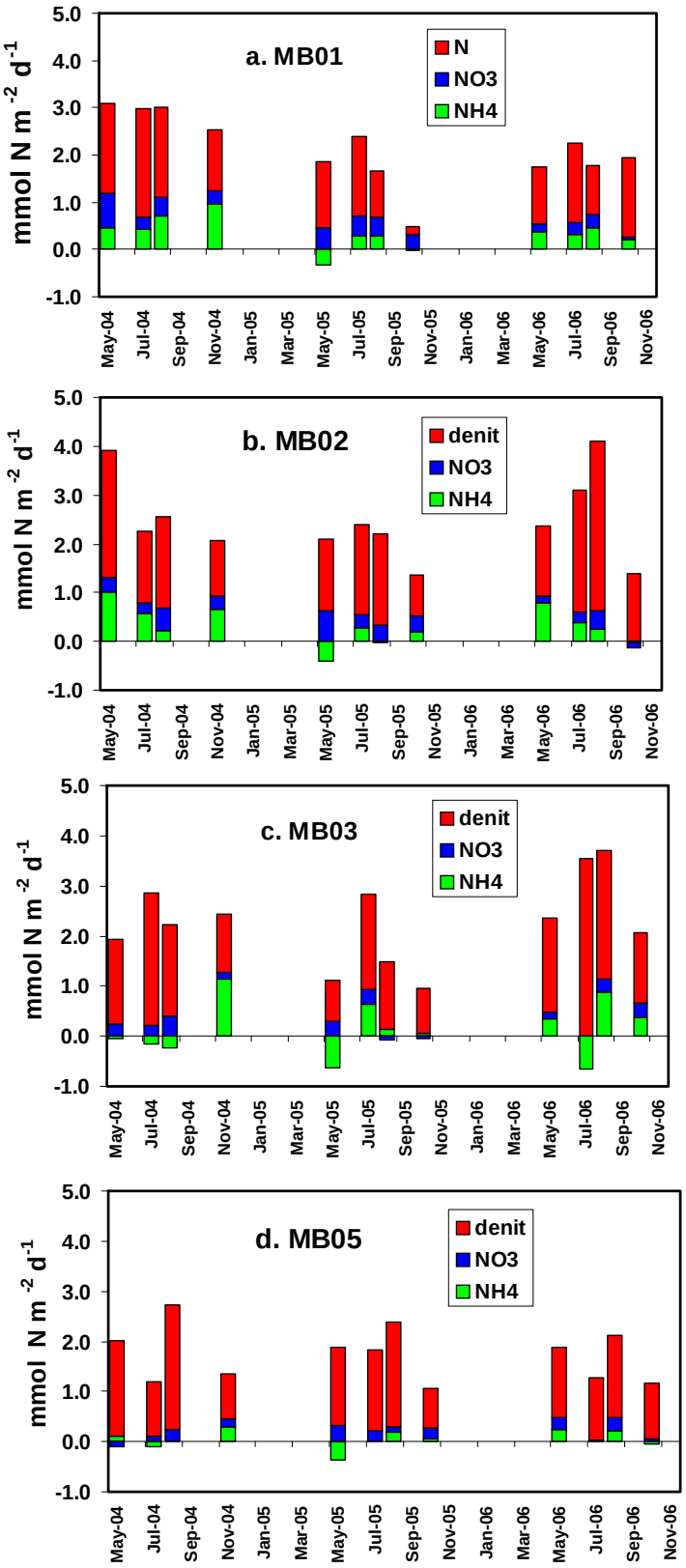


**Figure 14. Nitrogen flux at all four Massachusetts Bay Stations in 2004, 2005, and 2006, partitioned into components of N from denitrification, $NH_4$+ flux, and $NO_3^-$ flux**

## 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 and Eh.

### 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 (Fig. 15; note that $CO_2$ data are not available for 1995-1998). In the early years of monitoring (1992-1994), seasonal average RQs (omitting winter) were often greater than 1.0, indicating that anaerobic processes were important. 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 2006, average RQs returned to values close to 1.0 from the low values we observed in 2005 (Fig. 15). With this return, it seems clear that those low values may be attributed to the resuspension and oxygenating of the surface sediments by the stormy 2005 season. 2006 was a more typical year, and RQs in the nearfield were above 1.0 during all surveys except in July, when they were all less than 1.0. In particular, RQ was quite low, 0.5, at Station MB03 in July. However, it was followed in August by the high value of the season, 1.4, producing the "seesaw" seasonal pattern noted for DIN and $PO_4^-$ flux at this station. Photosynthesis would help explain this low value, but again, our dark incubations make this explanation implausible.

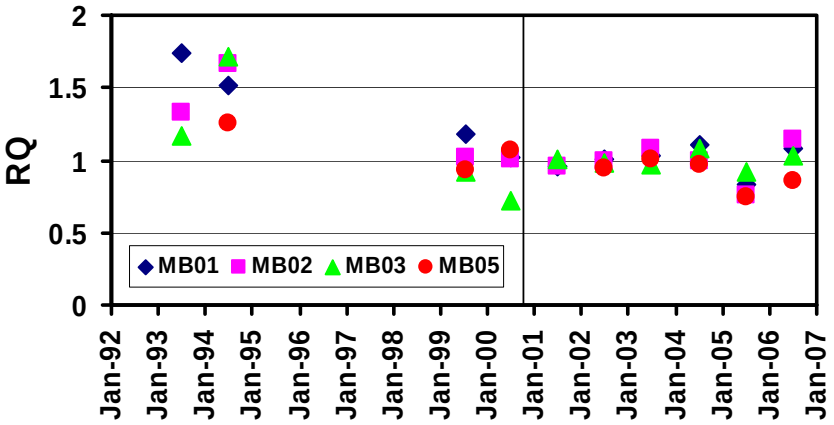


**Figure 15. Seasonal (May-October) average respiratory quotients for Nearfield stations MB01, BM02, MB03, and Farfield station MB05 from 1993-2006. The vertical line marks the transition from baseline to post-relocation observations.**

### 2.5.2 Eh profiles

Oxidation-reduction potential measured as Eh in 2006 continued to be indicative of highly oxidized conditions in sediment cores from Massachusetts Bay (Fig. 16). We have not observed any tendency towards decreased oxygen levels in these sediments. In fact, there has typically been no distinct color change that would mark a redox potential discontinuity (RPD) within the 18-20 cm depths of our cores, and that is still the case six years after relocation of the outfall. Values continue to be well above those that would indicate the presence of dissolved sulfides (-100 to -200 mV). Nearfield profiles of Eh in 2006 were in general least positive in July and most positive in October. At the farfield station, most positive values occurred in August.

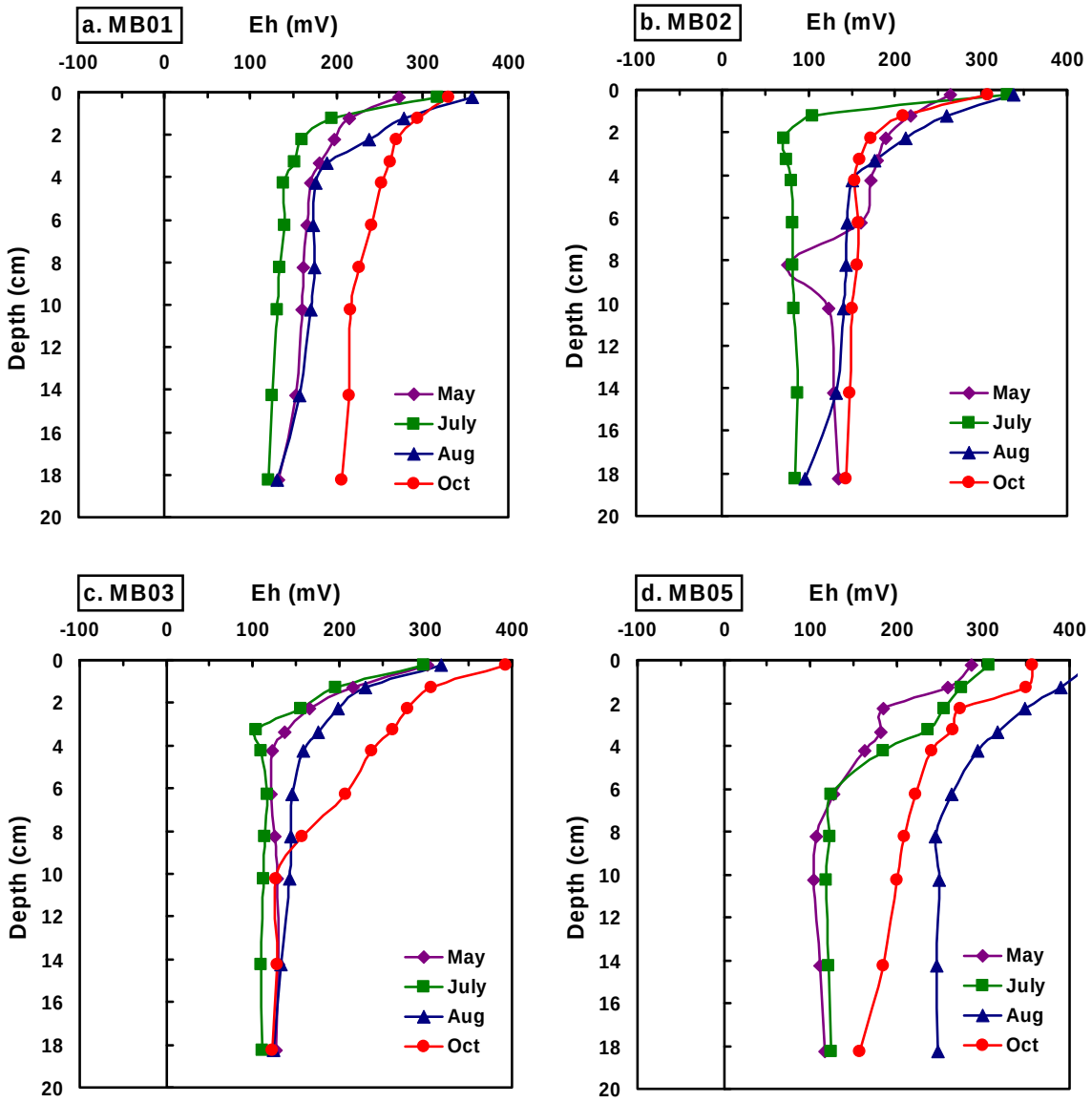


**Figure 16. Eh profiles for May through October, 2006, from Nearfield stations a.) MB01, b.) MB02, c.) MB03, and Farfield station d.) MB05.**

# 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 less change during this time.

The diversion of all MWRA effluent offshore marked the final phase in MWRA's Deer Island project, and has resulted in dramatic improvements in water quality in the harbor. For example, after five years, DIN concentrations had shown a decrease of 55% (Taylor, 2006). Accordingly, primary production has decreased, and the prolonged summer bloom that had been characteristic of the harbor is no longer typical (Libby et al, 2007).

Four harbor stations have been repeatedly sampled in the benthic nutrient cycling program throughout the monitoring period (Fig. 17). 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. In 2004, the October survey was delayed by weather, and instead took place during the first week of November.

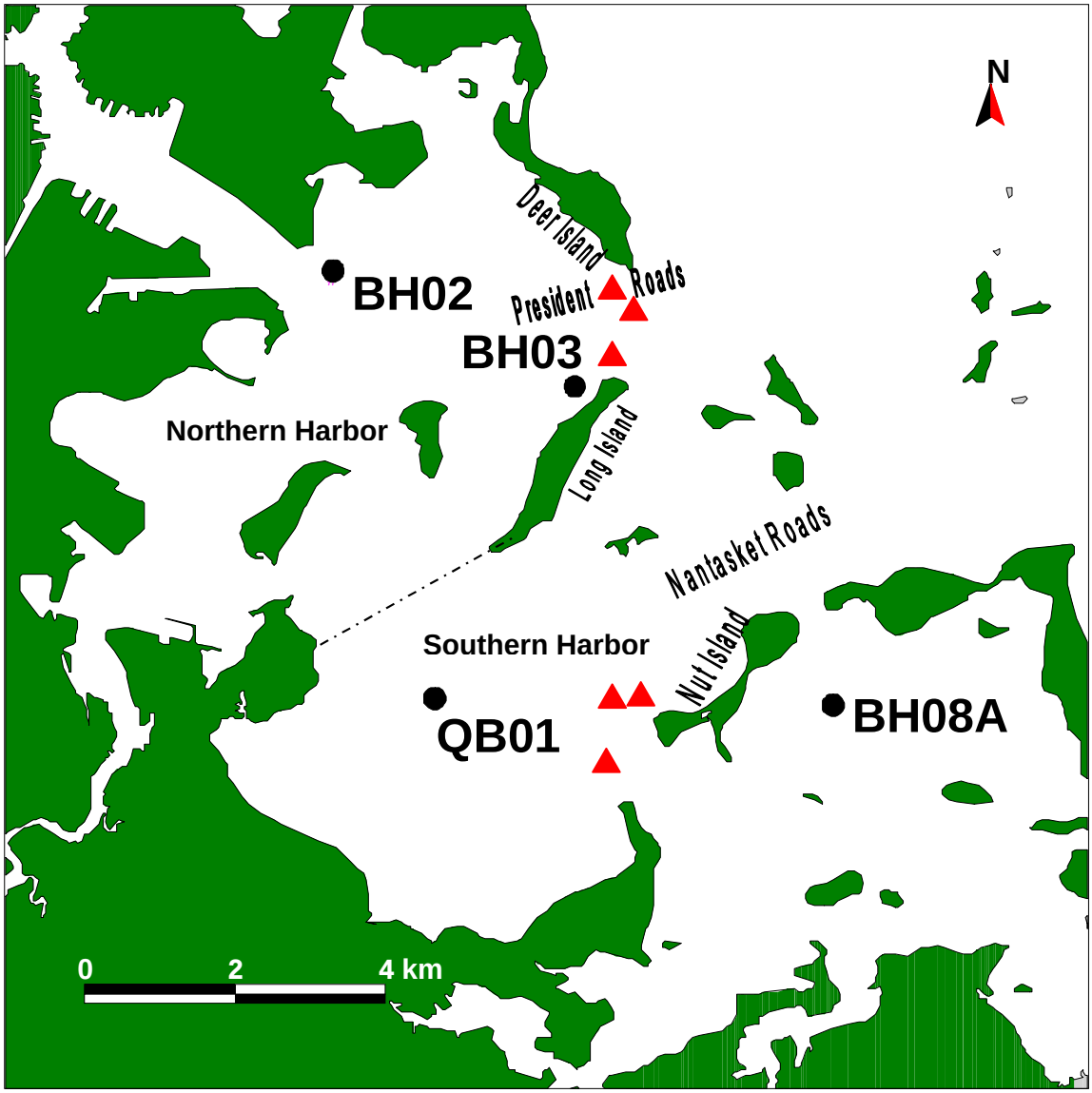


**Figure 17. Locations of four Boston Harbor stations. Triangles (▲) mark the location of the out-of-service Harbor outfalls, the last of which was taken out of service on Sept. 6, 2000.**

## 3.1 Organic Matter Loading

### 3.1.1 Total Organic Carbon

Reductions in organic matter content in Boston Harbor sediments became apparent before the MWRA outfall was relocated offshore because other improvements in sewage treatment were implemented during that baseline period. Of principle importance to the benthos was the reduction of solids discharge, which began at the end of 1991 with the cessation of sludge disposal in the harbor, and continued as full primary and then full secondary treatments came on line. 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. The very high percentages of organic carbon (over 4%) that were observed at these stations at various times before 1999 have not recurred. Temporal and spatial variability have also decreased.

In 2006, seasonal averages of total organic carbon (TOC) varied little across the four stations, ranging only from 1.7% at BH08A to 2.3% at QB01 (Fig. 18). At Station BH02, average TOC was 2.1 % , continuing a trend of almost no change since 2000. At Stations BH03 and BH08A, the slight increase this year from 2005 marks the first year the trend at these stations has not continued to decline. Within the season, highest TOC content, 2.7%, was observed at Station QB01 in July. Lowest, 1.4%, was measured at Station BH03 in October, when values from all stations were lowest. At Station BH03, coarse sediments and the absence of amphipods had been noted for 2004-2005. In August and October 2006, field observations recorded a return to muddier sediments, and amphipods, though not mats, were present.

As mentioned above, TOC content in harbor sediments seemed to reflect the changes in solids loading to the harbor. In fact, if we look at the harbor data relative to that time line, we do see a stepwise decrease in TOC. We have divided the data according to the time line of changes in solids loading (Figs. 18 and 19). Period 1 is the period before 1995. Sludge discharge into the harbor had ended at the end of 1991, and with it a reduction in solids loading from about 150 to 110 tons per day. Period 2 is from 1995 to 1997. In 1995, full primary treatment came on line, with a smaller reduction in solids, from about 110 to 90 tons per day . Period 3, 1998-2000, marks the beginning of secondary treatment and the transfer of all Nut Island discharge to Deer Island. This combination resulted in the largest decrease in solids loading, from around 85 tons per day in 1997 to about 40 tons per day in 1998. The final period starts in 2001, after the divergence of all discharge from Deer Island to the ocean outfall, which effectively ended the solids loading from effluent.

Data from Station BH03 provide the best comparison to this time line (Fig. 19). Unfortunately, we have only one data point from the time when sludge was still being discharged near this station (from September, 1991, and the carbon content was 3.8%), so we are unable to make a real pre- vs post-sludge disposal comparison. TOC remained high and variable through periods 1 and 2, and there was no real difference between the periods. However there was a large decrease between periods 2 and 3, after secondary treatment came on line, from an average of 3.8% TOC to 2.8%. Period 3 also followed the years of peak abundances of individuals and tube mats of the amphipod *Ampelisca*, which we believe accelerated the respiration of carbon in these sediments. A further decrease in TOC occurred between period 3 and 4, however variability increased over the six years of this period at this station. Inspection of the data shows little change during the first three years of period 4, followed by a decreasing trend starting in 2004 that was associated with a change to coarser sediments at this site (Tucker et al, 2006).

Similar series of changes were observed in the other stations as well (Fig. 19), especially at Station BH08A where there were stepwise decreases between periods 2, 3, and 4. At QB01, a large decrease occurred between periods 2 and 3, but there has been little change thereafter. Little change has been discernable at BH02 over the four periods, in part due to the large variability observed at this station before 2001. For this comparison we have included the two data points we had for BH02 from 1992, measured in April and August, which indicate a pattern in TOC parallel to that at BH03. Without these points, the average for this period appears, in our judgment, artificially low.

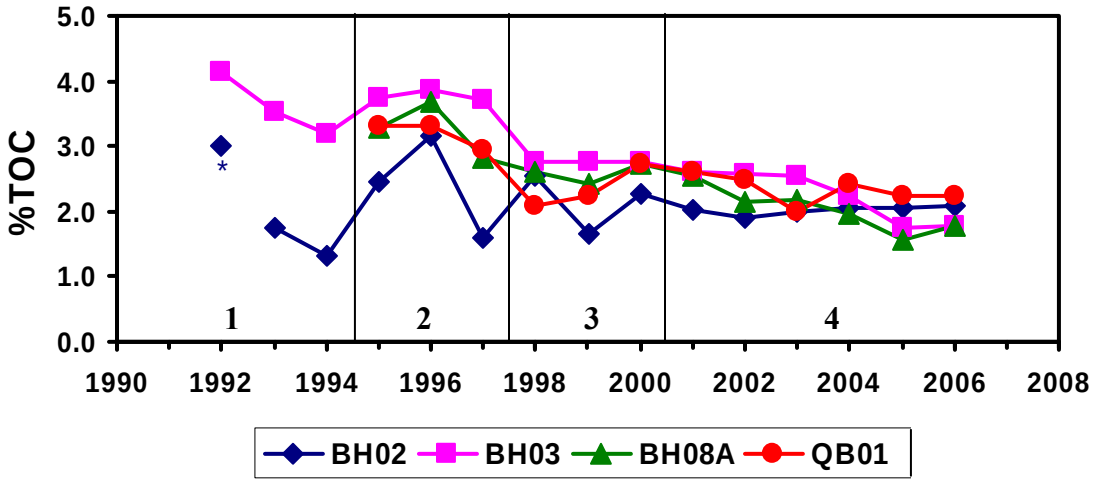


**Figure 18. Seasonal average TOC (% dry weight) for top 2 cm of sediment, with time divided into treatment periods 1-4 (see text for details). The asterisk beside the 1992 data point for BH02 denotes a two-point rather than a 4-point average.**

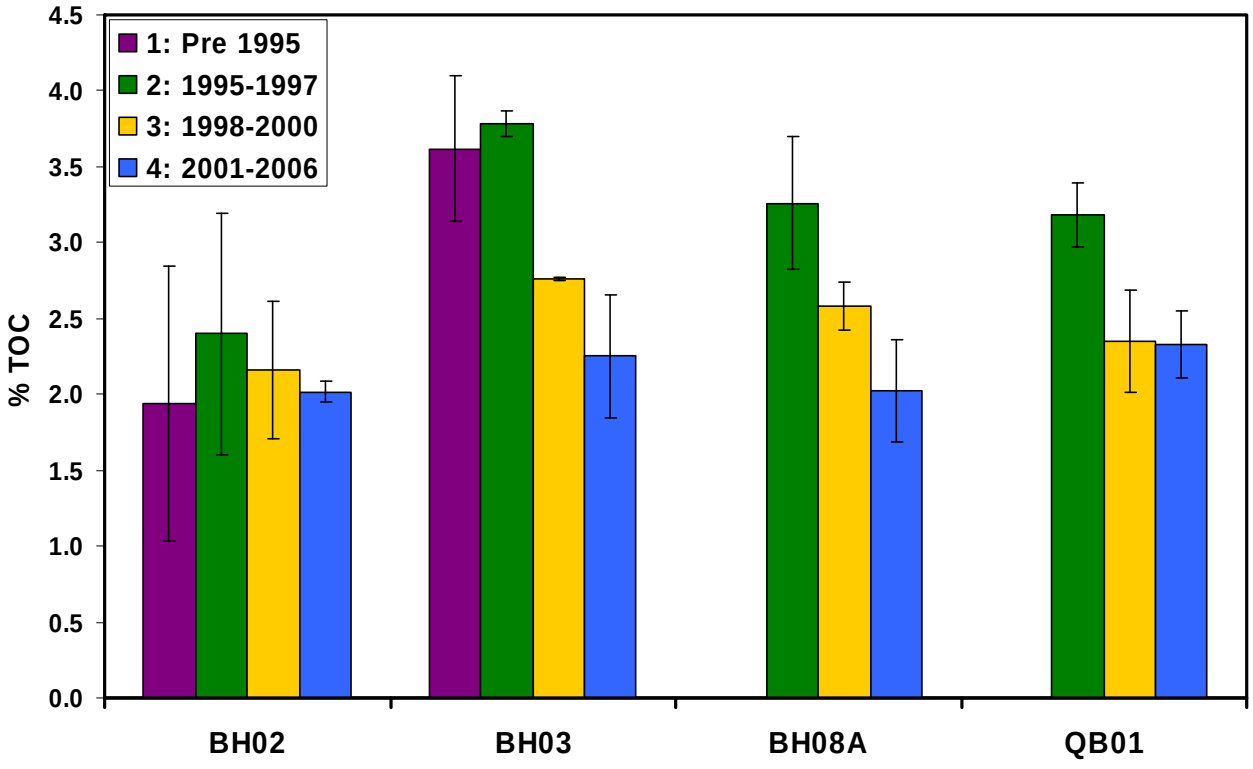


**Figure 19. Sediment TOC for each station by treatment periods 1-4 (see text for details). Data are seasonal averages over years for each period. Error bars represent one standard deviation of the mean.**

### 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.

Throughout the baseline period, there was no discernible temporal trend in sediment total pigment inventories (concentrations integrated over the top 5 cm). That is, there was no pattern that seemed to be directly related to sewage treatment improvements. Instead, the observed effects may have been mediated through the benthic community. Low inventories for all four stations occurred in 1995-1996, during the peak of harbor coverage of the amphipod mat community, which presumably would graze down the benthic microfauna as well as filter water column phytoplankton. (Note that a difference in extraction of pigments during this time may have caused the phaeophytin *a* fraction of the total pigments to be artificially low. However, chlorophyll inventories were also low at this time.) Highs (1997-1999) were more variable from station to station, but a release from grazing pressure as the mat community declined doubtless played a role. In fact, increases were often most apparent in the chlorophyll *a* ("fresh") fraction, and often associated with observations of benthic diatoms. This was especially and surprisingly true for Station BH02, where other sediment parameters had shown little "improvement".

For the first two years after the outfall relocation, there was no apparent change in chlorophyll inventories compared to the year before relocation. However, in 2002-2003, an upward trend, especially in the chlorophyll *a* fraction, began at Station BH02 and QB01. In 2004, this trend peaked, with highest levels yet observed at BH02, although similar inventories had been reached in 1998-1999. Curiously, largest chlorophyll *a* inventories of the four stations have been measured at Station BH02 consistently since 1998; these measurements have been accompanied by observations of benthic diatoms. For QB01, the upward trend resulted in inventories of total pigments as well as chlorophyll *a* alone that were unprecedented during baseline. Again, we believe much of this chlorophyll was derived from *in situ* production, as diatoms were also often observed at this station. A possible explanation for the difference in chlorophyll levels at Stations BH02 and QB01 compared to Stations BH03 and BH08A may be differences in grazing pressure. Dense animal communities have been rarely observed at BH02 and QB01, but often observed at BH03 and BH08A.

In 2006, chloropyll *a* inventories (integrated over the top 5 cm of sediment) were typical of the previous three years at QB01, and for the entire monitoring period for the other three stations. Largest inventories for the season occurred in May at all stations, and smallest in October. Concentration profiles for the top 5 cm showed surface maxima at all stations in May. At BH02 , May surface (0-1 cm) concentration of chlorophyll *a* was quite high at 27.9 µg $cc^{-1}$, over twice the levels at the other three stations. These high surface levels were not sustained throughout the season, but concentrations remained high enough even through October that the highest seasonal average inventory was once again found at BH02 (35.2 µg $cm^{-2}$). At QB01, strong profiles persisted from May through August, with surface concentrations peaking at 17.5 µg $cc^{-1}$ in August. October profiles showed very low concentrations throughout the profile. Seasonal average chlorophyll inventory at QB01 was 27 µg $cm^{-2}$. At BH03 and BH08A inventories were 10.7 and 12.7 µg $cm^{-2}$, respectively.

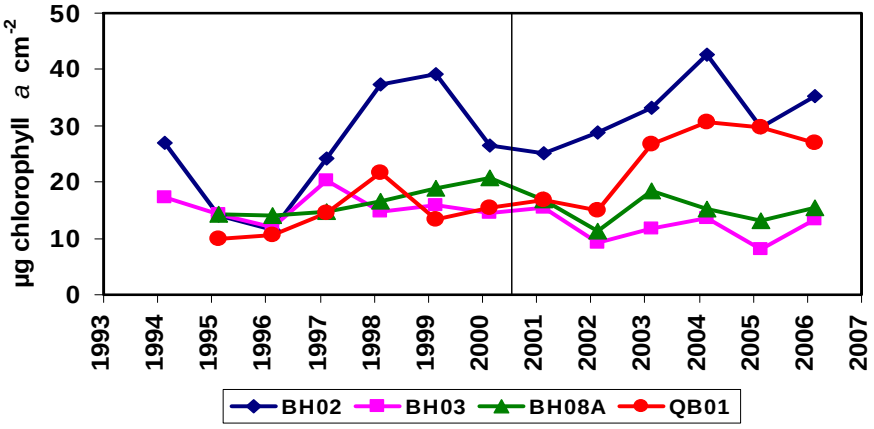


**Figure 20. Average chlorophyll a inventory for top 5 cm of sediment at harbor stations The vertical line marks the transition from baseline to post -relocation observations.**

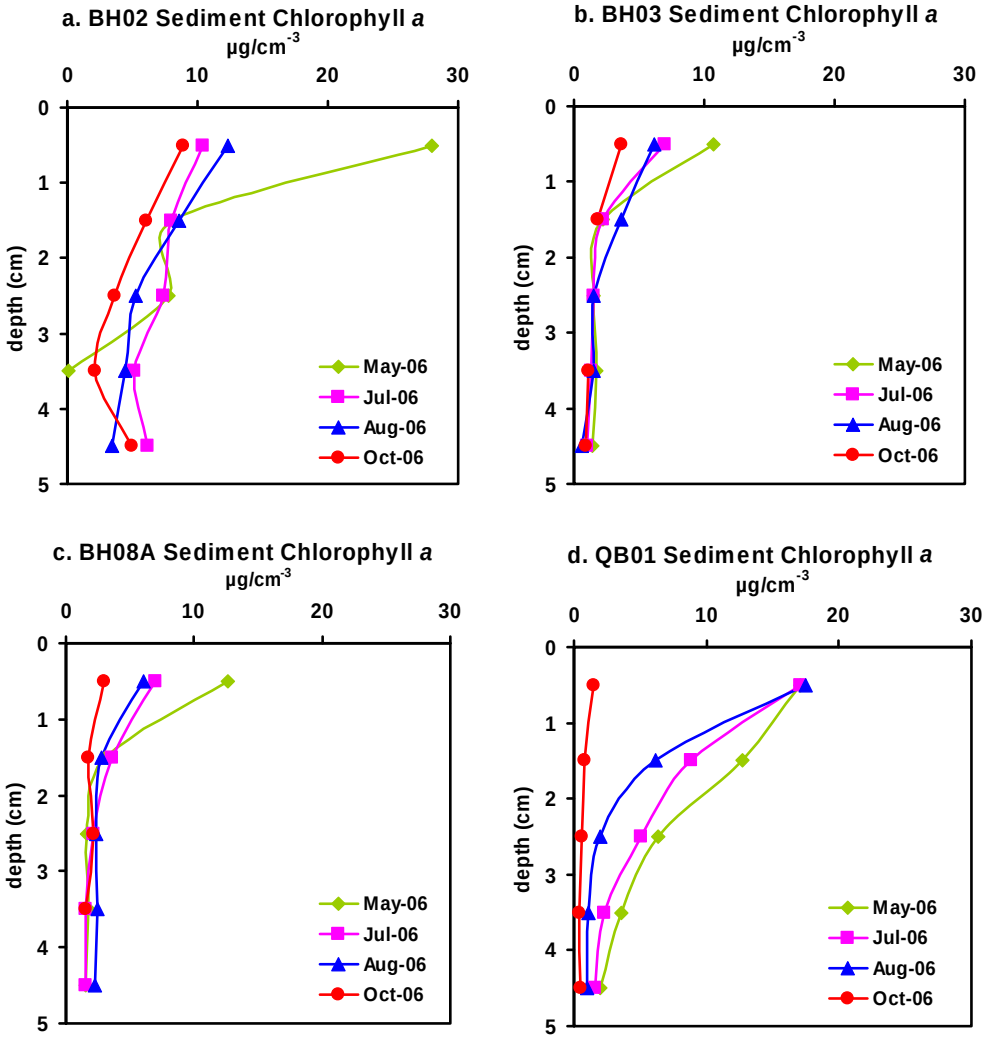


**Figure 21. Profiles of chlorophyll *a* in top 5 cm of sediment at Boston Harbor stations in 2006 a.) BH02, b.) BH03, c.) BH08A, and d.) QB01.**

## 3.2 Sediment Oxygen Demand

Since the beginning of the monitoring program, sediment oxygen demand (SOD) or benthic respiration has decreased dramatically from an average high across our four stations of 99.6 mmol $m^{-2}$ $d^{-1}$ in 1995 (this was the first year that data were available for all four stations; in 1993, the average for BH02 and BH03 was 133.2 mmol $m^{-2}$ $d^{-1}$) to the low in 2005 of 22.5 mmol $m^{-2}$ $d^{-1}$ (Fig. 23a). In 2006, that average increased slightly to 29.1 mmol $m^{-2}$ $d^{-1}$. The average for the post-relocation period is 34 mmol $m^{-2}$ $d^{-1}$ as compared to the pre-relocation average of 69 mmol $m^{-2}$ $d^{-1}$. However, as we discussed for organic carbon, changes in SOD and nutrient fluxes began before relocation; that is, as other treatment improvements were implemented.

For 2006, SOD was below the baseline range for Stations BH02, BH03, and BH08A. Seasonal averages at these three stations varied little, ranging only from 24.5 mmol $m^{-2}$ $d^{-1}$ at BH08A to 27.7 mmol $m^{-2}$ $d^{-1}$ at BH03. There was little seasonal variability at BH03, with rates ranging only from 30.3 mmol $m^{-2}$ $d^{-1}$ in August to 25.0 in October. Both BH02 and BH08A showed a more pronounced seasonal pattern, with maximum rates in July (36.7 mmol $m^{-2}$ $d^{-1}$ at BH02) and, like BH03, minima in October (17.5 mmol $m^{-2}$ $d^{-1}$ at BH08A). At Station BH03, the return of amphipod individuals, but not mats, and to muddier sediments was noted in August and October.

At the fourth station, QB01, which never exhibited the extremely high rates of the other three stations, SOD was typical except in August, when the average of the measured rates was unusually high. The resulting seasonal average, 38.9 mmol $m^{-2}$ $d^{-1}$, was the highest of the four stations. The cause of the high August rate, which was 64.9 mmol $m^{-2}$ $d^{-1}$, was the presence of macrofauna in one of the two experimental cores. The description of this core at the time of incubation noted a large burrow in the core as well as a shrimp. Benthic respiration (as well as other fluxes; see Sections 3.3.1 and 3.3.2) in this particular core was very high: 104.9 mmol $m^{-2}$ $d^{-1}$. In contrast, the duplicate core, without macrofauna, had a respiration rate of a very typical 24.8 mmol $m^{-2}$ $d^{-1}$. We have not omitted the high rates because animal respiration is an important part of total SOD. However, inclusion certainly overestimates the average flux because we do not think this high rate is characteristic of 50% of the bottom. Lowest SOD for the season at this station was 18.5 mmol $m^{-2}$ $d^{-1}$, and occurred in October as it did for the other three stations.

We have been unable to identify a primary control on SOD in these harbor sediments. We have often reported on the temporal and spatial variability in the relationship with potential controls such as temperature, %TOC, and sediment chlorophyll pigments. In 2006, SOD was strongly correlated with temperature at Stations BH02 and BH08A, less strongly at Station QB01, and not at all at Station BH03 (Table 1). Organic carbon content was very important at BH02, but not at the other three stations. One station, BH03, showed a reasonable correlation with sediment chlorophyll *a*, but at the same time a very strong but negative correlation with total chlorophyll pigments (chlorophyll *a* + phaeophytin *a*). At Station BH08A, total chlorophyll was very strongly correlated with SOD, whereas chlorophyll *a* alone was not.

In at attempt to examine these relationships over a longer and more stable time frame, we ran these correlations for the post-diversion period (2001-2006). In this analysis, temperature could account for only 8%-12% of the variability in sediment respiration across the four stations. The importance of other controls varied more widely across stations. Highest correlations of TOC, chlorophyll *a*, and phaeophytin *a* with SOD were found at Station BH08A, where the $r^2$s were 0.39, 0.21, and 0.27, respectively. Relationships with these parameters were weak or nonexistent at the other stations, with $r^2$s ranging from 0.15 for phaeophytin *a* at BH03, to 0.00 for chlorophyll *a* at Station BH02. It is clear that multiple factors interact to determine S.O.D. at these stations, and that these factors may vary annually and across stations.

**Table 1. Coefficients of determination ($r^2$) for relationships between SOD and temperature (ºC), TOC (% dry weight, top 2 cm), and chlorophyll *a* and total chlorophyll pigment inventories (ug $cm^{-2}$ for top 5 cm), in 2006. Gray shading denotes regressions with negative slopes.**

| SOD vs: | Station | | | |
|---|---|---|---|---|
| | BH02 | BH03 | BH08A | QB01 |
| Temp | 0.699 | 0.001 | 0.775 | 0.381 |
| TOC | 0.838 | 0.442 | 0.278 | 0.182 |
| Chl a | 0.050 | 0.546 | 0.125 | 0.199 |
| Chl + Phaeo a | 0.083 | 0.979 | 0.969 | 0.157 |

## 3.3 Nutrient Fluxes

Like sediment respiration, benthic fluxes of DIN, phosphate and silica (Fig.21b-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 temporal and spatial variability we observed 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

In 2006, DIN flux at three of the four harbor stations was typical of recent years, but in general lower than the baseline range (Fig.23b). The one exception was a higher than usual flux at Station QB01. As discussed for SOD, the high seasonal average flux at this station of 2.8 mmol $m^{-2}$ $d^{-1}$ was driven by the high August rate (9.2 mmol $m^{-2}$ $d^{-1}$; Fig 24h), which in turn was driven by very large fluxes from one of the duplicate cores. In this core, DIN flux (almost all $NH_4^+$) was very large, 16.8 mmol $m^{-2}$ $d^{-1}$, whereas the rate from the other core was a typical 1.7 mmol $m^{-2}$ $d^{-1}$. Also as previously discussed, we include this rate because it represents a real element of benthic nutrient cycling, however because of small sample numbers, we believe inclusion may result in an over-estimation of the true average flux. Even so, the 2006 rate did not exceed all previous observations; in 1995, average DIN flux at Station QB01 was 4.1 mmol $m^{-2}$ $d^{-1}$.

For the remainder of the sampling dates and stations, rates ranged from a low DIN flux of less than 0.1 mmol $m^{-2}$ $d^{-1}$ in October at QB01, to a high of 7.2 mmol $m^{-2}$ $d^{-1}$ at BH02 in August (Fig. 24 e-g) . Seasonal averages ranged from 1.2 mmol $m^{-2}$ $d^{-1}$ at BH03 to 4.1 mmol $m^{-2}$ $d^{-1}$ at BH02. All stations showed a seasonal pattern with high rates in August, such that temperature could explain between 45% and 60% of the DIN flux.

Nitrate comprised a relatively small portion of the overall DIN flux in 2006. It was a major component , 52%, only at Station BH03. It accounted for 23% and 10% of the flux at Stations BH08A andBH02, respectively, and less than 1% at Station QB01. At BH03, both physical and biological processes may be acting to oxygenate the sediments. Field and lab notes describe surface sediments with small rocks and pebbles, attached macroalgae, and no amphipods in May and July, but some amphipod tubes reappearing in August and October. At BH08A, there was little note of small infauna, but Cerianthids were noted by divers in May, July, and August. These larger infauna may produce deeper but very local patches of oxygenated sediments around their burrows. No amphipods and few biological features were noted at the other two stations.

### 3.3.2 Phosphate and Silica

Seasonal average phosphate fluxes in 2006 varied across the four stations but were typical of post-relocation observations. Averages ranged from 0.04 mmol $m^{-2}$ $d^{-1}$ at Station BH03 to 0.41 mmol $m^{-2}$ $d^{-1}$ at BH02 (Fig. 23c). The harbor average for 2006 was 0.19 mmol $m^{-2}$ $d^{-1}$, higher than the previous year's all-time low of 0.09 mmol $m^{-2}$ $d^{-1}$. Within the year, observations were within or below baseline ranges except for a large flux at BH02 in October (1.18 mmol $m^{-2}$ $d^{-1}$) and a just-above-the-range value at QB01 in May (0.26 mmol $m^{-2}$ $d^{-1}$) (Fig. 25 a-d). There was no apparent bioturbation-enhanced $PO_4^-$ flux at QB01 in August as there was for the other nutrients. However, the large flux at BH02 in October may have been caused by a small shrimp swimming in one of the duplicate cores, although in this case similar increases were not observed in the other fluxes. There was no seasonal pattern other than $PO_4^-$ fluxes were extremely small (BH03) or directed into the sediments (uptake) in July.

Silica flux, as a harbor-wide average for the season, increased in 2006 from the very lowest measured rate of the previous year (2.7 mmol $m^{-2}$ $d^{-1}$) to a more typical 4.3 mmol $m^{-2}$ $d^{-1}$ (Fig. 23d). Seasonal average rates were similar across the four stations, ranging from 3.9 mmol $m^{-2}$ $d^{-1}$ at BH08A to 5.0 mmol $m^{-2}$ $d^{-1}$ at QB01. Within the year, Si fluxes were within or below the baseline range, except for the August rate at QB01 (Fig. 25e-h). This high rate of 10.8 mmol $m^{-2}$ $d^{-1}$ comes from the same pair of cores in which one core had very high SOD and $NH_4^+$ fluxes, and that we attributed to bioturbation (see Sections 3.2 and 3.3.1). However, in the case of Si, both cores had similarly high fluxes, even though macrofauna were observed in only one. The lowest rate of the season was an uptake of 1.3 mmol $m^{-2}$ $d^{-1}$ at Station BH02 in May. Small uptake was also observed at Station BH08A in May.

Largest Si fluxes at all stations occurred with the warmest temperatures in August, so although there was a seasonal pattern to the fluxes, the direct relationship with temperature was variable depending on station. The correlation was strongest at Station BH02, where the $r^2$ was 0.80 and weakest at Station BH03, where it was only 0.22. For the post-relocation years 2001-2006, temperature could explain between 16% and 26% of the variability in Si fluxes.

### 3.3.3 Benthic Flux Contribution to Primary Production

The relocation of the sewage outfall ended the direct input of a large source of nutrients to the Harbor. With this change, we expected that the relative contribution of nutrients supplied to the water column by benthic recycling might increase. We can use Redfield relationships to make rough estimates of these contributions using pre- and post- relocation rates of primary production and benthic fluxes. Annual average primary production at water column station F23 at the mouth of the harbor has decreased from a pre-relocation average of about 572 g C $m^{-2}$ $y^{-1}$ to a post-relocation average of 361 g C $m^{-2}$ $y^{-1}$ (Libby et al., 2007). Seasonal average nutrients fluxes have also decreased, and in some cases relatively more than has primary production. The result is that the potential contribution of recycled DIN and $PO_4^-$ to primary production has actually decreased. Before relocation, even with benthic fluxes declining, we calculated a potential contribution of 30% and 41% for DIN and $PO_4^-$, respectively. After relocation, we calculate a potential contribution of 23% for DIN and 22% for $PO_4^-$. In contrast, the contribution of dissolved silica fluxes has not changed, being about 41% during both periods.

As noted for similar estimates made for our bay sites (Section 2.2.3) 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 in Boston Harbor.

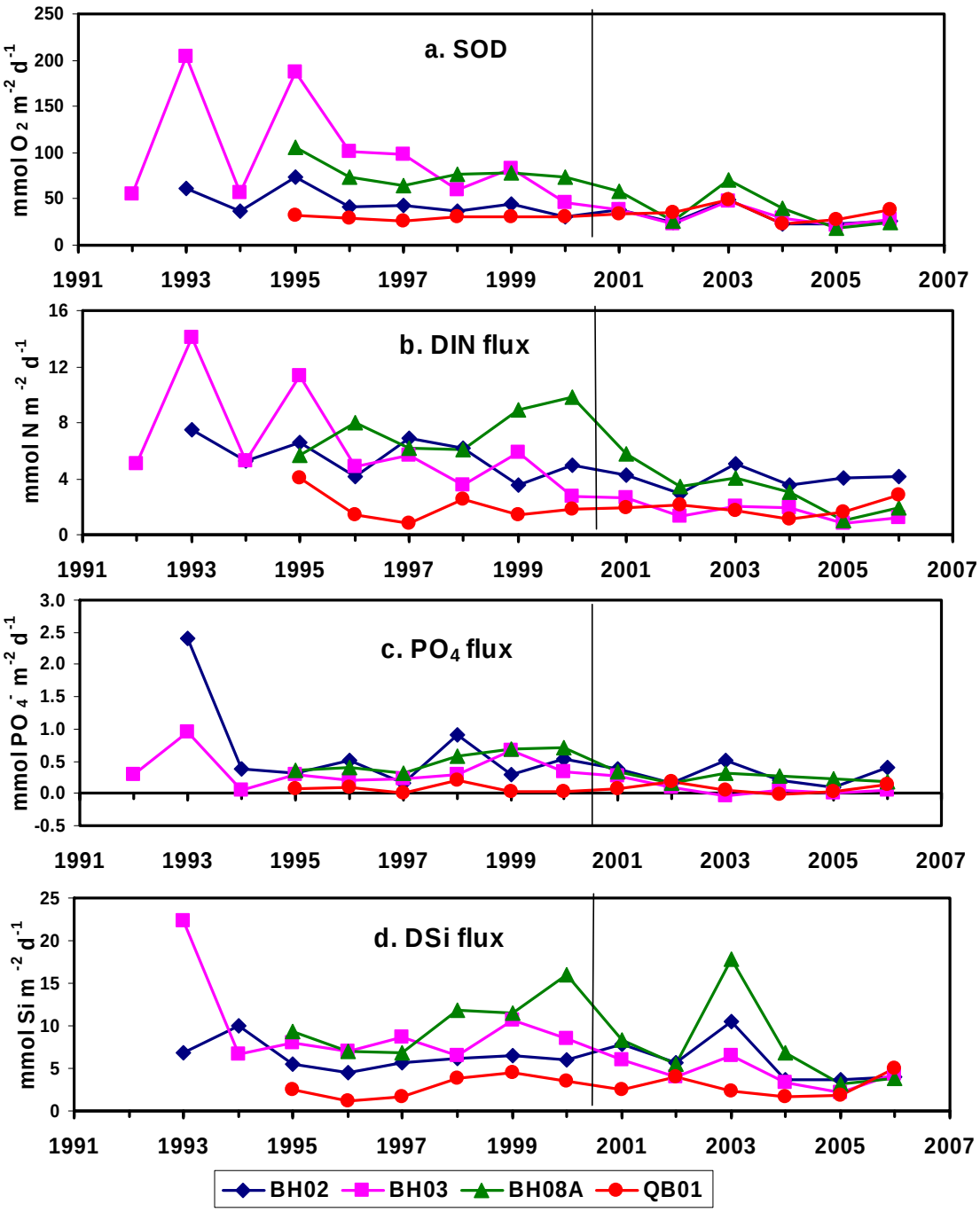


**Figure 22. Seasonal (May-October) averages of a.) sediment oxygen demand (SOD), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Boston Harbor stations in 1993-2006. The vertical lines mark the transition between baseline and post-relocation observations.**

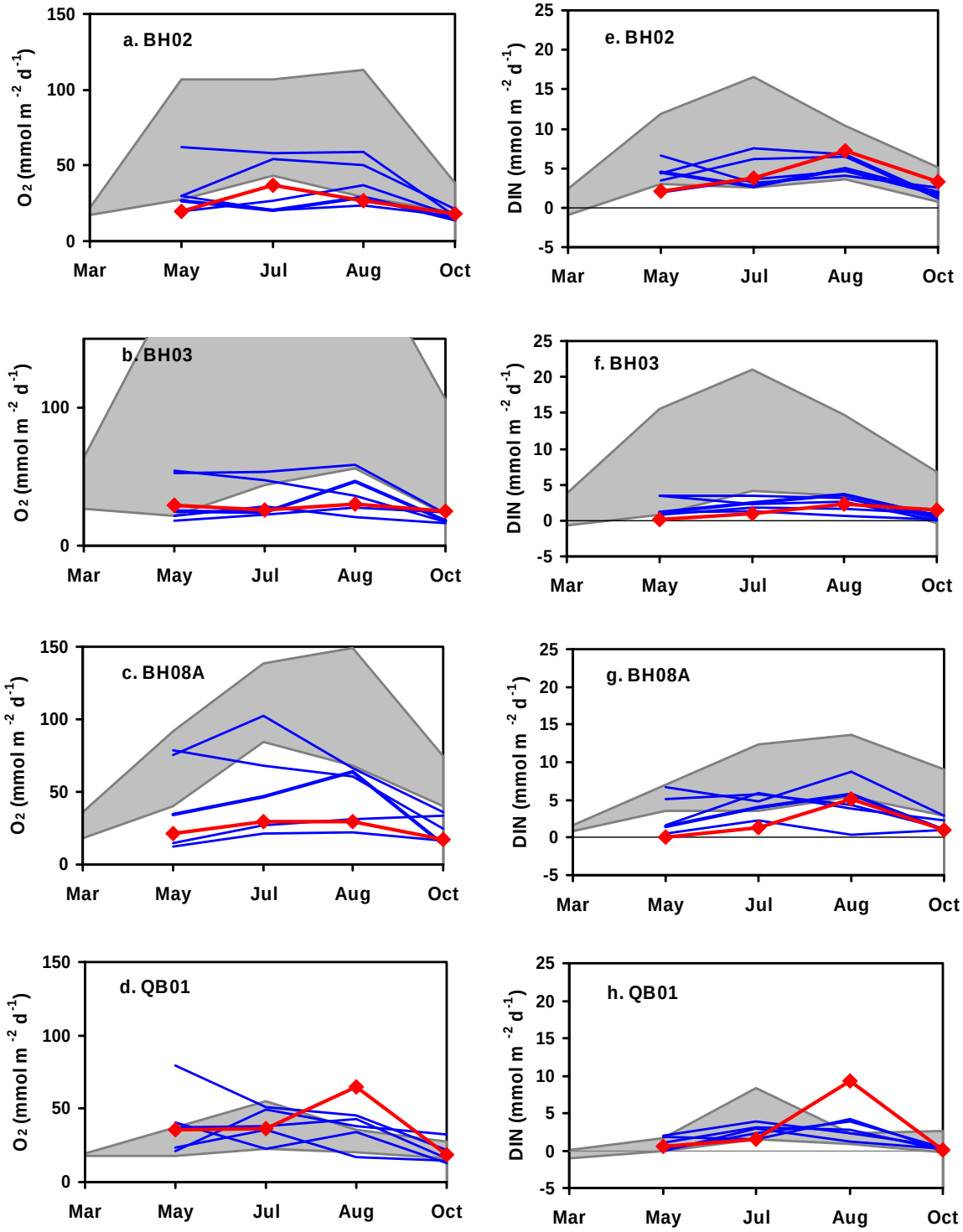


**Figure 23. Sediment oxygen demand ($O_2$ flux) and DIN flux for 2006 compared to all other post relocation years (2001-2005, solid lines) and maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations BH02, BH03, BH08A, and QB01, respectively.**

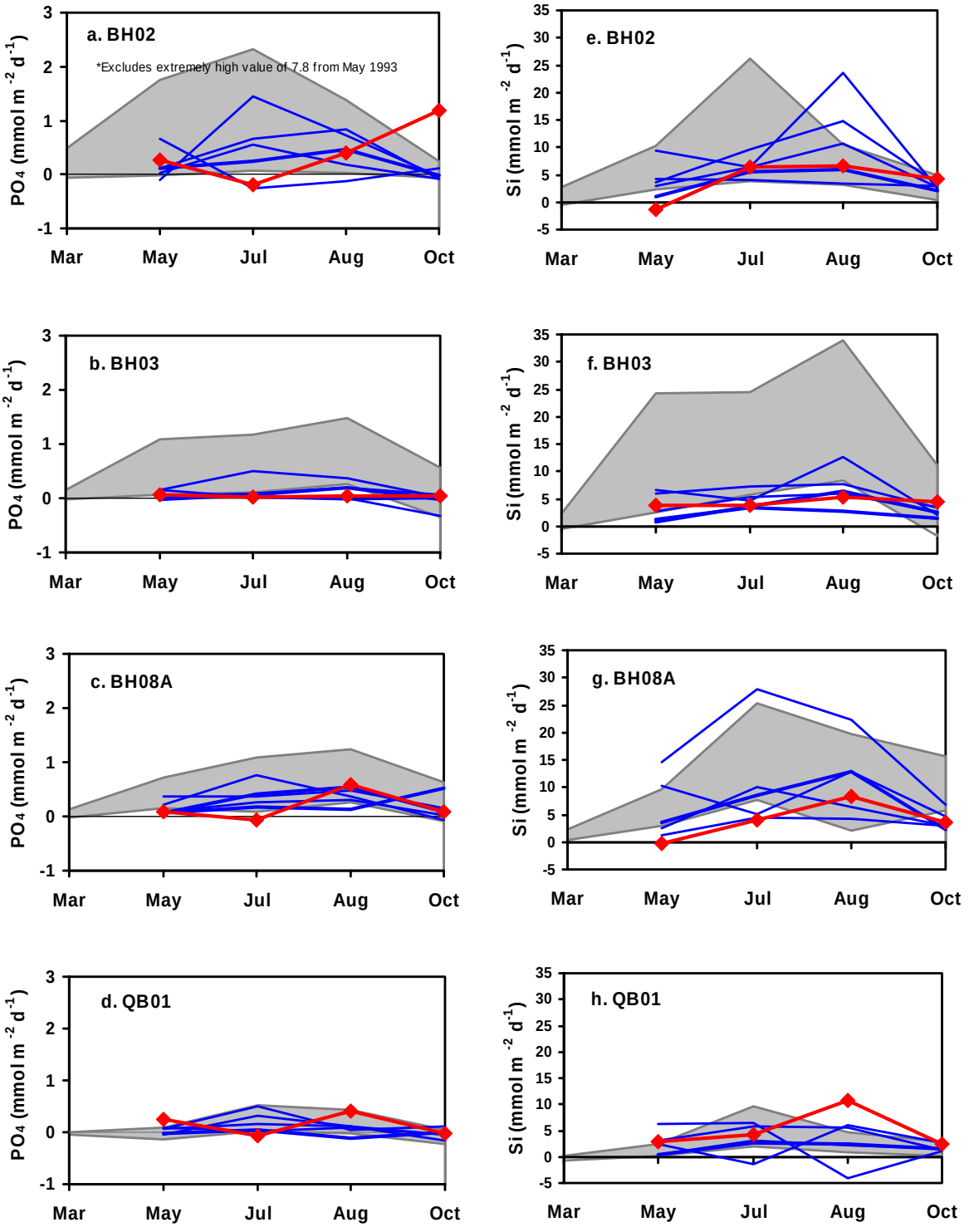


**Figure 24. Phosphate ($PO_4$) and dissolved silica (DSi) flux for 2006 (-♦-) compared to all other post-relocation years (2001-2005, solid lines) maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict $PO_4$ and panels e-h depict DSi flux for stations BH02, BH03, BH08A, and QB01, respectively.**

## 3.4 Denitrification

Denitrification rates in 2006 were among the lowest of both baseline and post-relocation measurements for the third year running at Stations BH02 and BH03, where it has been measured throughout the monitoring program. In fact, seasonal average rates have been very similar over the past three years. In 2006, those rates were 1.4 mmol N $m^{-2}$ $d^{-1}$ and 1.8 mmol N $m^{-2}$ $d^{-1}$, for BH02 and BH03 respectively. (Fig 25a). Again we must note that the low rates may in part be a result of the new analytical method (see Tucker and Giblin, 2005). However, the timing is also coincident with the decline and even absence of the amphipod mats, which we believe were responsible for some of the very high rates observed early in the program.

The change in analytical method in 2004 allowed us to add measurements at southern harbor Stations BH08A and QB01 so we now have three years of data from all four stations and all surveys (Fig. 25b). In 2006, the four stations followed similar seasonal patterns. The highest rates at all stations occurred in May, with the maximum rate of 3.0 mmol N $m^{-2}$ $d^{-1}$ at QB01. Lowest rates occurred in August at all stations except BH02, which had a low rate in October. The minimum rate occurred at QB01, where in August there was essentially no denitrification. The overall average denitrification rate for 2006 was 1.4 mmol N $m^{-2}$ $d^{-1}$.

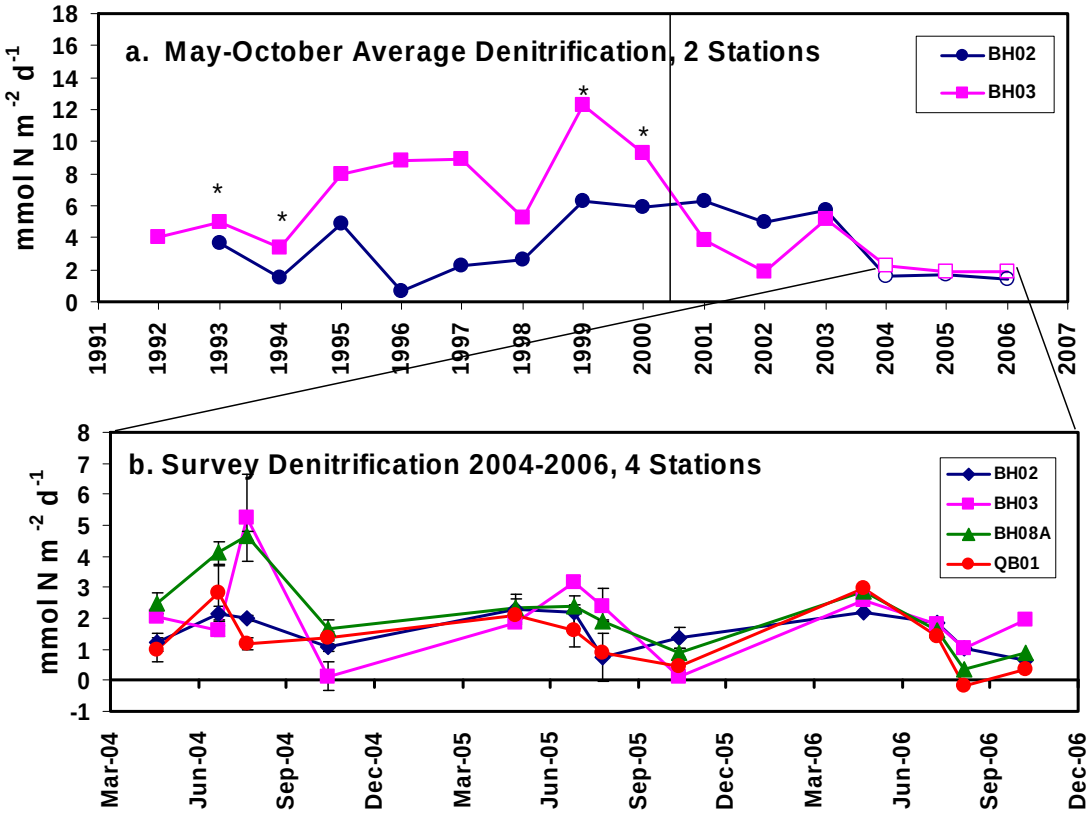


**Figure 25. Denitrification in Boston Harbor: a.) May-October seasonal averages for Station BH02 and BH03 from 1992-2005; * marks years when averages were of three ( 1993 and 1994) or two (1999, 2000) rather than four surveys; the vertical bar marks the outfall relocation. b.)Denitrification rates for all four harbor stations during 2004 - 2006. Error bars represent one standard error of the mean of two replicates. .**

High rates of denitrification in May and low rates in August led to inverse relationships with temperature that were relatively strong. However, this likely represents an indirect effect, mediated through DIN flux, which is positively correlated with temperature. In fact, in 2006 there was a very strong inverse relationship between denitrification and DIN flux at Stations BH03 and BH08A ( $r^2$s were 0.93 and 0.62, respectively). This relationship was even stronger when $NO_3^-$ alone was used as the independent variable ($r^2$s were 0.96 and 0.79 respectively) . At BH02 and QB01, the relationship was not as strong, but was best when $NH_4^+$ alone was used as the independent variable ($r^2$s were 0.24 and 0.38). When examined over the three years for which we have data from all four stations, the correlations were much weaker or, in the case of Station BH02, absent. At BH03, $NH_4^+$ flux could explain 38% of the variability in denitrification, whereas at Station QB01 it could account for only 17%. At BH08A, $NO_3^-$ flux was more important, explaining about 34% of denitrification.

As a proportion of the total N efflux (DIN flux plus denitrification) from the sediments, denitrification in the harbor varies temporally and spatially (Fig. 26). Consistent with the inverse relationship noted above, denitrification was the largest component of the total N efflux in May, when DIN flux was low, ranging from 51% at BH02 to 96% at BH08A. In August, when DIN flux was highest, denitrification accounted for a much smaller percentage of the total flux. At Station BH03, where $NO_3^-$ flux was larger than $NH_4^+$ flux in August (suggesting good oxygen penetration and therefore nitrification) denitrification accounted for 30% of the flux. At the other stations, where the DIN flux was larger and comprised mostly of $NH_4^+$ (little nitrification), denitrification accounted for from 0% (QB01) to 13% (BH02) of the total efflux.

In general, denitrification has been proportionally most important at Station BH03 and BH08A, least at Station BH02 , and most variable at Station QB01. This pattern held in 2006, except at Station BH08A, which was as seasonally as variable as Station QB01 this year. We have explained the relative importance of denitrification at Stations BH03 and BH08A as being related to increased oxygen penetration into the sediments enhanced by either bioturbation (in particular, the amphipod mats) or physical processes. At Station BH03, we have observed the replacement of the biological effects by physical effects. In contrast, at BH08A, we have observed the decrease in biological processes, but no change in physical disturbance. This may help explain the apparent change in the relative importance of various components of the nitrogen flux at BH08A in 2006 to a pattern more similar to that of Stations BH02 and QB01, where bioturbation has typically played a smaller role. At Station QB01, the presence or absence of benthic microalgae plays an additional role. Denitrification may become relatively more important at sites such as this when DIN flux is intercepted by micro-algal uptake of these nutrients (e.g. in May).

The decrease in N loading to the harbor caused by the relocation of the sewage outfall should shift the role of denitrification in the overall N budget. In an earlier paper (Giblin et al, 1994) we constructed a nitrogen budget for the harbor in which denitrification accounted for 14% of total nitrogen inputs from land. Export, calculated as the N not accounted for by denitrification or burial, was the major sink during this period (1991-1994) and burial was minor (Fig. 27a). We have constructed a new budget for the post-diversion period (2001-2006). We assumed that burial rate has not changed, and used the average denitrification rate at Station BH02 and BH03 (3.2 mmol N $m^{-2}$ $d^{-1}$ as compared to 5.5 mmol N $m^{-2}$ $d^{-1}$ in the early model). We compared the new rate to the new loading rate for total nitrogen inputs to the harbor (338 kmol $d^{-1}$ as compared to 1842 kmol $d^{-1}$ ; Taylor, 2005). In this new budget, denitrification has become the major N sink, accounting for about 60% of the total inputs (Fig 27b).

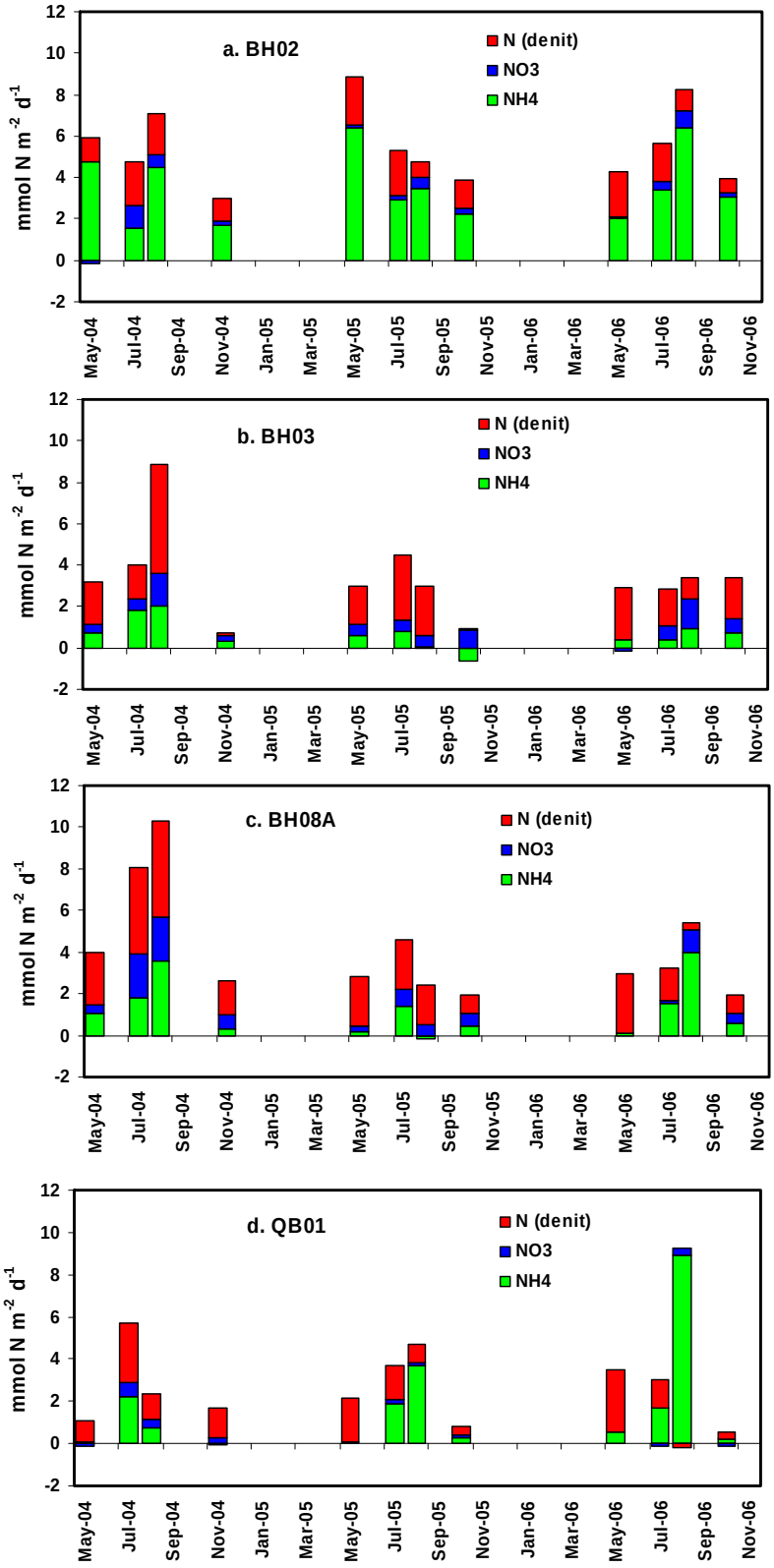


**Figure 26. Nitrogen flux at all four Boston Harbor Stations in 2004, 2005, and 2006, partitioned into components of N from denitrification, $NH_4^+$ flux, and $NO_3^-$ flux.**

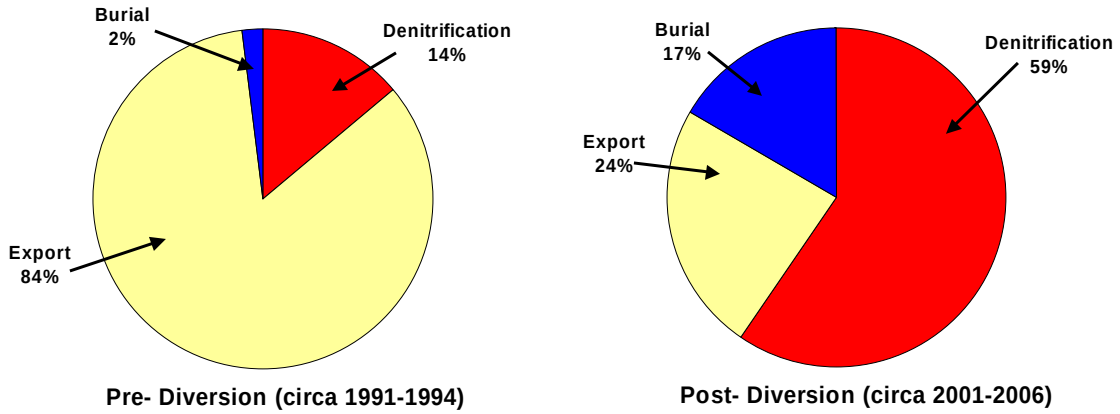


**Figure 27. Nitrogen budgets for Boston Harbor, showing change in relative importance of denitrification after outfall diversion.**

## 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 dense infaunal populations (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 lower than 1.0 in recent years. In addition, high concentrations of dissolved sulfides (> 0.5mM) are no longer detected in the porewaters at Station BH03. At Station BH02, where the amphipod community is 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 2006 average respiratory quotients (RQs) ranged from 0.8 at Station BH03 to 1.6 at Station BH02 (Fig. 28). Values were typical for a given station. At BH03, RQs less than 1.0 throughout the season (ranging only narrowly from 0.77 in August to 0.89 in July) continued to indicate reoxidation of sediments at that site. In contrast, values consistently greater than 1.0 (1.34 in July to 1.85 in October) at Station BH02 indicate storage of reduced endproducts of anaerobic respiration at this site, which continues to have more reducing sediments than the other three sites. At Stations BH08A andQB01, RQs were more variable throughout the season; these stations exhibited values both greater than and less than 1.0. Highest RQs (~1.5) for these stations occurred in August. The low for BH08A occurred in July (0.67) whereas at QB01 it occurred in October (0.83)

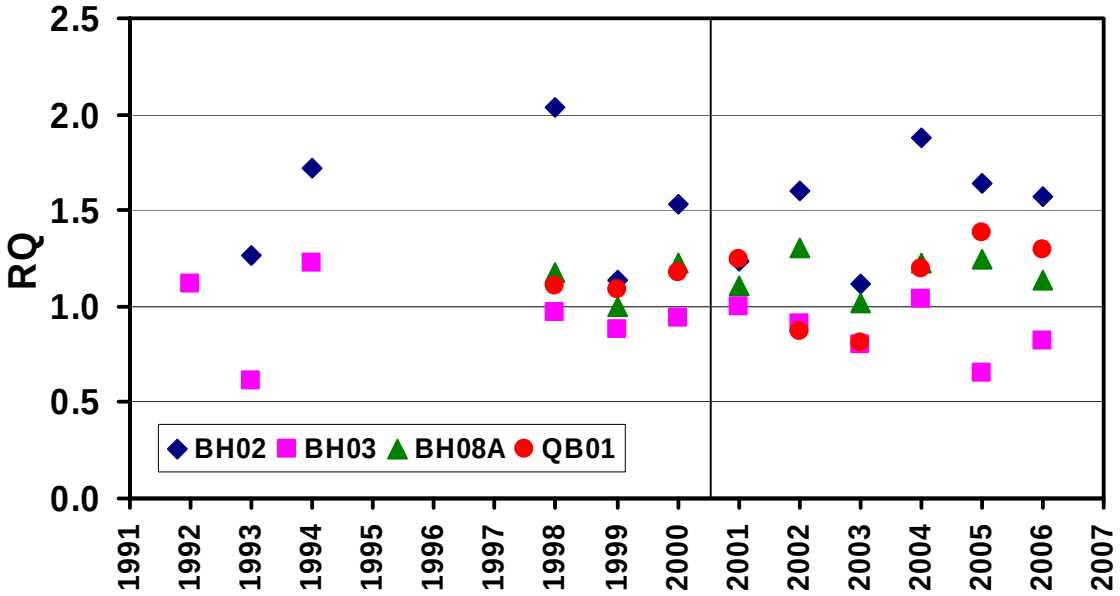


**Figure 28. Seasonal (May-October) average respiratory quotients for Boston Harbor stations BH02, BH03, BH08A, and QB01 from 1993-2006. The vertical line marks the transition from baseline to post-relocation observations.**

### 3.5.2 Eh Profiles

Profiles of oxidation-reduction potential (Eh) (Fig. 29) taken from within sediment cores during 2006 fell within baseline and post-relocation ranges, but were temporally and spatially variable. Sediments at Station BH03 continued to be the most highly oxidized of the four stations, with no negative values within the length of cores we were able to obtain. Highly oxidized conditions at this station are consistent with the coarser grain size that has developed there, as is the difficulty in obtaining cores. Very positive values throughout the profiles were notable at Stations BH08A and QB01 in May. Otherwise, Eh profiles were typical of coastal marine sediments, with the stations other than BH03 showing conditions favorable for sulfate reduction (Eh = -150 to –200) at one or more times during the season. However, these conditions were reached at relatively deep (8 – 10 cm) positions in the cores. In 2006, profiles at Station BH02, which often has more reducing conditions than the other stations, were not very different from those at Stations BH08A and QB01.

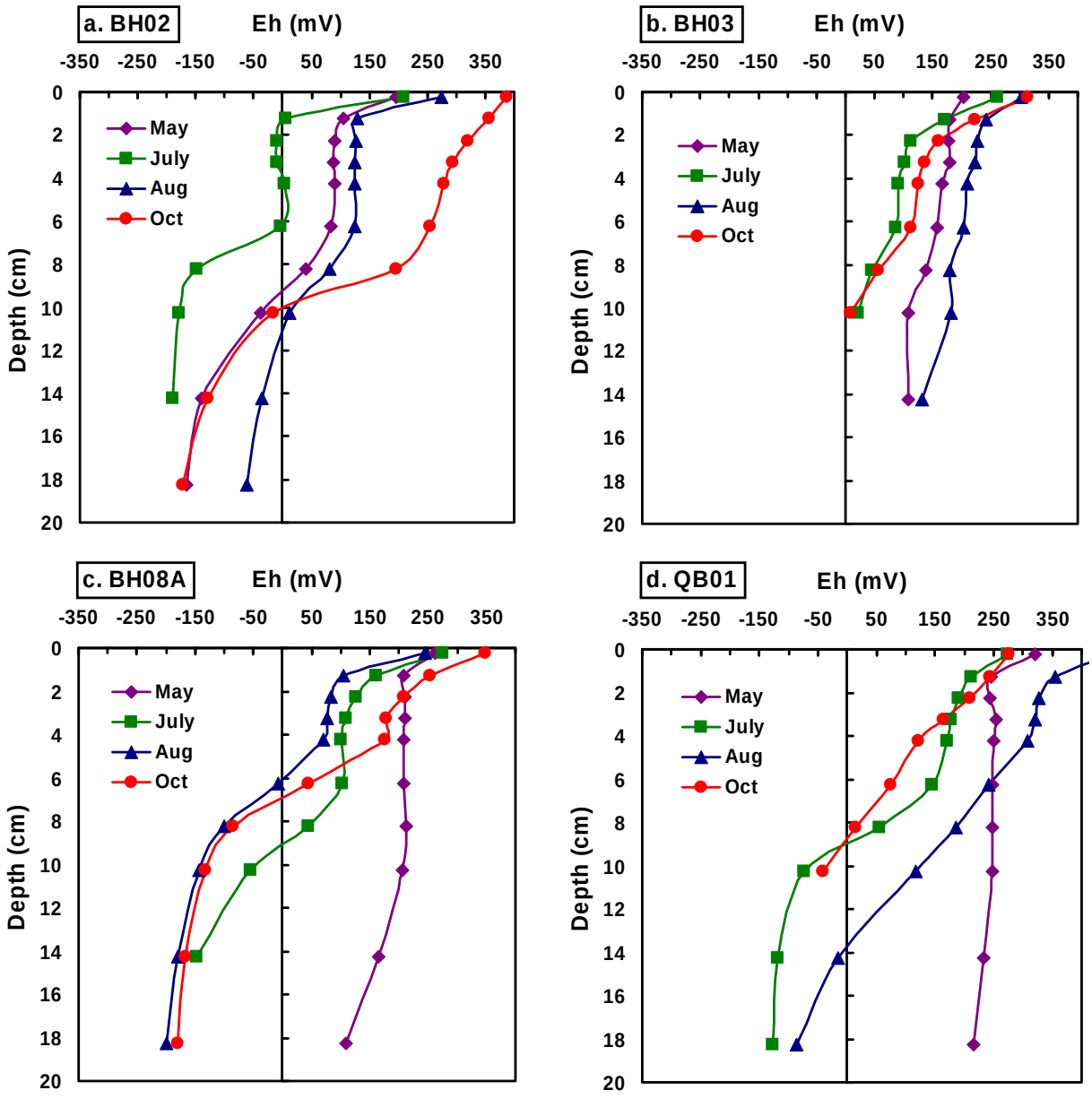


**Figure 29. Eh profiles for May through October, 2006, from Harbor stations a.) BH02, b.)BH03, c.) BH08A, and d.) QB01.**

# 4.0 SUMMARY

## 4.1 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.

In 2006, physical/climatological factors that affected Massachusetts Bay were not as dramatic as the storms of the previous year, but they were important. The relatively quiet conditions were favorable for the development of a large winter/spring (largely diatom) bloom. It was also a very wet year, with record-high river discharge in May, along with overall high discharge for the year, which presumably carried significant load of terrestrially derived nutrients, organic matter, and fresh water to the system. In July, strongly upwelling-favorable conditions likely contributed to the unusual subsurface summer chlorophyll bloom that was observed south of the outfall.

As a nearfield average, organic matter measured as TOC in 2006 was typical at 1.1%. Although two of the stations (MB02 and MB03) seem to have been varying up and down together since 2002, the third station, MB01, has been slowly declining over the same period. Average TOC at this station was only 1.0%, and was only lower in 1999 (0.9%). In contrast, there has been little change in TOC at our deeper, Stellwagen Basin station. Here the TOC averaged 1.6% for the season, very similar to the previous five years. We have detected no change in TOC between the pre- and post-diversion periods at any of the stations.

Inventories of chlorophyll *a* in nearfield sediments in 2006 were among the highest observed during the monitoring period. Highest inventories occurred in May, reaching 13.5µg $cm^{-2}$ at Station MB03. These high inventories were in large part due to very high surface concentrations, which occurred in May at all stations but also in July at Station MB03. These surface concentrations averaged 10.5 µg $cc^{-1}$, whereas they are usually less than half that amount. Large concentrations of "fresh" chlorophyll *a* in May resulted from the deposition of the large winter/spring diatom bloom. Similarly; the elevated signal in July at Station MB03 originated from the summer, subsurface bloom that was present in the water column above this station. At the Stellwagen station, chlorophyll *a* inventories were much lower than in the nearfield, averaging about 2.5 µg $cm^{-2}$ but typical for this station. Even so, some expression of the two phytoplankton blooms was suggested by slightly elevated surface concentrations in May and July. There has been no change in average sediment chlorophyll content since the relocation of the outfall.

Rates of SOD in 2006 were typical. The average for the May to November sampling period for the nearfield stations was 15.6 mmol $m^{-2}$ $d^{-1}$, whereas the baseline mean is 17.2 mmol $m^{-2}$ $d^{-1}$. Rates varied only narrowly over the season, ranging from 12.2 to 20.7 mmol $m^{-2}$ $d^{-1}$. At Stellwagen Station MB05, seasonal average SOD was 12.2 mmol $m^{-2}$ $d^{-1}$, lower than the nearfield average but nearly identical to the previous year. The baseline average for this station is 11.6 mmol $m^{-2}$ $d^{-1}$.

Fluxes of DIN in 2006 were also quite typical. The seasonal average across the nearfield stations was 0.5 mmol $m^{-2}$ $d^{-1}$ as compared to a baseline average of 0.9 mmol $m^{-2}$ $d^{-1}$. The seasonal average for each station was very similar, but included uptake of DIN (primarily $NH_4^+$) at Station MB03 in July and MB02 in October. $NO_3^-$ comprised on average 36% flux, much less than in the previous year, but more

consistent with typical conditions. At station MB05, average DIN flux for 2005 was 0.25 mmol $m^{-2}$ $d^{-1,}$ the same as the baseline mean. At this station, $NO_3^-$ comprised 57% of the seasonal average efflux.

In 2006, $PO_4^-$ fluxes at the nearfield stations were characteristically small and/or negative, resulting in a small seasonal average uptake of 0.02 mmol $m^{-2}$ $d^{-1}$ compared to a baseline mean efflux of 0.06 mmol $m^{-2}$ $d^{-1}$. At Station MB05, the seasonal average flux was negligible (< 0.01 mmol $m^{-2}$ $d^{-1}$).

Average nearfield Si flux were 3.5 mmol $m^{-2}d^{-1}$ compared to the baseline average of 5.1 mmol $m^{-2}d^{-1}$ , and varied little across stations. At MB05, Si fluxes in 2006 were 4.6 mmol $m^{-2}d^{-1}$ , quite typical as compared to the baseline average of 4.3 mmol $m^{-2}d^{-1}$.

The potential contribution of nutrients recycled in the benthos to water column primary production remained small in 2006. Seasonal average nutrient fluxes compared to annual average primary production indicated that the DIN flux could account for less than 5% of primary production, and since there was average uptake of $PO_4^-$, there was no contribution of this nutrient. Dissoved silica could contribute about 34% of phytoplankton requirements. There has been no change in the potential contributions between pre-relocation (1995-1998) and post-relocation periods (2001-2006). Those comparisons are (pre- vs. post-) 3.7% vs. 4.3% for nitrogen, and 24% vs. 26% for silica. For the years with average efflux of PO4-, the potential contribution was 0.04% for both periods.

The average denitrification rate for 2006 at the two nearfield stations where it has traditionally been measured was 2.2 mmol N $m^{-2}d^{-1}$ , very similar to the baseline mean of 2.7 mmol N $m^{-2}d^{-1}$ . At the third nearfield station, the seasonal average was lower 1.4 mmol N $m^{-2}d^{-1}$. At the Stellwagen station the rate was also 1.4 mmol N $m^{-2}d^{-1}$. In 2006, denitrification accounted for 78% of the average total inorganic nitrogen (DIN + $N_2$) flux at the nearfield stations, and 86% at the Stellwagen station.

There was no indication of decreased sediment oxidation in any of our measurements. Respiratory quotients ranged from 1.0 to 1.2 in the nearfield and at the Stellwagen station was 0.85. Eh profiles indicated oxidizing sediment conditions.

There has been no indication of increased SOD or increased nutrient fluxes from nearfield sediments. Table 2 shows a summary of pre- ( 1993-2000) and post- (2001-2006) relocation fluxes. Instead, these data trend towards decreases especially for $NH_4^+$ (and therefore DIN) and Si fluxes. Decreases in the other data have been small compared to the variability, and we would suggest there has been no real change in SOD, $NO_3^-$ fluxes, $PO_4^-$ fluxes or denitrification.

**Table 2. Average fluxes for all nearfield stations over the pre-diversion (1993 through 2000) or post-diversion (2001-2006) time periods (flux units are mmol $m^{-2}$ $d^{-1}$). The asterisk denotes the denitrification averages are from only two rather than four stations, and for May and October only.**

| | SOD | NH4 | NO2+NO3 | PO4 | Si | Denit (N)* |
|---|---|---|---|---|---|---|
| **Flux Pre-diversion** | 17.2 | 0.7 | 0.2 | 0.1 | 5.1 | 3.4 |
| **Flux Post-Diversion** | 15.6 | 0.3 | 0.3 | 0 | 3.4 | 2.3 |

## 4.2 Boston Harbor

The diversion of wastewater disposal from the mouth of Boston Harbor to the offshore location was the final step in minimizing the impacts of the Deer Island Treatment Facility on the harbor, but recovery in the harbor began before this event as various stages of treatment improvements were initiated. In particular, reductions in solids loading to the harbor were very significant to the benthic community, contributing to decreases in sediment organic carbon that were observed well before outfall relocation. Very high rates of benthic respiration "burned off" much of the carbon stores within the sediments, and were enhanced by the bioturbating effects of the *Ampeliscid* amphipod community that bloomed in the harbor during this period. With the diversion, a large source of nutrients to the water column was removed, leading to decreases in primary production, and thereby further decreases in inputs to the sediments. The cumulative effects are that now, six years after outfall relocation, organic carbon content of the sediments, benthic respiration, and other nutrients have seemingly stabilized at a level quite typical of many coastal marine environments.

In 2006, the total organic carbon content (TOC) at our four stations was very similar, ranging only from 1.7% to 2.3%. At two stations, BH02 and BH03, these values represented slight increases from the previous year, and marked the first year that the trend at these stations has not continued to decline. At Station BH03, coarse sediments and the absence of amphipods had been noted for 2004-2005. In August and October 2006, field observations recorded a return to muddier sediments, and amphipods, though not mats, were present. Decreases in TOC from the very high values in the early 1990s seem to reflect the step-wise reductions in solids loadings that resulted from treatment improvements. This pattern was followed most closely at Station BH03, followed by BH08A and QB01, whereas TOC content at station BH02 has varied. Along with reductions in TOC, the large range of values observed across the four stations early in the monitoring program has narrowed in the past several years (2000-2006).

Sediment chlorophyll *a* inventories in 2006 were typical for the trends observed at each station for the previous three years at Station QB01, and for essentially the entire monitoring period for the other three stations. It has been characteristic at Station BH02 and has become so at Station QB01 to have higher chlorophyll levels than the other two stations. In 2006, the average seasonal inventory for these two stations was 31.1 μg $cm^{-2}$ compared to 11.7 μg $cm^{-2}$ at BH03 and BH08A. Much of this chlorophyll may be attributed to benthic diatoms that are commonly observed at these stations, but we are unable to differentiate benthic from water column origins. Smaller inventories of chlorophyll at Stations BH03 and BH08A may be related to higher grazing pressure at these sites.

Sediment oxygen demand in 2006 was typical of the post-relocation period, but slightly higher than in 2005, which had the lowest SOD yet observed. SOD was lower than the baseline range at all stations except Station QB01, which was generally within the baseline range. This station never exhibited the extremely high rates of the other stations, so it has been typical for pre-and post- relocation rates to be similar. The harbor-wide average was 29.1 mmol $m^{-2}d^{-1}$, compared to a post-relocation average of 34 mmol $m^{-2}d^{-1}$, whereas the baseline mean was 69.4 mmol $m^{-2}d^{-1}$.

Fluxes of DIN, $PO_4^-$, and dissolved Si in 2006 were also typical of the post-relocation period, averaging 2.5, 0.2, and 4.3 mmol $m^{-2}d^{-1}$, respectively, as compared to the averages for the period of 2.7, 0.2 and 5.2 mmol $m^{-2}d^{-1}$. In contrast the averages for the baseline period were 5.8, 0.5, and 8.0 mmol $m^{-2}d^{-1}$. We continue to note that the large variability between stations and years that was observed early in the monitoring program has largely disappeared for DIN and $PO_4^-$ fluxes. Si fluxes have shown larger variability within the post-relocation period (2003), but in 2006, average fluxes were quite consistent across all stations.

Since outfall diversion, water column primary production has also decreased in the harbor. We expected that benthic remineralization might provide a relatively more important source of nutrients to the phytoplankton after outfall diversion, but in fact fluxes have decreased so much that these potential contributions have decreased. Using rates of primary production from a station at the mouth of the harbor and seasonal averages of fluxes, we calculate that these fluxes could have supplied about 23% and 22% of phytoplankton N and P requirements, respectively, for the post-relocation period. Before relocation, the potential contributions were 30% for DIN and 41% for $PO_4^-$. The potential contribution of silica fluxes has not changed, being about 41% for both periods.

In 2006, rates of denitrification at the two harbor stations where it has traditionally been measured, BH02 and BH03, were within baseline measurements but among the lowest of both baseline and post-relocation measurements. The average for the two stations in 2006 was 1.6 mmol N $m^{-2}d^{-1}$ as compared 3.2 mmol N $m^{-2}d^{-1}$ for the post-relocation period and to 5.5 mmol N $m^{-2}d^{-1}$for the baseline period. Low rates may have been partly due to the new analytical method. This method enables us to measure denitrification at the other two harbor stations, BH08A and QB01. Including all four stations, the harborwide average for 2006 becomes 1.4 mmol N $m^{-2}d^{-1}$, which is very similar to the average of 1.8 mmol N $m^{-2}d^{-1}$ for the three years for which we have data for all stations. As a percentage of the combined DIN + denitrification flux of N from the sediments, denitrification can vary widely; in 2006 it represented on average 47% of the combined flux. Due to the large change in loading to the harbor, denitrification is now the major sink of nitrogen, accounting for about 60% of the total inputs, whereas before relocation it accounted for 14%.

Patterns in redox measurements varied across stations. At three of the stations, average respiratory quotients (RQs) for the season were greater than 1.0, ranging from 1.1 to 1.6 in a pattern not atypical for the harbor. RQs at one of these stations, Station BH02, were greater than 1.0 throughout the season and the highest of all four stations, as is also typical. At this station evidence of anaerobic respiration is often found in Eh profiles. At the other two stations, RQs were more variable through the season, and exhibited values both above and below 1.0. In contrast, at the fourth station, BH03, RQs were always less than 1.0, averaging 0.8 for the season and suggesting ongoing reoxidation of sediments at this site.

Consistent with the RQs, oxidation-reduction potential measured as Eh profiles in the top 10 –20 cm of sediment cores revealed most highly oxidized sediments at Station BH03 and most reduced at Station BH02. Eh values low enough to suggest sulfate reduction were encountered one or more times during the season at all stations except BH03, but only at relatively deep positions (8 cm or more) in the profile. These profiles are not atypical of those observed in muddy coastal sediments.

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. The role that infauna has played has been significant in areas like BH08A and BH03, and the presence or absence of those benthic communities will no doubt continue to impact benthic nutrient cycling.

Table 3 is a summary of the flux data for the pre- (1992-1995 through 2000) and post-(2001 through 2006) diversion years. We have observed between a 35% and 67% reduction between the two time periods, depending on the flux. Much of this decrease actually happened during the pre-diversion period and was related to the first phases of sewage disposal improvements. However, the relocation of the outfall marked a final phase to this part of the Boston Harbor project, so the pre-diversion years integrate all of the changes. Insofar as our four sampling stations are representative, we have witnessed a remarkable change in rates of metabolism and nutrient cycling in the sediments of Boston Harbor.

**Table 3. Average fluxes for all harbor stations over the pre-diversion (1992-1995 through 2000) or post-diversion (2001-2006) time periods, and the % reduction in fluxes between the two periods. Flux units are mmol $m^{-2}$ $d^{-1}$. Note that denitrification averages are from only two rather than four stations.**

| | SOD | NH4 | NO2+NO3 | DIN | PO4 | Si | Denit (N) |
|---|---|---|---|---|---|---|---|
| **Flux Pre-diversion** | 69.4 | 3.6 | 2.2 | 5.8 | 0.5 | 8.0 | 5.5 |
| **Flux Post-Diversion** | 34.0 | 2.0 | 0.7 | 2.7 | 0.2 | 5.2 | 3.2 |
| **%Reduction** | 51 | 45 | 67 | 54 | 65 | 35 | 42 |

## 4.3 Cross-System Overview

In 2006, we observed a continuation of the patterns we have observed in previous annual reports. These patterns are summarized in Fig. 30, which shows flux averages over time for Boston Harbor and Massachusetts Bay, with the bay separated into the nearfield and farfield. The farfield (Stellwagen Basin) station is considered to be beyond the range of any sewage influence, and serves as a reference.

Most noticeable is the decrease in SOD and nutrient fluxes that has been observed at the harbor stations. At the beginning of the monitoring program, these fluxes were much greater than those in Massachusetts Bay. Currently, SOD and DIN fluxes (Fig 30 a and b) have decreased nearly to the level of Massachusetts Bay, and $PO_4^-$ and Si fluxes (Fig 30 c and d) are virtually the same. As the magnitude of the fluxes has decreased, so has the temporal and spatial variability.

Fluxes of SOD and DIN from the Massachusetts Bay nearfield stations are typically slightly higher than those from the Stellwagen station, but $PO_4^-$ and Si fluxes have been similar. Importantly, there have been no increases observed in bay fluxes since the bay outfall became operational in September 2000.

It is also interesting to look at these changes in the context of other, similar coastal systems. We have compared Boston Harbor and Massachusetts Bay SOD, both pre- and post-diversion, to a range of other estuaries (Nixon, 1981) (Fig. 31). Our data are averages of July and August data, created to better compare with Nixon's data, which are referred to as "summer". Data from the pre-diversion period are shown from 1995 for both Boston Harbor and the Massachusetts Bay nearfield. This was the first year we had data from all four stations in the harbor and the three nearfield stations, and it was also a year with very high SOD in the harbor. We also present data for the current year, 2006, as well as the three previous years for the harbor.

This comparison shows there has been little change in Massachusetts Bay between the two periods. In Boston Harbor, however, there has been a remarkable change. The 1995 data for the harbor exceeded the range of the other estuaries presented. Since then, however, SOD in Boston Harbor has decreased dramatically, reaching its lowest point to date in 2005, when the only two systems that had lower SOD were Kaneohe Bay, HI, and our own Massachusetts Bay. (2005 was also the lowest year to date for Massachusetts Bay.) In 2006, summer SOD was higher than in 2005 and was similar to that measured in 2004. We may find that 2004 and 2006 are the more typical years in a system that seems to be stabilizing at a new equilibrium.

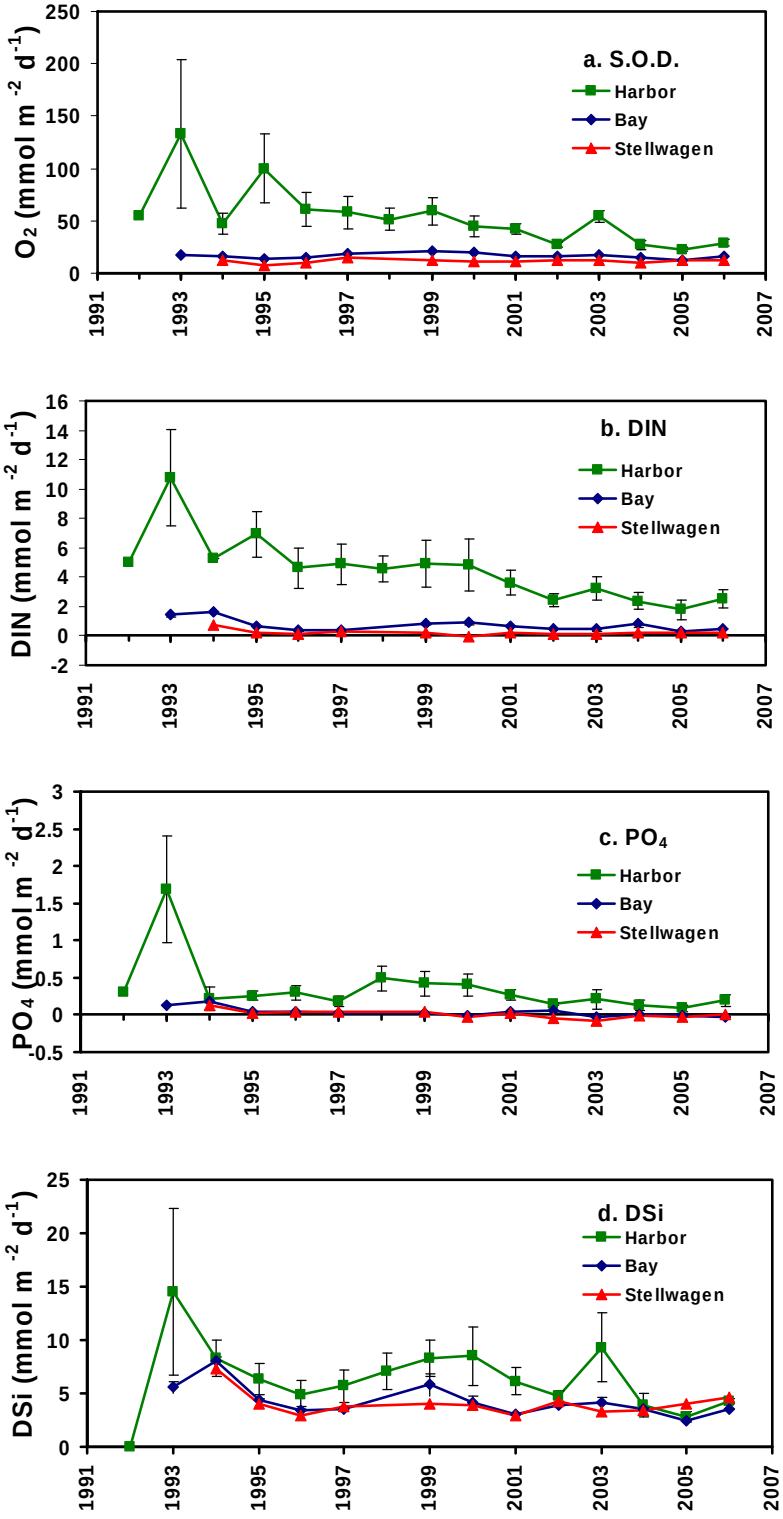


**Figure 30. Survey averages of a.) S.O.D., b.) DIN flux, c.) PO4 flux, and d.) DSi flux for Boston Harbor (■), Massachusetts Bay (♦), and Stellwagen Basin (▲) . Error bars represent the standard error of the mean.**

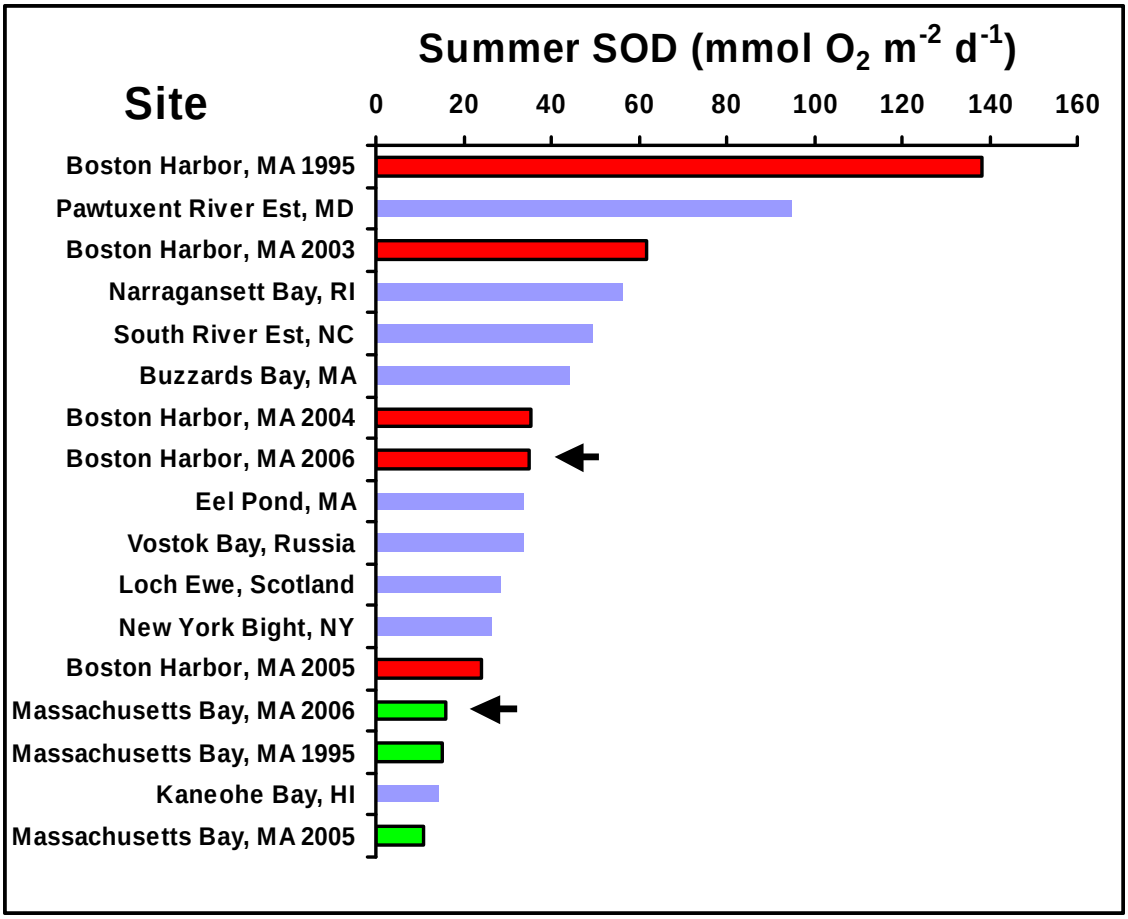


**Figure 31. Sediment oxygen demand in Boston Harbor and the nearfield of Massachusetts Bay compared to summer SOD reported for other coastal ecosystems (Nixon 1981). Data for Boston Harbor and Massachusetts Bay are July-August averages. Arrows point to 2006 data.**

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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 2006.

## 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 2006.*

| Station | Survey | Date | Latitude | Longitude | Depth (m) | Temp (°C) | D.O. (mg/L) | Salinity (psu) |
|---|---|---|---|---|---|---|---|---|
| BH02 | NC061 | 5/4/2006 | 42.34378 | -71.00227 | 8.3 | 9.9 | 9.08 | 30.7 |
| | NC062 | 7/17/2006 | 42.34362 | -71.00210 | 10.0 | 16.3 | 9.73 | 31.0 |
| | NC063 | 8/14/2006 | 42.34378 | -71.00197 | 7.9 | 17.8 | 7.81 | 27.6 |
| | NC064 | 10/17/2006 | 42.34369 | -71.00198 | 10.5 | 12.8 | 8.54 | 30.7 |
| BH03 | NC061 | 5/4/2006 | 42.33075 | -70.96188 | 7.9 | 9.9 | 9.08 | 30.4 |
| | NC062 | 7/17/2006 | 42.33087 | -70.96178 | 10.0 | 15.6 | 9.81 | 30.9 |
| | NC063 | 8/14/2006 | 42.33072 | -70.96181 | 6.7 | 17.7 | 7.89 | 27.7 |
| | NC064 | 10/17/2006 | 42.33070 | -70.96190 | 9.5 | 12.8 | 8.55 | 31.0 |
| BH08A | NC061 | 5/4/2006 | 42.29111 | -70.92236 | 8.6 | 9.6 | 9.15 | 31.1 |
| | NC062 | 7/17/2006 | 42.29097 | -70.92208 | 8.0 | 17.0 | 10.09 | 31.1 |
| | NC063 | 8/14/2006 | 42.29102 | -70.92230 | 6.7 | 17.8 | 7.89 | 27.7 |
| | NC064 | 10/17/2006 | 42.29108 | -70.92194 | 9.2 | 12.7 | 8.75 | 31.5 |
| QB01 | NC061 | 5/4/2006 | 42.29352 | -70.98788 | 3.4 | 10.1 | 8.77 | 30.4 |
| | NC062 | 7/17/2006 | 42.29362 | -70.98772 | 3.0 | 17.2 | 10.29 | 30.8 |
| | NC063 | 8/14/2006 | 42.29360 | -70.98795 | 2.6 | 18.8 | 8.31 | 27.7 |
| | NC064 | 10/17/2006 | 42.29347 | -70.98777 | 5.0 | 12.6 | 8.97 | 30.7 |
| MB01 | NC061 | 5/8/2006 | 42.40318 | -70.83753 | 32.2 | 7.2 | 9.82 | 32.1 |
| | NC062 | 7/18/2006 | 42.40307 | -70.83728 | 28.2 | 8.2 | 7.29 | 33.3 |
| | NC063 | 8/15/2006 | 42.40310 | -70.83739 | 30.4 | 8.8 | 7.87 | 29.7 |
| | NC064 | 10/16/2006 | 42.40307 | -70.83728 | 31.5 | 10.4 | 6.57 | 32.1 |
| MB02 | NC061 | 5/8/2006 | 42.39252 | -70.83447 | 33.6 | 7.0 | 9.74 | 32.3 |
| | NC062 | 7/18/2006 | 42.39247 | -70.83415 | 27.4 | 8.4 | 7.81 | 33.3 |
| | NC063 | 8/15/2006 | 42.39258 | -70.83438 | 32.2 | 8.8 | 8.04 | 30.0 |
| | NC064 | 10/16/2006 | 42.39262 | -70.83438 | 32.0 | 10.7 | 6.29 | 32.1 |
| MB03 | NC061 | 5/8/2006 | 42.34780 | -70.81620 | 34.5 | 6.7 | 9.99 | 31.9 |
| | NC062 | 7/18/2006 | 42.34787 | -70.81605 | 29.5 | 8.4 | 7.79 | 33.1 |
| | NC063 | 8/15/2006 | 42.34783 | -70.81620 | 29.1 | 9.4 | 7.76 | 29.9 |
| | NC064 | 10/16/2006 | 42.34782 | -70.81610 | 34.3 | 10.7 | 7.00 | 31.7 |
| MB05 | NC061 | 5/8/2006 | 42.41655 | -70.65225 | 45.2 | 6.7 | 9.92 | 32.2 |
| | NC062 | 7/18/2006 | 42.41662 | -70.65205 | 40.1 | 7.3 | 7.60 | 33.4 |
| | NC063 | 8/15/2006 | 42.41650 | -70.65200 | 46.3 | 7.6 | 8.38 | 30.3 |
| | NC064 | 10/16/2006 | 42.41637 | -70.65195 | 44.5 | 9.9 | 7.39 | 31.9 |


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