2005 Annual benthic nutrient flux monitoring report

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2005Annual
Benthic Nutrient Flux
Monitoring Report

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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 2005, the overriding influence on benthic nutrient cycling was the two early and one late season northeast storms. These storms produced large enough waves and were of sufficient duration to impact the benthos in the nearfield area. The year was marked by a coarsening of sediments in the nearfield, an increase in physical over biological processes acting on the sediment surface, and a decrease in biogenic structures (Maciolek et al, 2006). Decreases in most parameters measured in the benthic nutrient cycling studies can be attributed at least in part to the effects of these storms.

Organic matter measured as TOC was lower than usual in 2005, averaging 1.1% for the nearfield. It is likely that some scouring of surface sediments resulted from the northeast storms. In contrast, there was little change in TOC at our deeper, Stellwagen Basin station, which was presumably unaffected by the storms. Here the TOC averaged 1.5% for the season. We have detected no change in TOC between the pre- and post-diversion periods.

Inventories of total sediment pigments also decreased in 2005, with the seasonal averages for the nearfield being 90.7 µg pigment cm^{-2} for the top 5 cm, down from 112.8 µg cm^{-2} in 2004. Curiously, the chlorophyll *a* fraction showed an increase over the previous year, from 3.8 µg cm^{-2} to 5.5µg cm^{-2}. However, there was little expression of a spring bloom in May sediment profiles from the nearfield stations. At the Stellwagen station, there was a smaller decrease in total pigments (from 86.9µg cm^{-2} in 2004 to 77.1µg cm^{-2} in 2005), but a similar change in chlorophyll (from 5.7µg cm^{-2} to 7.1µg cm^{-2}). At this station, however, there was a pronounced surface elevation of chlorophyll concentration in May.

Rates of SOD in 2005 were low. The average for the May to November sampling period for the nearfield stations was 12.6 mmol m^{-2} d^{-1}, nearing the bottom of the baseline range of 12.4 to 24.7 mmol m^{-2} d^{-1}. At Stellwagen Station MB05, the seasonal average was 12.9 mmol m^{-2} d^{-1}, very similar to the nearfield average. The baseline average for this station is 11.6 mmol m^{-2} d^{-1}.

Fluxes of DIN in 2005 were also quite low. The seasonal average across the nearfield stations was 0.3 mmol m^{-2} d^{-1} , the lowest to date, as compared to a baseline average of 0.9 mmol m^{-2} d^{-1}. NO_3^- comprised the major fraction of the flux, contributing between 71% and 99% of the total. These small DIN fluxes included periods of uptake; in particular, in May, sediments from all stations exhibited NH_4^+ uptake. At station MB05, average DIN flux for 2005 was 0.22 mmol m^{-2} d^{-1} as compared to the baseline average of 0.25 mmol $m^{-2}d^{-1}$. At this station, NO_3^- comprised 100% of the seasonal average efflux.

In 2005, PO_4^- fluxes at the nearfield stations were nearly undetectable, and the small fluxes that we did measure were on average negative for all four stations; that is, there was on average uptake of PO_4^- rather than release.

Average nearfield Si fluxes were 2.4 mmol $m^{-2}d^{-1}$ compared to the baseline average of 5.1 mmol $m^{-2}d^{-1}$, and lower than the previous year. At MB05, Si fluxes in 2005 were 4.1 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 was small in 2005. Seasonal average nutrient fluxes compared to annual average primary production indicated that the DIN flux could account for only 4% of primary production, and since there was average uptake of PO_4^-, there was no contribution of this nutrient. Dissoved silica could contribute about 28% of phytoplankton requirements.

The average denitrification rate for 2005 at the two nearfield stations where it has traditionally been measured was 1.3 mmol N $m^{-2}d^{-1}$ as compared to the baseline mean for the two stations of 2.7 mmol N $m^{-2}d^{-1}$. Somewhat lower rates in 2005 may have been partly due to the use of an improved analytical method, which tends to yield lower rate estimates than the previous method. At the third nearfield station, the average rate was 1.1 mmol N $m^{-2}d^{-1}$. At the Stellwagen station the rate was 1.5 mmol N $m^{-2}d^{-1}$. In 2005, denitrification accounted for between 60% and 82% of the total inorganic nitrogen (DIN + N_2) flux at the nearfield stations, and 85% at the Stellwagen stations.

There was no indication of decreased sediment oxidation in any of our measurements. In fact, respiratory quotients were on average lower than 1.0, and Eh profiles indicated oxidizing sediment conditions.

BOSTON HARBOR

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

In 2005, the two early and one late season storms were major events that shaped the whole season for the benthos of Boston Harbor. The physical disturbance not only scoured the sediments and flushed porewaters, it evidently prevented the *Ampeliscid* amphipod community, which has been very important in the biogeochemistry of the harbor, from colonizing and forming mats. These mats were absent from all our stations for the entire season.

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring, including the five years since diversion. In 2005, storms likely contributed to further decreases which were most noticeable at Stations BH03 and BH08A. The range of TOC in the harbor was 1.6% to 2.2%, approaching Massachusetts Bay values. A comparison of averages pre-and post -diversion show that overall, decreases in TOC have been most pronounced at Stations BH03, followed by BH08A and QB01, whereas TOC content at station BH02 has varied. The large range of values observed across the four stations early in the monitoring program has narrowed in the past several years (2000-2005).

Along with changes in TOC at Station BH03 and BH08A has been an increase in grain size of the sediments at these two sites. In particular, sediments at Station BH03 have changed from mostly silt and clay to currently mostly sand, and including gravel. BH08A has experienced similar changes, although there is little gravel present at this time. At Station QB01, we have observed the reverse trend, whereas BH02 has exhibited little change.

Sediment chlorophyll *a* inventories were lower than usual in 2005 for three of the four harbor stations. At the fourth station, QB01, inventories were normal, and only at this station was there a strong surface signal of chlorophyll in May, when divers described a benthic diatom mat (unidentified species) at this site. It has become common to observe benthic diatoms at Station BH02 as well, but they were not noted in May this year, nor were they noted at the other two stations. It may be that at this more protected site in Quincy Bay, the sediments experienced less storm disturbance.

Sediment oxygen demand in 2005 was the lowest yeat observed. The harbor-wide average was 22.5 mmol $m^{-2}d^{-1}$, whereas the baseline mean was 69.4 mmol $m^{-2}d^{-1}$. There was little variability across stations in seasonal averages. Fluxes of DIN , PO_4^- , and dissolved Si were also the lowest to date, averaging 1.8, < 0.1, and 2.7 mmol $m^{-2}d^{-1}$, respectively, as compared to baseline averages of 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.

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 at the mouth of the harbor and seasonal averages of fluxes, we calculate that these fluxes could have supplied about 21% and 25% 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 2005, 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 2005 was 1.8 mmol N $m^{-2}d^{-1}$ as compared 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, where average rates for the season were 1.9 and 1.2 mmol N $m^{-2}d^{-1}$. The average across all four stations was 1.6 mmol N $m^{-2}d^{-1}$, nearly equivalent to the DIN flux.

Patterns in redox measurements varied across stations. At three of the stations, average respiratory quotients for the season were greater than 1.0, a pattern not atypical for the harbor. Highest RQs were observed at Station BH02, as is also typical, where evidence of anaerobic respiration is often found in Eh profiles. In contrast, very low RQs (< 1.0) were observed at Station BH03 in 2005. A partial explanation may be that the coarsening of the grain size and increasing dominance of physical processes at this site (enhanced by this year's storms?) are providing a situation where these sediments are continually flushed, resulting in the reoxidation of stored products of anaerobic respiration.

Oxidation-reduction potential measured as profiles in sediment cores from the harbor was fairly typical for recent conditions. Of note was the evidence of storm-induced oxidation of sediments at some sites in May. At BH02, the profile revealed that oxidizing conditions penetrated more deeply than is typical for this site. At BH03 and QB01, the May profiles showed little change in Eh from the sediment surface to the bottom of the core sample.

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.

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. Whereas in the pre-diversion period, SOD in some areas of Boston Harbor exceeded the range presented by Nixon, current rates are now at the bottom of the range. These results are illustrative of a compelling story of recovery in the harbor that is rare in its long-term and thorough documentation. Certainly from the point of view of benthic nutrient cycling (a few isolated areas notwithstanding), the clean-up of Boston Harbor is a genuine success story.

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1.0 INTRODUCTION

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

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

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

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

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

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

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

II. Have the rates of these processes changed?

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

The annual report written for the year 2001 (Tucker et al. 2002) provides a thorough review of our understanding of both the Boston Harbor and Massachusetts Bay systems during baseline monitoring, and our observations during that first year after the outfall was relocated. In this report we compare the results from 2004 to those baseline studies and to the previous three 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 1998-2003 (Giblin et al., 1992; Kelly and Nowicki 1992; Giblin et al., 1993; Kelly and Nowicki, 1993; Giblin et al., 1994; Giblin et al., 1995; Tucker et al., 1999; Tucker et al, 2000; Tucker et al, 2001; Tucker et al., 2002; Tucker et al., 2003, Tucker et al., 2004). 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. The general circulation pattern is that GOM water flowing to the south may enter Massachusetts Bay near Cape Ann, setting up a weak counterclockwise circulation that exits off the tip of Cape Cod. The temperature and salinity of this water, together with wind and climatological factors, determine the timing and strength of seasonal (summer) stratification patterns within Massachusetts Bay. Data gathered during baseline monitoring demonstrated that concentrations of dissolved oxygen present in GOM water at the onset of stratification in the spring contributed directly to the degree of seasonal O_2 depletion in the bottom waters of the bay (Geyer et al., 2002). In addition, nutrients are delivered to the bay in GOM water. Discharge from the bay outfall represents a perturbation to this system, the significance of which is 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 2005, the importance of the physics of the system was much in evidence. Two northeast storms in May played a critical role in shifting circulation patterns landward and thereby rapidly transported an extremely intense *Alexandrium* bloom occurring in the southern Gulf of Maine into Massachusetts and Cape Cod Bays (Anderson et al, 2006). These storms were also the major driving influence for benthic processes in 2005, both in Massachusetts Bay and Boston Harbor. They lasted long enough and generated waves of sufficient height to resuspend bottom sediments in the nearfield. Benthic surveys in August reported that grain size was higher and biogenic structures were less numerous than usual, and these effects were attributed to a scouring of sediments in the early season (Maciolek et al, 2006) Another strong nor'ester in October also impacted the nearfield benthos. Our May survey occurred between the two early season storms, and the October survey occurred after (was delayed by) the late season storm.

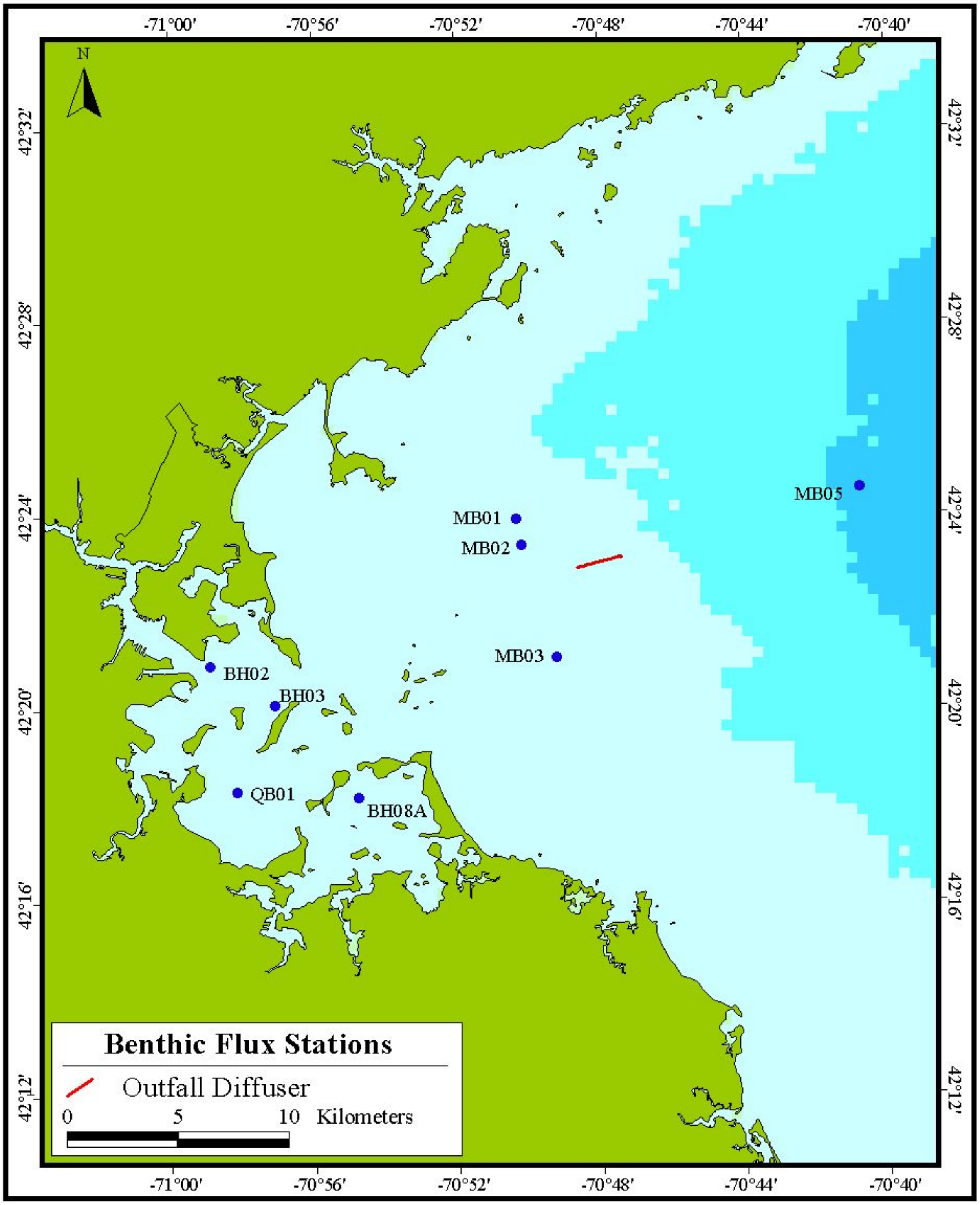

Figure 2-1. Benthic nutrient cycling stations in Massachusetts Bay and Boston Harbor.

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 2005, TOC was a bit lower on average than usual, and this we attribute to surface scouring caused by the stormy season noted above (Fig. 2). Average sediment TOC for the May to October period was similar across the nearfield stations and ranged only from 1.0 to 1.2 %. These values represented declines from the previous year for Stations MB02 and MB03; in particular, they marked a return to more typical values for MB03 after the all time high of 1.9% observed in 2004. At the Stellwagen station, the 2005 average TOC was 1.5%, quite typical for this station, which is in deeper water (75m vs 33m) and less susceptible to disturbance by storm.

Within the season, TOC content varied from station to station and, on a survey by survey basis, did not correlate well with water column events. Values ranged from 0.7 to 1.8 % across all four stations (Fig. 2). The three nearfield stations did not display similar seasonal patterns. At MB02, TOC was quite constant from May through August, with a value of just above 1%, and only decreased slightly to 0.9% in October. TOC at the other two nearfield stations showed much larger changes over the season, but in contrasting patterns. At station MB01, highest TOC (1.8%) occurred in May. Levels decreased through August, reaching a low for the year of 0.7%, and then increased again to 1.2%in October. At MB03, lowest TOC occurred in May, was similar in July, and then increased to a high of 1.8% in October. Attempts to correlate TOC with events such as the spring *Phaeocystis* blooms that have now occurred for 6 consecutive years are made difficult by this station to station variability.

Ratios of TOC to total N (C/N: Fig. 3) in 2005 were elevated at MB01 and MB02, reaching values of 13.8 and 14.4 (averaged over the May to October period), respectively, which were as high or higher than any observed at these two nearfield stations. At MB03, C/N was 11.5, which was lower than the other two stations but higher than in the previous year, when a low value of 9.8 suggested “fresh” inputs to the sediments. At farfield station MB05, C/N was a bit lower than in the nearfield at 10.5 and typical for this station. It has been a consistent pattern over the entire monitoring program that C/N has been lower at MB05 than at the nearfield stations.

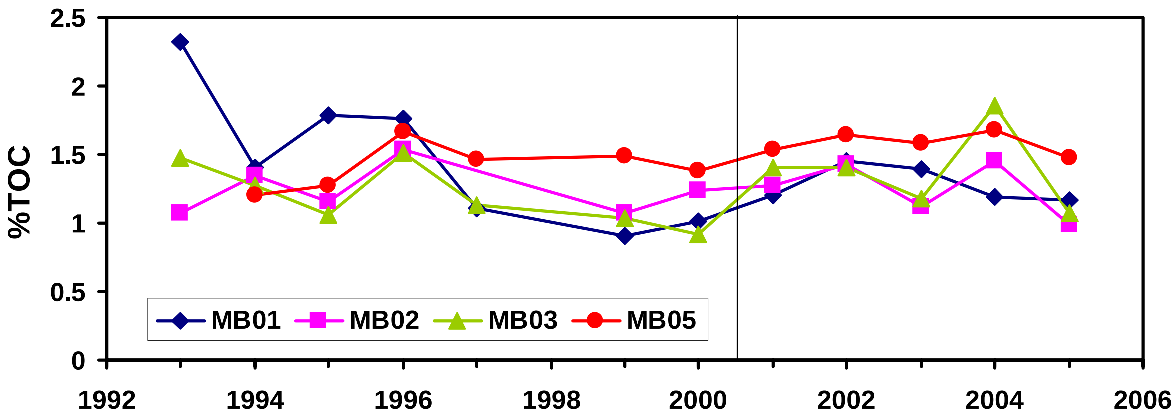

Figure 2-2. Organic carbon content of top 2 cm of sediment at Nearfield stations MB01, MB02, and MB03 and Farfield station MB05. The vertical line marks the transition from baseline to post-relocation observations.

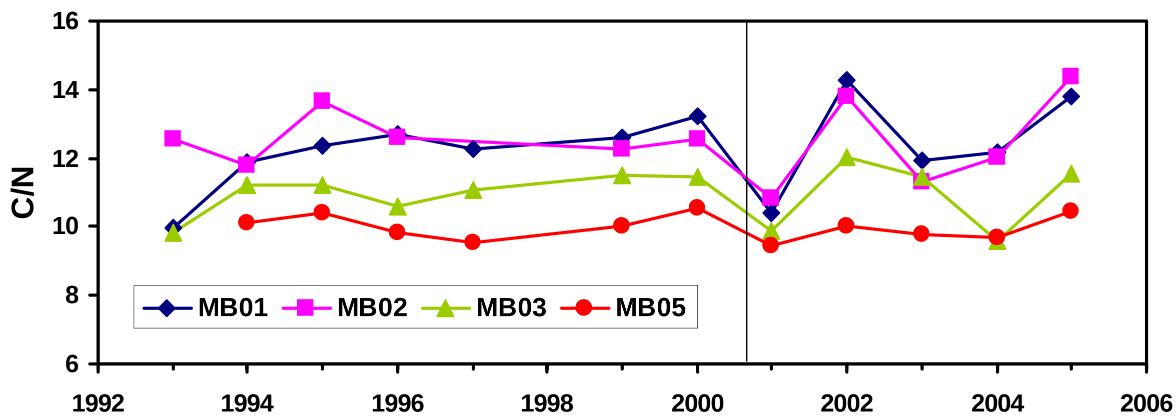

Figure 2-3. Molar TOC/TON for top 2 cm of sediment. The vertical line marks the transition from baseline to post-relocation observations.

2.1.2 Sediment Pigments

In 2005, chlorophyll *a* content, measured as inventory over the top 5 cm of sediment, was well within the monitoring baseline, although higher than in the previous year (Fig. 4). Average chlorophyll *a* inventory for the season at Station MB03 was 8.5 µg cm^{-2}, just over twice that at the other two nearfield stations. At the Stellwagen station MB05, chlorophyll *a* inventory was 7.1 µg cm^{-2}, similar to that at MB03. It has been the general pattern that among the four Massachusetts Bay stations, pigment concentrations are typically highest at Station MB03. In terms of total chlorophyll pigments (chlorophyll a + phaeophytin a), the inventory at MB03 was 104.3 µg cm^{-2} as compared to a range of 81 to 87 µg cm^{-2} at the other three stations.

In spite of 2005 being the sixth consecutive year of a spring *Phaeocystis* bloom, we have been unable to discern a clear signal of the blooms in these inventories, probably for the same reasons as suggested above for lack of a signal in the TOC. However, we sometimes observe an indication of fresh deposition as elevated concentrations of chlorophyll *a* in the surface two to three cm of sediment profiles. We most often observe this in May, presumably following the spring bloom. By July, surface concentrations have often decreased to background (5 cm depth) levels. In 2005, this surface signal was not very apparent in nearfield profiles. We think it is likely that the northeast storm that occurred in May just before we sampled resuspended sediments at the three nearfield stations. In July, however, there was elevated surface chlorophyll *a* at Station MB03, and to a lesser degree at the other two nearfield stations as well (Fig. 5 a-c). A mixed bloom of pennate diatoms and dinoflagellates that occurred after the second storm and lasted until mid-June may have been the origin (Libby et al, 2006b).

In contrast, a surface signal was observed at the farfield station MB05 in May. Presumably the storm had little effect on the sediments at this deeper Stellwagen station. In fact, at MB05 we observed a surface signal that persisted throughout the season; this is not atypical for this station and may reflect less biological activity (consumption and/or burial) in these deeper sediments.

Over the years, we have attempted to correlate sediment chlorophyll, as an expression of water column productivity, to TOC content, but with little success. 2005 marked the sixth consecutive year of large spring *Phaeocystis* blooms, which are rich in carbon relative to chlorophyll. We thought the possibility of finding a correlation during this period might be improved. In 2004, we reported a hint of this at one station , Station MB03, where we observed elevated TOC and total pigments and a quite low C/N. In 2005, we found a reasonable correlation between C/N and chlorophyll *a* inventory at Station MB03 (r^2 = 0.62), but the relationship this year was positive; ie, higher C/N occurred with higher chlorophyll inventory. In contrast, the strongest relationship between C/N and chlorophyll inventory in 2005 was found for Stations MB01 (r^2 = 0.82), but in this case the relationship was negative. Although it is accepted that water column production fuels the benthos, it is difficult to demonstrate it. In the case of *Phaeosystis* blooms, part of the difficulty may be that these are surface, buoyant blooms that may be advected far from their origin, and be slow to sink to the bottom. The additional complication in 2005 was the spring 's that may have scoured the bottom sufficiently to remove signs of recent deposition.

2.1.3 Pre- and Post- Relocation Comparison

By our measures of TOC and pigment inventories, 2005 was a very typical year in terms of organic matter loading to the benthos of Massachusetts Bay. These data add to the previous four 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.

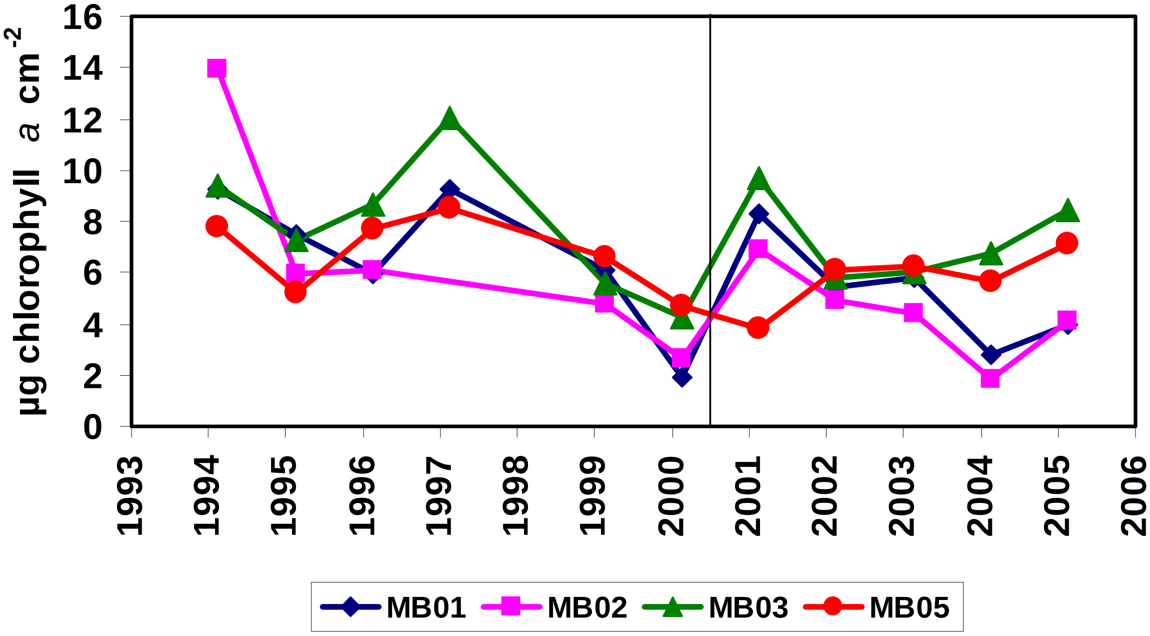

Figure 2-4. Chlorophyll *a* inventory for top 5 cm of sediment at Nearfield stations a.) MB01, b.) MB02, and c). MB03, and Farfield station c). MB05. The vertical line marks the transition from baseline to post-relocation observations.

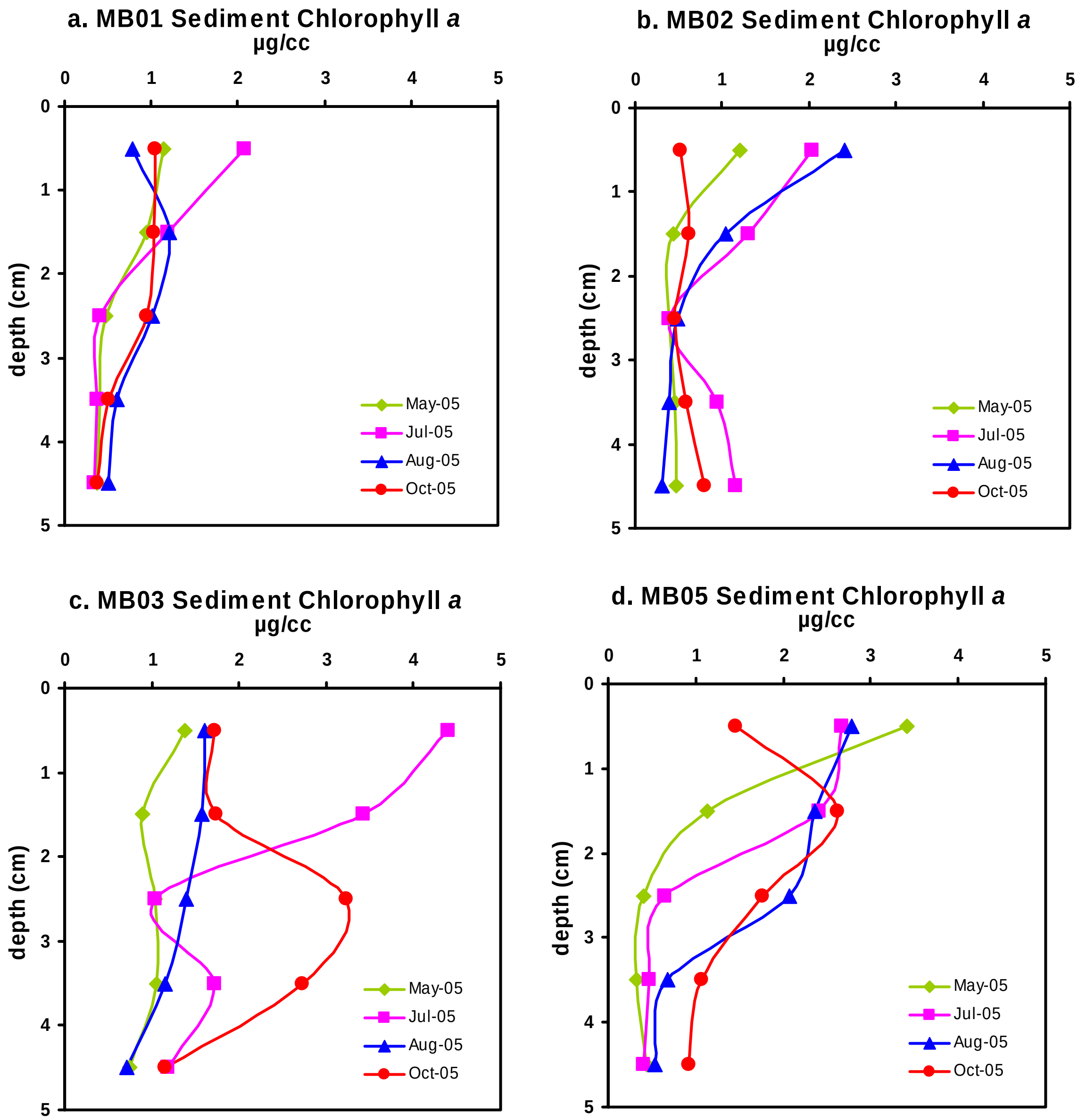

Figure 2-5. Profiles of chlorophyll a concentration (µg/cc) in top 5 cm of sediment in 2005 from Massachusetts Bay Stations a.) MB01, b.) MB02, c.) MB03, and d.) MB05.

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 2005, seasonal average SOD ranged from 11.7 mmol m^{-2} d^{-1} at MB01 to 13.5 at MB03, and the average across the three stations was 12.6 mmol m^{-2} d^{-1}(Fig. 8 a). Clearly observations in 2005 were well within baseline. In fact, these rates were some of the lowest ever observed at these stations.

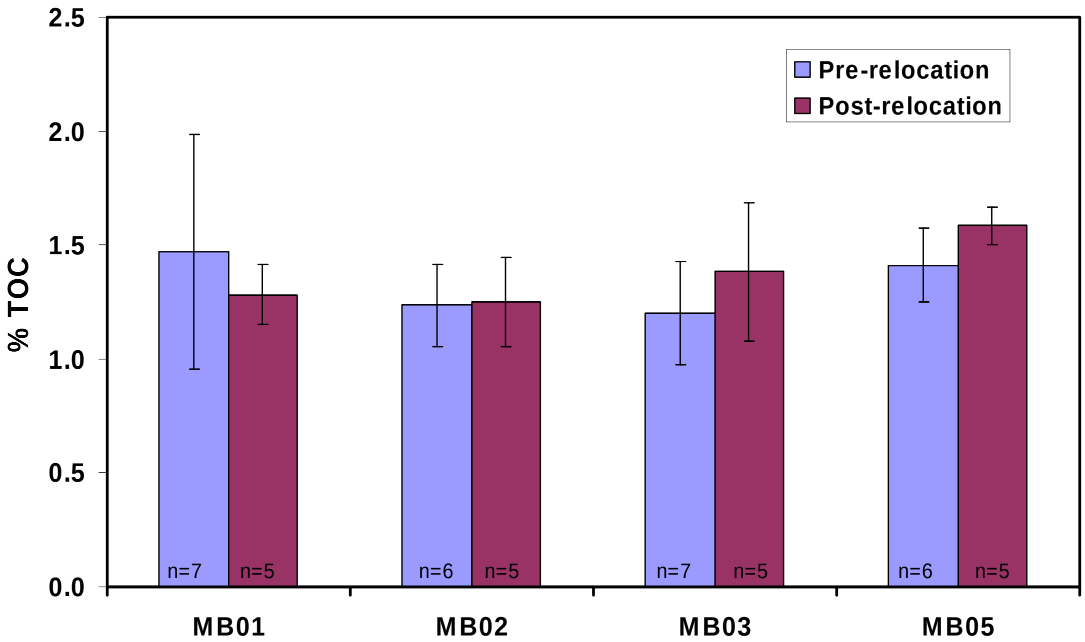

Figure 2-6. Sediment TOC pre- and post- relocation of the outfall. Data are seasonal averages over all available years for each station. Error bars represent one standard deviation of the mean.

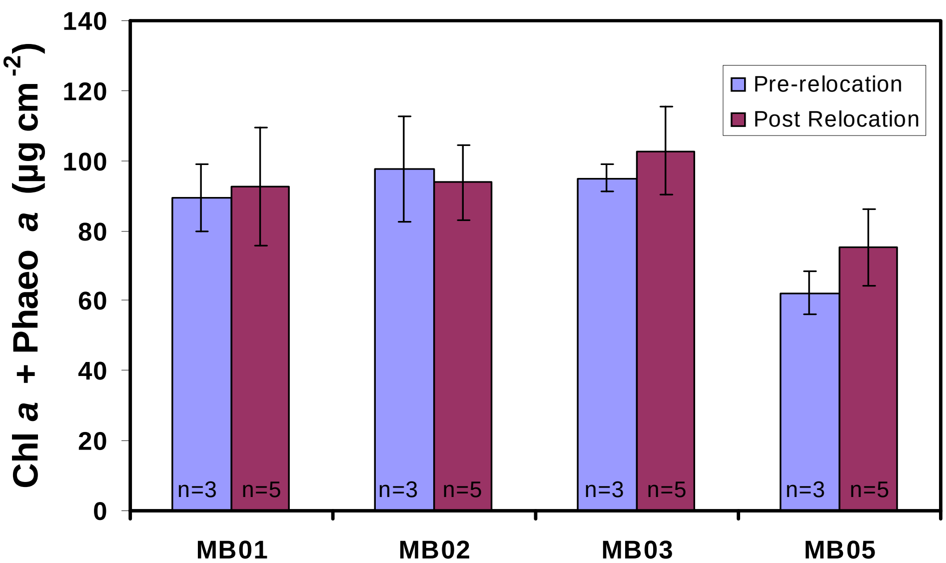

Figure 2-7. Sediment total chlorophyll pre- and post- relocation of the outfall. Data are seasonal averages over all available years for each station (data from 1995-1997 are omitted due to possible differenced in phaeopigment measurements). Error bars represent one standard deviation of the mean.

The seasonal pattern that resulted in these low averages was interesting. In May, SOD was in the mid to high end of the baseline ranges at Stations MB01 and MB02 (14.4 and 17.9 mmol m^{-2} d^{-1}, respectively) and exceeded the baseline range at MB03 (18.9 mmol m^{-2} d^{-1}) (Fig. 9a-c). For the rest of the season (July-October) however, SOD at all three stations fell to very near the bottom of or below the baseline ranges. Lowest SOD of the year was 9.4 mmol m^{-2} d^{-1} and occurred in July at Station MB01.

At farfield station MB05, seasonal average SOD was very typical of baseline (Fig 8a). We have seen little variability in fluxes at this station, with the seasonal average during the baseline period ranging only from 7.8 mmol m^{-2} d^{-1} in 1995 to 15.3 mmol m^{-2} d^{-1} in 1997, with all other values falling between 10 and 13 mmol m^{-2} d^{-1}. In 2005, the seasonal average was a very typical 12.9 mmol m^{-2} d^{-1}. However, as was the case for nearfield station MB03, the May SOD at MB05 of 16.5 mmol m^{-2} d^{-1} was higher than the baseline range for this month, and among the highest recorded for any time of the season. For the rest of the year, rates were typical of baseline, ranging from a low of 10.1 mmol m^{-2} d^{-1} in July to 12.7 mmol m^{-2} d^{-1} in October (Fig. 9d).

We continue to analyze the data to look for correlations between SOD and expected controls on SOD. As we have reported before (eg. Tucker et al, 2005), a strong correlation was found between temperature and SOD for the first three years of the monitoring program (1993-1995), but this correlation became very inconsistent in the following years. Often, in fact, we observed *negative* correlations. This was the case in 2005, with all four stations showing strong but negative correlations between SOD and temperature (r^2s between 0.500 and 0.830). In this case, the relationship was heavily weighted by the very high SOD we observed in May, when temperatures were still very cool. In fact , if the May data are omitted, the regression becomes positive and relatively strong at two of the stations, MB02 and MB03, explaining 27% and 65% of the variability, respectively. These results point to other controlling factors present in May.

We would expect that benthic respiration would respond to fresh inputs of carbon from the spring phytoplankton bloom. As noted above, however, we observed little indication of such inputs in the TOC or pigment data. However, regressions of SOD vs TOC or total pigments did show strong positive correlations at one nearfield station, Station MB01, and the farfield station MB05. At MB01, the r^2 for the relationship between TOC and SOD was 0.49 and between total pigments and SOD it was 0.78. At MB05, the correlation with TOC was very strong, resulting in an r^2 of 0.92, while the regression with total pigments was weaker ($r^2 = 0.61$). At the other two nearfield stations, these relationships were very weak or were negative. Over all years, a weak correlation between SOD and total pigments exists ($r^2 = 0.34$) at Station MB02 only. For the other stations and with TOC, the relationships are insignificant.

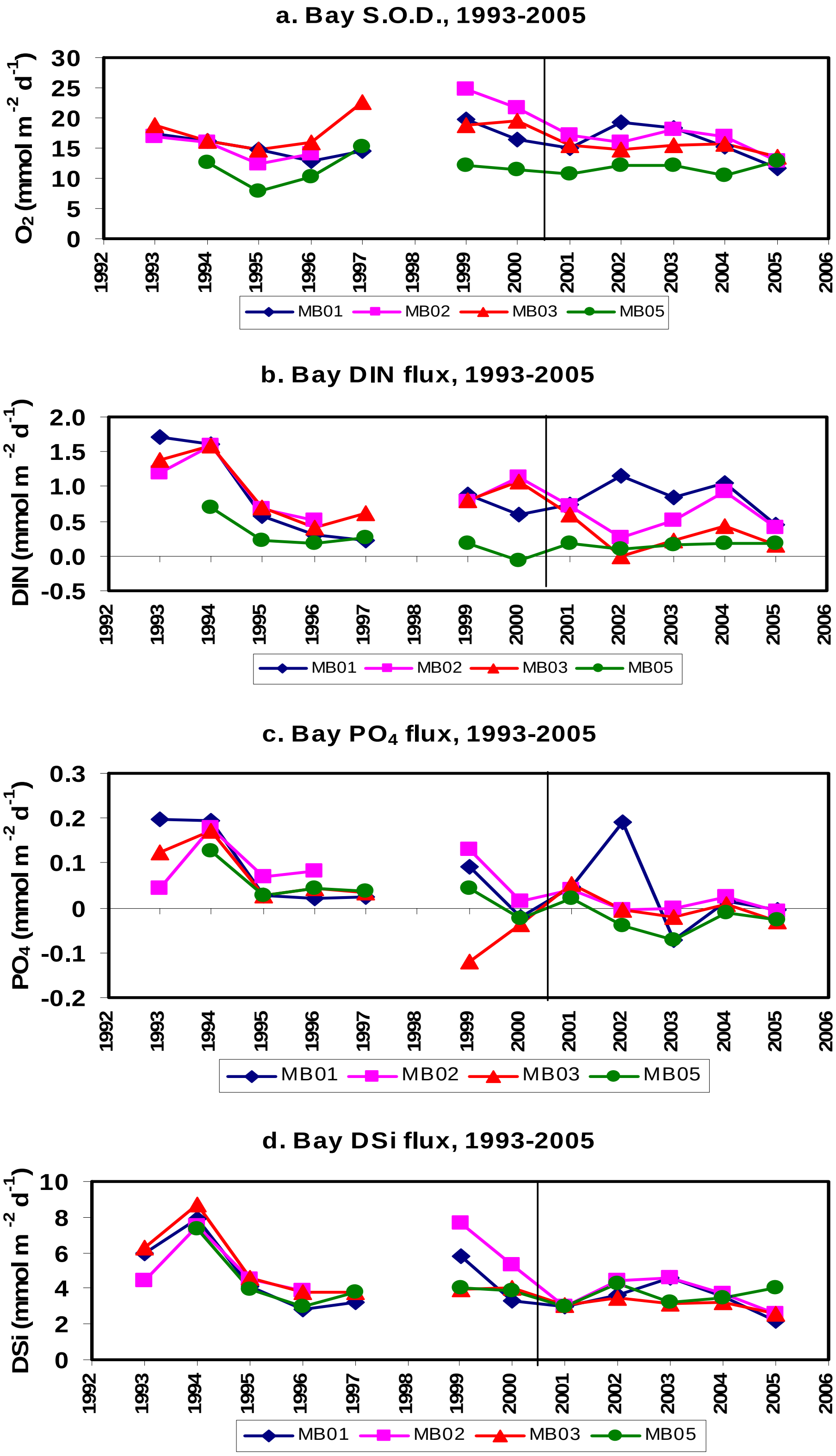

Figure 2-8. Seasonal (May-October) averages of a.) sediment oxygen demand (S.O.D.), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Massachusetts Bay stations in 1993-2005. The vertical lines mark the transition between baseline and post-relocation observations.

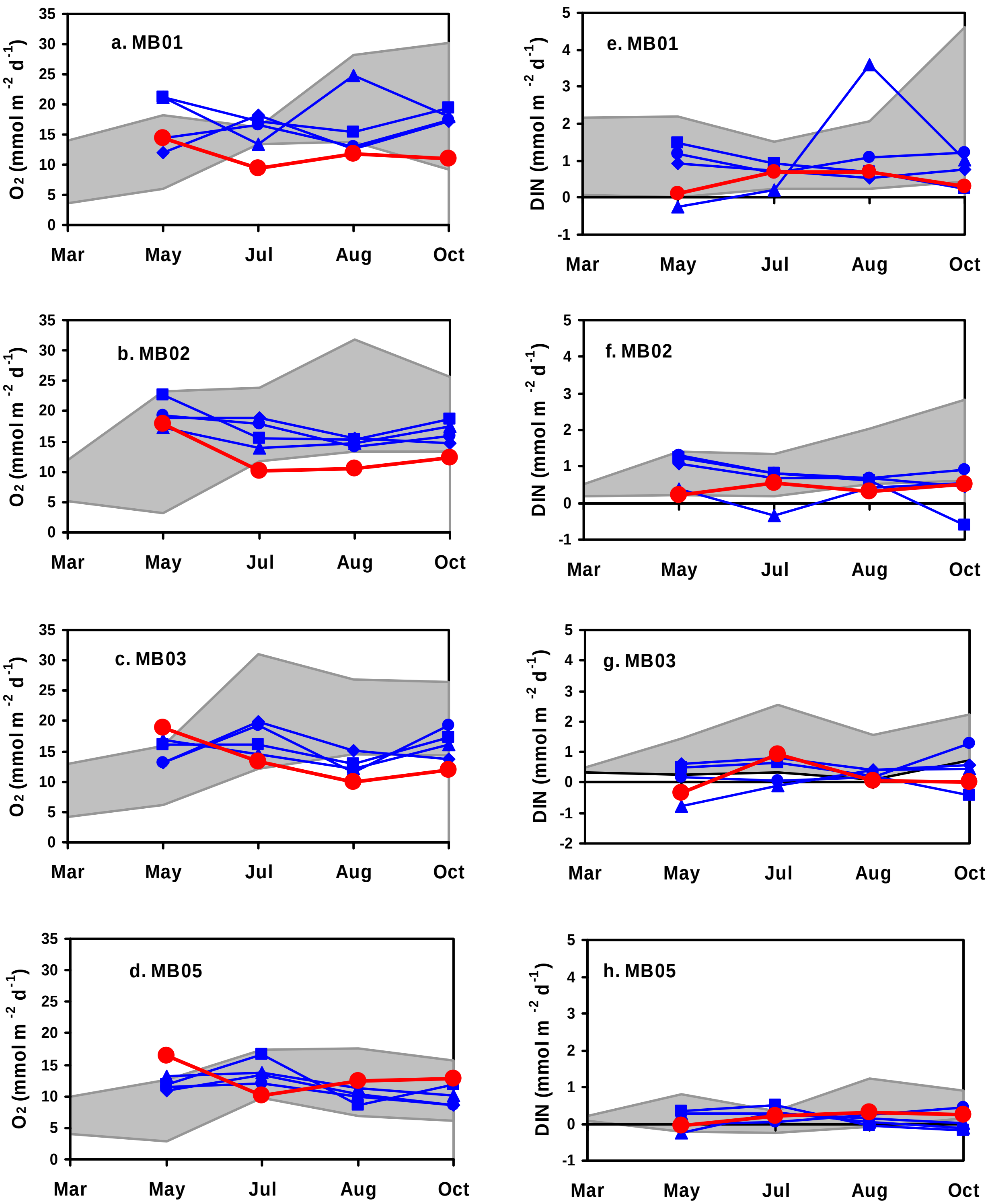

Figure 2-9. Sediment oxygen demand (O_2 flux) and DIN flux for 2001 (♦), 2002 (▲), 2003 (■), 2004 (●) and 2005 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations MB01, MB02, MB03, and MB05, respectively.

2.2.1 Contribution to Oxygen Drawdown in Bottom Water

Of concern to the monitoring program is the role that sediment oxygen demand plays in the seasonal drawdown of oxygen in the bottom waters of Massachusetts Bay. The mean annual drawdown in the nearfield is about 0.04 mg L^{-1} d^{-1} (Geyer et al., 2002). For comparison, the May to October average SOD for 2002-2004 was 16.4 mmol m^{-2} d^{-1}, which translates to about 0.05-0.1 mg L^{-1} d^{-1}, depending on the depth of the stratified layer used in the conversion (5-10 meters, respectively). In 2005, even the low nearfield average SOD of 12.6 translates to 0.04 mg L^{-1} d^{-1} (stratified layer of 10 m). Thus, SOD measured in these muddy sediments is comparable to the annual drawdown. Although these rates are sizable, the bay does not experience oxygen depletion. Geyer et al (2002) have used statistical models to show that physical processes rather than biological ones control the bottom water oxygen concentrations. That is, despite substantial rates of respiration, both in the water column and the sediments, there is sufficient replenishment of oxygen-rich water, advected from of Gulf of Maine, to prevent oxygen drawdown to biologically unhealthy levels.

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 five 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 2005, DIN fluxes from nearfield sediments were in the low end of the baseline range (Fig 8b and 9e-g), and varied from uptake of 0.31 mmol m^{-2} d^{-1} at Station MB03 in May to 0.9 mmol m^{-2} d^{-1} at the same station in July. In general, fluxes this year were lowest in May and highest in July. Low DIN fluxes in May resulted from NH_4^+ uptake at all three nearfield stations, ranging from 0.3 to 0.6 mmol m^{-2} d^{-1}. Seasonal averages of DIN flux varied across the three nearfield stations, with stations MB01 and MB02 similar at 0.45 and 0.4 mmol m^{-2} d^{-1} and MB03 less than half that at 0.2 mmol m^{-2} d^{-1}; these rates were each just under half what they were the year before. The nearfield seasonal average in 2005 was 0.3 mmol m^{-2} d^{-1}, the lowest yet observed.

Nitrate (used throughout text as shorthand for NO_3^- + NO_2^-) comprised nearly all of the seasonal average DIN flux in 2005, ranging from a contribution of 71% of the flux at MB03 to 99% at MB02(Fig 10a-c). Large proportions of nitrate as compared to ammonium fluxes usually indicate that sediments are well oxygenated. Often we attribute this to high levels of biological activity, but in 2005, physical processes dominated biological ones (Maciolek et al, 2006), and were likely responsible.

At MB05, DIN fluxes were about average of those observed during baseline (Fig. 8b and 9h), ranging from -0.04 mmol m^{-2} d^{-1} to 0.30 mmol m^{-2} d^{-1} (the overall range at this station is -0.26 to 1.24 mmol m^{-2} d^{-1}). Lowest rates (uptake) occurred in May and increased through the rest of the season (Fig. 9h). Negative DIN fluxes in May were driven by NH_4^+ uptake similar to that observed in the nearfield. Seasonal average DIN efflux was comprised entirely of the NO_3^- flux; NH_4^+ flux was directed into the sediments (Fig. 10d).

2.3.2 Phosphorus and Silica

Phosphate fluxes remained very small and/or negative in 2005, following the pattern we have observed for the past five years (with one exception at MB01 in 2002), and were typical of or lower than observed during baseline monitoring, (Fig. 8c and 11a-d). Fluxes ranged from an uptake of 0.22 mmol m^{-2} d^{-1} in October at MB03 to an efflux of 0.06 mmol m^{-2} d^{-1} in July at the same station. There was little seasonal pattern evident. Seasonal averages were all negative (overall uptake), ranging from -0.00(3) to -0.03 mmol m^{-2} d^{-1} (Fig. 8c). At the farfield station MB05, the seasonal average was also negative (-.03 mmol m^{-2} d^{-1}), and similar in magnitude and seasonal pattern to that observed at Station MB03.

Dissolved silica fluxes at the nearfield stations in 2005 were mostly below the baseline range (Fig. 8d). Fluxes ranged from a low of 1.6 mmol m^{-2} d^{-1} in May at MB02 to a high of 3.6 mmol m^{-2} d^{-1} in August at the same station. There was no consistent seasonal pattern across stations (Fig. 11e-g). The May-October averages for the nearfield stations were very similar and together averaged 2.4 mmol m^{-2} d^{-1}, less than half the baseline average of 5.1 mmol m^{-2} d^{-1} (Fig. 8d). At the farfield station MB05, silica fluxes were low compared to baseline in May but fairly typical for the rest of the season. (Fig. 11h). Rates varied only from 3.0 to 5.2 mmol m^{-2} d^{-1}, with the lowest rates in May and highest in October. The seasonal average of 4.1 mmol m^{-2} d^{-1} was higher than the nearfield average, and very similar to the baseline average for MB05.

2.3.3 Nutrient Flux Contribution to Primary Productivity

Average annual primary production in the nearfield area in 2005 was 246 g C m^{-2} y^{-1} (or 56 mmol C m^{2} d^{-1}) (average production from Stations F23, N04 and N18; Oviatt, pers. com). Following Redfield considerations, this amount of production would require 8.5 mmol m^{-2} d^{-1} of N or Si, and 0.5 mmol m^{-2} d^{-1} of P . Using the seasonal average DIN flux from our three nearfield stations of 0.34 mmol m^{-2} d^{-1}, we find that benthic DIN flux represented only 4% of phytoplankton requirements. Because there was seasonal average *uptake* of PO_4^- by the benthos in 2005, there was no contribution to the water column. Fluxes of dissolved silica, however, could account for 28% of requirements, assuming a 1:1 relationship between silica and nitrogen. There are several caveats on this calculation, including the fact that we used annual rates for primary productivity compared to seasonal (May through October only) rates for benthic fluxes, which would cause an overestimation of the contribution of benthic fluxes. Another reason this may be an overestimation is that our sampling sites are biased to the depositional, and presumably more active sediments of the bay.

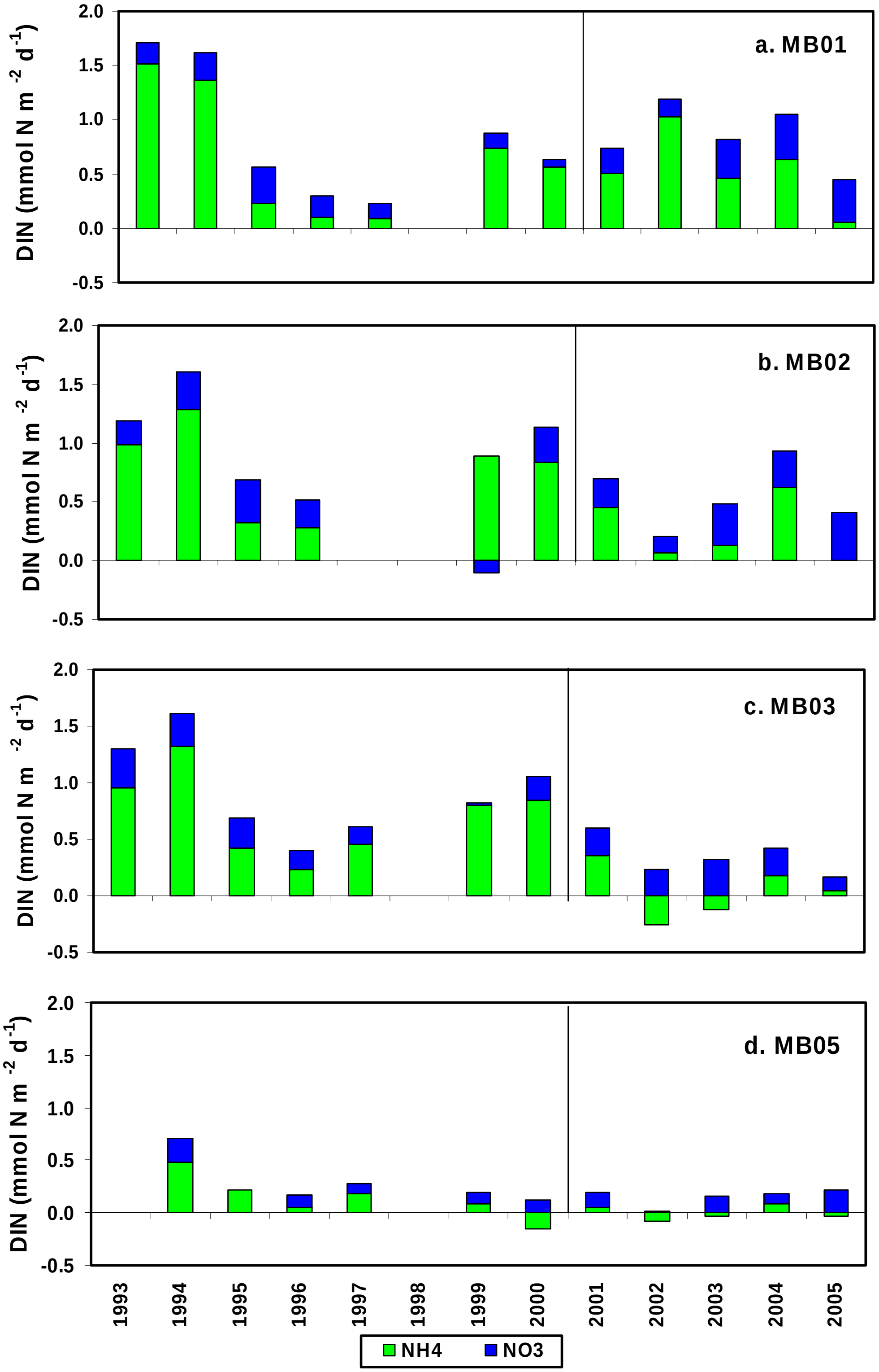

Figure 2-10. May-October seasonal average DIN flux from 1993-2005 at bay stations, partitioned into NH_4^+ and NO_3^-+NO_2^- a.) MB01, b.) MB02, c.) MB03, d.) MB05. The vertical line marks the transition from baseline to post-relocation observations.

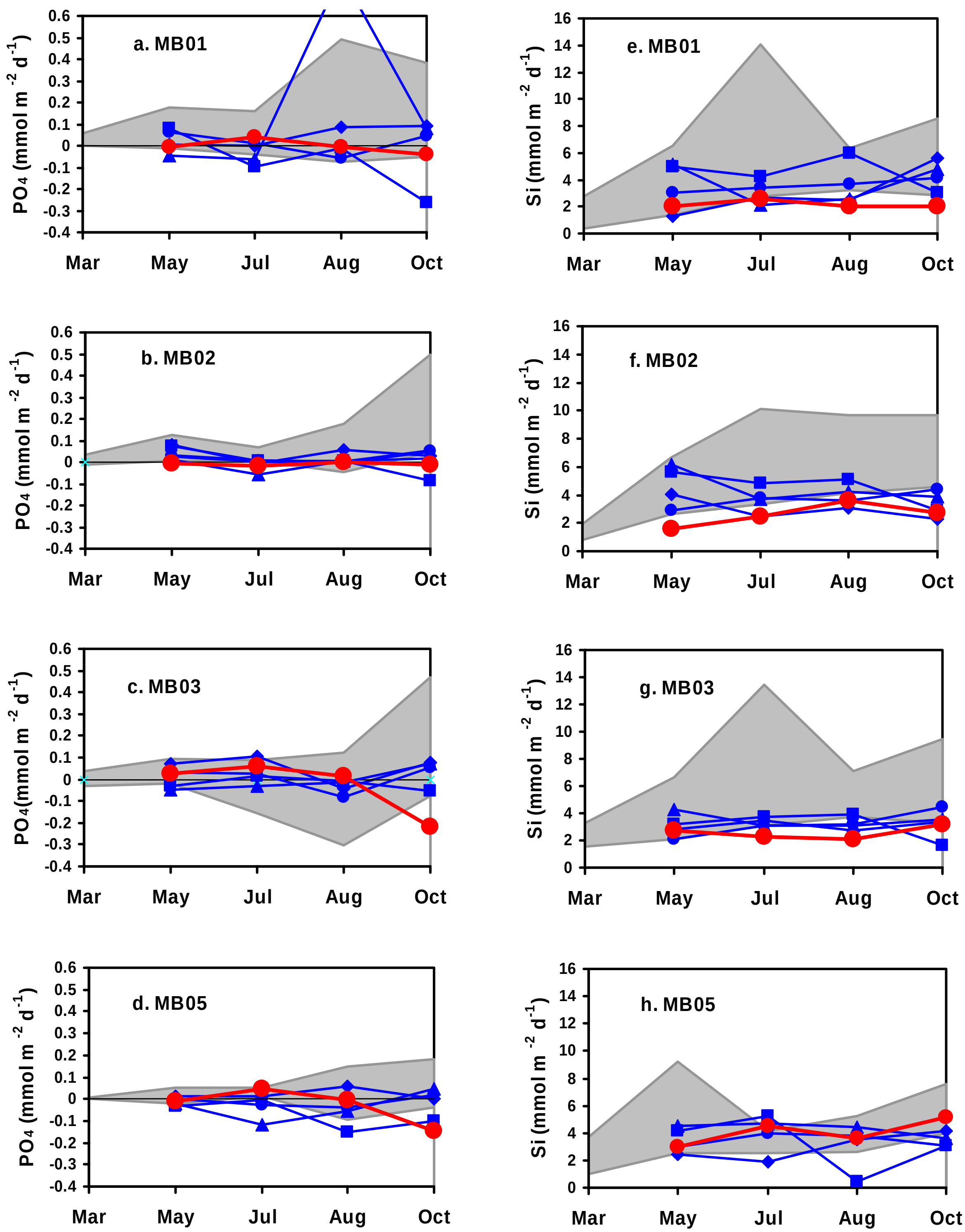

Figure 2-11. Phosphate and dissolved silica for 2001 (♦), 2002 (▲), 2003 (■), 2004 (●) and 2005 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO4 flux and panels e-h depict DSi flux for stations MB01, MB02, MB03, and MB05, respectively.

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 (now 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.

Denitrification rates at our long-term nearfield stations MB02 and MB03 in 2005 were low but within the overall baseline ranges (Fig. 12), with seasonal averages of 1.5 and 1.2 mmol N m^{-2} d^{-1}, respectively. The highest rate observed from these two stations was 1.9 mmol N m^{-2} d^{-1}, occurring in July at Station MB03. Similar rates were observed in July and August at MB02. Lowest rates were 0.8 mmol N m^{-2} d^{-1} , occurring in May at MB03 and October at MB02. For comparison, the highest rate observed during the May to October period, and over the entire monitoring program was 6.0 mmol N m^{-2} d^{-1} (at MB02, October 1999) and the lowest was 0.7 mmol N m^{-2} d^{-1} (also in October at MB02, 1993). We must note that the new method tends to produce lower estimates (Tucker and Giblin, 2005), and our results for 2005 (as well as 2004) may be due in part to the method change. At this point, however, we do not think there has been a significant change in denitrification rates.

Adding the "new" data from Station MB01 to the observations from the nearfield stations gives us a new low rate for the year. Denitrification in October at MB01 was very low, only 0.2 mmol N m^{-2} d^{-1} (Fig.13). This rate was as low as any observed, including March data from the 1992-1997 period. All of the stations had lowest rates of the year in October, following highest rates in July or August. This seasonal pattern, with lower rates early and late in the season and higher in summer in was also observed at the farfield station MB05. At this station, denitrification reached 2.1 mmol N m^{-2} d^{-1} in August, then fell to 0.8 mmol N m^{-2} d^{-1} in October. Seasonal averages for Stations MB01 and MB05 were 1.0 and 1.5 mmol N m^{-2} d^{-1}, respectively.

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) in the soft sediments of Massachusetts Bay. 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 continued to see this pattern in 2005. If we break these fluxes into their components of N(gas), NH_4^+, and NO_3^-(Fig. 14), we see that for 2004 and 2005, when we have data for all stations and all surveys, the N flux from denitrification is almost always the largest component. During this period denitrification accounted for between 60% and 82 % of the efflux (as seasonal averages). At MB05, denitrification is even more important, accounting for about 85% of the N efflux.

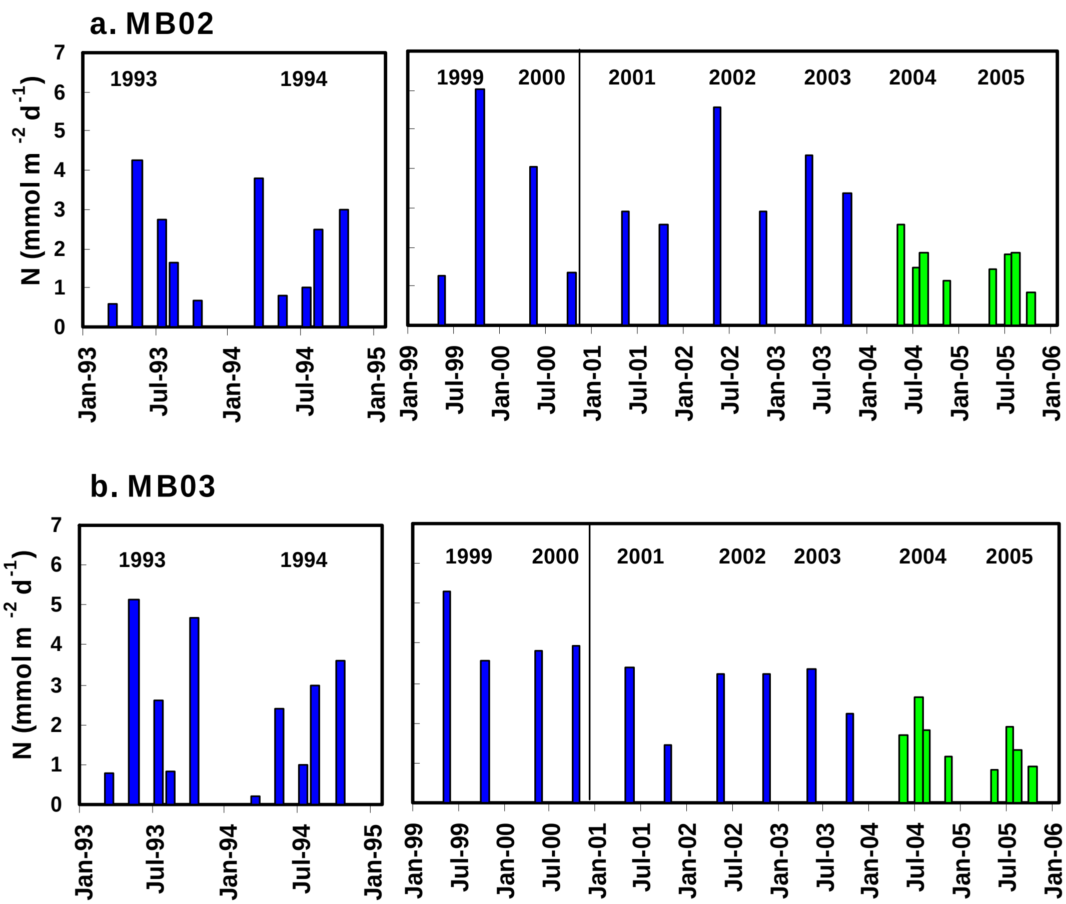

Figure 2-12. Denitrification at two nearfield stations, a.) MB02, and b.) MB03. Denitrification measurements were not conducted in Massachusetts Bay in 1995-1998. 2004 and 2005 data were produced using the new analytical method and are highlighted in green. The vertical line marks the transition between baseline and post-relocation of the outfall.

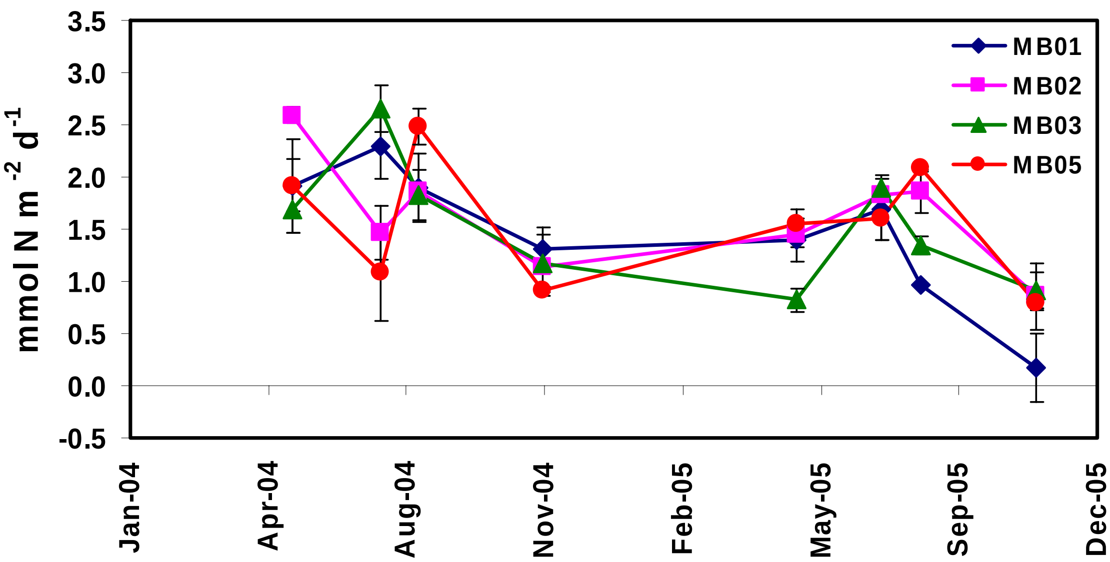

Figure 2-13. Denitrification at all four Massachusetts Bay Stations in 2004 and 2005.

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.

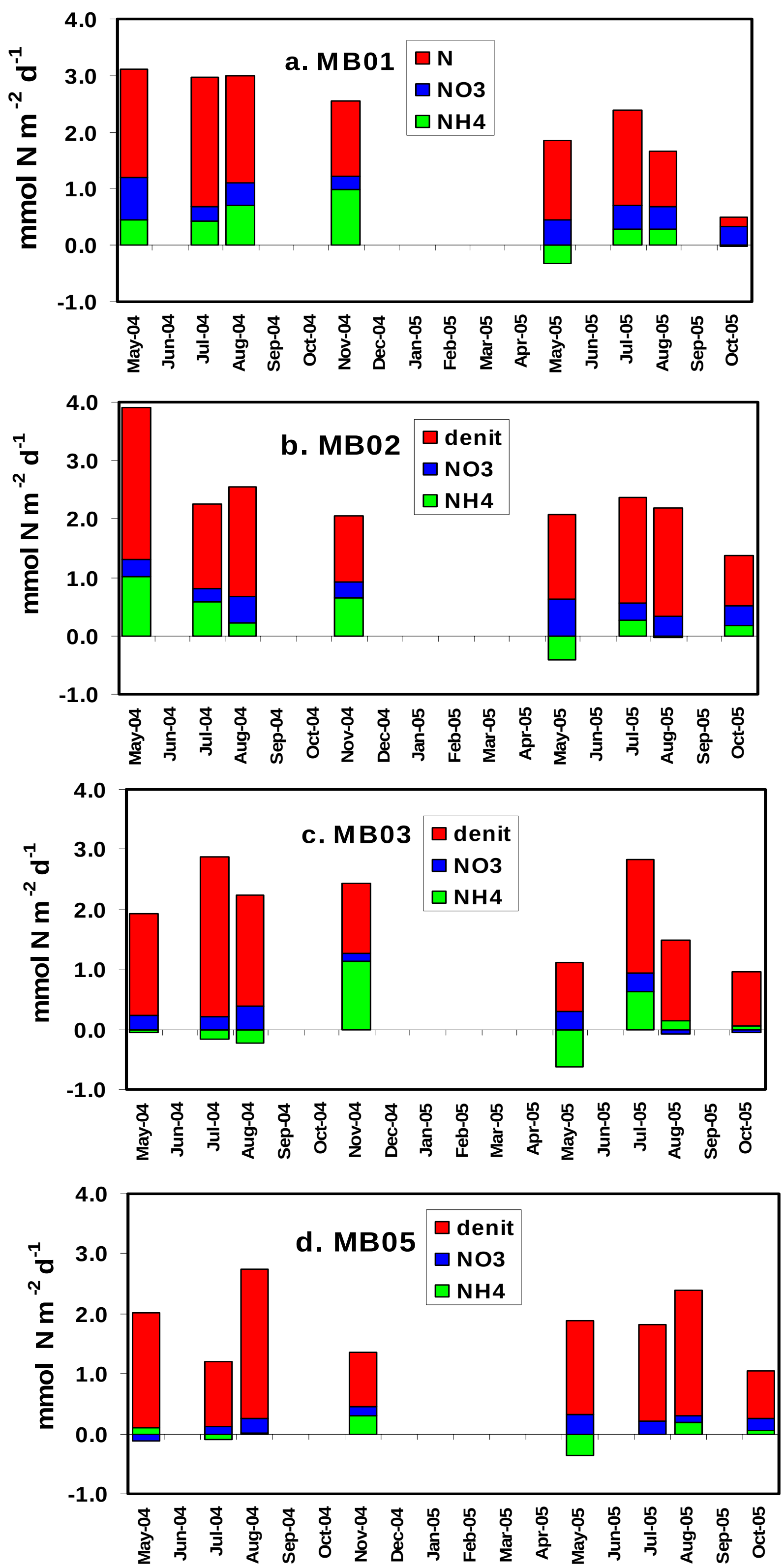

Figure 2-14. Nitrogen flux at all four Massachusetts Bay Stations in 2004 and 2005, partitioned into components of N from denitrification, NH_4+ flux, and NO_3^- flux.

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), respiratory quotients measured during core incubations were often greater than 1.0. Seasonal averages (omitting winter) were also 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 2005, RQs were less than 1.0 during all surveys except July. In particular, May values were quite low at three of the four stations, ranging from 0.56 and 0.57 at MB02 and MB05, respectively, to 0.70 at MB01. At MB03, RQ was 0.87, closer but still less than 1.0. During August and October, values at all four stations ranged from 0.68 to 0.88. During July, RQs were greater than 1.0 at three of the four stations: 1.1, 1.2, and 1.1 at MB01, MB03, and MB05, respectively. At MB02, RQ in July was 0.90, which was higher than during the rest of the season but still less than 1.0. Resulting seasonal average RQ at all stations was less than 1.0, ranging from 0.74 at MB05 to 0.92 at MB03 (Fig. 15).

2.5.2 Eh profiles

Oxidation-reduction potential measured as Eh in 2005 continued to be indicative of highly oxic conditions in sediment cores from Massachusetts Bay (Fig. 16). We have not observed any tendency towards decreased oxygen levels in these sediments in the five years post-relocation of the outfall. Values continue to be well above those that would indicate the presence of dissolved sulfides (-100 to -200 mV). Profiles of Eh in 2005 were in general similar to those observed in recent years, although in this year we did observe more of what would be expected as a typical seasonal progression towards lower Eh at depth in our cores than we typically see. Again we see the effects of the early season storms resuspending and oxidizing these sediments , creating very high Eh values at all depths in the May profiles. This is not surprising given the highly oxic and therefore “poorly poised (buffered)” state of the sediments.

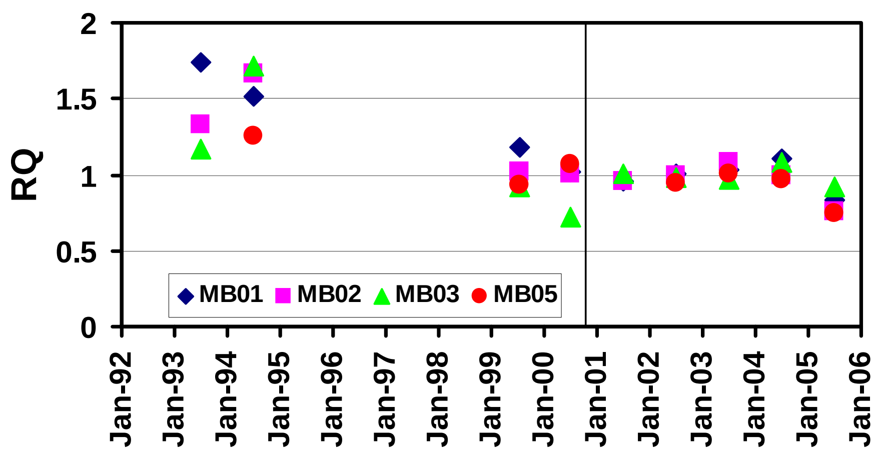

Figure 2-15. Seasonal (May-October) average respiratory quotients for Nearfield stations MB01, MB02, MB03 and Farfield station MB05 from 1993-2005. The vertical line marks the transition from baseline to post-relocation observations.

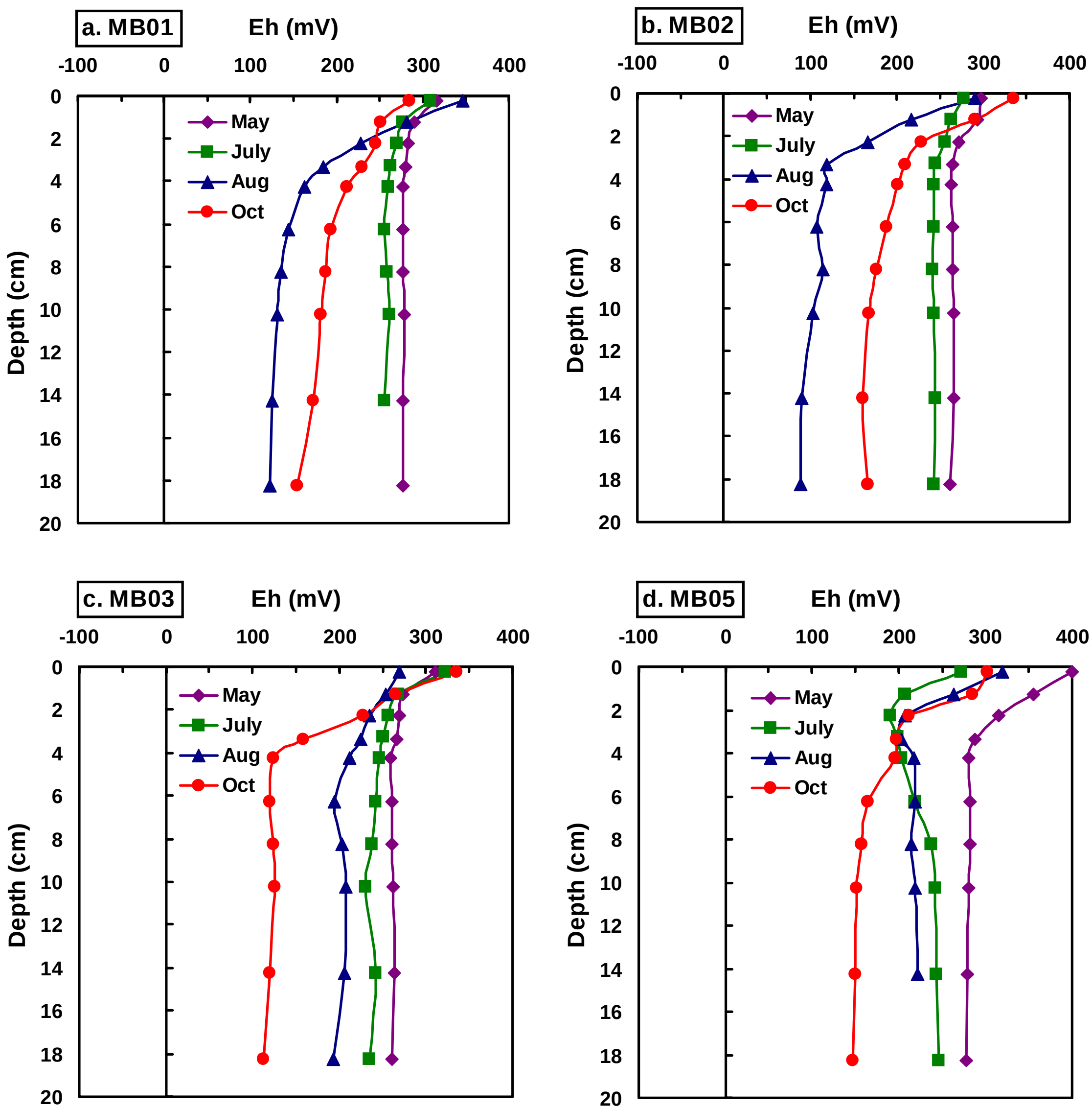

Figure 2-16. Eh profiles for May through October, 2005, from Nearfield stations a.) MB01, b.) MB02, c.) MB03, and Farfield station d.) MB05.

3.0 BOSTON HARBOR

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

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

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

The diversion of all MWRA effluent offshore marked the final phase in MWRA's Deer Island project, and has resulted in dramatic improvements in water quality in the harbor. For example, after three years, DIN concentrations had shown a decrease of 59% (Taylor, 2004). Accordingly, primary production has decreased, and the prolonged summer bloom that had been characteristic of the harbor is no longer typical (Libby et al, 2006b).

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.

In 2005, the two May and one October storms affected the harbor benthos and therefore its biogeochemistry significantly. These storms resuspended bottom sediments, certainly displacing and redistributing the fine fraction, as well as flushing porewaters. In addition, the May storms evidently disturbed the bottom sufficiently to prevent successful colonization of the sediments by the amphipod mat community that has been so important to benthic processes in much of the harbor. The amphipod mat was not present at any of our stations during any survey in 2005. Additionally, for the first time since Sediment Profile Imaging monitoring in the Harbor began in 1989, amphipod mats were not observed at any of 60 harbor stations imaged in August 2005 (Diaz, pers. com).

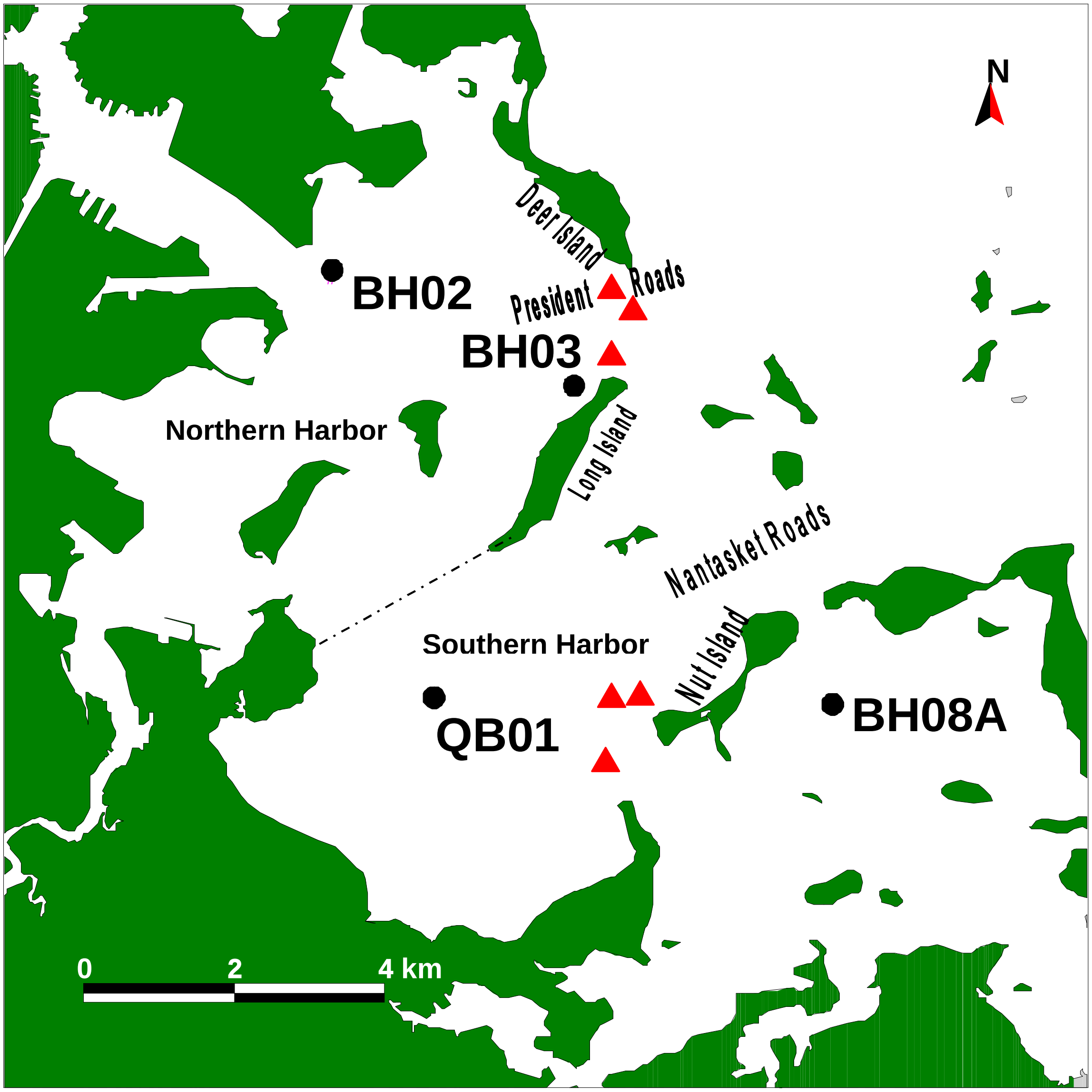

Figure 3-1. Locations of four Boston Harbor stations. Triangles (▲) mark the location of the out-of-service Harbor outfalls, the last of which was taken out of service on Sept. 6, 2000.

3.1 Organic Matter Loading

3.1.1 Total Organic Carbon

Organic matter loading to Boston Harbor decreased significantly over the baseline monitoring period due to the cessation in late 1991 of sludge disposal in the harbor and with subsequent improvements in sewage treatment. Accordingly, we observed a decrease in the organic matter content of sediments in the Harbor over the baseline period as these direct inputs decreased and carbon stores were metabolized. Beginning in 1999, reductions in sediment TOC from year to year continued but became smaller, and the variability across stations decreased. The very high percentages (over 4%) that were observed at these stations at various times before 1999 have not recurred. There has been no observable change in this pattern after the MWRA outfall was relocated offshore in September 2000. However, there is potential to see further reductions if the relocation results in any reductions in primary productivity and thereby decreases in organic matter deposition to the benthos.

Relative to the baseline period, there has been little interannual variability within or among the four harbor stations (Fig. 18). In 2005, seasonal averages of total organic carbon (TOC) were typical of observations from the last several years at Stations BH02 and QB01 (2.0% and 2.2%, respectively), but were low at Stations BH03 and BH08A (1.8% and 1.6% respectively). These latter two stations have shown a progressive decline in TOC over the monitoring period. In fact, the seasonal average TOC at both of these stations was lower than in the previous year, which had been the lowest. Across all four stations, lowest TOC was observed at Station BH08A, and the highest was at Station QB01. A comparison of TOC between the pre-and post-diversion periods (Fig. 19) shows a significant decrease at Stations BH03 and BH08A. TOC at QB01 also appears to have declined, athough pre-and post- averages overlap. There has been no real change at Station BH02.

Although TOC has declined and become less variable at all four harbor stations, the continued decline at Stations BH03 and BH08A is notable and corresponds to changes in sediment grain size at these stations (Fig. 20). The most dramatic example is Station BH03, where a very muddy, silty site has become sandy and gravelly, to the point that the SCUBA divers find it difficult to core here (Fig. 20b) A similar change has occurred at Station BH08A, although the gravel component is absent (Fig. 20c). We attribute some of the change at these two stations to the rise and fall of the *Ampelisca* mat, which, when present, not only accelerated the "burning off" of organic matter normally associated with the silt and clay fractions, but also damped physical winnowing of the sediments. As these mats became less robust, beginning around 2000 for BH03 and a little later for BH08A, or absent, as in 2005, sediments became more exposed to physical disturbance. In contrast, Station QB01 has experienced a change towards more silty sediments, and the gravel component that was present in the early part of the monitoring program is now nearly absent (Fig. 20d). Less change in sediment size distribution has occurred at Station BH02 (Fig. 20a).

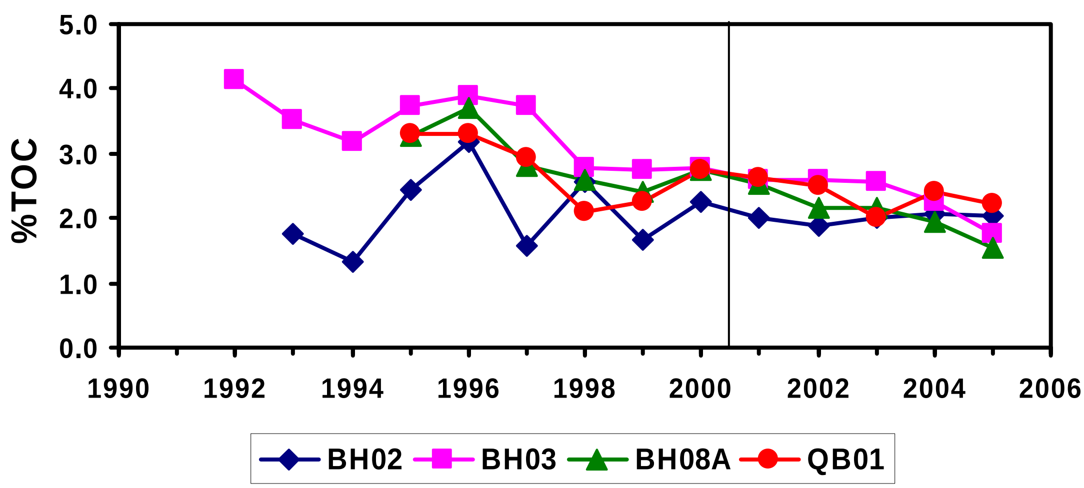

Figure 3-2. Seasonal average TOC (% dry weight) for top 2 cm of sediment.

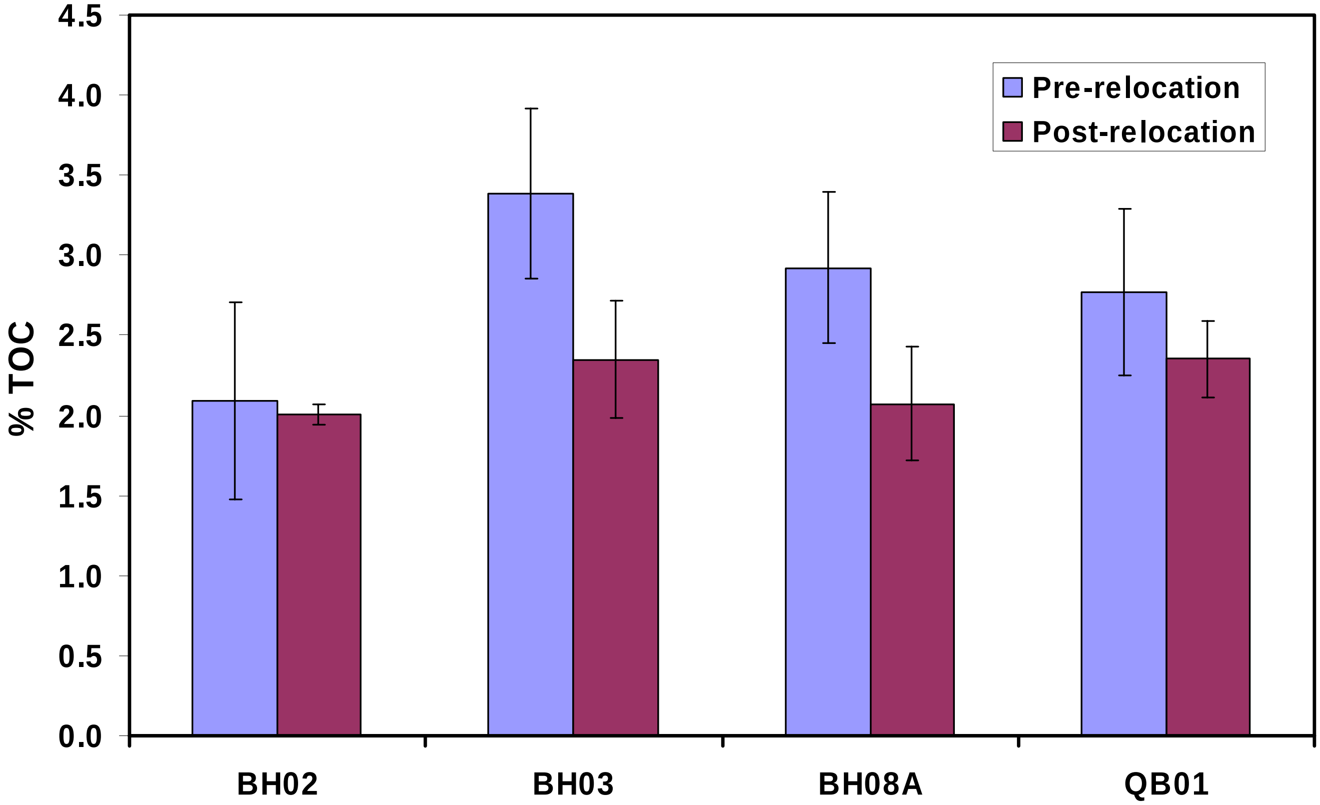

Figure 3-3. Sediment TOC pre- (1993 or 1995-2000) and post-(2001-2005) relocation of the outfall. Data are seasonal averages over all available years for each station. Error bars represent one standard deviation of the mean.

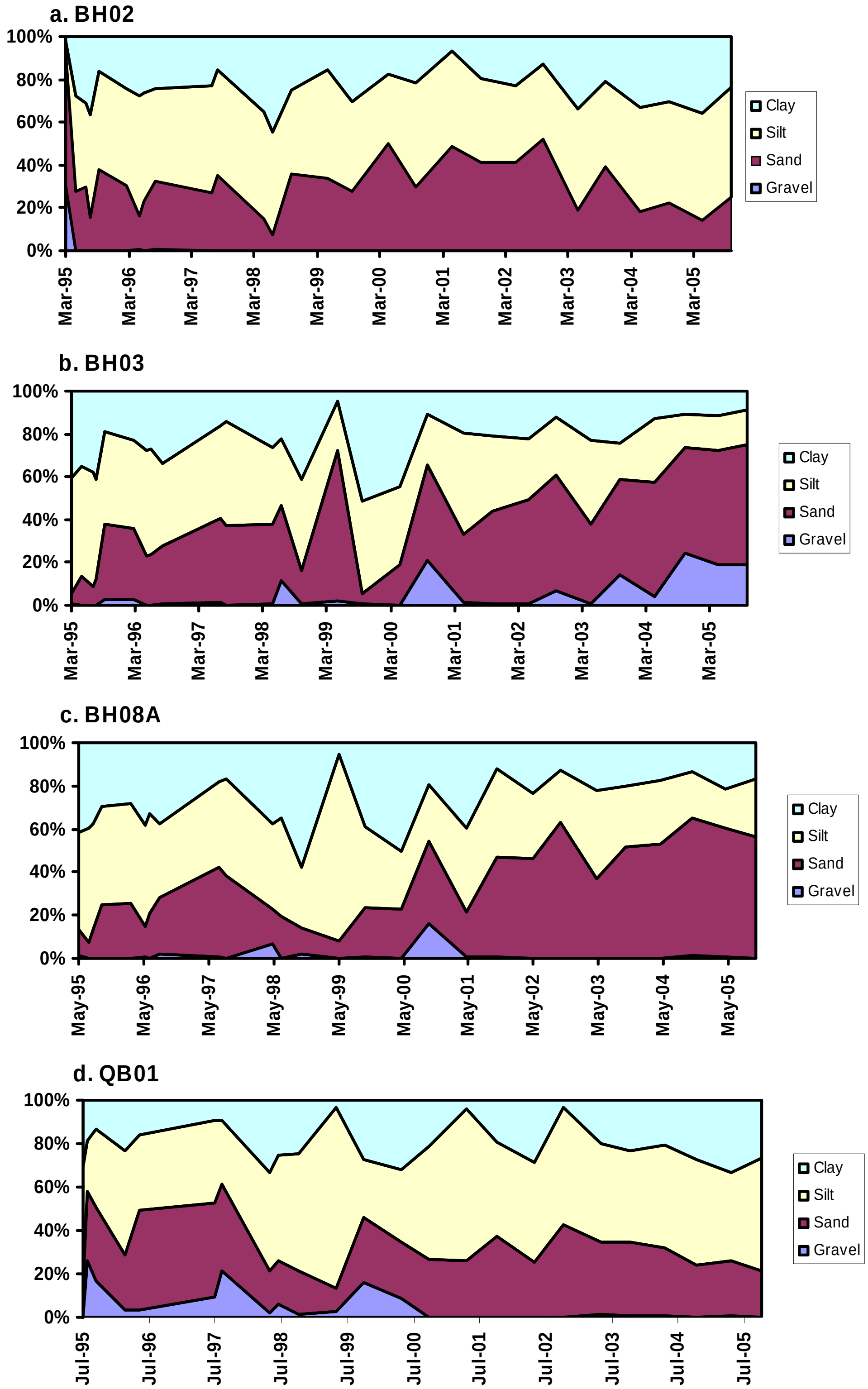

Figure 3-4. Grain size distribution at harbor stations.

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 variability in sediment pigment concentrations, but no trend up or down with time. For the first two years after the outfall relocation, there still was no apparent change. In 2003 and 2004, we observed an increase in total sediment pigments (chlorophyll *a* + phaeophytin *a*) in all stations except Station BH03. At BH02 and QB01, the increase was especially noticeable in the chlorophyll *a* fraction, and seemed to correlate with observations of benthic diatoms. (Fig.21). In 2005, total pigments declined from the high levels of the two previous years at all stations except at QB01, where levels stayed about the same.

In 2005, chloropyll *a* inventories (integrated over the top 5 cm of sediment) were highest in May at Stations BH02 and QB01, where levels were 37.0 and 42.5 µg chl *a* cm^{-2},respectively. Inventories at Stations BH03 and BH08A at the same time were much lower, only 7.7µg chl *a* cm^{-2} at BH03 and 13.9µg chl *a* cm^{-2} at BH08A. Lowest levels for the year were observed at Station BH03, when in July, chlorophyll inventory was only 5.5µg chl *a* cm^{-2} (Fig 21). Average inventories for the May-October season were also quite low at Station BH03 (8.2 µg cm^{-2}), and lower than the previous year at Station BH02 and BH08A. Only at Station QB01 were seasonal averages comparable to those in 2004.

Sediment profiles of chlorophyll *a* revealed elevated levels at the sediment surface in May at all stations, and was most pronounced at Station QB01 where surface concentrations were over 16 µg cm^{-3} (Fig. 22). Divers remarked on a "thick diatom mat" at QB01, and benthic diatoms were noted in the laboratory at the surface of cores. Chlorophyll *a* profiles from QB01 showed elevated surface concentrations throughout the year. Station BH02 showed somewhat high concentrations (~5ug cm^{-3}) throughout the profile for the rest of the season, with a subsurface peak in July. Profiles from Stations BH03 and BH08A revealed "background" chlorophyll concentrations (~1-2 ug cm-2) below the surface in May, and for the rest of the season, with the exception of a surface peak at BH03 in October. We have previously attributed low chlorophyll concentrations at Stations BH03 and BH08A to grazing pressure by the amphipod mat community; however in 2005, a mat never formed.

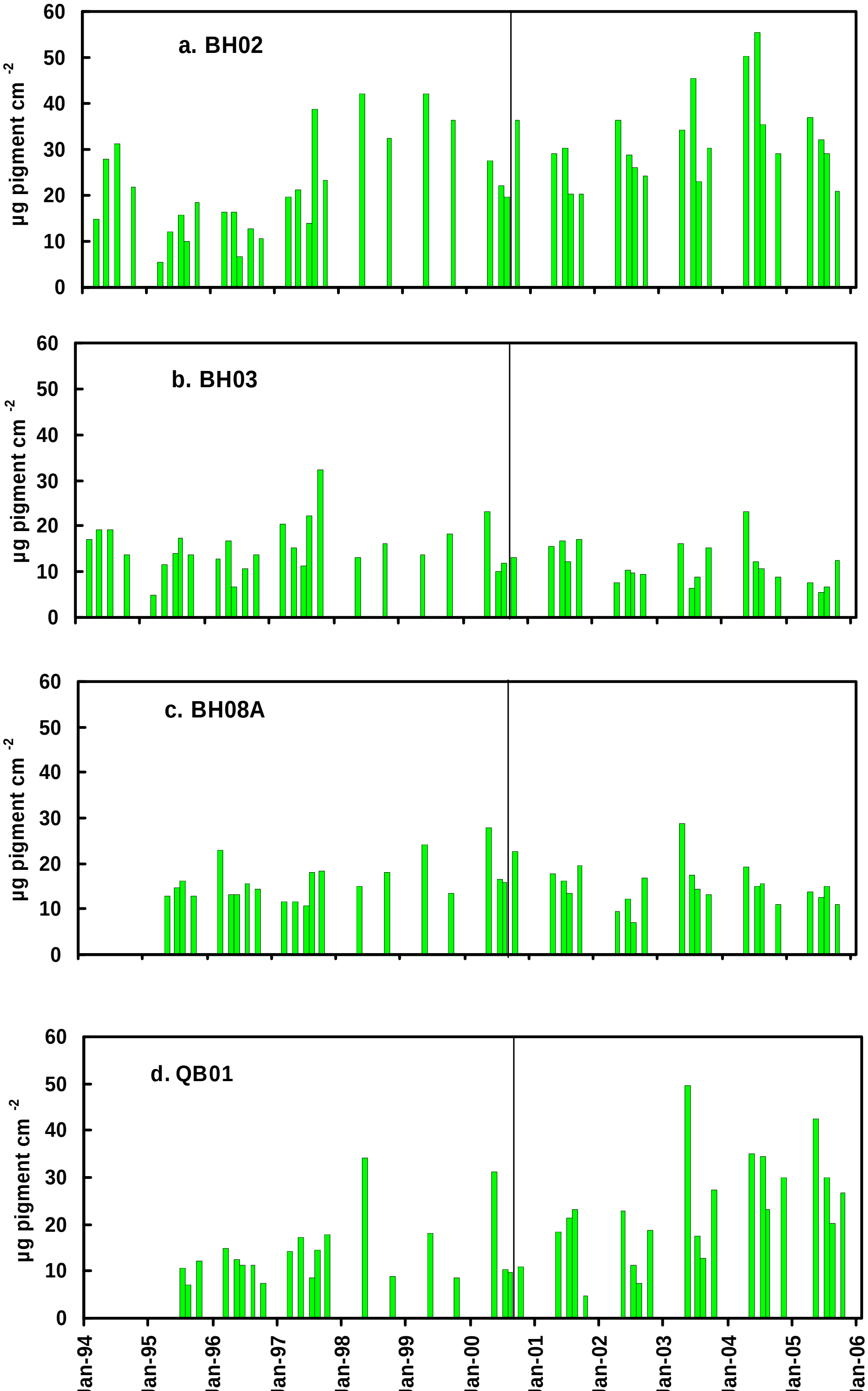

Figure 3-5. Chlorophyll *a* inventory for top 5 cm of sediment at northern harbor stations a.) BH02, b.) BH03, and southern harbor stations c.) BH08A, d.) QB01. The vertical line marks the transition from baseline to post -relocation observations.

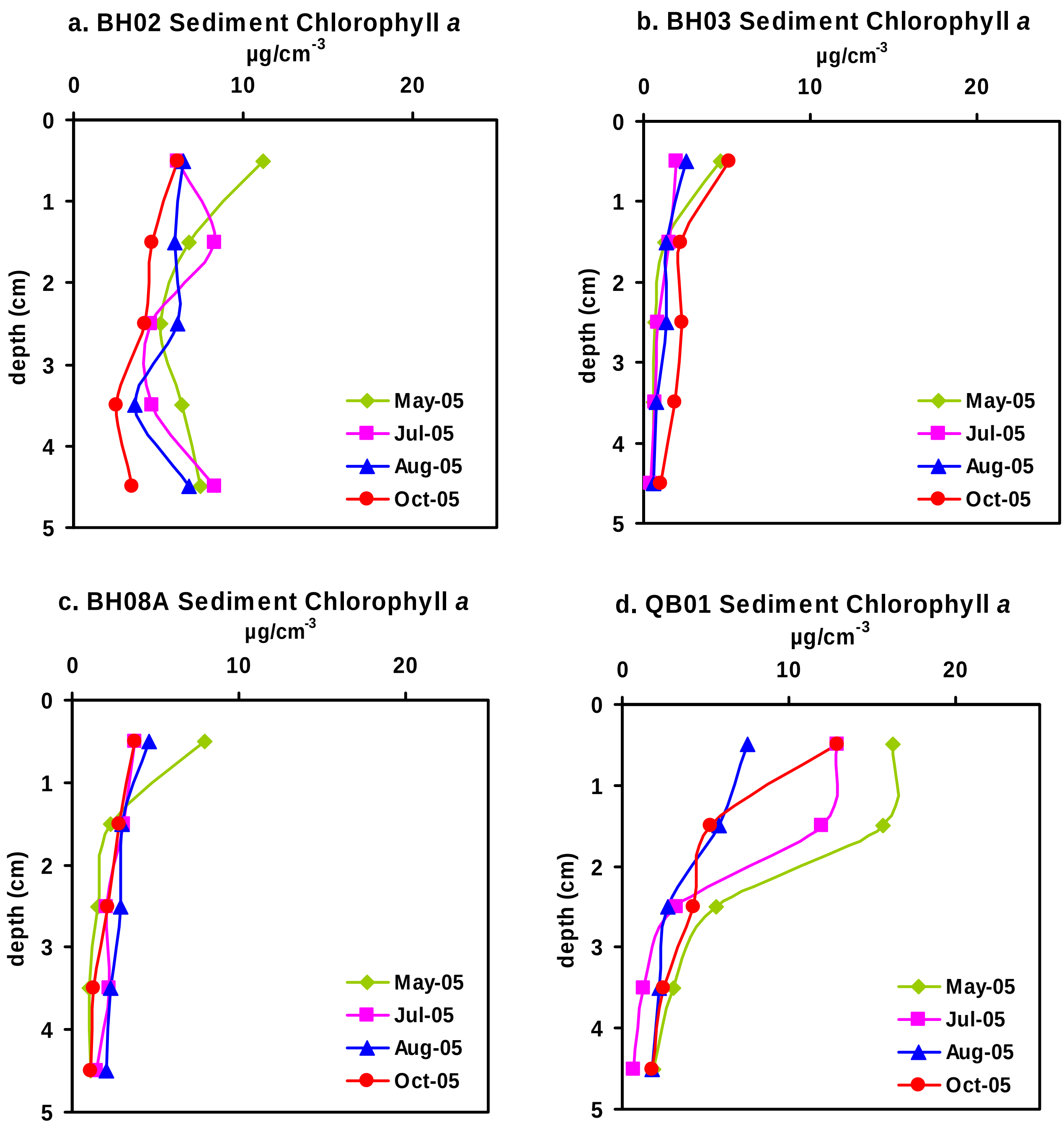

Figure 3-6. Profiles of chlorophyll *a* in top 5 cm of sediment at Boston Harbor stations in 2005 a.) BH02, b.) BH03, c.) BH08A, and d.) QB01.

3.2 Sediment Oxygen Demand

SOD in the harbor has been decreasing over the past several years, and 2005 results continued that trend (Fig. 23a). As a harbor-wide average of our four stations, sediment oxygen demand in Boston Harbor in

2005 was the lowest yet observed during the monitoring program. That average was 22.5 mmol m^{-2} d^{-1} as compared to the highest observed average of 99.6 mmol m^{-2} d^{-1}, seen 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}) The only station that did not exhibit the lowest seasonal average yet reported was Station QB01, and even here rates were among the lowest. Seasonal averages ranged from the high at QB01 of 27.7 mmol m^{-2} d^{-1} to the lowest at BH08A of 18.3 mmol m^{-2} d^{-1}. This rate at BH08A was less than half of the previous year.

For all stations except Station QB01, rates were at the bottom of or lower than the entire range of data throughout the 2005 season (Fig. 24 a-d). Highest and lowest rates of the season occurred in May, and were 40.1 mmol m^{-2} d^{-1} at QB01 and 12.7 mmol m^{-2} d^{-1} at BH08A .

The absence of the amphipod mat combined with probable loss of some of the fine fraction of the sediment were the major drivers setting the low SOD in 2005. When we look at other likely drivers, such as temperature, %TOC, and sediment chlorophyll *a*, we get varied results (Table 1). For example, in 2005, temperature was positively correlated with SOD at Stations BH03 and BH08A, but the relationship was very weak and negative at BH02 and QB01. Instead, %TOC and pigments were more important at these two stations although the relationships were not strong except for chlorophyll *a* at Station BH02. The weak relationship with chlorophyll at QB01 was surprising given the higher concentrations observed at this site. We have often reported on the interannual and spacial variability in these relationships. 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 (°C), TOC (% dry weight, top 2 cm), and chlorophyll *a* (ug cm^{-2} for top 5 cm) in 2005. Gray shading denotes regressions with negative slopes.

	Station			
SOD vs:	**BH02**	**BH03**	**BH08A**	**QB01**
Temp	0.047	0.493	0.861	0.004
TOC	0.326	0.876	0.343	0.326
Chl *a*	0.813	0.692	0.045	0.198

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

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 variability we observed from station to station and year to year early in the monitoring program has abated, such that flux rates across all four harbor stations are now very similar. It appears that conditions in the harbor are entering a new equilibrium.

3.3.1 DIN

In 2005, DIN flux averaged across the four harbor stations and the May to October season was the smallest yet observed during the monitoring program (Fig. 23b). Although seasonal averages for Stations BH02 and QB01 were fairly typical for those stations (4.0 and 1.6 mmol m^{-2} d^{-1}, respectively), fluxes at Station BH03 and BH08A were the smallest to date (0.8 and 1.0 mmol m^{-2} d^{-1}, respectively). A large decrease occurred at Station BH08A, where 2005 rates were one third of those in the previous year.

Despite having a typical seasonal average, Station QB01 had essentially no DIN flux in May (< 0.1 mmol m^{-2} d^{-1}), and only a small flux in October (0.41 mmol m^{-2} d^{-1}) (Fig. 24d). July and August rates, however, were substantial (2.2 and 3.8 mmol m^{-2} d^{-1}). This pattern, with highest rates co-occurring with warmest bottom water temperatures, resulted in a strong relationship with temperature ($r^2 = 0.736$), a seasonal pattern observed only at this station this year. Station BH02 had the largest fluxes throughout the season, ranging from 6.6 mmol m^{-2} d^{-1} in May to 2.5 mmol m^{-2} d^{-1} in October, but with a negative relationship with temperature. There was less change over the season at the other two stations, with rates ranging between 0.3 mmol m^{-2} d^{-1} (BH08A, August) and 2.2 mmol m^{-2} d^{-1}, (BH08A, July), resulting in weak relationships with temperature (Fig. 24b).

The composition of the DIN flux varied according to station in 2005. At Stations BH02 and QB01, NO_3^- comprised only about 7% of the seasonal average flux. In contrast, NO_3^- was the major component of the average DIN fluxes at Station BH03 and BH08A, contributing 75% and 55% , respectively. At times, $N0_3^-$ comprised 100% of the DIN efflux at these two stations (October at BH03 and August at BH08A). We have often observed proportionally large NO_3^- fluxes at these two stations, but have normally attributed them to bioirrigation and oxidation of the sediments by the amphipod mat community that has characterized these sites in the past. In 2005, however, the mats were absent. At station BH03, we have noticed the waning of the mat community over recent years, and noted that the sediments have become coarser over time, with divers often reporting a cobbly surface and difficulty in obtaining cores . We think sediments here are currently oxygenated by physical processes rather than biological ones. The sand component has also increased at Station BH08A, but not to the same degree as BH03, and there had not been the same degree of decline in the amphipod mat. Even though there was never a mat formed at this site in 2005, divers did report biological features, especially in August when Cerianthid burrows were noted. This station may now be in transition, and we may be seeing a mix of biological and physical processes.

3.3.2 Phosphate and Silica

Seasonal average phosphate fluxes in 2005 were among the lowest observed for each station throughout the monitoring program (Fig. 23c). A harbor average across all four stations was less than 0.1 mmol m^{-2} d^{-1}, lower even than the previous two years, each of which had been described as the " lowest yet observed". Seasonal average fluxes in 2005 ranged from essentially no flux at Station BH03 (< 0.01 mmol m^{-2} d^{-1}) to 0.2 mmol m^{-2} d^{-1} at Station BH08A.

Within the year, fluxes fell near or below the bottom of the baseline range (Fig 25a-d). At most stations and during much of the season, fluxes were weak (that is, the change in concentration over time in our incubated cores was often not linear) and/or variable (for example, one replicate showing efflux and the other influx). Linear and consistent fluxes were observed at Statiaon BH02 in May, Station BH08A in July, August, and October, and QB01 in August and October. Among these results, fluxes ranged from an uptake of 0.05 mmol m^{-2} d^{-1} at QB01 in October to 0.5 mmol m^{-2} d^{-1} at BH08A, also in October. In contrast to the previous three years, there was no correlation with temperature.

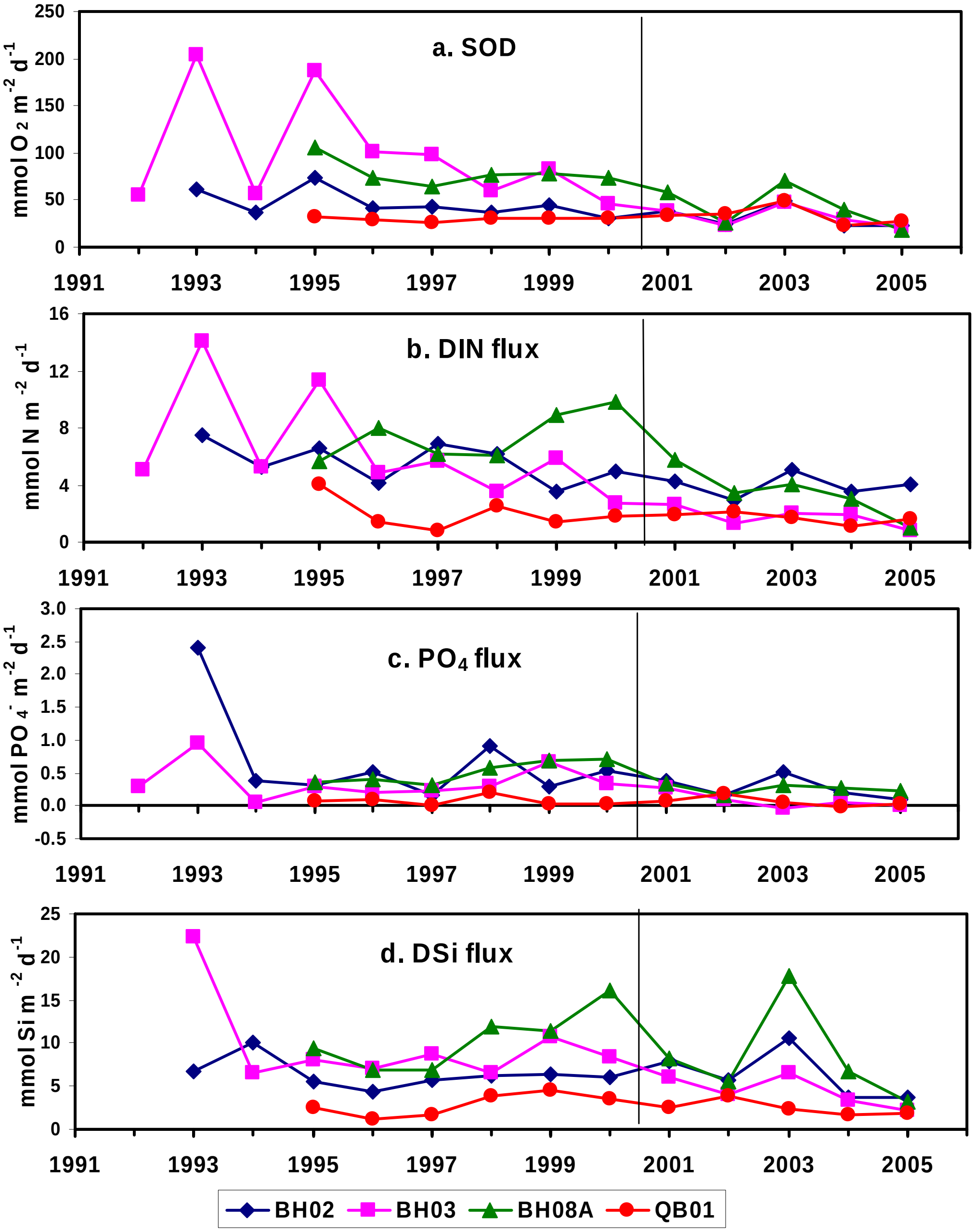

Figure 3-7. Seasonal (May-October) averages of a.) sediment oxygen demand (SOD), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Boston Harbor stations in 1993-2005. The vertical lines mark the transition between baseline and post-relocation observations.

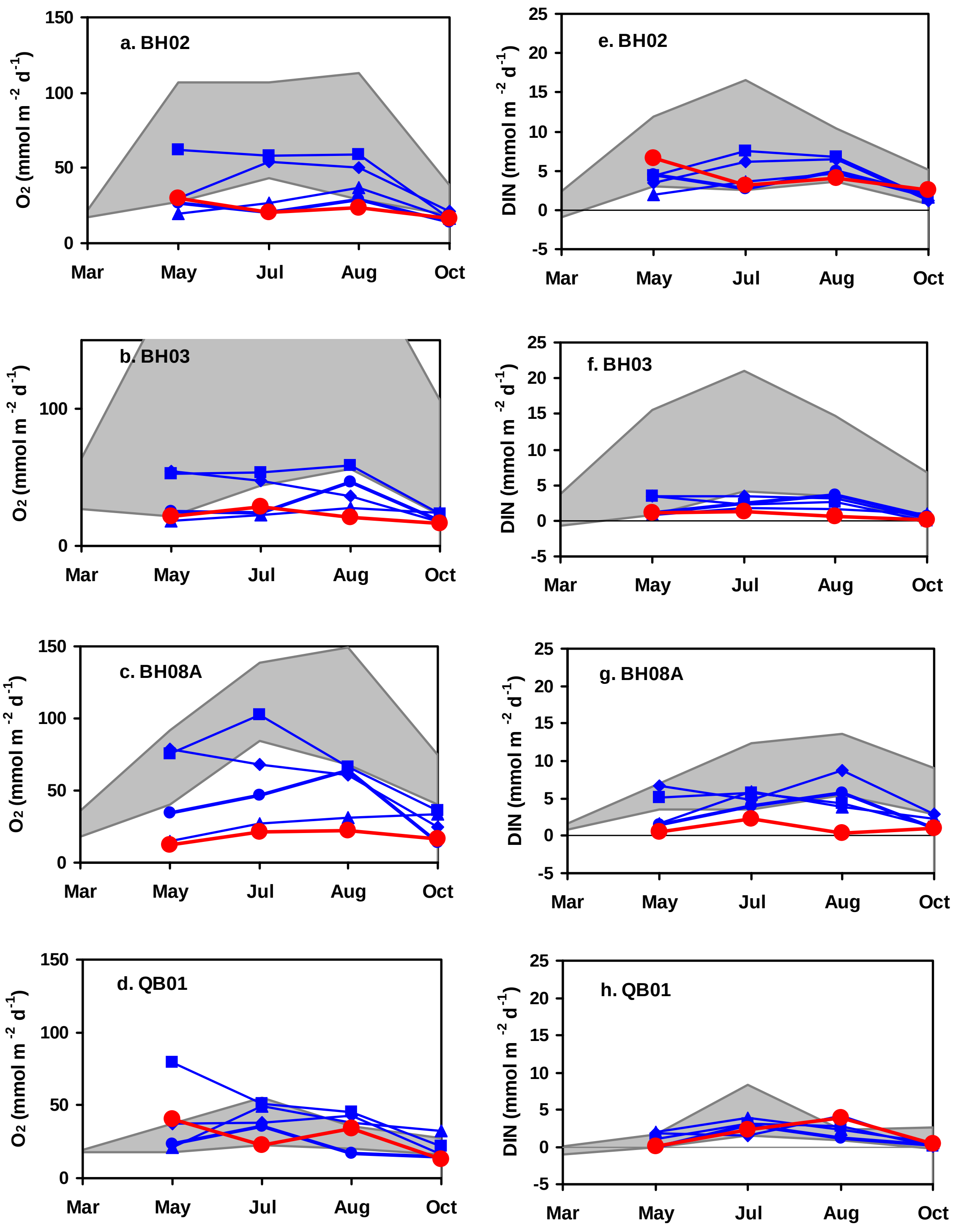

Figure 3-8. Sediment oxygen demand (O_2 flux) and DIN flux 2001 (♦), 2002 (▲) , 2003 (■), 2004 (●), and 2005 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations BH02, BH03, BH08A, and QB01, respectively.

Silica fluxes in 2005, as a harbor-wide average for the season, were the smallest yet observed (2.7 mmol m^{-2} d^{-1})(Fig. 23d). The largest change was observed at Station BH08A, where the seasonal average flux of 3.2 mmol m^{-2} d^{-1} was less than half the value of the previous year. Fluxes were also lower than baseline and lower than most previous observations at Stations BH02 and BH03, averaging 3.6 and 2.2 mmol m^{-2} d^{-1}, respectively. At Station QB01, silica fluxes of 1.8 mmol m^{-2} d^{-1} were similar to the previous year and were near the lower end of the baseline range for the station. (Fig 23d)

Even though fluxes were small, a strong seasonal pattern was observed in the 2005 silica fluxes (Fig. 25e-h) at all stations except Station BH02. At BH02, largest fluxes of 4.3 mmol m^{-2} d^{-1} occurred in May, and decreased through the season to 2.9 mmol m^{-2} d^{-1} in October. At the other three stations, high rates occurred in July, and were highest at Stations BH08A where they reached 4.4 mmol m^{-2} d^{-1}. Lowest rates for these three stations occurred in May, with a rate of 0.4 mmol m^{-2} d^{-1} at QB01 being the lowest. Temperature could explain from 80% to 99% of the variability in 2005 at these three stations. As for the other fluxes, this relationship with temperature varies temporally and spatially. After including 2005 data, the relationship over all years suggested that temperature explains between about 27% to 34 % of the variability we see in Si fluxes, somewhat less than reported last year.

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 378 g C m^{-2} y^{-1} (Libby et al., 2006a and Oviatt, pers. com.). 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 21% for DIN and 25% 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.

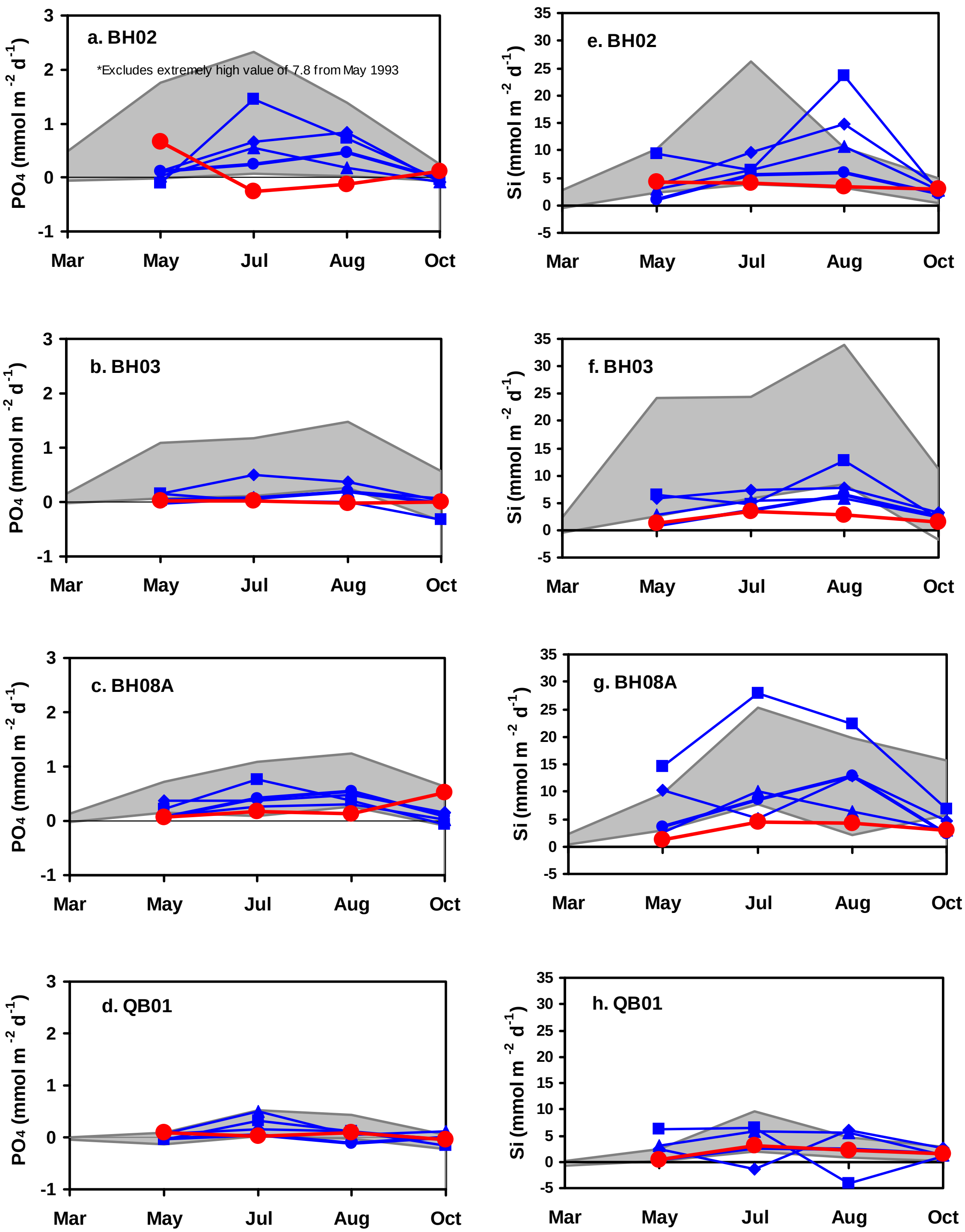

Figure 3-9. Phosphate (PO_4) and dissolved silica (DSi) flux for 2001 (♦), 2002 (▲), 2003 (■), 2004 (●) and 2005 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO_4 and panels e-h depict DSi flux for stations BH02, BH03, BH08A, and QB01, respectively.

3.4 Denitrification

For the second year, rates of denitrification at the two harbor stations where it has traditionally been measured, BH02 and BH03, were among the lowest of both baseline and post-relocation measurements (Fig 26a). The seasonal average rate at BH02 of 1.6 mmol N m^{-2} d^{-1}, was the same as in 2004, and was lower only twice during the baseline period (1.5 in 1994 and 0.7 ion 1996). At BH03, the seasonal average of 1.9 mmol N m^{-2} d^{-1} for 2005 matched the lowest rate previously observed in 2002 and was similar to the 2004 rate of 2.2 mmol N m^{-2} d^{-1}. Rates this low were not observed during baseline. Again we must note that the low rates may in part be a result of the new analytical method (see Tucker and Giblin, 2005).

Various controls on denitrification could account for these patterns. Increases in oxygen penetration of the sediments, which would facilitate nitrification, could result in increased rates of denitrification. Improvements in redox conditions at these two stations, earlier and more dramatically at BH03 due to bioirrigation, are likely responsible for increased rates of denitrification we observed, first at BH03 and later at BH02. Decreases in more recent years might be the result of decreasing organic matter availability as well as changes in bioturbation as the successional stage of the benthic community advances.

In 2004, the change in analytical method allowed us to add measurements at southern harbor Stations BH08A and QB01 so we now have two years of data from all four stations and all surveys (Fig. 26b). In 2005, there was less variability across the four stations than in the previous year. Seasonal averages ranged only from 1.3 mmol N m^{-2} d^{-1} at QB01 to 1.9 mmol N m^{-2} d^{-1} at both BH03 And BH08A. We believe the absence of the amphipod mats is largely the reason for the decreased rates.

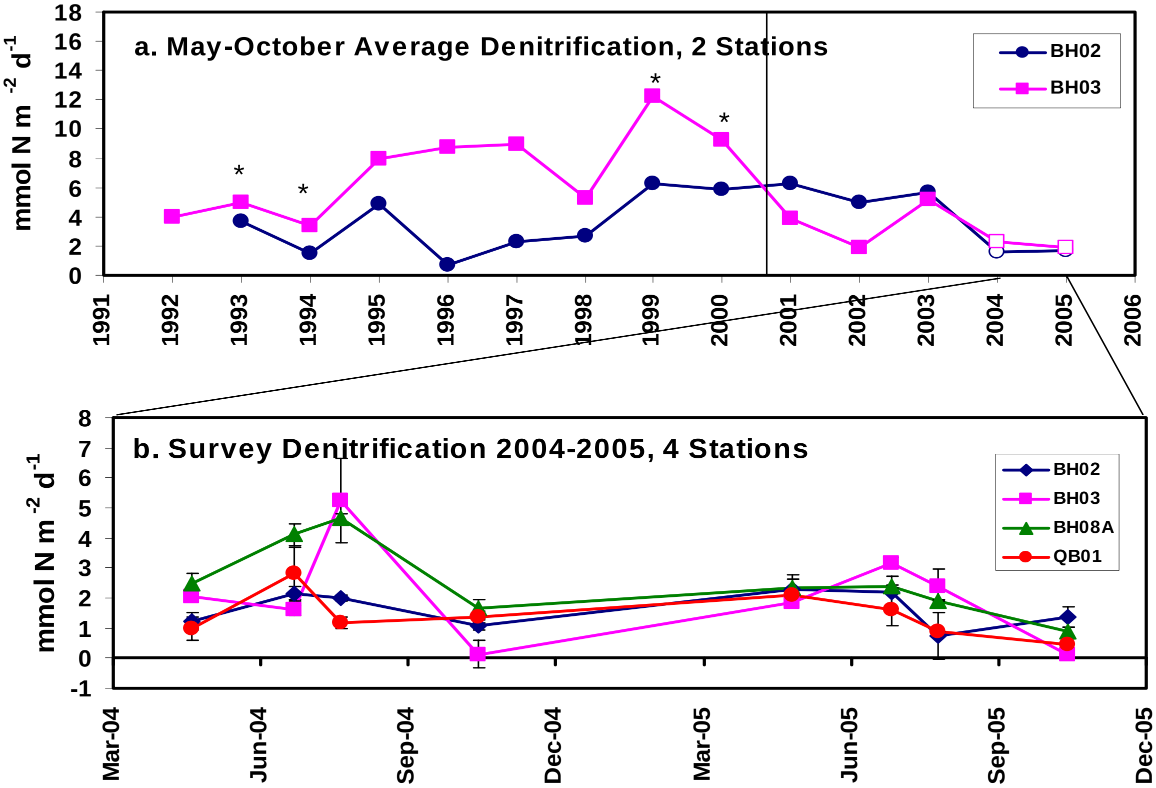

Figure 3-10. Denitrification in Boston Harbor: a.) May-October seasonal averages for Station BH02 and BH03 from 1992-2005; * marks years when averages were of three (1993 and 1994) or two (1999, 2000) rather than four surveys; the vertical bar marks the outfall relocation. b.)Denitrification rates for all four harbor stations during 2004 and 2005. Error bars represent one standard error of the mean of two replicates. .

The four stations started the season with very similar rates of denitrification in May, averaging 2.1 mmol N m^{-2} d^{-1} (Fig. 26b). Later in the season, rates became variable across the stations. Highest rates of 3.2 mmol N m^{-2} d^{-1} occurred at Station BH03 in July. Lowest rates of the season of only 0.1 mmol N m-2 d-1 were also observed at BH03 in October; we observed similarly low rates at this station in the fall of 2004. Station BH03 was the only station in 2005 where rates were correlated with temperature, and the relationship was not very strong ($r^2 = 0.62$). For the other three stations, highest rates occurred in May, and in general declined through the season.

Relative to DIN flux, denitrification in the harbor varies across sites and seasonally within sites (Fig. 27). For 2004 and 2005, it was most consistent at Station BH02, where it ranged from 20% to 45% of the total of denitrification and DIN efflux. At this site, DIN fluxes are typically larger than at the other three sites, and NH_4^+ comprised most of the flux. At Station BH08A, denitrification was usually the major component of the flux, ranging from 45% to 84% of the total. This was the case for Station BH03 as well, except in October, when all fluxes were very small and denitrification contributed less than 20%. At QB01, the proportion of the flux that was denitrification was usually large, but varied widely. In May of both years it comprised over 90%; in August 2005, however, it comprised only 19%. This variability may be accounted for by a number of processes that affect various components of the nitrogen cycle. For example, increased oxygen penetration produced by either biological or physical processes often enhances denitrification by increasing nitrification. This likely accounts for higher proportions of denitrification at Station BH03 And BH08A. In contrast, Station BH02 typically has shallower oxygen penetration, accounting for the dominance of NH_4^+ flux at this site. At Station QB01, the presence or absence of benthic microalgae plays a role. Denitrification becomes relatively more important when DIN flux is damped 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. 28a). We have now constructed a new budget for the post-diversion period (2001-2005). We assumed that burial rate has not changed, and used the average denitrification rate at Station BH02 and BH03 (3.5 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 65% of the total inputs (Fig 28b).

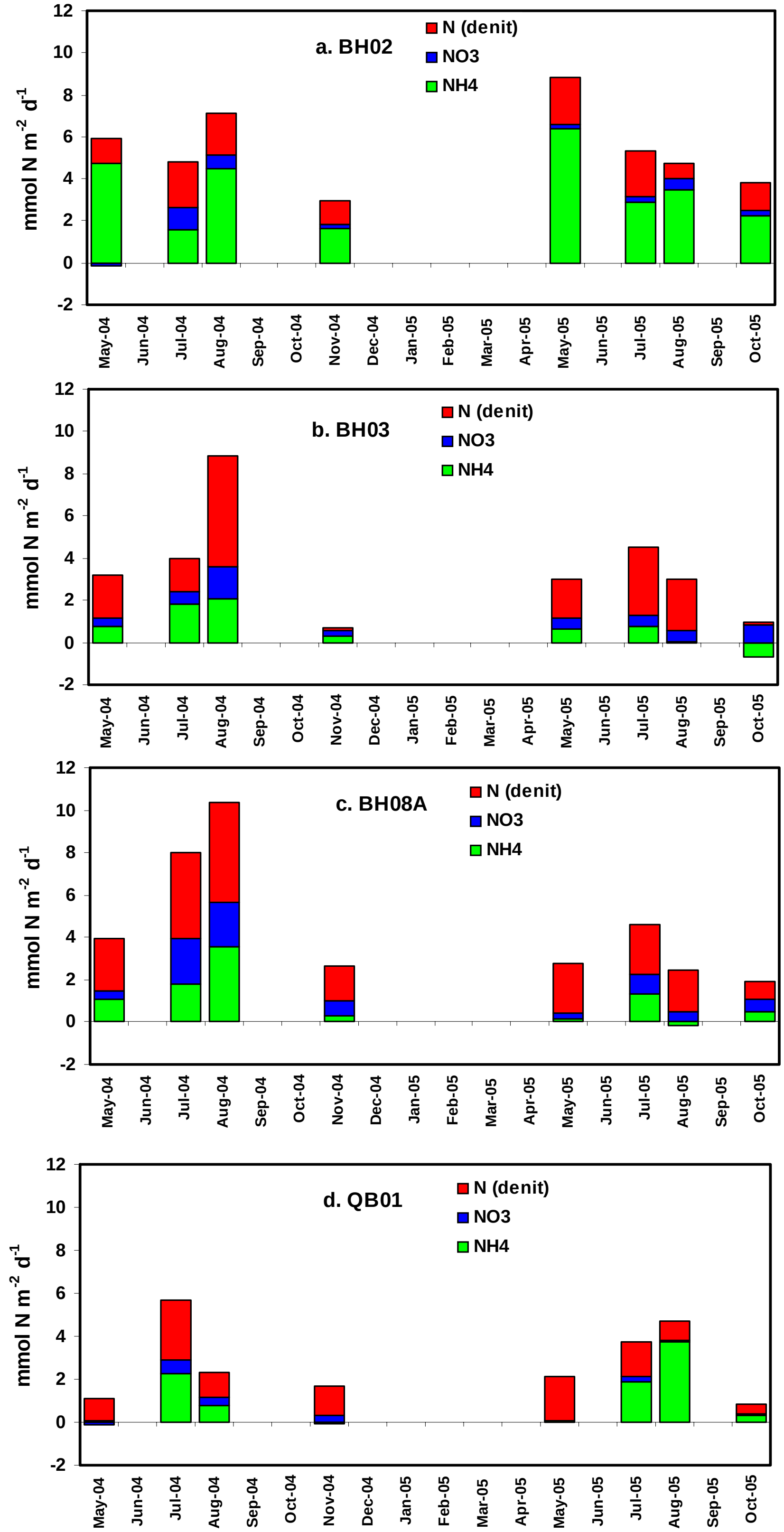

Figure 3-11. Nitrogen flux at all four Boston Harbor Stations in 2004 and 2005, partitioned into components of N from denitrification, NH_4+ flux, and NO_3^- flux.

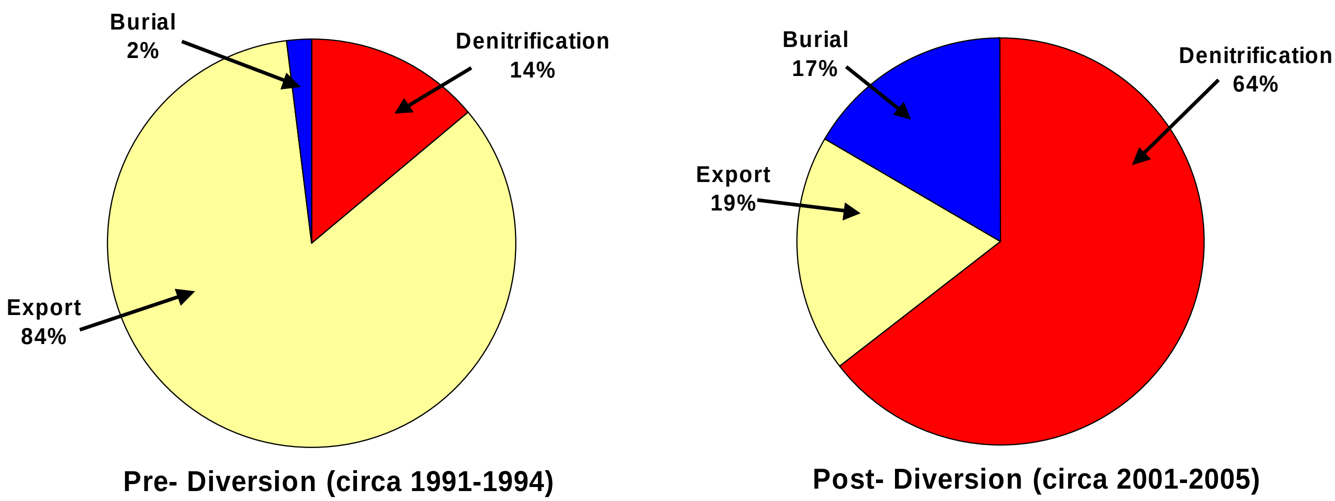

Figure 3-12. Nitrogen budgets for Boston Harbor, showing change in relative importance of denitrification after outfall diversion.

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 a dense infaunal population (the amphipod mat) that helped reoxidize the sediments through bioturbation. The effects of the infaunal community included deeper oxidized layers at these sites, and changes in RQs from values well over 1.0 early in the monitoring program to values close to or somewhat lower than 1.0 in recent years. High concentrations of dissolved sulfides (> 0.5mM) are no longer detected in the porewaters at Station BH03. At Station BH02, where the amphipod community 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 2005, average respiratory quotients (RQs) were among the higher values observed at Stations BH02, BH08A, and QB01, but nearly the lowest ever observed at Station BH03 (Fig. 29). At Station BH03, RQ averaged over the May to October period was 0.6, with the only value above 1.0 occurring in May. Averages for the other three stations ranged from 1.2 to 1.6, with higher RQs occurring in May at Station BH02 and QB01, but in October for Station BH08A. RQs were especially high at BH02 and QB01 in

May, reaching 2.2 and 1.7, respectively. Again, we suggest that the stormy season played a role in these high values. After a "flushing" of the porewaters as may have occurred during the storms, the sediments would tend to resettle, developing new redox profiles and storing sulfides and other endproducts of anaerobic respiration. Thus, more DIC would be released than O_2 consumed. The exception of Station BH03 is unexplained but may be related to the changing nature of this station; for example, the change to coarser sediments and shift towards a dominance of physical processes may facilitate a continual flushing of porewaters here.

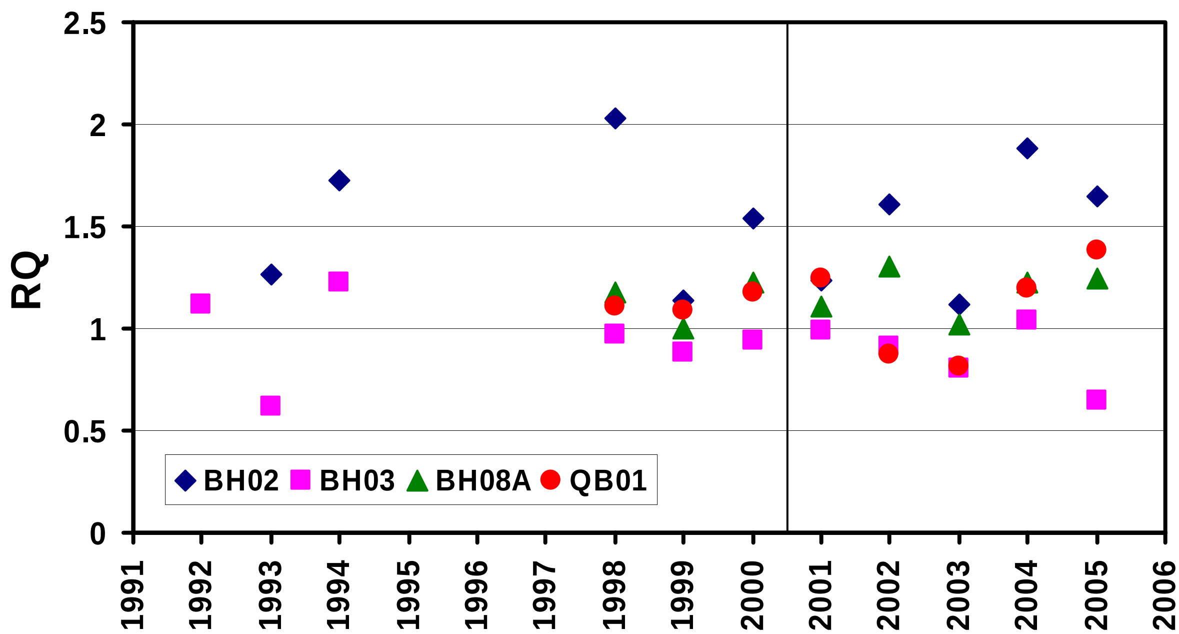

Figure 3-13. Seasonal (May-October) average respiratory quotients for Boston Harbor stations BH02, BH03, BH08A, and QB01 from 1993-2005. The vertical line marks the transition from baseline to post-relocation observations.

3.5.2 Eh Profiles

Profiles of oxidation-reduction potential (Eh) (Fig. 30) taken from within sediment cores during 2005 fell within baseline and post-relocation ranges. Surface sediments (0-4cm) were highly oxidized throughout the season and at all stations. This 4 cm depth is typical of the depth to which small animal borrow penetrate our core samples. However, in 2005, physical disturbance of the surface sediments by storms probably contributed to the oxic nature of the Eh profiles. This effect was particularly evident in May, after one of that month's northeast storms, at Stations BH03 and QB01, where the Eh profile changed little with depth to 15 cm (bottom of the cores) (Fig. 30 b and d). Strongly oxidizing conditions persisted at these stations throughout the season.

At Station BH02, which usually exhibits the most reducing conditions of the stations, the May profile had high Eh values to over 10 cm (Fig. 30a). More typical profiles for this stations developed during the summer, with Eh reaching values that would indicate sulfate reduction (-150mV) at about 8 cm. After the October storm, surface sediments at this stations were reoxidized.

At Station BH08A, Eh profiles for the top 4 cm were nearly identical through the season (Fig. 30c). In contrast to the other stations, the most oxidizing conditions at this station were observed in July. A large burrow hole within the core sample that was used for this measurement was probably the cause, and illustrates the effect animal burrows may have on sediment biogeochemistry, as well as on the small-scale heterogeneity of these sediments. Eh values low enough to indicate sulfate reduction were only observed in August at this station, occurring at about 8-10 cm depth.

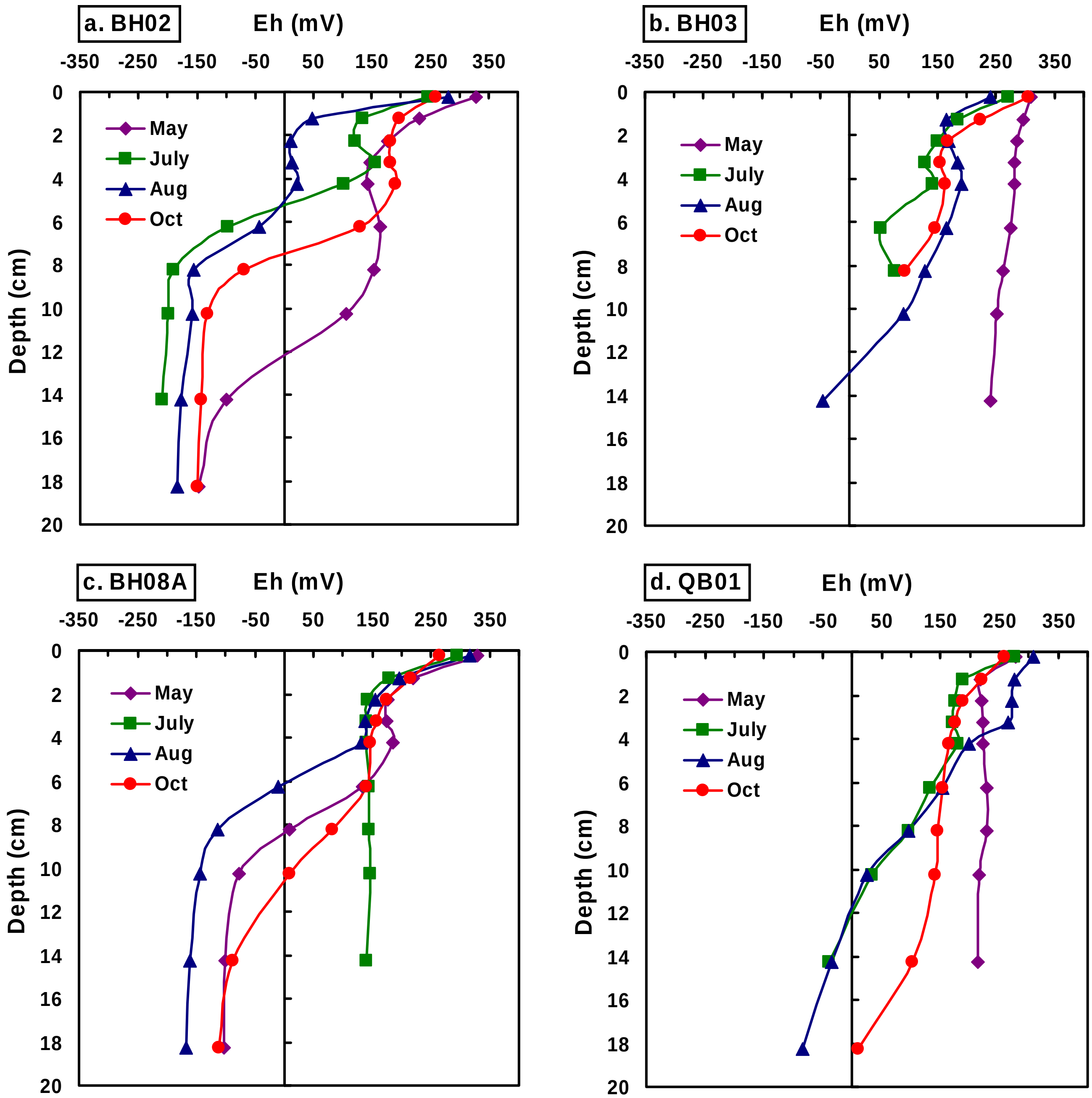

Figure 30. Eh profiles for May through October, 2005, from Harbor stations a.) BH02, b.)BH03, c.) BH08A, and d.) QB01.

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 2005, the overriding influence on benthic nutrient cycling was the two early and one late season northeast storms. These storms produced large enough waves and were of sufficient duration to impact the benthos in the nearfield area. The year was marked by a coarsening of sediments in the nearfield, an increase in physical over biological processes acting on the sediment surface, and a decrease in biogenic structures (Maciolek et al, 2006). Decreases in most parameters measured in the benthic nutrient cycling studies can be attributed at least in part to the effects of these storms.

Organic matter measured as TOC was lower than usual in 2005, averaging 1.1% for the nearfield. It is likely that some scouring of surface sediments resulted from the northeast storms. In contrast, there was little change in TOC at our deeper, Stellwagen Basin station, which was presumably unaffected by the storms. Here the TOC averaged 1.5% for the season. We have detected no change in TOC between the pre- and post-diversion periods.

Inventories of total sediment pigments also decreased in 2005, with the seasonal averages for the nearfield being 90.7 µg pigment cm^{-2} for the top 5 cm, down from 112.8 µg cm^{-2} in 2004. Curiously, the chlorophyll *a* fraction showed an increase over the previous year, from 3.8 µg cm^{-2} to 5.5µg cm^{-2}. However, there was little expression of a spring bloom in May profiles from the nearfield stations. At the Stellwagen station, there was a smaller decrease in total pigments (from 86.9µg cm^{-2} in 2004 to 77.1µg cm^{-2} in 2005), but a similar change in chlorophyll (from 5.7µg cm^{-2} to 7.1µg cm^{-2}). At this station, however, there was a pronounced surface elevation of chlorophyll concentration in May.

Rates of SOD in 2005 were low. The average for the May to November sampling period for the nearfield stations was 12.6 mmol m^{-2} d^{-1}, nearing the bottom of the baseline range of 12.4 to 24.7 mmol m^{-2} d^{-1}. At Stellwagen Station MB05, the seasonal average was 12.9 mmol m^{-2} d^{-1}, very similar to the nearfield average. The baseline average for this station is 11.6 mmol m^{-2} d^{-1}.

Fluxes of DIN in 2005 were also quite low. The seasonal average across the nearfield stations was 0.3 mmol m^{-2} d^{-1} , the lowest to date, as compared to a baseline average of 0.9 mmol m^{-2} d^{-1}. NO_3^- comprised the major fraction of the flux, contributing between 71% and 99% of the total. These small DIN fluxes included periods of uptake; in particular, in May, sediments from all stations exhibited NH_4^+ uptake. At station MB05, average DIN flux for 2005 was 0.22 mmol m^{-2} d^{-1} as compared to the baseline average of 0.25 mmol $m^{-2}d^{-1}$. At this station, NO_3^- comprised 100% of the seasonal average efflux.

In 2005, PO_4^- fluxes at the nearfield stations were nearly undetectable, and the small fluxes that we did measure were on average negative for all four stations; that is, there was on average uptake of PO_4^- rather than release.

Average nearfield Si fluxes were 2.4 mmol $m^{-2}d^{-1}$ compared to the baseline average of 5.1 mmol $m^{-2}d^{-1}$, and lower than the previous year. At MB05, Si fluxes in 2005 were 4.1 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 was small in 2005. Seasonal average nutrient fluxes compared to annual average primary production indicated that the DIN flux could account for only 4% of primary production, and since there was average uptake of PO_4^-, there was no contribution of this nutrient. Dissoved silica could contribute about 28% of phytoplankton requirements.

The average denitrification rate for 2005 at the two nearfield stations where it has traditionally been measured was 1.3 mmol N $m^{-2}d^{-1}$ as compared to the baseline mean for the two stations of 2.7 mmol N $m^{-2}d^{-1}$. Somewhat lower rates in 2005 may have been partly due to the use of an improved analytical method, which tends to yield lower rate estimates than the previous method. At the third nearfield station, the average rate was 1.1 mmol N $m^{-2}d^{-1}$. At the Stellwagen station the rate was 1.5 mmol N $m^{-2}d^{-1}$. In 2005, denitrification accounted for between 60% and 82% of the total inorganic nitrogen (DIN + N_2) flux at the nearfield stations, and 85% at the Stellwagen stations.

There was no indication of decreased sediment oxidation in any of our measurements. In fact, respiratory quotients were on average lower than 1.0, and 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- (2001-2005) relocation fluxes. The changes in most of these fluxes has 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. For NH_4^+ (and therefore DIN) and Si fluxes, there appears to have been a decrease. The suggestion that there has been an increase in NO_3^- fluxes is interesting and bears watching. Change was not assessed for PO_4^- fluxes because these fluxes vary from positive to negative and are often negligible.

Table 2. Average fluxes for all nearfield stations over the pre-diversion (1993 through 2000) or post-diversion (2001-2005) time periods, and the % reduction in fluxes between the two periods. Flux units are mmol m^{-2} d^{-1} and (nc) denotes no detectable change. (*Note that 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	15.7	0.3	0.3	0	3.4	2.5
%Reduction	(nc)	61	(nc)	(nc)	33	(nc)

4.2 Boston Harbor

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

In 2005, the two early and one late season storms were major events that shaped the whole season for the benthos of Boston Harbor. The physical disturbance not only scoured the sediments and flushed porewaters, it evidently prevented the *Ampeliscid* amphipod community, which has been very important in the biogeochemistry of the harbor, from colonizing and forming mats. These mats were absent from all our stations for the entire season.

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring, including the five years since diversion. In 2005, storms likely contributed to further decreases which were most noticeable at Stations BH03 and BH08A. The range of TOC in the harbor was 1.6% to 2.2%, approaching Massachusetts Bay values. A comparison of averages pre-and post - diversion show that overall, decreases in TOC have been most pronounced at Stations BH03, followed by BH08A and QB01, whereas TOC content at station BH02 has varied. The large range of values observed across the four stations early in the monitoring program has narrowed in the past several years (2000-2005).

Along with changes in TOC at Station BH03 and BH08A has been an increase in grain size of the sediments at these two sites. In particular, sediments at Station BH03 have changed from mostly silt and clay to currently mostly sand, and including gravel. BH08A has experienced similar changes, although there is little gravel present at this time. At Station QB01, we have observed the reverse trend, whereas BH02 has exhibited little change.

Sediment chlorophyll *a* inventories were lower than usual in 2005 for three of the four harbor stations. At the fourth station, QB01, inventories were normal, and only at this station was there a strong surface signal of chlorophyll in May, when divers described a benthic diatoms mat at this site. It has become common to observed benthic diatoms at Station BH02 as well, but they were not noted in May this year, nor were they noted at the other two stations. It may be that at this more protected site in Quincy Bay, the sediments experienced less storm disturbance.

Sediment oxygen demand in 2005 was the lowest yet observed. The harbor-wide average was 22.5 mmol $m^{-2}d^{-1}$, whereas the baseline mean was 69.4 mmol $m^{-2}d^{-1}$. There was little variability across stations in seasonal averages. Fluxes of DIN, PO_4^- , and dissolved Si were also the lowest to date, averaging 1.8, < 0.1, and 2.7 mmol $m^{-2}d^{-1}$, respectively, as compared to baseline averages of 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.

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 at the mouth of the harbor and seasonal averages of fluxes, we calculate that these fluxes could have supplied about 21% and 25% 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 2005, 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 2005 was 1.8 mmol N $m^{-2}d^{-1}$ as compared 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, where average rates for the season were 1.9 and 1.2 mmol N $m^{-2}d^{-1}$. The average across all four stations was 1.6 mmol N $m^{-2}d^{-1}$, nearly equivalent to the DIN flux.

Patterns in redox measurements varied across stations. At three of the stations, average respiratory quotients for the season were greater than 1.0, a pattern not atypical for the harbor. Highest RQs were observed at Station BH02, as is also typical, where evidence of anaerobic respiration is often found in Eh profiles. In contrast, very low RQs (< 1.0) were observed at Station BH03 in 2005. A partial explanation may be that the coarsening of the grain size and increasing dominance of physical processes at this site (enhanced by this year's storms?) are providing a situation where these sediments are continually flushed, resulting in the reoxidation of stored products of anaerobic respiration.

Oxidation-reduction potential measured as profiles in sediment cores from the harbor was fairly typical for recent conditions. Of note was the evidence of storm-induced oxidation of sediments at some sites in May. At BH02, the profile revealed that oxidizing conditions penetrated more deeply than is typical for this site. At BH03 and QB01, the May profiles showed little change in Eh from the sediment surface to the bottom of the core sample.

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 2005) diversion years. For most of the fluxes, we have observed between a 45% and 65% reduction between the two time periods. For instance, we have observed a reduction of 50% in SOD and 54% in DIN. Only silica fluxes and denitrification have changed less (note that denitrification averages are based on two rather than four stations). 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 (2001-2005) 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	34.9	1.9	0.8	2.7	0.2	5.4	3.5
%Reduction	50	46	63	54	66	32	36

4.3 Cross-System Overview

In 2005, we observed a continuation of the patterns we have observed in previous annual reports. These patterns are summarized in Fig. 31, 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 31 a and b) have decreased nearly to the level of Massachusetts Bay, and PO_4^- and Si fluxes (Fig 31 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. 32). 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, 2005, as well as the two 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. However, SOD in Boston Harbor has progressively decreased, noticeably so even during the past three years, and is now only higher than Kaneohe Bay, HI, of the Nixon estuaries, and than our own Massachusetts Bay. These results are illustrative of a compelling story of recovery in the harbor that is rare in its long-term and thorough documentation. Certainly from the point of view of benthic nutrient cycling (a few isolated areas notwithstanding), the clean-up of Boston Harbor is a genuine success story.

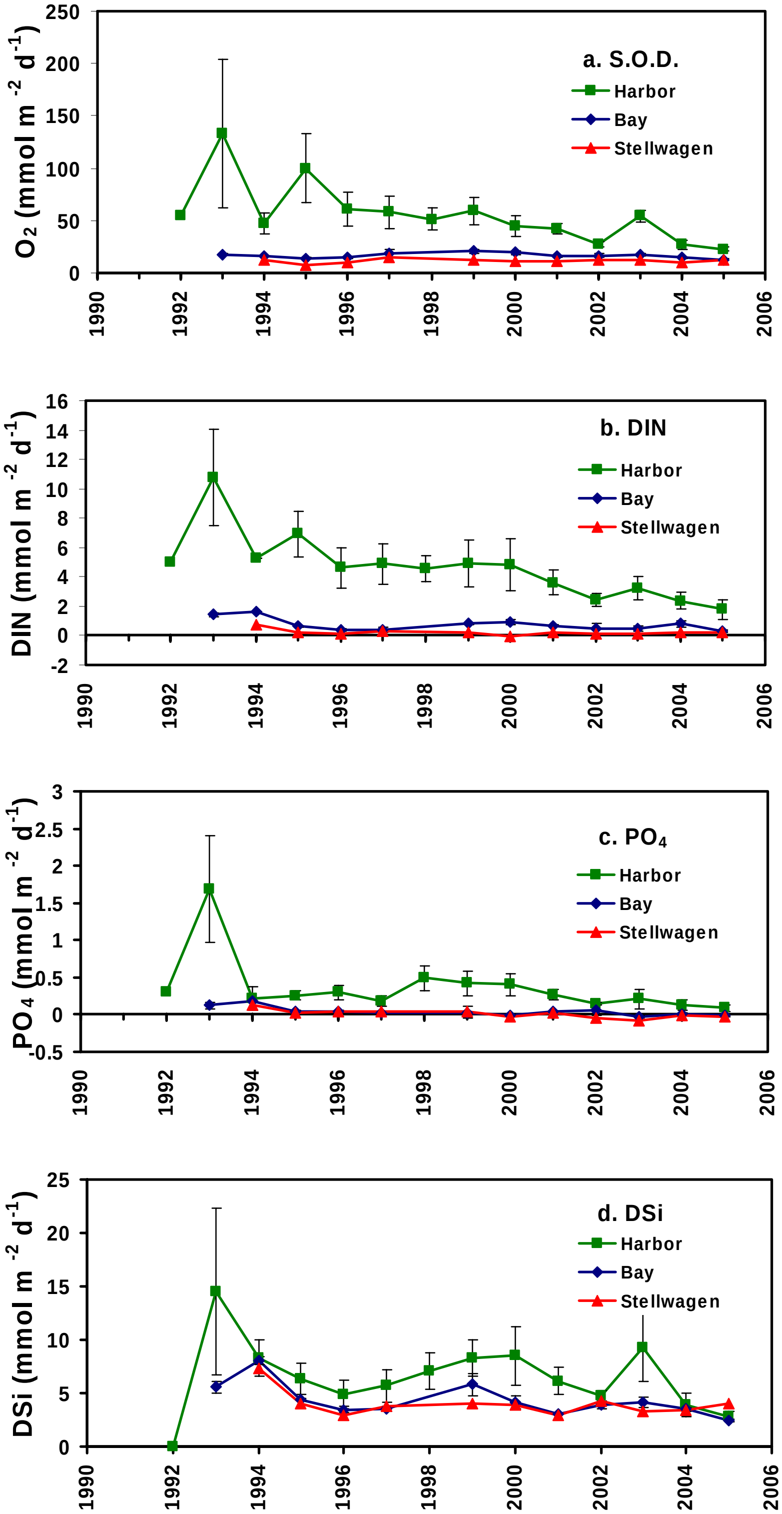

Figure 31. Survey averages of a.) S.O.D., b.) DIN flux, c.) PO4 flux, and d.) DSi flux for Boston Harbor (■), Massachusetts Bay (♦), and Stellwagen Basin (▲) . Error bars represent the standard error of the mean.

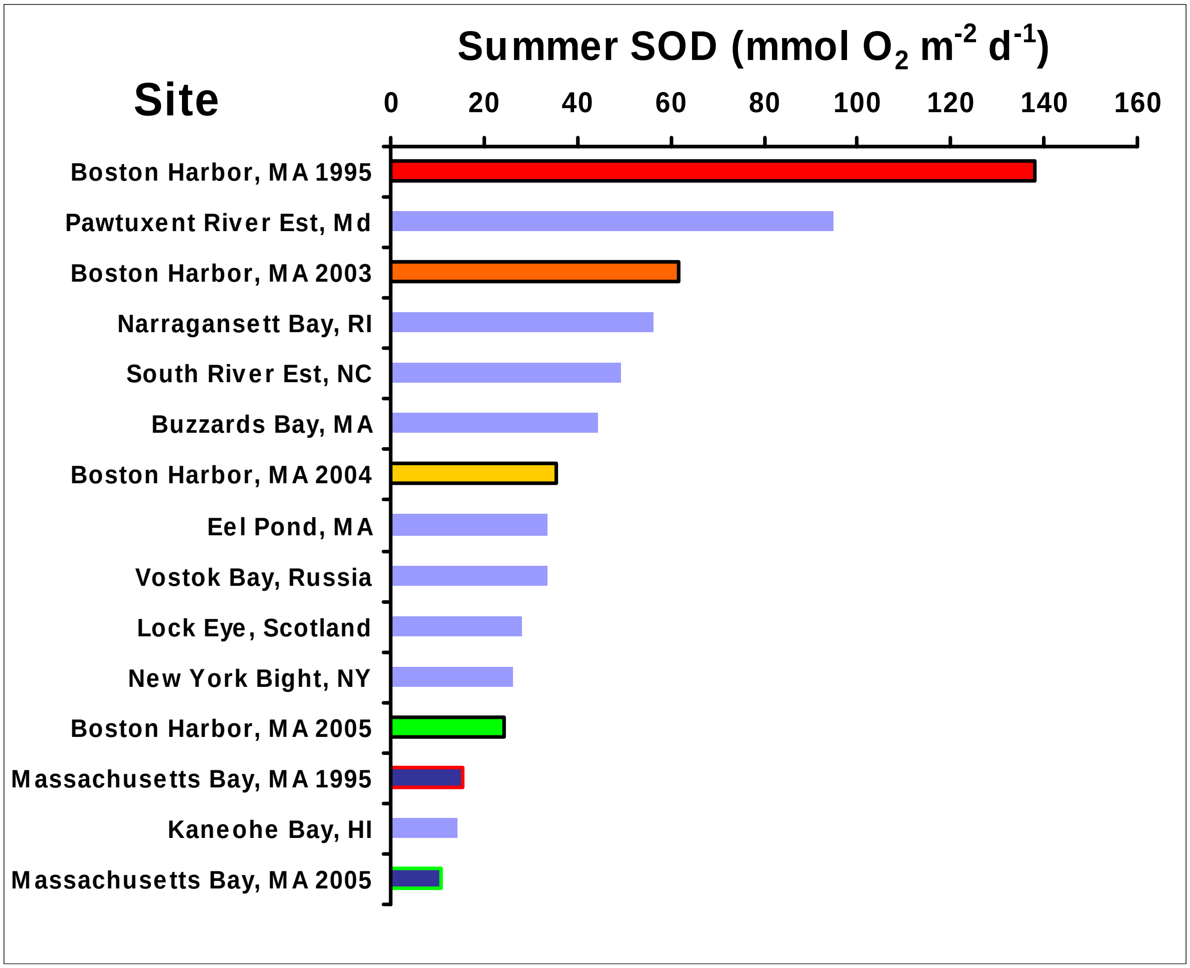

Figure 32. Sediment oxygen demand in Boston Harbor and the nearfield of Massachusetts Bay compared to summer SOD reported for other coastal ecosystems (Nixon 1981). Data for Boston Harbor and Massachusetts Bay are July-August averages.

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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 2005.

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 2005.

Station	Survey ID	Date	Latitude	Longitude	Depth (m)	Temp (^oC)	D.O. (mg L^{-1})	Salinity (psu)
BH02	NC051	5/12/2005	42.34352	-71.00225	6.0	9.7	10.24	28.5
	NC052	7/12/2005	42.34352	-71.00220	9.0	17.7	7.40	30.0
	NC053	8/9/2005	42.34380	-71.00200	8.2	15.3	8.34	31.9
	NC054	10/27/2005	42.34650	-71.00191	10.1	10.3	9.29	30.3
BH03	NC051	5/12/2005	42.33075	-70.96163	5.1	10.2	10.15	28.0
	NC052	7/12/2005	42.33070	-70.96207	7.5	17.8	7.80	30.0
	NC053	8/9/2005	42.33058	-70.96190	7.6	16.7	7.98	31.6
	NC054	10/27/2005	42.33085	-70.96181	9.6	10.4	9.17	30.7
BH08A	NC051	5/12/2005	42.29113	-70.92215	8.1	9.6	9.44	29.1
	NC052	7/12/2005	42.29105	-70.92215	7.5	18.6	7.80	30.0
	NC053	8/9/2005	42.29092	-70.92207	7.2	16.6	8.28	32.0
	NC054	10/27/2005	42.29123	-70.92212	8.7	9.7	9.33	28.9
QB01	NC051	5/12/2005	42.29343	-70.98779	2.0	10.5	9.40	28.8
	NC052	7/12/2005	42.29360	-70.98808	3.0	19.5	7.76	29.1
	NC053	8/9/2005	42.29342	-70.98797	3.3	18.3	7.79	31.2
	NC054	10/27/2005	42.29370	-70.98772	4.6	10.2	9.47	29.3
MB01	NC051	5/10/2005	42.40298	-70.83730	32.2	6.4	10.08	30.3
	NC052	7/11/2005	42.40307	-70.83728	23.9	8.9	8.66	31.7
	NC053	8/8/2005	42.40308	-70.83743	32.2	6.8	8.19	33.0
	NC054	10/31/2005	42.40303	-70.83727	32.8	10.8	8.29	30.5
MB02	NC051	5/10/2005	42.39235	-70.83434	33.9	6.3	9.96	30.4
	NC052	7/11/2005	42.39245	-70.83440	30.4	7.8	8.59	32.3
	NC053	8/8/2005	42.39255	-70.83432	33.9	6.9	8.05	33.0
	NC054	10/31/2005	42.39257	-70.83420	33.6	10.8	8.39	30.1
MB03	NC051	5/10/2005	42.34777	-70.81612	31.7	6.2	10.05	30.3
	NC052	7/11/2005	42.34775	-70.81557	21.9	9.7	8.67	31.2
	NC053	8/8/2005	42.34782	-70.81609	32.8	7.2	7.92	33.0
	NC054	10/31/2005	42.34778	-70.81606	34.6	10.9	8.39	30.5
MB05	NC051	5/10/2005	42.41638	-70.65220	45.5	6.1	10.29	30.7
	NC052	7/11/2005	42.41637	-70.65203	34.4	6.5	9.33	33.3
	NC053	8/8/2005	42.41665	-70.65205	47.1	6.2	8.64	33.5
	NC054	10/31/2005	42.41663	-70.65228	45.7	10.5	8.24	31.0

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