2004 Annual benthic nutrient flux monitoring report

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2004 Annual
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.

Organic matter measured either as TOC or sediment pigments in the nearfield sediments has been variable and although we have observed some higher values in the post-relocation period, through 2003 none had exceeded the range observed during the baseline period. In fact, averages of pre-relocation vs. post-relocation years are not significantly different for either measure.

In 2004, however, seasonal average TOC at one station, Station MB03, did exceed previous observations. At the same time, C/N for these sediments decreased and sediment total chlorophyll *a* levels were high, suggesting that elevated TOC may have resulted from deposition of the large spring *Phaeocystis* bloom. We are uncertain why indications of the bloom would only be present at this station, but it may be related to highest densities of *Phaeocystis* occurring in Boston Harbor and Broad Sound and the more southerly ("down-current") position of Station MB03.

Rates of SOD in 2004 were typical of the post-relocation period and in the low end of the baseline range. Although the rates of sediment oxygen demand would be high enough to affect the seasonal drawdown of

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

Fluxes of DIN in 2004 were in the mid to low end of the range observed during baseline monitoring. NO_3^- comprised less of the DIN flux than it had in the previous two years, averaging about 43% of the flux. The most noticeable change was at Station MB03, where in 2002 and 2003, NO_3^- had comprised all of the DIN efflux but in 2004 was 57%. Small DIN fluxes resulted in a contribution of nitrogen amounting to less than 9% of the requirements for nearfield primary production. At station MB05, average DIN flux for 2004 was low compared to the baseline average, with NO_3^- comprising 56% of the flux.

In 2004, PO_4^- fluxes at the nearfield stations were low compared to the baseline range, resulting in a potential contribution to primary production of only 3% of requirements. At MB05, the 2004 average PO_4^- flux was slightly negative (uptake). Nearfield Si fluxes were also low compared to baseline, but could account for nearly 40% of 2004 primary production. At MB05, Si fluxes in 2004 were moderate compared to the baseline average.

The average denitrification rate for 2004 at the two nearfield stations where it has traditionally been measured was 1.8 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 2004 may have been partly due to the use of an improved analytical method, which tends to yield lower rate estimates than the previous method. The new method allowed denitrification to be measured for the first time at Stations MB01 and MB05 in 2004. The seasonal average rate of 1.8 at MB01 compared well with the other two Nearfield stations, and the rate at Stellwagen station MB05 was only slightly lower, 1.6 mmol N $m^{-2}d^{-1}$. In 2004, denitrification accounted for 69% and 89% of the total inorganic nitrogen (DIN + N_2) flux at the nearfield and Stellwagen stations, respectively.

There was no indication of decreased sediment oxidation in any of our measurements. Respiratory quotients were very close to 1.0, and Eh profiles indicated oxidizing sediment conditions.

A comparison of pre- (1993-2000) and post- (2001-2004) relocation fluxes reveal there has been no discernable change in SOD, NO_3^- fluxes, or denitrification, and for all other fluxes there has been a decrease. Change was not assessed for PO_4^- fluxes because these fluxes vary from positive to negative and are often negligible.

BOSTON HARBOR

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

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring, including the four years since diversion. A comparison of averages pre-and post diversion shows that 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 five years (2000-2004).

For the second year, we have observed increased chlorophyll *a* content in surface sediments at two of the four harbor stations, BH02 and QB01. Inventories over the top 5 cm of sediment at these two stations for 2004 were the highest yet observed. Observations of benthic diatoms and sediment profiles of chlorophyll suggest that *in situ* production is important at these sites. Similar increases at the other two sites, BH03 and BH08A, have not been seen, presumably prevented by grazing pressure by the infaunal community.

Sediment oxygen demand in 2004 was low compared to previous years; only 2002 rates were lower. There was little variability across stations in seasonal averages, which had decreased somewhat from the high rates observed in 2003. Fluxes of DIN and PO4 were the lowest to date, although only slightly lower than 2002 observations. Fluxes of dissolved silica decreased from high values observed in 2003, and were also the lowest reported. We continue to note that the large variability between stations and years that was observed early in the monitoring program has largely disappeared.

Using rates of primary production at the mouth of the harbor and seasonal averages of DIN and PO_4^- fluxes, we calculate that these fluxes could contribute about 21% and 18% of phytoplankton N and P requirements for 2004. Silica fluxes from the sediment were large enough in 2004 to support 34% of primary production, down from a possible 100% contribution in 2003. With the reduction in nutrient inputs to the harbor after the relocation of the outfall, these contributions may become significant, however oceanic and remaining terrestrial inputs still exceed the needs of primary production.

In 2004, 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 2004 was 1.9 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 implementation of a new analytical method. This method enables us to measure denitrification at the other two harbor stations, BH08A and QB01 for the first time. BH08A had somewhat higher rates and QB01 lower, resulting in an overall average of 2.2 mmol N $m^{-2}d^{-1}$, essentially equivalent to the average DIN flux.

Patterns in redox measurements varied across stations. At BH02, respiratory quotients were elevated throughout the 2004 season. Further evidence of reducing conditions was supplied by Eh measurements that indicated sulfate reduction beginning within the top 10 cm of sediments from this station. These conditions are not atypical for this station, but they indicate the relative importance of anaerobic process at this site continues to vary from year to year. Respiratory quotients at BH08A and QB01 were somewhat elevated, but not unusually so for these stations. At BH03, the RQ averaged the theoretical 1.0 in 2004. Eh profiles at these stations were generally more positive than at BH02, but at certain times reached low enough values to suggest the presence of sulfides at depths of 15 cm or greater.

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 status of those benthic communities will no doubt continue to mediate changes in benthic nutrient cycling.

A comparison of the flux data for the pre- (1992-1995 through 2000) and post-(2001 through 2004) diversion years reveals that, for most of the fluxes, we have observed between a 40% and 60% reduction. For instance, we have observed a reduction of 45% in SOD and 50% 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.

CROSS SYSTEMS COMPARISONS

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

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. 23). Our data are seasonal averages (May-October) whereas Nixon's data are referred to as "summer". 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. During the pre-diversion years, Boston Harbor had among the highest rates of SOD, whereas it is now in the middle of the range. The change is even more dramatic if only the early part of the pre-diversion period (1993-1995) is considered; during those years, the average SOD in Boston Harbor (93 mmol m^{-2} d^{-1}) was equivalent to that of the Pawtuxent River. 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 still in question.

We have monitored three stations, MB01, MB02, MB03, in the nearfield region of Massachusetts Bay and one station, MB05, in the farfield (Stellwagen Basin) (Fig. 1). Stations MB01, MB02, and MB03 have been monitored nearly every year since fall of 1992, and Station MB05 has been monitored since fall of 1993. Station MB02 was not visited in 1997, and no stations in Massachusetts Bay were sampled in 1998. Through 1997, all stations were sampled in March, May, July, August, and October. After 1997, the March surveys were discontinued. In 2004, the October survey was delayed by weather, and actually took place during the first week of November.

The three nearfield stations are located in depositional areas in about 33 meters of water. Two of these, MB01 and MB02, are located approximately 4 and 3.6 km, respectively, northwest of the center of the bay outfall array, and the third, MB03, is 4.6 km southwest of the site. The Stellwagen station, MB05, is 12 km northeast of the site, in a depositional area about 75 meters deep.

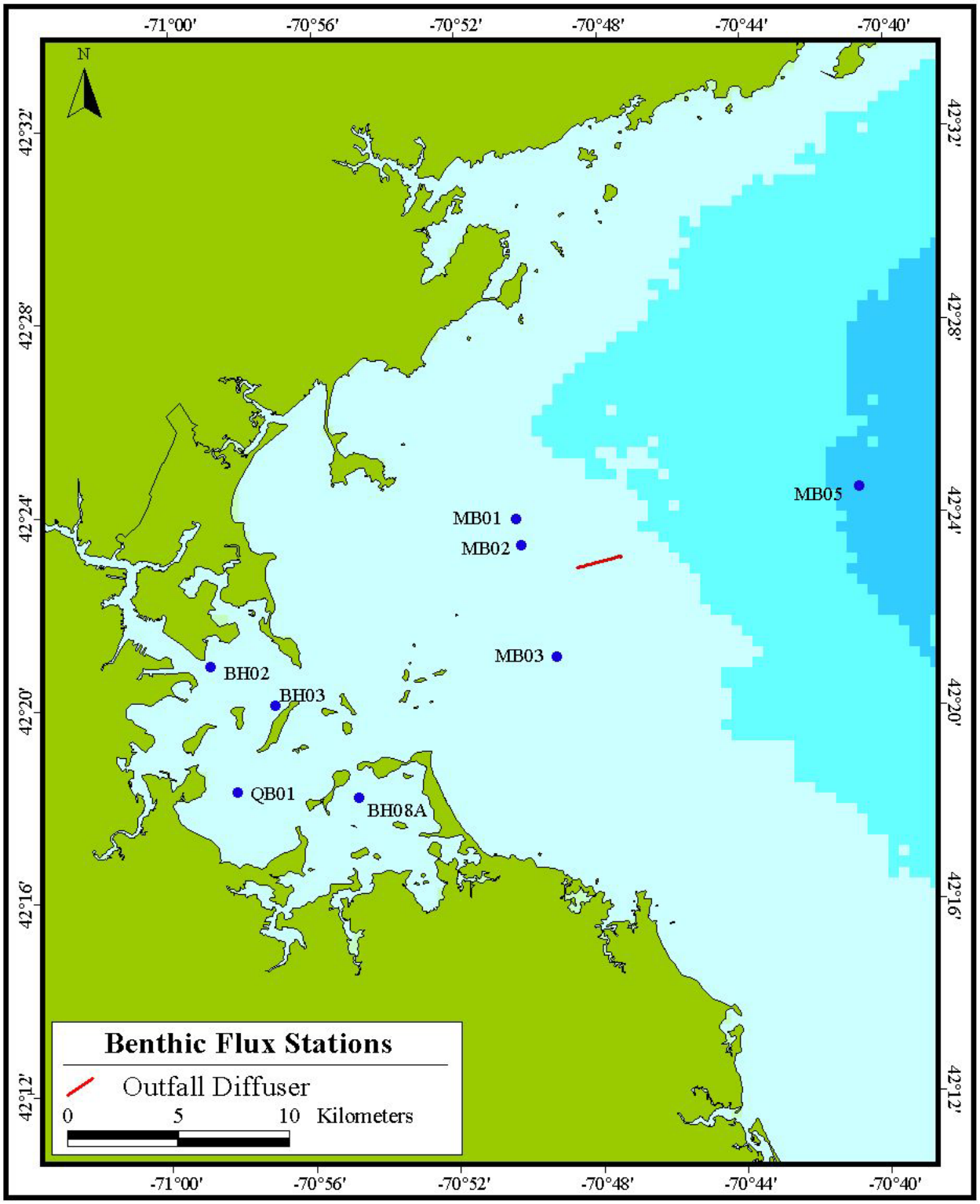

Figure 1. Benthic nutrient cycling stations in Massachusetts Bay and Boston Harbor.

2.1 Organic Matter Loading

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

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

2.1.1 Total Organic Carbon

During baseline monitoring, organic carbon (OC) content in the sediments of the four Massachusetts Bay stations ranged from 0.4% to 4.3%, but with values more typically between 1.0% and 2.9%. 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 2004, TOC content ranged from 1.0 to 2.4 % across all four stations. Peak levels occurred in July and August at Station MB03 (2.4 and 2.2 %, respectively) , and in August at MB02 (2.0%). In this case, these higher values may have been related to a very large spring *Phaeocystis* bloom (Libby *et al*., 200X), although TOC was not elevated at the third nearfield station (MB01) or the Stellwagen station (MB05) at these times.

Seasonal (May-October) average sediment TOC from the three Nearfield stations ranged from 1.2% to 1.9% (Fig. 2), and was 1.7 % at Station MB05. The high seasonal average of 1.9 at Station MB03 was the highest we have observed at this station, and was driven by the high concentrations in July and August. It was also the highest of any of the stations in 2004, including Stellwagen Station MB05, which often has higher sediment carbon content than the nearfield stations. It is at this single nearfield station MB03 that we may be seeing an increase in the carbon content of the sediments; however, high intra-annual variability makes this trend insignificant. Recent observations at the other two stations are typical of baseline. At the farfield station MB05, there appears to have been a slow increase over the entire monitoring period, from 1.2 % in 1994 to 1.7 % in 2004.

Insight into the quality of organic matter may be gained from ratios of organic carbon to nitrogen. Higher ratios reflect organic matter that is relatively depleted in nitrogen, and therefore considered to be of lower quality or lability. In 2001 and 2002, we had observed some variability in seasonal average C/N ratios at the three nearfield stations, with first low values and then high, which seemed to return to "normal" in 2003. In 2004, C/N at Stations MB01 and MB02 remained typical of baseline for those stations at 12.3 and 12.1. At MB03, however, C/N dropped to 9.8, which was low compared to the other two stations and to typical baseline values for this station. The C/N at MB03 was very similar to that at the farfield MB05. At MB05, C/N appears to have decreased slightly with time over the monitoring period (as %C has increased; see above). These lower values are indicative of higher quality carbon, and may be further support for a phytoplankton source (Fig. 3).

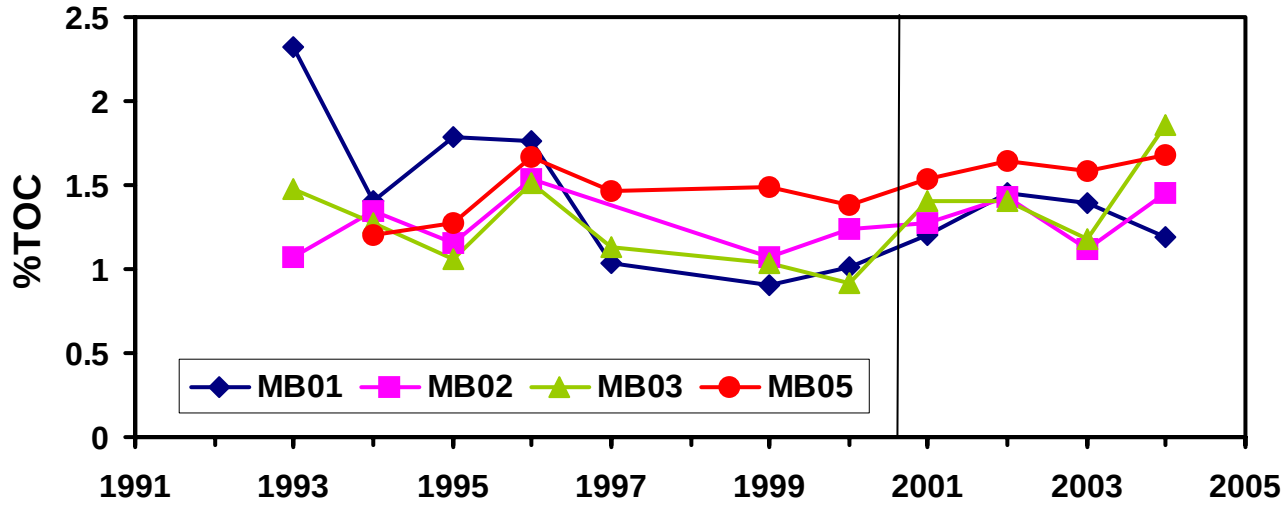

Figure 2. Organic carbon content of top 2 cm of sediment at Nearfield stations MB01, MB02, and MB03 and Farfield station MB05. The vertical line marks the transition from baseline to post-relocation observations.

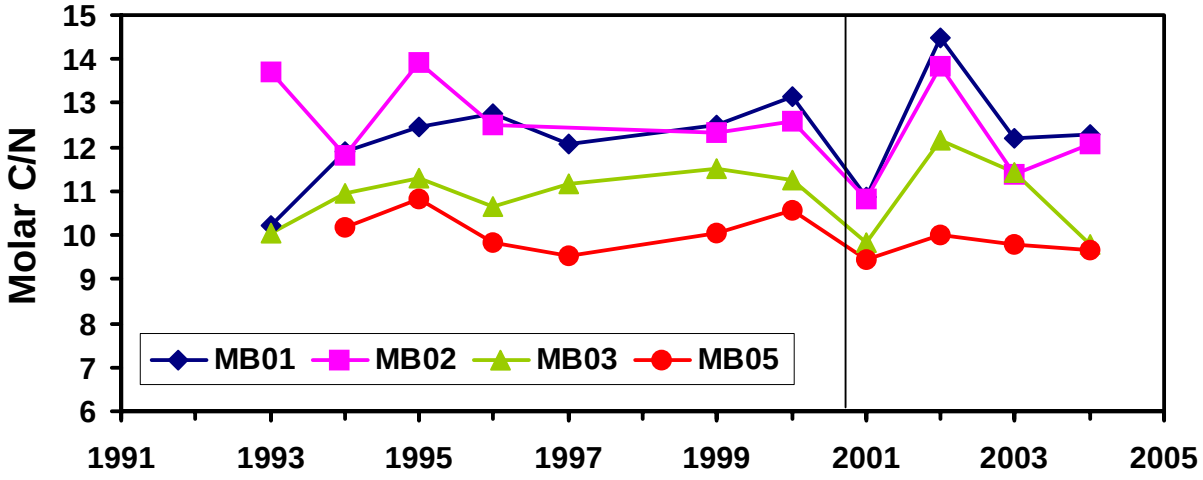

Figure 3. Molar TOC/TON for top 2 cm of sediment. The vertical line marks the transition from baseline to post-relocation observations.

2.1.2 Sediment Pigments

In 2004, chlorophyll *a* content, measured as inventories over the top 5 cm of sediment, was well within the monitoring baseline (Fig. 4). In fact, at two of the three nearfield stations, MB01 and MB02, chlorophyll inventories were quite low compared to most years, with averages for the season of 2.8 and 1.8 ug cm^{-2}, respectively. This was the case in spite of the large spring *Phaeocystis* bloom. At the third nearfield station, MB03, and at the Stellwagen station MB05, inventories were typical of those stations, with seasonal averages of 6.7 and 5.7 ug cm^{-2}. Again, there was no strong signal of the *Phaeocystis* bloom in the sediment chlorophyll *a* inventories, although there was more chlorophyll present in the sediments in spring/early summer than in late summer/early fall.

There was, however, some indication of the bloom in the total (chlorophyll *a* + phaeophytin *a*) chlorophyll inventories (Fig. 4), in particular at Station MB03, where we measured the highest seasonal average to date, 129 µg cm-2. Total pigment levels were also high at Station MB05 compared to most previous years, although similar to levels measured in 2003. Profiles of pigment concentrations provide some insight into these inventories, showing highest concentrations through the top 3 cm in May and July at Station MB03 (Fig. 5). Near-surface peaks were also observed at Stations MB01and MB05 in May. Curiously, no such peaks were obvious in the profiles from MB02.

Signals of recent phytoplankton deposition are not normally noticeable in our measures of sediment TOC but at times may be seen in the pigment data. In 2004, it may have been evident in both measurements, at least at one station. This may be due to the fact that the spring bloom was comprised of *Phaeocystis*. During such blooms elevated POC is often reported in the water column (Libby et al., 2004). However, elevated levels of TOC or pigments were not observed at all our stations. Although the three nearfield stations are all in about 30 m of water and might be expected to receive similar deposition from the water column, patterns in chlorophyll and TOC are often dissimilar among the stations. We are uncertain why indications of the bloom would only be present at MB03, but it may be related to highest densities of *Phaeocystis* occurring in Boston Harbor and Broad Sound (Libby et al., 2005) and the more southerly ("down-current") position of Station MB03.

2.1.3 Pre- and Post- Relocation Comparison

Has organic carbon loading to the sediments increased since the relocation of the outfall? Although we observed some elevated levels of TOC and total pigments at one nearfield station in 2004, overall there has not been a change. Figures 6 and 7 show the mean seasonal average for each station over the pre-relocation (baseline) years compared to the post-relocation years for TOC and total pigments. There is no statistical difference between the pre- and post- years for either measure given the variability around each of these means**.**

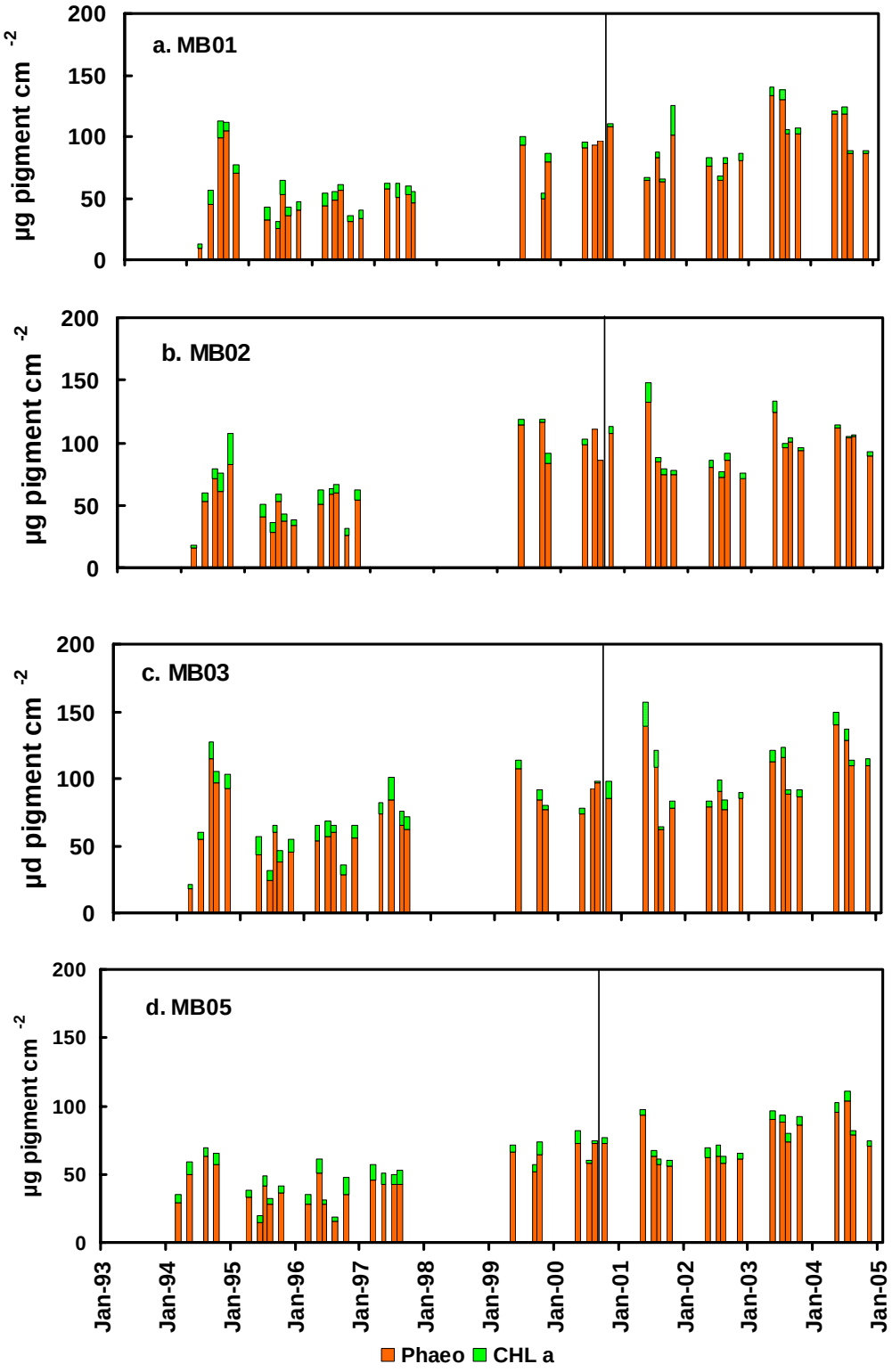

Figure 4. Chlorophyll a and phaeophytin inventory for top 5 cm of sediment at Nearfield stations a.) MB01, b.) MB02, and c). MB03, and Farfield station c). MB05. Vertical lines mark the transition from baseline to post-relocation observations.

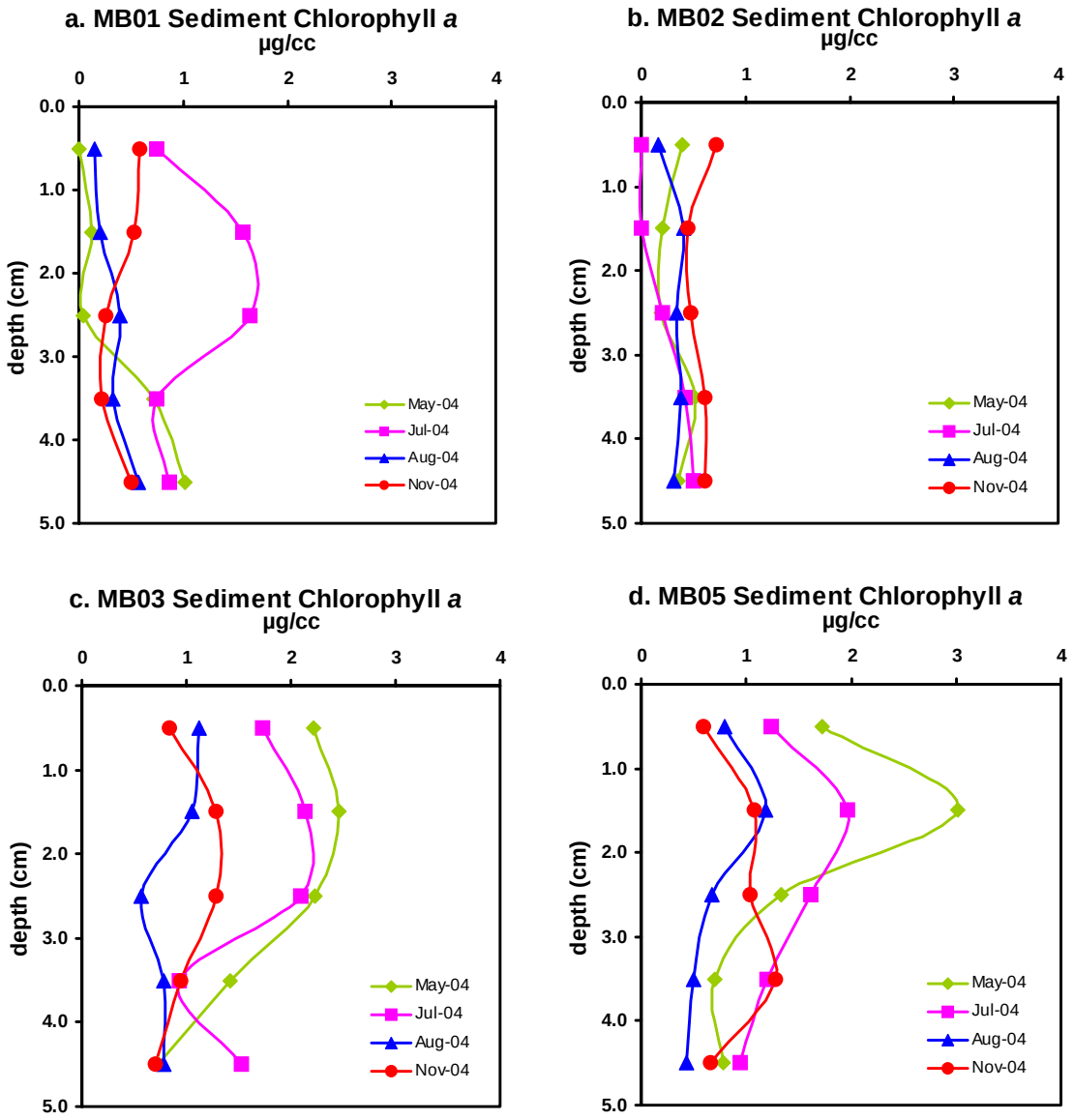

Figure 5. Profiles of chlorophyll a concentration (µg/cc) in top 5 cm of sediment in 2004 from Massachusetts Bay Stations a.) MB01, b.) MB02, c.) MB03, and d.) MB05.

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), with a grand mean across stations and years of 17.2 mmol m^{-2} d^{-1}. In 2004, seasonal average SOD ranged from 15.3 mmol m^{-2} d^{-1} at MB01 to 16.8 at MB02, and the average across the three stations was 16.0 mmol m^{-2} d^{-1}(Fig. 8 a-c). Clearly observations in 2004 were well within baseline. Additionally, the nearfield mean for 2004 was very typical of the mean for the 4-year, post-relocation period, which is 16.5 mmol m^{-2} d^{-1} as well as to the pre-location mean.

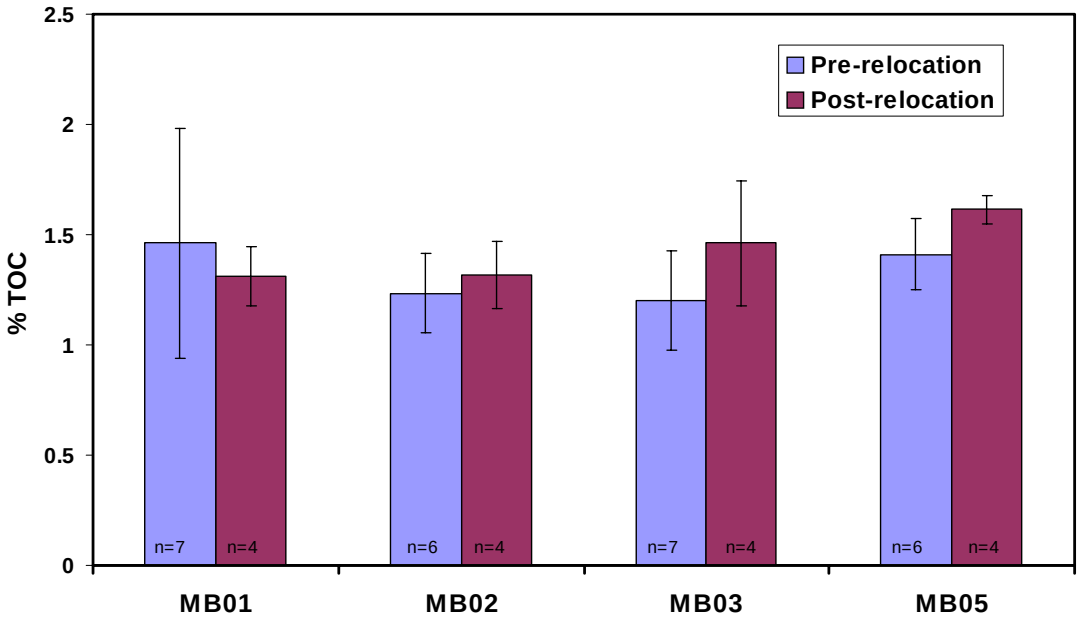

Figure 6. Sediment TOC pre- and post- relocation of the outfall. Data are seasonal averages over all available years for each station. Error bars represent one standard deviation of the mean.

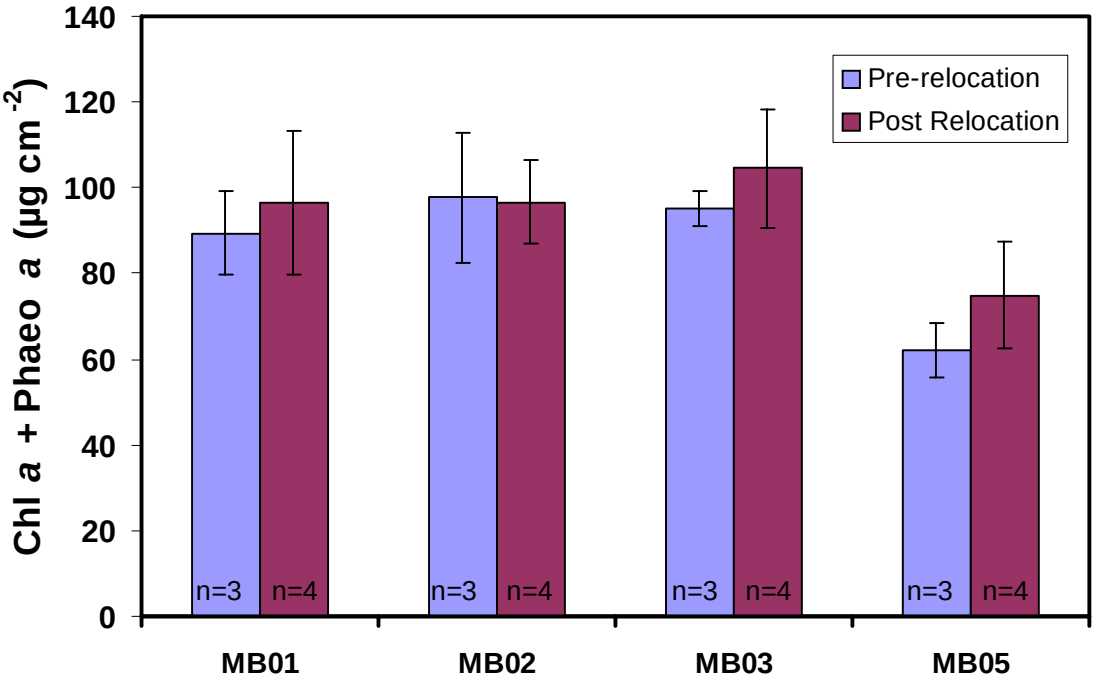

Figure 7. Sediment total chlorophyll pre- and post- relocation of the outfall. Data are seasonal averages over all available years for each station. Error bars represent one standard deviation of the mean.

Highest nearfield rates for 2004 reached 19.3 mmol m^{-2} d^{-1} in May at Stations MB02 and in July at MB03 (Fig. 9a-c) and were well within the baseline range. The lowest rate occurred in August at Stations MB03 and was 11.6 mmol m^{-2} d^{-1}, which was below the baseline range for that station and time of year. Most measurements for 2004 fell in the mid to low end of the baseline range.

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 baseline ranging only from 7.8 to 15.3 mmol m^{-2} d^{-1}. In 2004, the seasonal average was 10.5 mmol m^{-2} d^{-1}, with rates declining over the season from a July high of 12.1 mmol m^{-2} d^{-1} to an October low of 8.5 mmol m^{-2} d^{-1} (Fig. 9d).

Multiple factors influence SOD. Primary among these are temperature and organic matter supply. Indeed, in the first years of the monitoring program, temperature was a strong predictor for SOD. However, a shift in this relationship seemed to occur after 1995. Using only May through October data, which are available for all years, we found that temperature explained on average 45% of the variability in S.O.D. that we observed from 1993 through 1995. From 1996 on, however, that relationship failed; through 2004 the r^2 for the relationship was only about 0.03. We cannot explain this shift, but until 2004, we suggested that it might be related to warmer early season bottom water temperatures in the later years that narrowed the temperature range over which we made these measurements. For example, in Stellwagen Basin where bottom water temperatures vary little over the season, temperature has never been a strong predictor of SOD. In 2004, there still was not a correlation between SOD and temperature, even though early spring bottom water temperatures were cold and fall temperatures were warm, leading to a difference large enough that one might expect some correlation with SOD.

Organic matter is the next likely factor controlling SOD. Correlation analysis of SOD versus TOC or total pigments, however, yield inconsistent results. When the May through October data are analyzed for all years at each of the four Massachusetts Bay stations, we find only one significant correlation . At station MB02, there was a significant relationship between SOD and total chlorophyll pigments (r2 = 0.41; 1993 – 2004, with data unavailable for 1997 and 1998). Taken year by year, however, we often find relationships with either chlorophyll or TOC, but usually not both (< 20% of observations). For example, total chlorophyll or TOC explained over 50% of the variability in SOD in 8 or 7, respectively, out of 39 observations. These relationships are generally not consistent across stations; for example, there was no year in which either total chlorophyll or TOC was significant across all four stations or even across the three nearfield stations. There was one year, 1997, when neither chlorophyll nor TOC was significant (note that Station MB02 was not sampled in 1997). The other pattern that stood out among the stations was that at Station MB03, the relationship between SOD and total chlorophyll was significant for only one year out of 10, 1995. For 2004, total chlorophyll was an important predictor of SOD only at Station MB05 ($r^2 = 0.95$), and more weakly correlated at Station MB02 ($r^2 = 0.20$). There was only a weak correlation with TOC at Station MB01 and MB05, (0.12 and 0.21, respectively). At Station MB02, there was a strong but negative correlation between SOD and TOC ($r^2 = 0.94$). The inconsistent nature of these relationships may be due to the fact that these measures are all of organic matter inventory, and therefore may not reflect the organic matter that is actually being used.

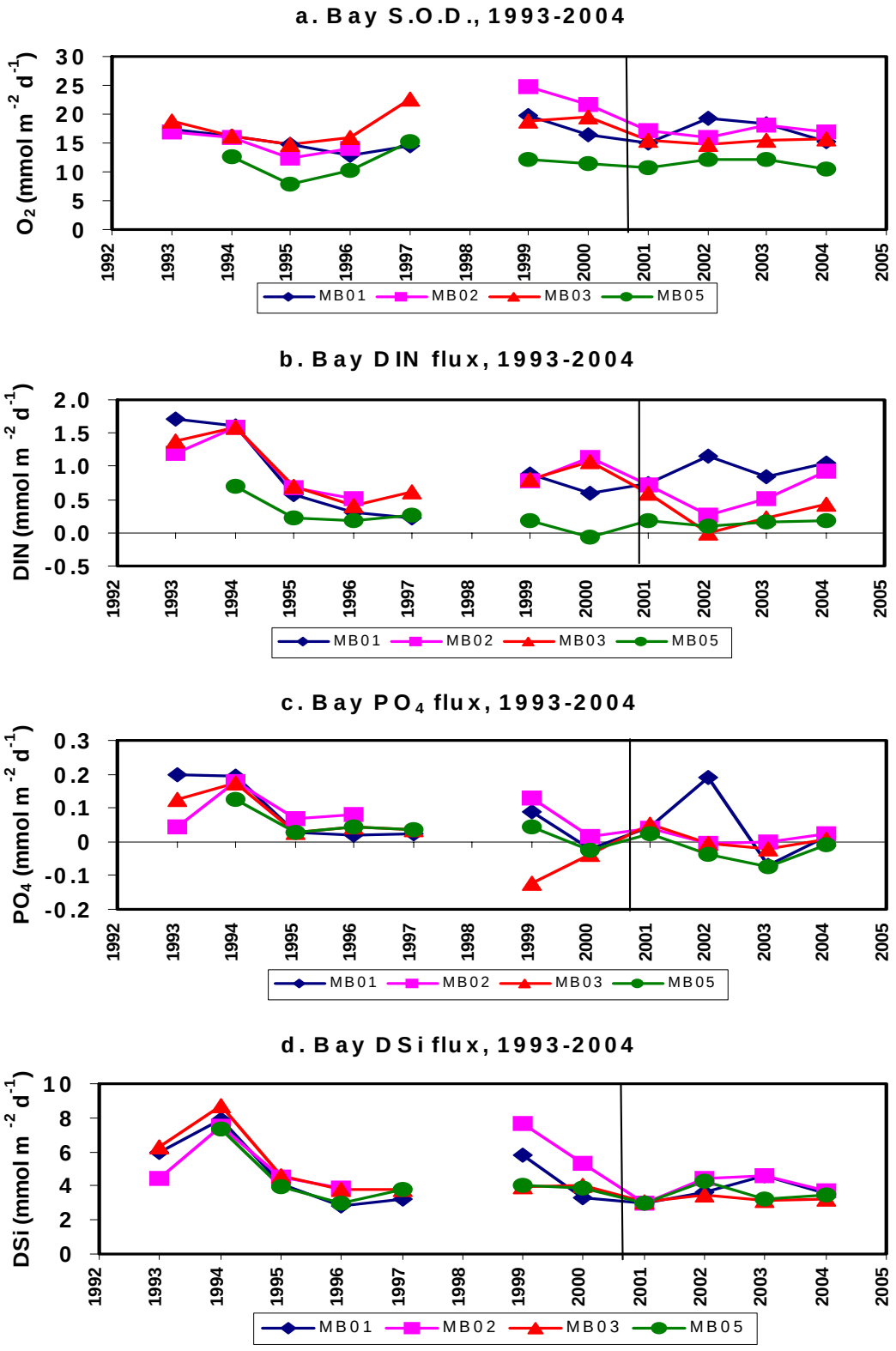

Figure 8. Seasonal (May-October) averages of a.) sediment oxygen demand (S.O.D.), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Massachusetts Bay stations in 1993-2004. The vertical lines mark the transition between baseline and post-relocation observations.

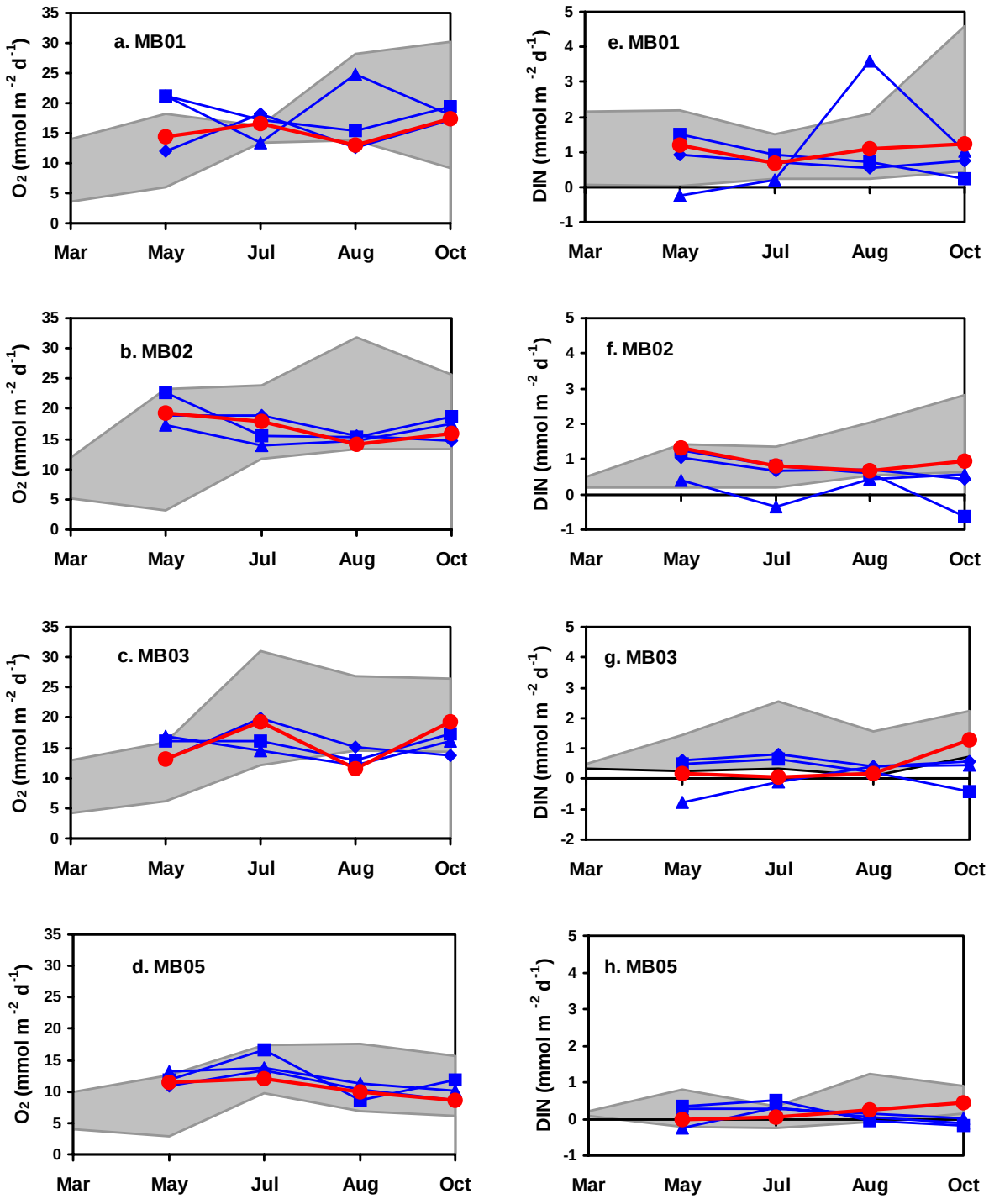

Figure 9. Sediment oxygen demand (O_2 flux) and DIN flux for 2001 (♦), 2002 (▲), 2003 (■), and 2004 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations MB01, MB02, MB03, and MB05, respectively.

2.2.1 Contribution to Oxygen Drawdown in Bottom Water

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

However, the contribution of the biological consumption should not be discounted. The temperature effect noted above acts partly through the fact that oxygen consumption (respiration) in both the bottom water and the sediments is temperature-sensitive. Also, the magnitude of sediment oxygen demand in the muddy sediments of the Nearfield typically equals or exceeds that of the annual drawdown, which is about 0.04 mg L^{-1} d^{-1} (Geyer et al., 2002). For example, in 2002 and 2003, the May to October average S.O.D. was 16.7 and 17.3 mmol m^{-2} d^{-1}, respectively, which translates to about 0.05-0.1 mg L^{-1} d^{-1}, depending on the depth of the stratified layer used (5-10 meters). In 2004, the average SOD of 16.0 translates to 0.05 mg/L/d for a stratified layer of 10 m.

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 four 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 2004, rates of dissolved inorganic nitrogen (DIN) flux from nearfield sediments were in the mid to low end of the baseline range (Fig 8b and 9e-g), ranging from a very low flux at Station MB03 in July of less than 0.1 mmol m^{-2} d^{-1} to a high of 1.3 mmol m^{-2} d^{-1} at MB02 in May. In general, fluxes this year were highest early (May) and late (Nov) in the season and lowest during the summer (July and Aug). Low rates at Station MB03 from May through August were in part caused by NH_4^+ uptake. Uptake of NH_4^+ was not observed at the other two nearfield stations in 2004. Seasonal averages of DIN flux varied across the three nearfield stations, with stations MB01 and MB02 similar at 1.0 and 0.9 mmol m^{-2} d^{-1} and MB03 less than half that at 0.4 mmol m^{-2} d^{-1}.

Nitrate comprised a smaller portion of the DIN efflux (Fig. 10) in the nearfield than in the previous year, ranging from 33% of the seasonal average flux at Station MB02 (Fig. 10b) to 57% at Station MB03 (Fig. 10c), and resulting in an overall average for the three nearfield stations of 43%. In particular, at Station MB03, NO_3^- had comprised all of the DIN efflux in 2002 and 2003. The lower 2004 percentages for nitrate are more typical of the pattern observed throughout the baseline period as the larger component of

the DIN flux was usually NH_4^+. In fact the percentages are driven more by variability in the NH_4^+ flux than by changes in NO_3^- flux. Over all the nearfield data, NH_4^+ flux has ranged from –0.9 to 4.0 mmol m^{-2} d^{-1}, for a total range of about 5 mmol m^{-2} d^{-1} , whereas NO_3^- flux has ranged only from –0.5 to 0.7 mmol m^{-2} d^{-1}, for a total of less than 1.0 mmol m^{-2} d^{-1}.

At MB05, DIN fluxes were about average those observed during baseline (Fig. 9h), ranging from -0.01 mmol m^{-2} d^{-1} to 0.44 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. 10d). Negative DIN fluxes in May were driven by NO_3^+ uptake whereas in July there was NH_4^+ uptake. Seasonal average DIN flux was spilt nearly evenly between NH_4^+ (44%) and NO_3- (56%).

2.3.2 Phosphorus and Silica

Like DIN fluxes, phosphate fluxes in Massachusetts Bay in 2004 were typical or lower than observed during baseline monitoring, (Fig 11a-d), following the pattern we have observed for the past four years. Fluxes ranged from an uptake of 0.08 mmol m^{-2} d^{-1} in August at MB03 to an efflux of 0.06 mmol m^{-2} d^{-1} in May at MB01. Generally, fluxes were highest at the beginning and end of the May to October season, and low in the summer, including no flux or uptake in August. Seasonal averages were among the lowest observed, but not as low as in the previous year (Fig. 8c). The nearfield stations all had seasonal average efflux from the sediments in contrast to uptake the previous year. At the farfield station MB05, the seasonal average was again negative (overall uptake) in 2004, but much smaller. In general, the pattern of PO_4^- flux (seasonal average) tends to follow the pattern of DIN flux.

Nearfield dissolved silica fluxes in 2004 were at the low end of the baseline range. In contrast to the pattern observed for DIN and PO_4^-, silica fluxes were lowest in the spring, and increased through the season. Lowest fluxes, 2.1 mmol m^{-2} d^-, occurred in May at MB03 and highest , 4.4 mmol m^{-2} d^- at MB02 and MB03, in October (Fig. 11e-g). The May-October averages for the nearfield stations were very similar and averaged 3.5 mmol m^{-2} d^-, lower than the baseline average of 5.1 mmol m^{-2} d^- (Fig. 8d). At the farfield station MB05, silica fluxes were low to intermediate as compared to the baseline range (Fig. 11f). Fluxes here did not show the same seasonal pattern as the nearfield. Rates varied only from 3.0 to 4.0 mmol m^{-2} d^-, with the lowest rates in May and highest in July. October fluxes fell below the baseline range. The seasonal average of 3.5 mmol m^{-2} d^- was very similar to the nearfield average, and well within the baseline range for MB05.

2.3.3 Nutrient Flux Contribution to Primary Productivity

Average annual primary production in the nearfield area in 2004 was 261 g C m^{-2} y^{-1} (or 60 mmol C m^{2} d^{-1}), low compared to the previous three years (Libby *et al.*, 2005). Following Redfield considerations, this amount of production would require 9.0 mmol m^{-2} d^{-1} of N or Si, and 0.6 mmol m^{-2} d^{-1} of P . Using the seasonal average DIN flux from our three nearfield stations of 0.8 mmol m^{-2} d^{-1}, we find that benthic DIN flux represented less than 9% of phytoplankton requirements. This is the second year in a row that this percentage has increased, but it still represents a small contribution towards primary production. Similar calculations revealed nearly a 3% potential contribution from PO_4^- fluxes in 2004, which although small, is more than the previous year when a seasonal average uptake of PO4 resulted in no contribution to the water column. Fluxes of dissolved silica, however, could account for nearly 40% of requirements, about the same as for the previous year, and 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.

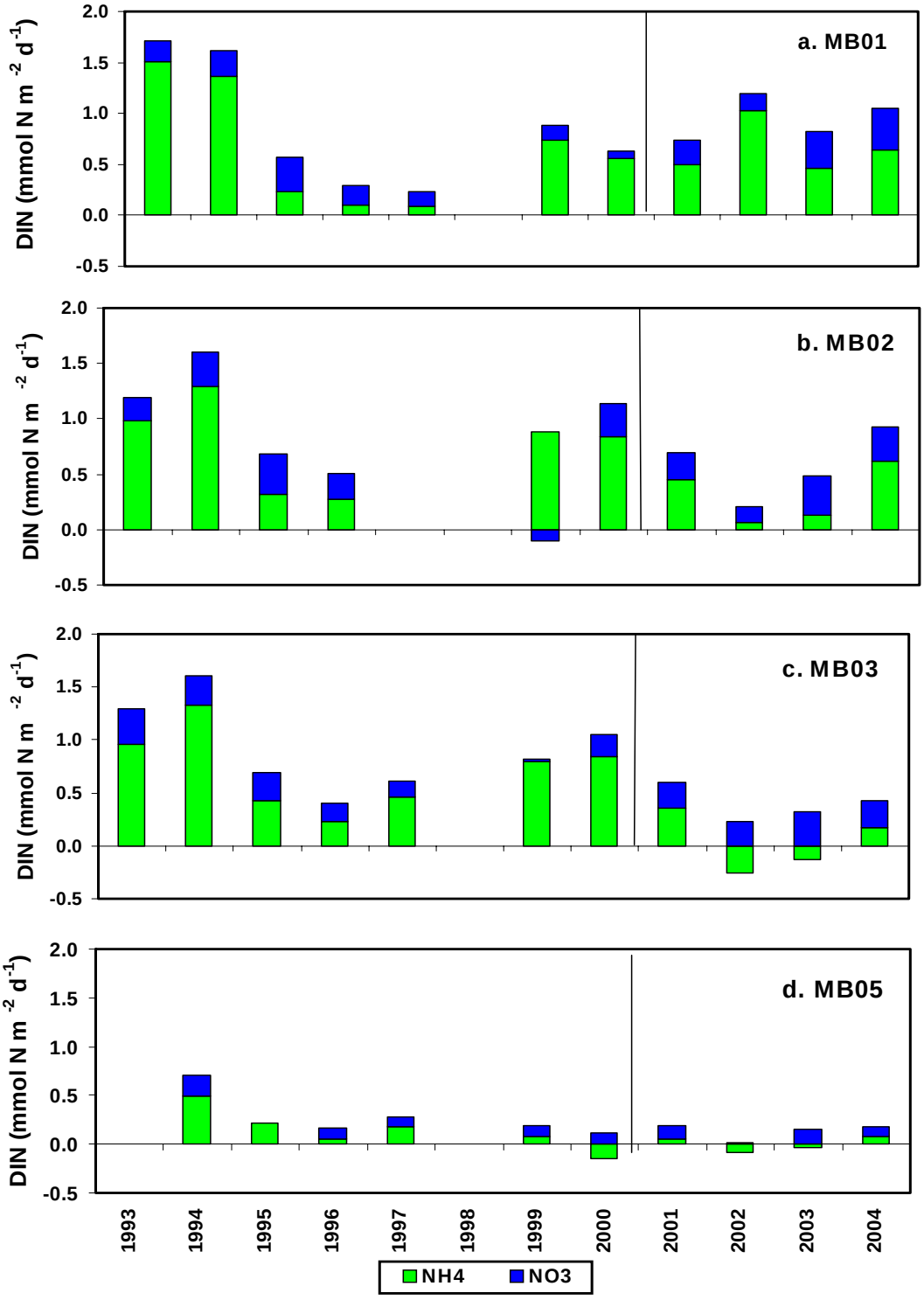

Figure 10. May-October seasonal average DIN flux from 1993-2004 at bay stations a.) MB01, b.) MB02, c.) MB03, d.) MB05. The vertical line marks the transition from baseline to post-relocation observations.

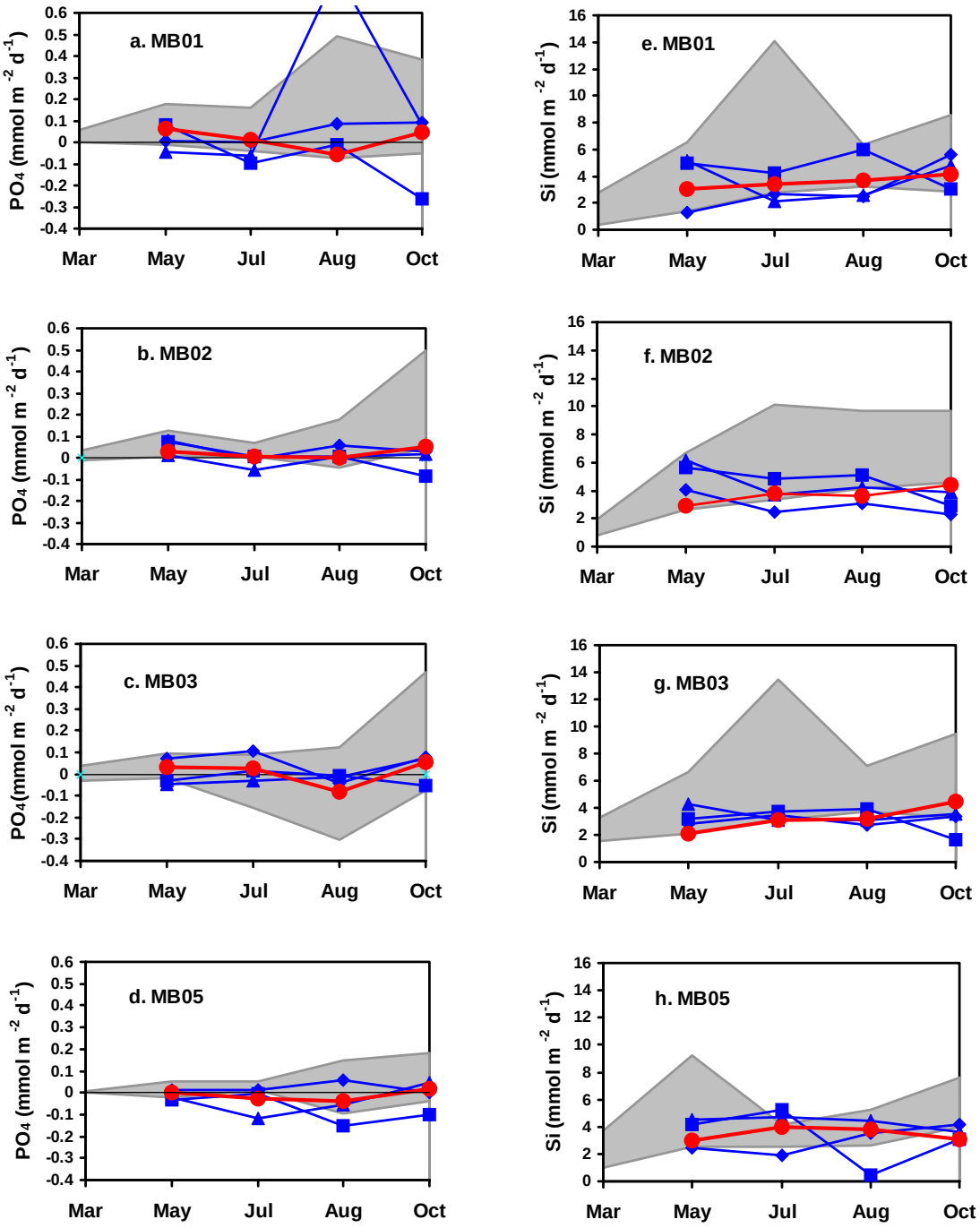

Figure 11. Phosphate and dissolved silica for 2001 (♦), 2002 (▲) , 2003 (■), and 2004 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO4 flux and panels e-h depict DSi flux for stations MB01, MB02, MB03, and MB05, respectively.

2.4 Denitrification

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). In 2004, however, the change in the 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 2004 were within the overall baseline ranges (Fig. 12) but were lower than the previous two years, especially at Station MB02. We must note, however, that the new method tends to produce lower estimates (Tucker and Giblin, 2005), and our results for 2004 may be due in part to the method change. At this point, we do not think there has been a significant change in denitrification rates.

High rates in 2004 were 2.6 mmol N m^{-2} d^{-1} at MB02 in May and MB03 in July, and low rates were about 1.1 mmol N m^{-2} d^{-1} at both stations in October. Denitrification at "new" Station MB01 was similar to the other two nearfield stations. Denitrification at the "new" farfield station MB05 was similar to the nearfield in May, but lower in July and October and higher in August (Fig. 13). The October rate of 0.9 mmol N m^{-2} d^{-1} at this station was the lowest overall for the 2004 season. There was not a clear seasonal pattern in denitrification rates, although lowest rates at all four stations occurred in November.

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.

In 2004, the new method allowed us to make this comparison for all four Massachusetts Bay stations and during all four surveys. At all four stations, denitrification played the larger role in the May through August period, but the two processes were more equivalent in October. Within this seasonal pattern, however, an interesting difference among stations emerged. Stations MB01 and MB02 were similar, with denitrification accounting for between about 60% and 75% of the total flux from May through August, falling to between 52% and 55% in October. In contrast, Stations MB03 and MB05 were similar, with denitrification accounting for between 90% and 100% of the total flux from May through August, and falling to 48% and 67% in October. Again, these differences are due mostly to the difference in the DIN flux, with Stations MB03 and MB05 having lower fluxes than the other two stations in 2004 (Fig. 8b). It is unclear why DIN fluxes at Station MB03 were so much smaller than at the other nearfield stations, especially in this year when there appeared to be evidence of recent carbon deposition (Sec. 2.1).

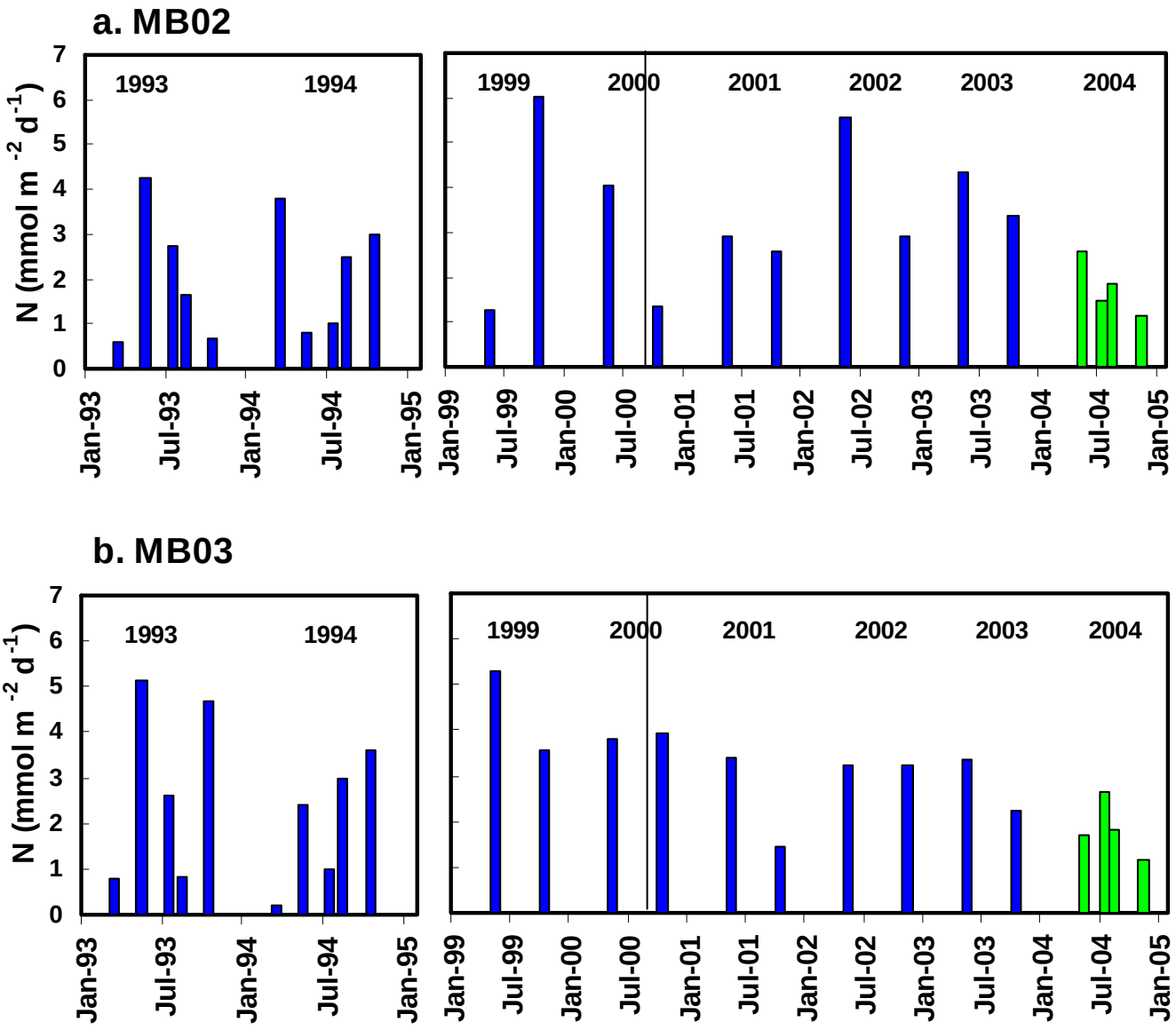

Figure 12. Denitrification at two nearfield stations, a.) MB02, and b.) MB03. Denitrification measurements were not conducted in Massachusetts Bay in 1995-1998. 2004 data were produced using the new analytical method and are highlighted in green. The vertical line marks the transition between baseline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

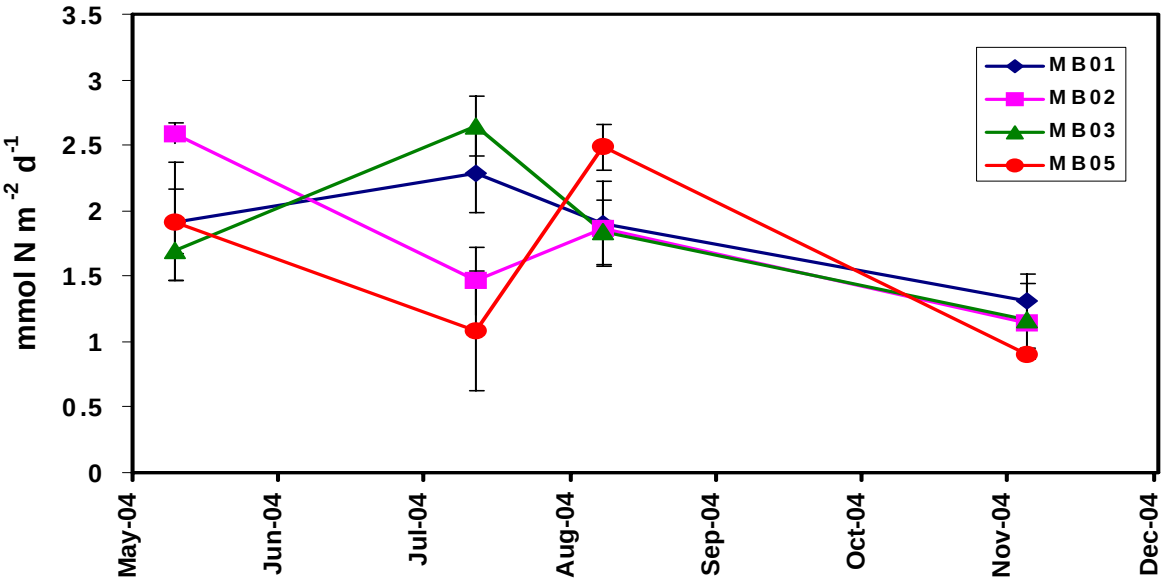

Figure 13. Denitrification at all four Massachusetts Bay Stations in 2004.

2.5 Redox

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

2.5.1 Respiratory Quotient

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

Respiratory quotients appear to have decreased over time since monitoring began (note that CO_2 data are not available for 1995-1998). In the early years of monitoring (1992-1994), respiratory quotients measured during core incubations of sediments from the three nearfield stations as well as from the farfield station were often greater than 1.0. Seasonal averages (omitting winter) were also greater than 1.0, indicating that anaerobic processes were important (Fig 14). 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 2004, seasonal average RQ at the three nearfield stations and at Station MB05 continued to be very close to 1.0, ranging only from 0.97 at MB05 to 1.10 at MB01 (Fig. 14). At all four stations, the low values of the season were occurred in July and were less than 1.0, ranging from 0.84 at MB03 to 0.92 at MB01. Otherwise there was little seasonal pattern. The low RQs in July would suggest reoxidation of the sediments by some sort of disturbance or bioturbation, but we have no direct evidence of such.

2.5.2 Eh profiles

Oxidation-reduction potential measured as Eh in 2004 continued to be indicative of highly oxic conditions in sediment cores from Massachusetts Bay (Fig. 15). We have not observed any tendency towards decreased oxygen levels in these sediments in the four 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 2004 were in general similar to those observed in recent years, although we have not observed any consistent seasonal pattern from year to year or among stations. This is not surprising given the highly oxic and therefore "poorly poised (buffered)" state of the sediments. (Note that relatively low values for Station MB02 in August (Fig. 15 b) are suspect and likely due to a poisoned Eh electrode.)

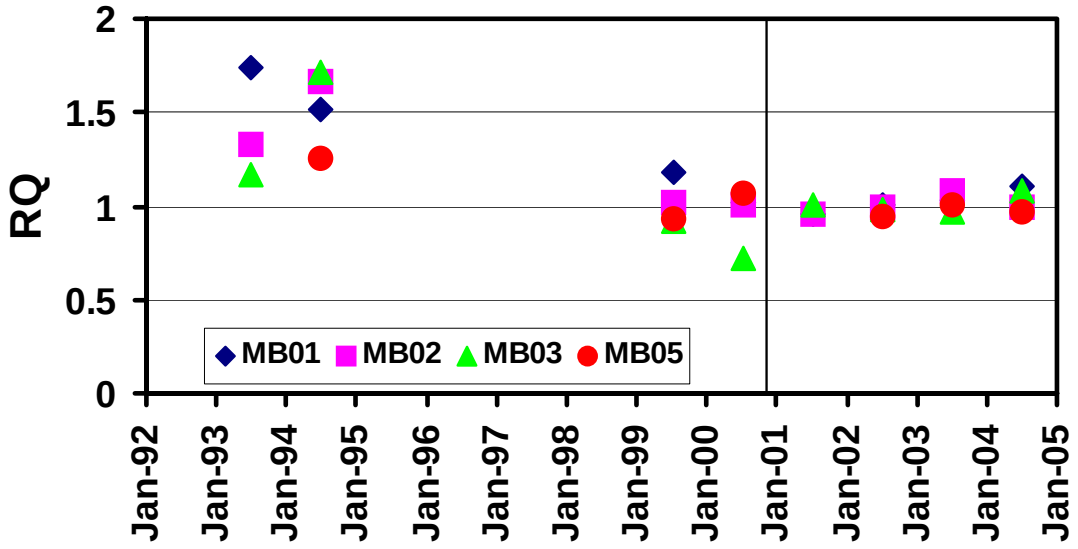

Figure 14. Seasonal (May-October) average respiratory quotients for Nearfield stations MB01, MB02, MB03, and Farfield station MB05 from 1993-2004. The vertical line marks the transition from baseline to post-relocation observations.

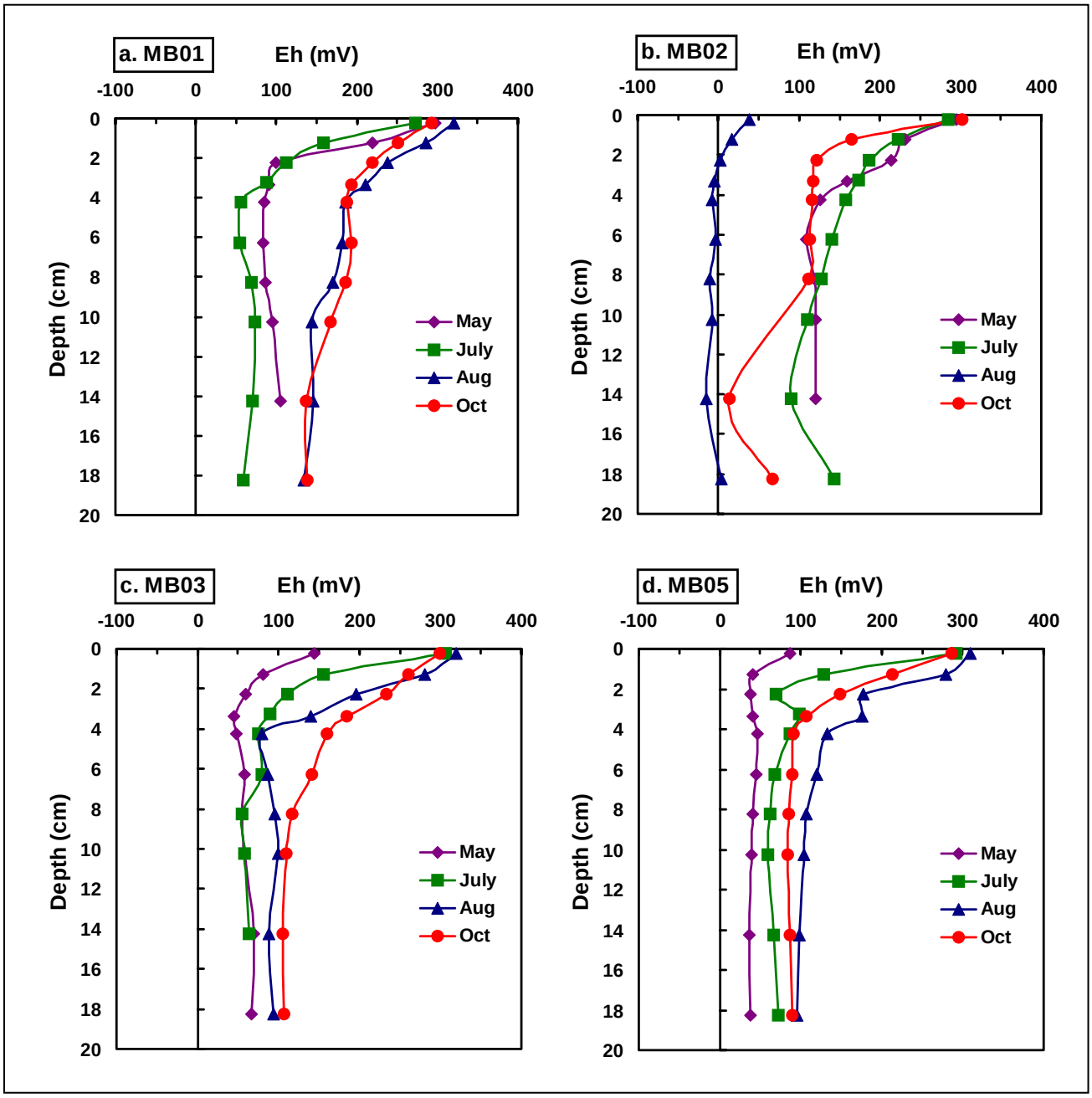

Figure 15. Eh profiles for May through October, 2004, from Nearfield stations a.) MB01, b.) MB02, c.) MB03, and Farfield station d.) MB05.

3.0 BOSTON HARBOR

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

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

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

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

Four harbor stations have been repeatedly sampled in the benthic nutrient cycling program throughout the monitoring period (Fig. 16). Two stations, BH02 and BH03, are located in the northern section of Boston Harbor and have been sampled routinely since September, 1991. The other stations, BH08A and QB01, are in the southern harbor, and have been visited since 1995. Through 1997, these stations were visited in March, May, July, August, and October. After that time, the March surveys were discontinued. In 2004, the October survey was delayed by weather, and instead took place during the first week of November.

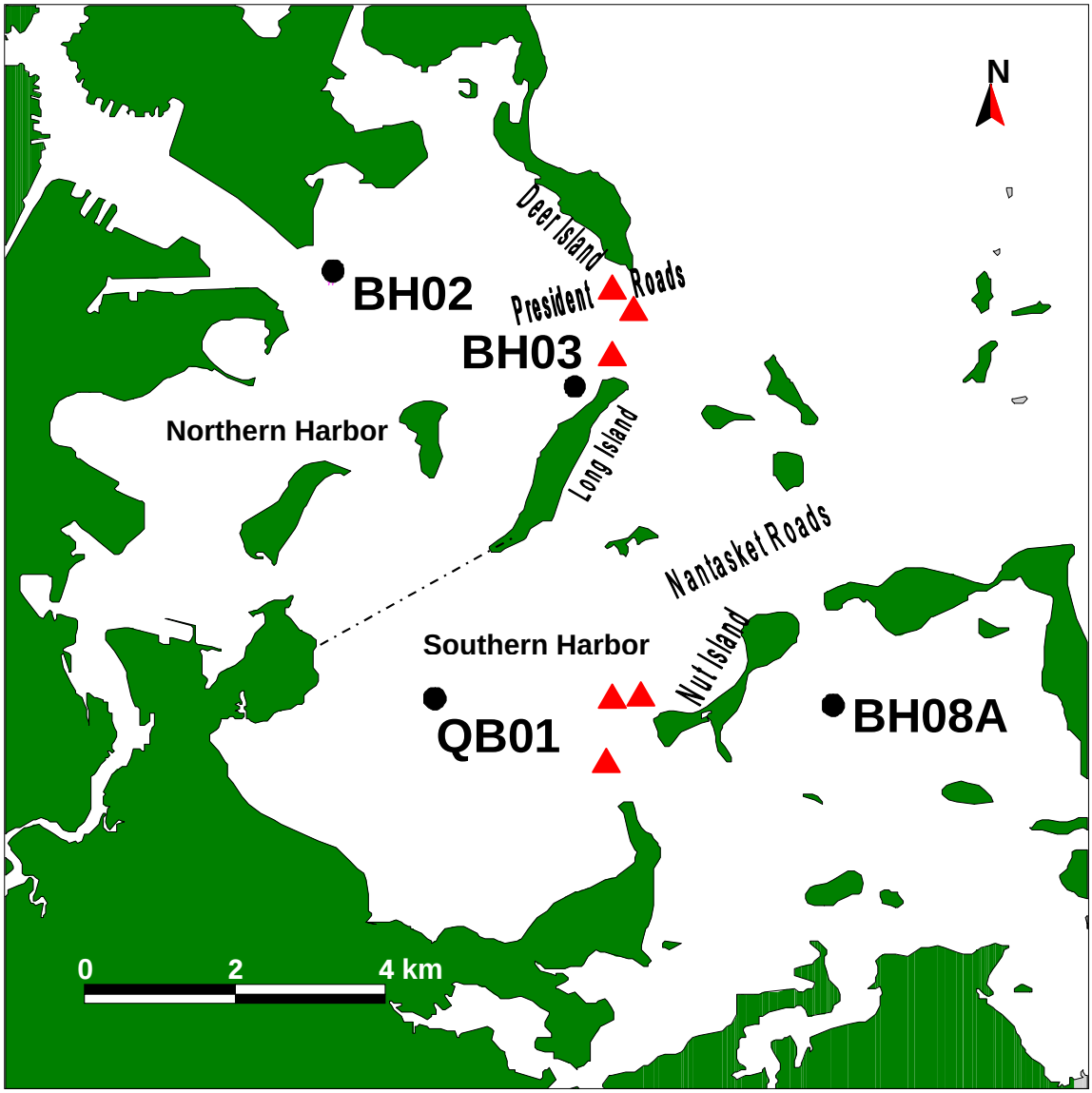

Figure 16. Locations of four Boston Harbor stations. Triangles (▲) mark the location of the out-of-service Harbor outfalls, the last of which was taken out of service on Sept. 6, 2000.

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. In 2004, seasonal averages of total organic carbon (TOC) were similar to those observed during the previous three post-relocation years, and ranged from 2.0% to 2.4% (Fig. 17). However, if one looks closely at the patterns exhibited at each station over the last 4 years, differences among stations are suggested. At Station BH02 there has been little change. At BH03 and BH08A, however, there appears to be a continuing, slow decrease in TOC over time. In fact , the seasonal average TOC at both of these stations was the lowest yet observed, and for the first time the lowest levels across all four stations was observed at Station BH08A. After a low year in 2003, QB01 had the highest TOC of the four stations in 2004 and was back to values similar to those of 2002

It is interesting to compare the data from the pre-relocation period to the post-relocation period (Fig.18) even while recognizing that the changes began before the relocation This comparison shows a large reduction in TOC at Station BH03, from a seasonal average of 3.4% to 2.5%, and a reduction in interannual variability. Note that we have data extending back to 1992 for this station; it was in these early years of the monitoring period that we observed very high levels of organic carbon in the sediments at this station. In contrast, at Station BH02, where we have a data record nearly as long (beginning in 1993), there has been little overall change in the organic carbon content, but a large reduction in interannual variability. The other two stations, where data collection began in 1995, fall between these two "endmembers".

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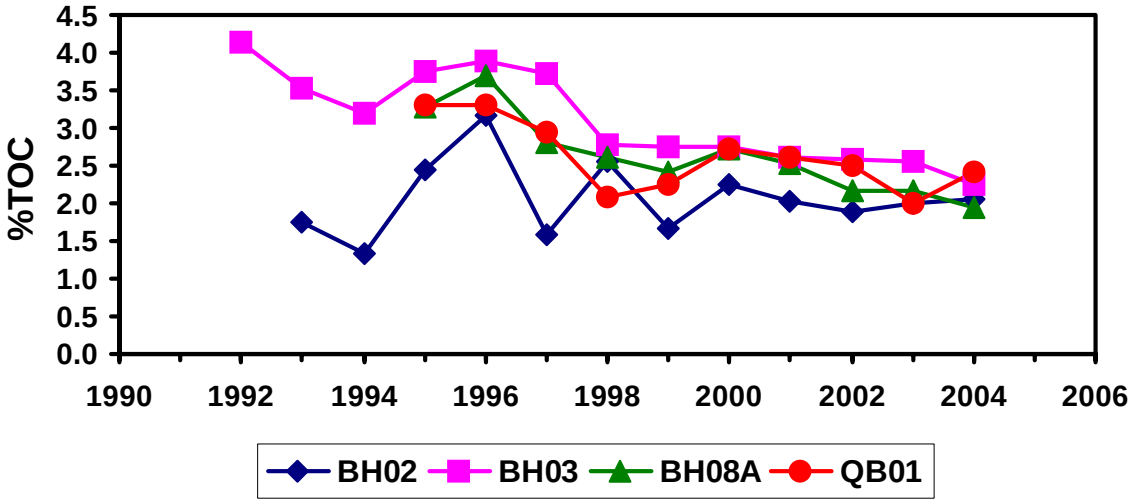

Figure 17. Seasonal average TOC (% dry weight) for top 2 cm of sediment.

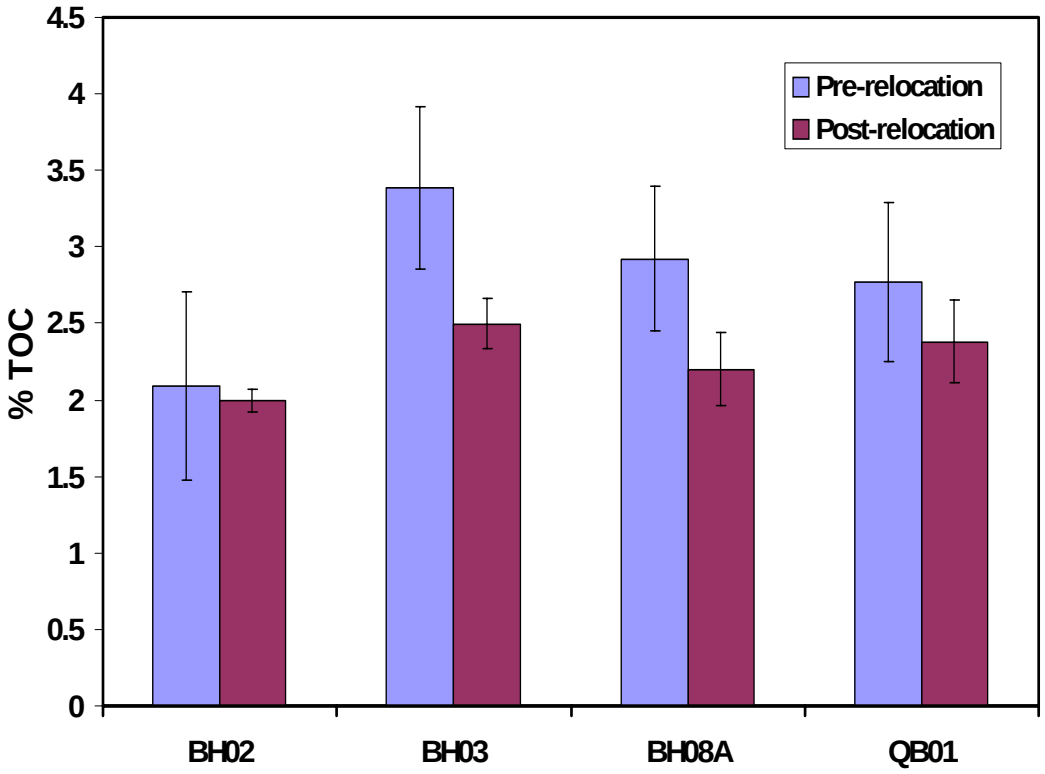

Figure 18. Sediment TOC pre- and post-relocation of the outfall. Data are seasonal averages over all available years for each station. Error bars represent one standard deviation of the mean.

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

In 2003 and now 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 noticeable in the chlorophyll *a* fraction alone (Fig. 19), where chlorophyll made up 20% and 17% of the total pigments, respectively. Higher chlorophyll *a* corresponded to frequent observations of benthic diatoms at these sites. At the other two sites, where amphipod mats are often present, chlorophyll concentrations were lower, accounting for less than 10% of the total, possibly resulting from heavier grazing pressure.

In 2004, chloropyll *a* inventories (integrated over the top 5 cm of sediment) at Station BH02 in May and July were 50.2 and 55.6 µg chl *a* cm^{-2}, the highest yet observed, surpassing the 2003 high value from QB01 (Fig 19). Accordingly, Station BH02 had the highest seasonal average of 42.6 µg chl *a* cm^{-2}. At BH02, large inventories over the entire season were consistent with observations of recent years. Since 1998, this station has had the highest seasonal average chlorophyll *a* inventories of the four harbor stations. High levels of sediment chlorophyll were also observed at Station QB01 throughout the season. Spring high levels were observed at Stations BH03 and BH08A, but were followed by lower inventories for the rest of the season. Lowest levels of sediments pigments were found at Station BH03, where the seasonal average for chlorophyll a was 13.7 ug chl *a* cm^{-2}.

Although we cannot directly determine how much of these elevated concentrations was derived from phytoplankton deposition and how much from *in situ* productiom, sediment profiles of chlorophyll *a* provide some insight (Fig. 20). In 2004, elevated surface concentrations were observed at all four stations in May, corresponding to the time when chlorophyll inventories were also high. Concentrations were very high at Station BH02 and QB01 (Fig. 20a and d) through the top two cm. In July, Station BH02 still had very high chlorophyll concentrations evident in the profile, showing a subsurface peak at 2 cm depth, and even in August surface concentrations remained high. At QB01, surface concentrations were high again in November. In these instances, since we did observe benthic diatoms, it was clear that the elevated chlorophyll levels were derived in large part from *in situ* production. In contrast, at Station BH03 where the lowest inventories of the four stations occurred, and BH08A, profiles did not show surface or subsurface peaks after May (Fig 20b and c). These two stations typically support large numbers of benthic amphipods and other infauna that presumably graze down diatom production.

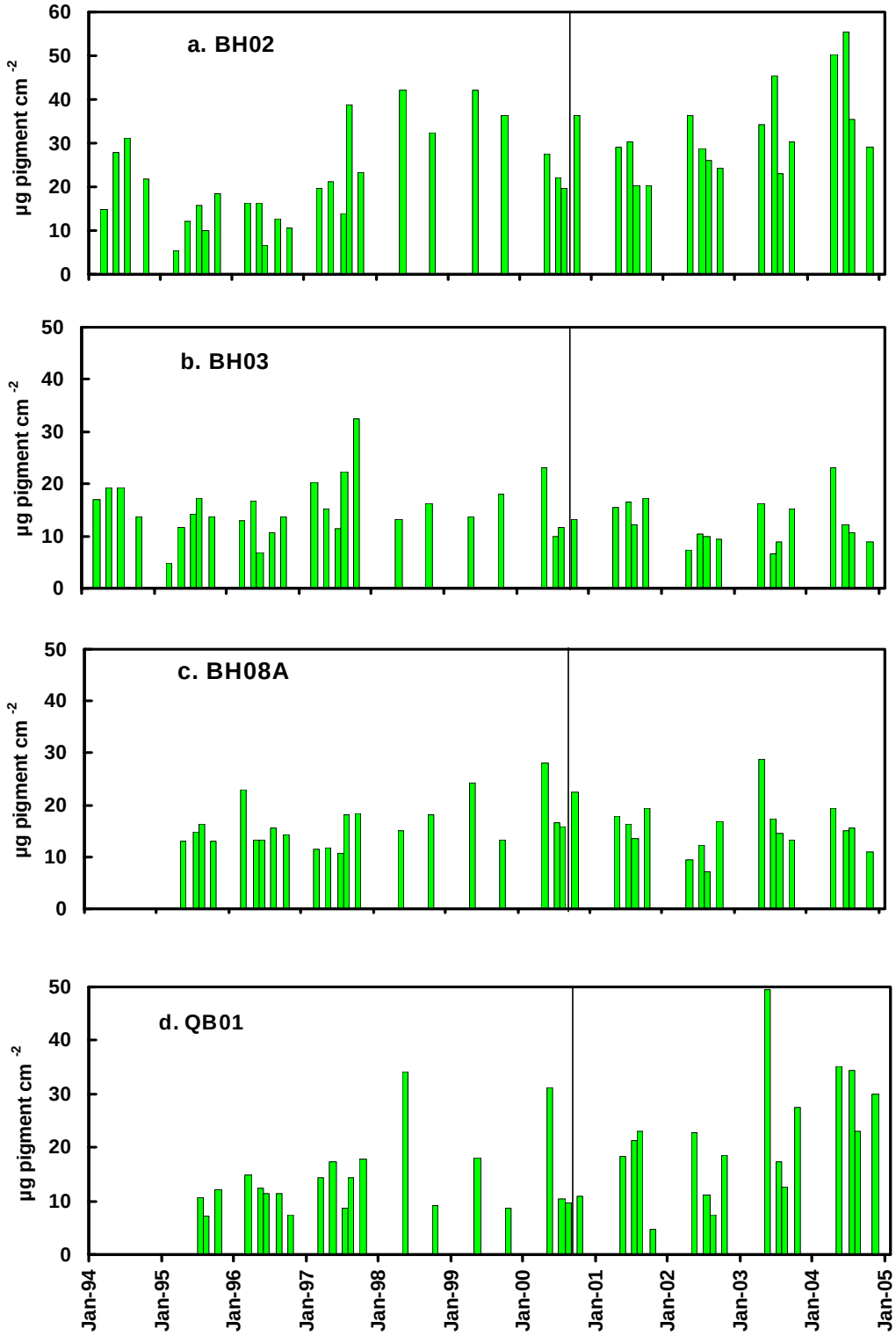

Figure 19. Chlorophyll *a* inventory for top 5 cm of sediment at northern harbor stations a.) BH02, b.) BH03, and southern harbor stations c.) BH08A, d.) QB01. The vertical line marks the transition from baseline to post -relocation observations.

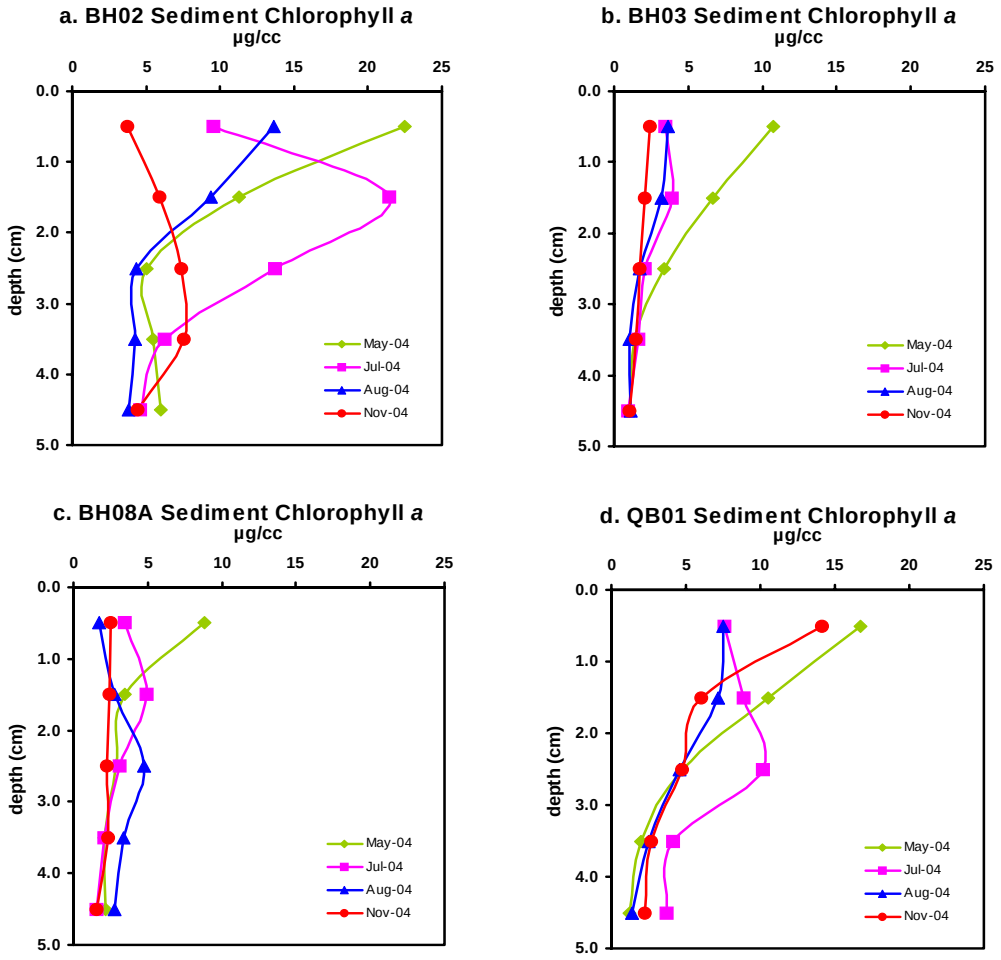

Figure 20. Profiles of chlorophyll a in top 5 cm of sediment at Boston Harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01.

3.2 Sediment Oxygen Demand

Sediment oxygen demand in Boston Harbor in 2004 was lower than it had been in 2003, and was more similar to the very low rates reported for 2002. Average rates for the May to October season were the lowest yet observed at Stations BH02 and QB01, at about 22 mmol m^{-2} d^{-1} (Fig. 21a). At BH03 and BH08A, only the 2002 rates were lower. The 2004 rates were 28.6 and 39.7 mmol m^{-2} d^{-1} at BH03 and BH08A, respectively. Averaged over all four stations, SOD in 2004 was 28.3 mmol m^{-2} d^{-1}, essentially the same as the all time low in 2002 of 27.5 mmol m^{-2} d^{-1}.

For all stations except Station QB01, rates were at the bottom of or lower than the baseline range throughout the season (fig. 22). At QB01, August and October rates were also below baseline, but May and July were mid-range. Highest rates of the season occurred in August at BH02, BH03, and BH08A, but in July at QB01. The highest SOD, 63.9 mmol m^{-2} d^{-1}, occurred at BH08A in August and the lowest, 14.0 mmol m^{-2} d^{-1} at BH02 in October.

Temperature explains some part of the patterns we have observed in SOD over time, but the strength of that relationship has varied among stations and years. In 2004, there was a strong relationship (as evaluated by the coefficient of determination, r2) at Stations BH03 and BH08A (r^2 = 0.53 and 0.74, respectively, but weak relationships at BH02 and QB01 (r2 0.15 and 0.06, respectively). In other years, eg. 2002, the reverse pattern was observed: strong relationships were found at BH02 and QB01, but weaker ones at BH03 and BH08A. Other years show intermediate patterns. When we look at all years combined, temperature explains between about 15% to 40% of the variability we see in rates of SOD.

We have compared low SOD for 2004 with observations from 2002 when the lowest SOD to date was observed. We had considered 2002 an anomalous year resulting from very low discharge from the Charles River, and the general absence of amphipod mats at our stations. In 2004, however, river discharge was normal (Libby et al. 200X) and amphipods were present for at least part of the year. Amphipods were noted by divers in the field and in our experimental cores at Station BH03 and BH08A in moderate numbers in July and at mat densities in August. For 2004, then, other drivers must be controlling SOD, and we are left to infer that declining amounts of labile organic carbon may be involved. 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.

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

Seasonal average DIN flux across the four harbor stations in 2004 were comparable to those of 2002 and the lowest N flux yet observed, ~2.4 mmol m^{-2} d^{-1}. Seasonal average rates ranged from a low of 1.1 mmol m^{-2} d^{-1} at QB01 to 3.5 mmol m^{-2} d^{-1} at BH02, (Fig. 21b). At BH02 and BH03, in the northern harbor, seasonal average DIN fluxes in 2004 were about average for the four post-relocation years, but were lowest of the four years at the southern harbor stations BH08A and QB01. In fact, average DIN flux at Station BH08A, 3.0 mol m-2 d-1, was the lowest yet measured over the entire monitoring program at that station, and at QB01, only the 1997 rate was lower (1997 = 0.8 mmol m^{-2} d^{-1}; 2004 = 1.1 mmol m^{-2} d^{1}).

For 2004, DIN fluxes were at the low end or lower than the baseline range (Fig. 22 e-h). Within the year, highest rates occurred in August at BH08A (5.66 mmol m^{-2} d^{-1}) and the lowest was actually a very small uptake of 0.04 mmol m^{-2} d^{-1} at QB01 in May.

Strong seasonal patterns in DIN flux were observed at three out of the four harbor stations in 2004, as high rates for the season occurred with warmer temperatures in August. Correlations (r^2) with temperature were 0.53 at QB01, 0.89 at BH03, and 0.95 at BH08A. In contrast to the other stations and to the two previous years, there was no relationship with temperature at Station BH02 (r^2 = 0.08). Most

of this decoupling occurred in the NH_4^+ fraction of the DIN flux, which decreased from (by far) the highest flux for May of the four stations of 4.7 mmol m^{-2} d^{-1} to the lowest (slightly) for July of 1.6 mmol m^{-2} d^{-1}. In August, NH_4^+ fluxes at BH02 returned to rates nearly as high as the May rates, and by early November had declined again. Uptake of NH_4^+ by the coating of benthic diatoms noted on the sediments at this station during May and July may have contributed to the May to July decline in flux. For all years combined, temperature explains about 30% to 50% of the variability we see in DIN fluxes.

Overall, the major component of the DIN flux in 2004 was NH_4, with NO_3^- comprising between 12% and 44% of the seasonal average flux. At specific times, however, NO_3^- flux was larger than NH_4^+ flux. This was particularly the case at Stations BH03 and BH08A , which shared very similar seasonal pattern in DIN flux in 2004. In July and August, when DIN fluxes were high and amphipods were present, NO_3^- accounted for up to 55% of the total flux . In early November, when fluxes had declined to the lowest point of the season, NO_3^- made up 50% and 69% of the flux at BH03 and BH08A, respectively. At BH02 , NH_4^+ comprised all of the DIN efflux in May (NO_3^- was taken up,) and remained the dominant form through out the season (60% to 89%). At QB01, DIN fluxes were lower in general than for the other three stations and were very low in May and November. In May, all of the efflux was NH_4^+, and in July and August it was predominantly NH_4^+ . In contrast, in November, all of the efflux was NO_3^-.

3.3.2 Phosphate and Silica

Seasonal average phosphate fluxes in 2004 were among the lowest observed for each station throughout the monitoring program (Fig. 21c). A harbor average across all four stations gave a rate of 0.13 mmol m^{-2} d^{-1}, the lowest yet observed. Prior to this, the lowest overall fluxes occurred in 2002. Fluxes in 2004 ranged from an uptake of PO_4^- at QB01 of 0.02 mmol m^{-2} d^{-1} (the lowest rate ever for this station) to an efflux of 0.28 mmol m^{-2} d^{-1} at Station BH08A.

Within the year, fluxes fell near the bottom of the baseline range, and with the exception of QB01, showed strong seasonality (Fig 23a-d). Of the three stations that did show strong seasonality, highest rates of 0.55 mmol m-2 d-1 were observed in August at Station BH08A, and lowest were uptake rates of 0.02 mmol m^{-2} d^{-1} in May and October at BH03. In contrast , August rates at QB01 were the lowest of the season for the station and overall (uptake of 0.12 mmol m^{-2} d^{-1}). High rates at this station were only 0.04 mmol m^{-2} d^{-1} and occurred in July. PO_4^- fluxes at this station are often characterized by poor r^2s for the regression of concentration vs. time, indicating that fluxes here are fairly negligible .

PO_4^- fluxes are controlled by a combination of biological and chemical factors, and therefore do not always correlate well with temperature. For example, at BH02, which often has quite reducing sediments, the regression with temperature for all years yields an r^2 of only 0.02. In 2004, however, a much stronger seasonal pattern was apparent such that temperature explained between 79% and 99% of the variability at all stations except Station QB01. We observed similarly strong relationships with temperature ($r^2 > 0.5$) in 2002 and 2003 for three out of four stations; in 2002, the "odd station out" was also QB01, but in 2003 it was BH03. In general, we seem to be seeing a stronger connection between temperature and PO_4^- flux than was typical for these stations. For all years combined, the r^2s ranged from 0.02 to 0.38.

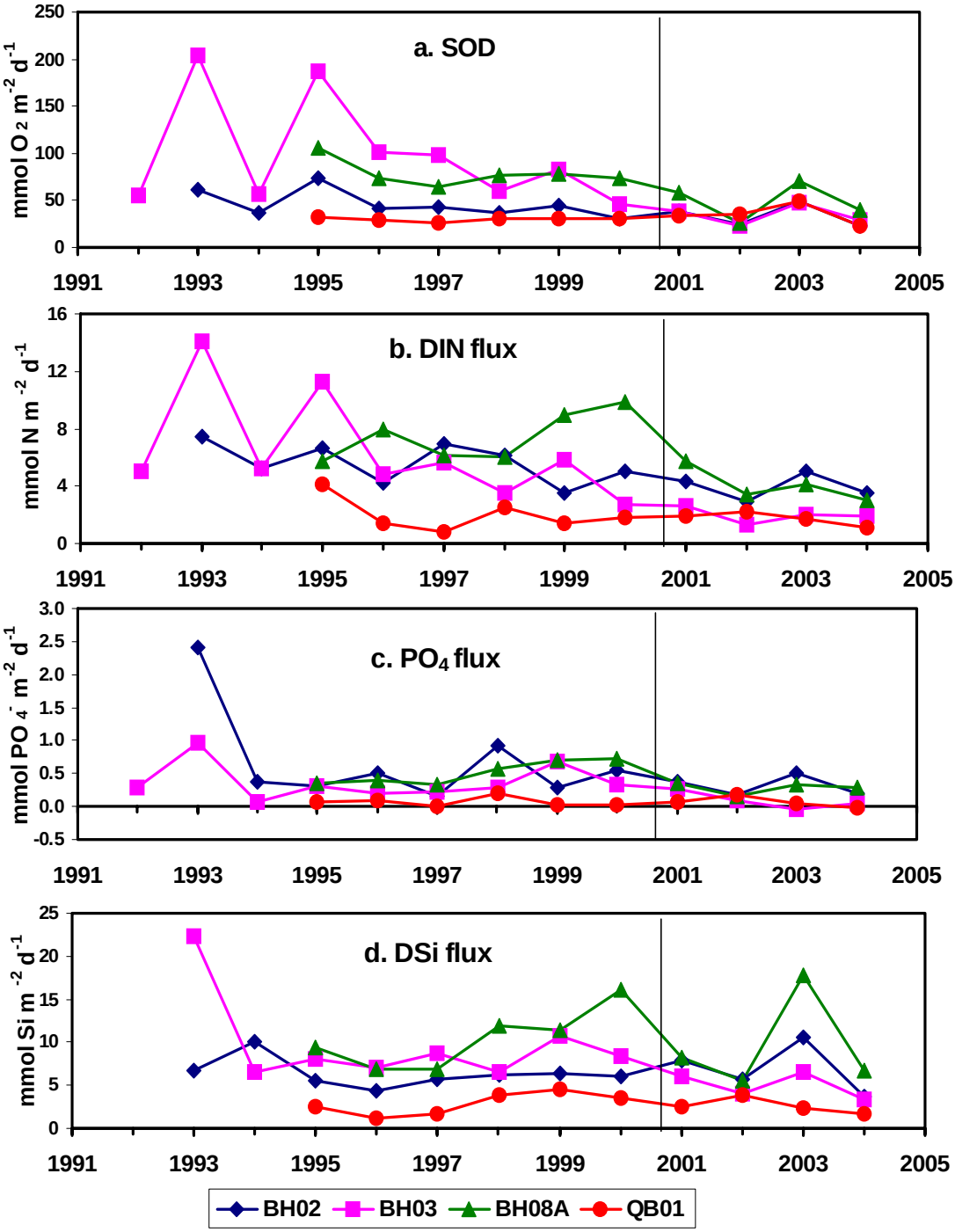

Figure 21. Seasonal (May-October) averages of a.) sediment oxygen demand (SOD), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Boston Harbor stations in 1993-2004. The vertical lines mark the transition between baseline and post-relocation observations.

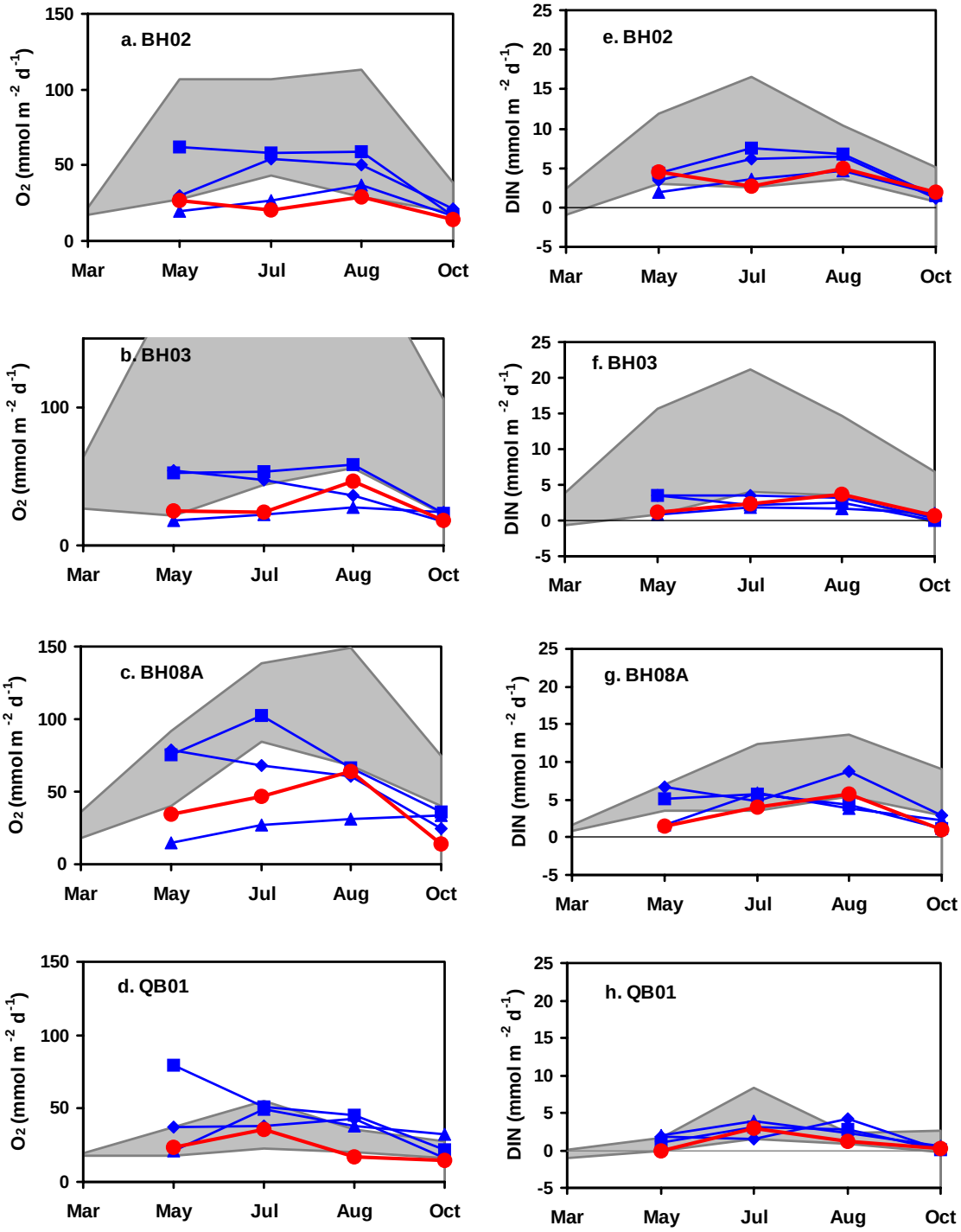

Figure 22. Sediment oxygen demand (O_2 flux) and DIN flux 2001 (♦), 2002 (▲) , 2003 (■), and 2004 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations BH02, BH03, BH08A, and QB01, respectively.

Silica fluxes in 2004 had moderated from the very large fluxes and high variability across stations that was observed in 2003. Seasonal average fluxes (Fig 21d) ranged from 1.7 mmol m^{-2} d^{-1} at QB01 to 6.7 mmol m^{-2} d^{-1} at Station BH08A, in contrast to the previous year when those averages were 2.4 and 17.9, respectively. In general, seasonal averages were lower than the baseline range and low for the four post-relocation years. The average across all four stations, 3.9 mmol m^{-2} d^{-1}, was, in fact, the lowest to date.

A strong seasonal pattern was observed in the 2004 silica fluxes (Fig. 22e-h). High rates occurred in August at all stations, but were highest at Stations BH08A where they reached 12.9 mmol m-2 d-1. Lowest rates for all stations occurred in May, with a rate of 0.32 mmol m^{-2} d^{-1} at QB01 being the lowest. Temperature could explain from 79% to 97% of the variability in 2004, whereas in the previous year, this relationship was only strong at Station BH08A. Over all years, temperature explains between about 30% to 40 % of the variability we see in Si fluxes. An additional explanation lies in the possibility than much of the Si flux was intercepted by benthic diatoms, particularly in May when diatoms were observed at BH02 and QB01 and chlorophyll *a* concentrations were high at all four stations.

3.3.3 Benthic Flux Contribution to Primary Production

The relocation of the sewage outfall has ended the direct input of a large source of nutrients to the Harbor. With this change, the relative contribution of nutrients supplied to the water column by benthic recycling may have increased. We can make a rough estimate of this contribution using post relocation rates of primary production and benthic fluxes. Annual average primary production rate from water column station F23 at the mouth of the harbor was 332 g C m^{-2} yr^{-1}, a little higher than the previous year but lower than the other two post-relocation years and baseline. (Libby *et al*., 2005). Using Redfield relationships, 11.4 mmol m^{-2} d^{-1} of nitrogen would be needed to support this production. Benthic fluxes in 2004 supplied on average 2.4 mmol DIN m^{-2} d^{-1} or about 21% or phytoplankton requirements. A similar calculation shows that about 18% of P requirements could be met by benthic recycling. The relatively small fluxes of dissolved silica in 2004 decreased the contribution these fluxes could make to water column primary production to about 34%, based on a 1:1 ratio with nitrogen requirements, whereas in 2003, Si flux was sufficient to support nearly all (98%)of the production. It is unknown how much of the Si flux may have been used in support of benthic primary production, but changes in its relative availability in the water column could shift the competitive balance there towards less desirable phytoplankton species.

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. Also, model estimates of inputs from other sources, including terrestrial and oceanic (which would include some contribution from the ocean outfall; Kelly, 1998), still exceed phytoplankton requirements and may render benthic fluxes less important. A post-relocation nutrient budget for the harbor is needed in order to better assess the current contribution of benthic fluxes.

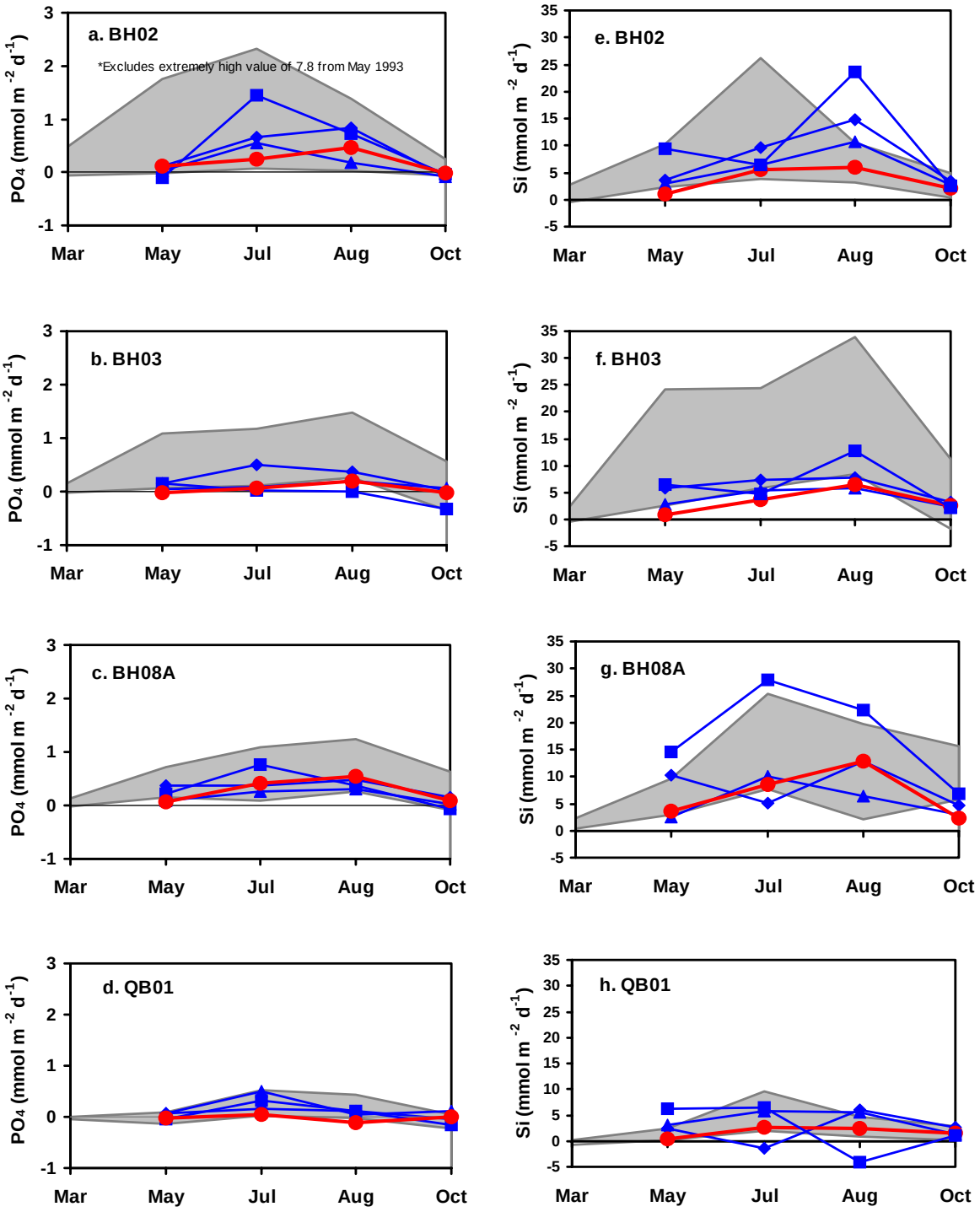

Figure 23. Phosphate (PO_4) and dissolved silica (DSi) flux for 2001 (♦), 2002 (▲) , 2003 (■), and 2004 (●) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO_4 and panels e-h depict DSi flux for stations BH02, BH03, BH08A, and QB01, respectively.

3.4 Denitrification

In 2004, 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. Again we must note that the low rates may in part be a result of the new analytical method (see Tucker and Giblin, 2005). Seasonal average rates were 1.6 and 2.2 mmol N m^{-2} d^{-1}, respectively (Fig. 24). At BH02, this marked a large decrease after 5 consecutive years when average denitrification rates were higher and fairly consistent from year to year, ranging only from 5.0 to 6.3 mmol N m-2 d-1. Instead, the 2004 rate was more similar to those sometimes observed during the baseline period. For BH03, the rate for 2004 was lower than the relatively high (for post-relocation) rate the previous year of 5.1 mmol N m^{-2} d^{-1} and much lower than the very high rates observed during the baseline period (reaching 12.2 mmol N m^{-2} d^{-1} in 1999).

Various controls on denitrification could account for these various 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 for the first time. Seasonal averages at these two stations compared well with the northern harbor stations (Fig. 25). At BH08A, where the benthic community is similar to that at BH03 although lagging a year or two behind in development, the average rate of 3.2 mmol N m^{-2} d^{-1} was the highest of all four stations. At QB01, where the animal community is sparse, the rate of 1.6 mmol N m^{-2} d^{-1} was the same as that observed at BH02.

For the year, highest rates occurred at BH03 and BH08A in August, averaging about 5.2 mmol N m^{-2} d^{-1}. Lowest rates of the season of only 0.14 mmol N m-2 d-1 were also observed at BH03 in early November. Denitrification rates correlated strongly with temperature at Stations BH02 and BH08A (r^2 = 0.86 and 0.88, respectively), but less so at Station BH03 (r^2 = 0.50). At Station QB01, the relationship was weak (r^2 = 0.16).

As discussed in a previous report (Tucker et al, 2002), the decrease in N loading to the harbor caused by the relocation of the sewage outfall may shift the role of denitrification in the overall N budget. In the cited report, estimates of harborwide denitrification rates were in excess of 1000 mmol m^{-2} y^{-1}; including the 2003 and 2004 observations did not significantly change this estimate. Estimates of the remaining terrestrial inputs of N were also on the order of 1000 mmol m^{-2} y^{-1}, suggesting that denitrification might act as a sink equivalent to inputs. However, model estimates suggest that oceanic inputs remain the overwhelming input to the system (Kelly, 1998), and decrease the N sink provided by denitrification to less than 10% of total nitrogen inputs.

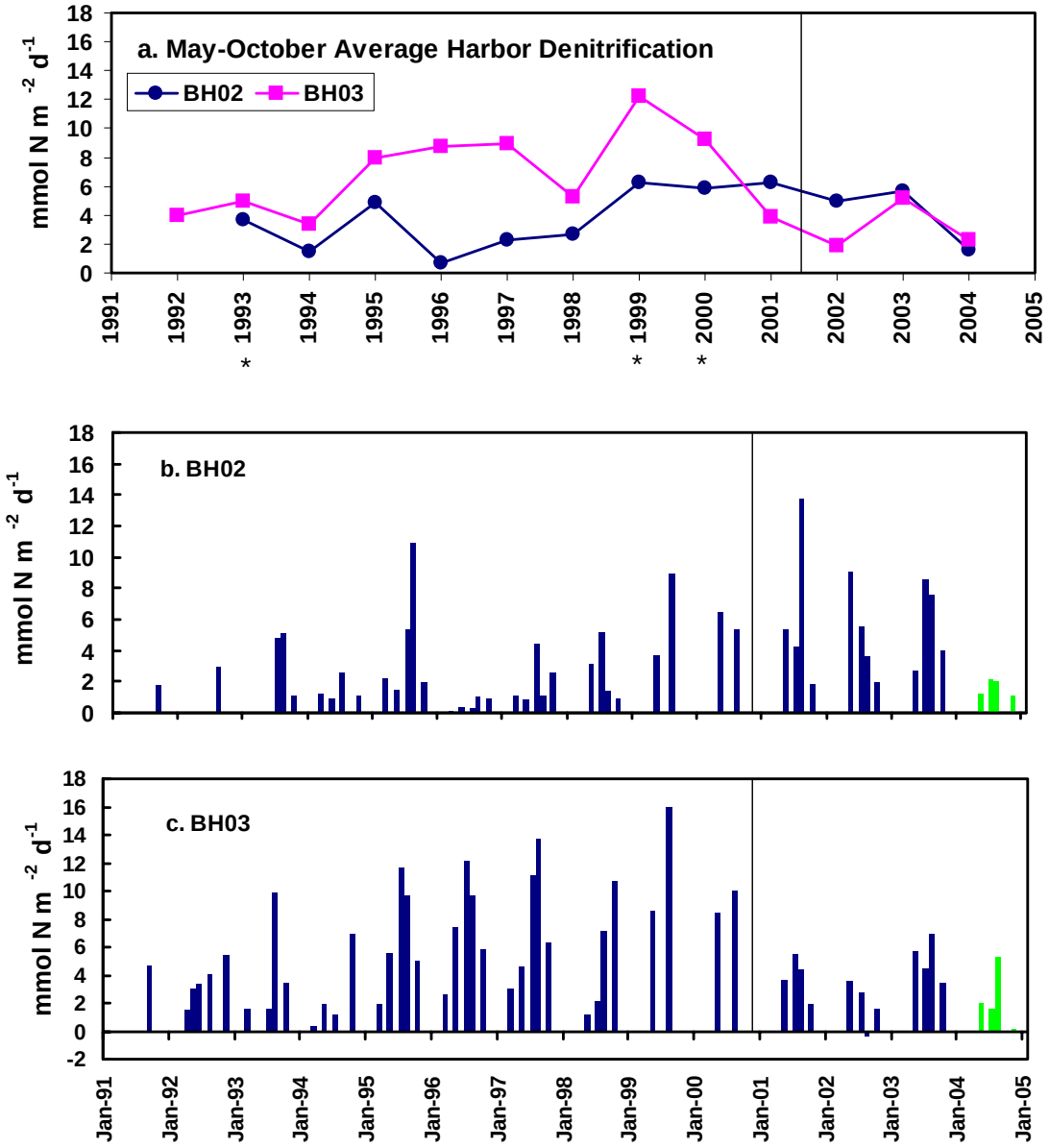

Figure 24. Denitrification in Boston Harbor: a.) May-October seasonal averages for Station BH02 and BH03 from 1992-2004; * marks years when averages were of three rather than four surveys; b.) survey means for BH02 and c.) BH03 from 1991-2004. Vertical lines mark the transition between baseline and post-relocation measurements.

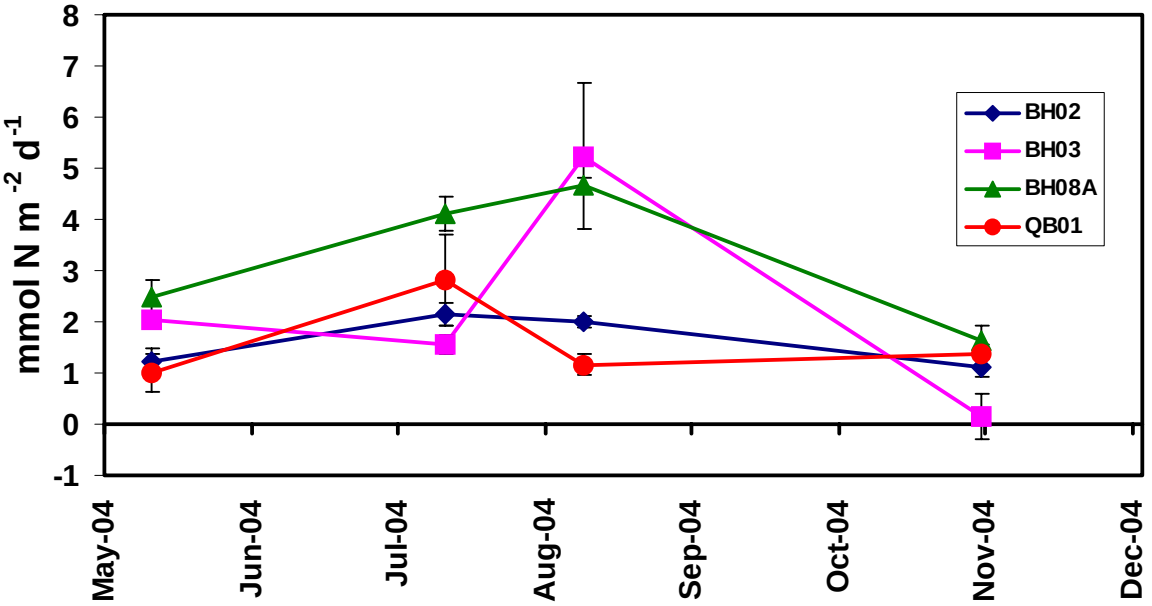

Figure 25. Denitrification at all four Boston Harbor Stations in 2004.

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 2004, average respiratory quotients (RQs) were higher than in the previous year, but generally typical of values we have observed over the past several years (Fig. 26). At Station BH03, RQ averaged over the May to October period was very close to the theoretical 1.0. At BH08A and QB01, the average was 1.2, with a tendency for higher RQs to occur in May and November and indicating some storage of anaerobic endproducts over the season. At BH02, the RQ was quite high at 1.9. High RQs at BH02 were observed

over the entire sampling season and suggest sulfur storage by these sediments. Although these values were not atypical for this station, they were among the higher values observed, and indicate that the relative importance of anaerobic processes at this site continues to vary from year to year.

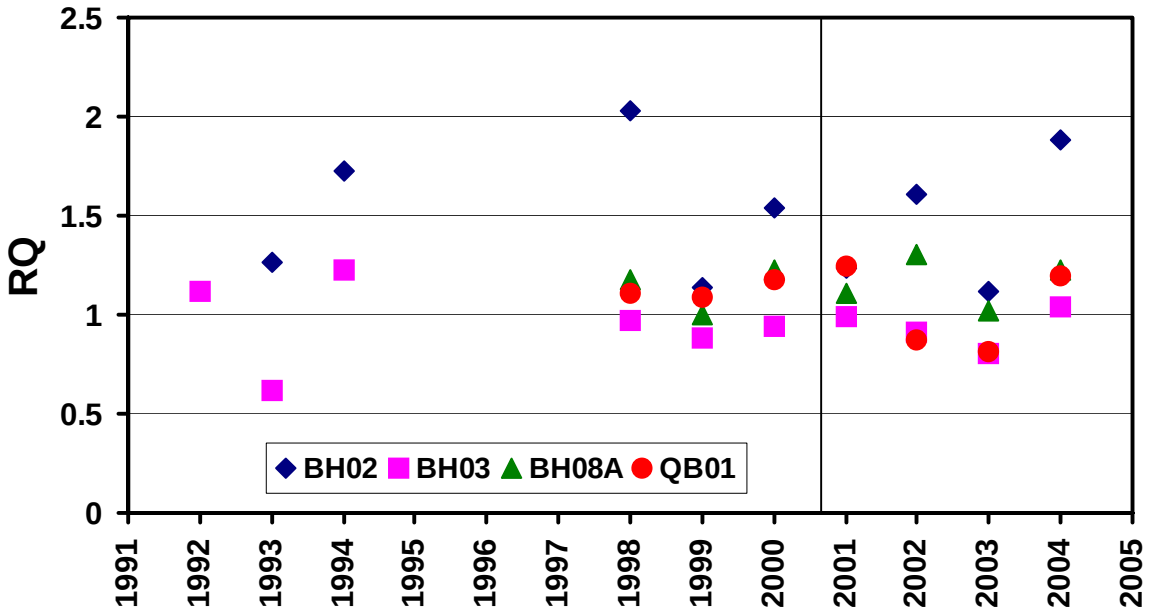

Figure 26. Seasonal (May-October) average respiratory quotients for Boston Harbor stations BH02, BH03, BH08A, and QB01 from 1993-2004. The vertical line marks the transition from baseline to post-relocation observations.

3.5.2 Eh Profiles

Profiles of oxidation-reduction potential (Eh) (Fig. 27) taken from within sediment cores during 2004 fell within baseline and post-relocation ranges. In fact, profiles from August, often the month with the most reducing conditions, fell in the middle of the range of August profiles from previous years (data not shown).

As has been typical throughout the monitoring program, Station BH02 exhibited the most reducing conditions of the four stations, with Eh reaching values (~-150mV) where sulfate reduction should occur by about 8 cm depth in the sediment for all sampling periods except May, when it did not reach those values until 14 cm depth. [Porewater sulfide concentrations were not measured in 2004.] In the surface sediments, the most oxidizing conditions at Station BH02 were observed in November.

At Station BH08A, Eh profiles varied from month to month, with more oxidizing conditions indicated in July and November, and more reducing conditions in May and August, when Eh values reached ~ -150 at 14 cm. At Stations BH03 and QB01, Eh did not show large changes over the season, and only in August at the bottom of the profiles approached values low enough to indicate sulfate reduction.

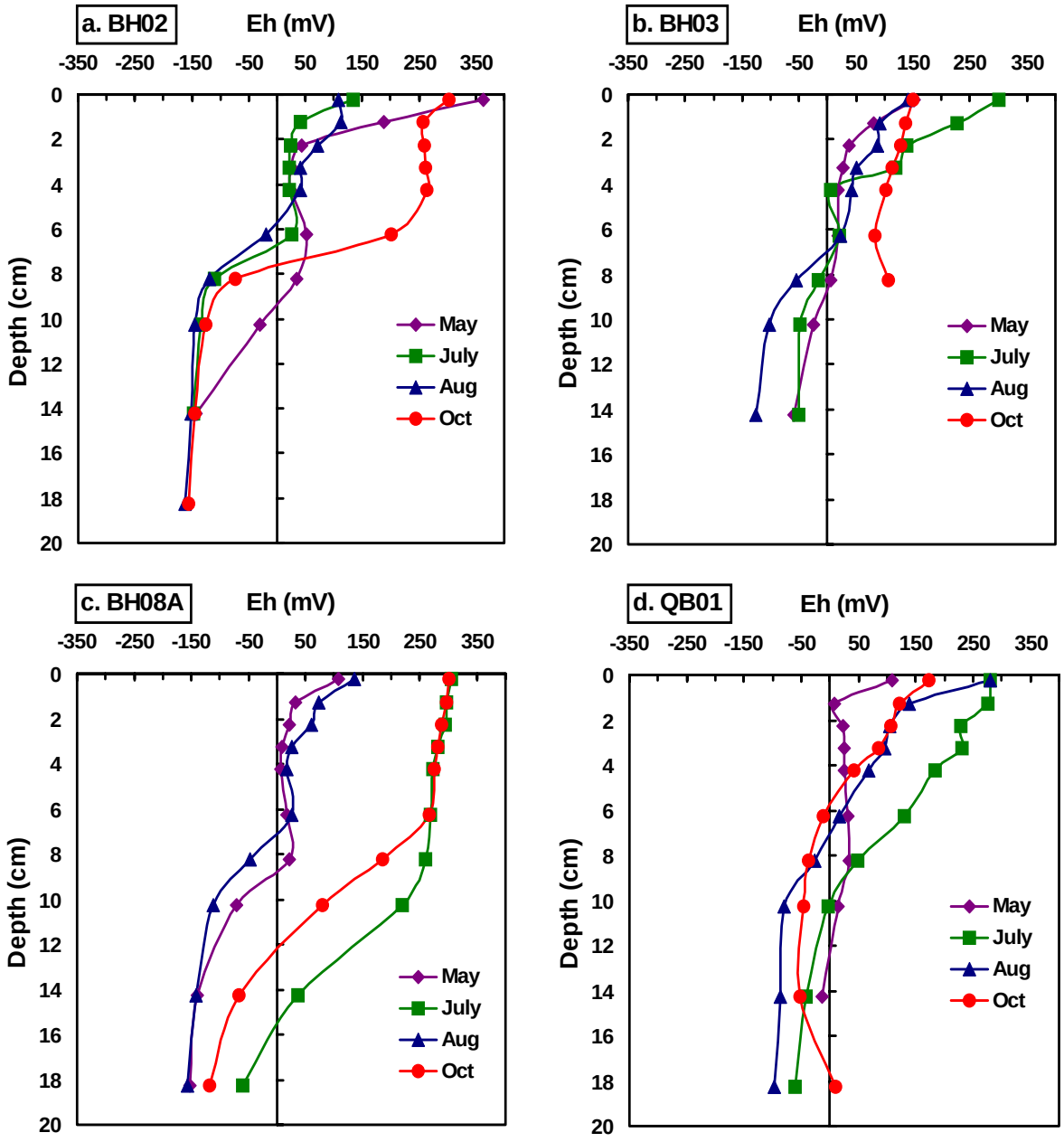

Figure 27. Eh profiles for May through October, 2004, from Harbor stations a.) BH02, b.)BH03, c.) BH08A, and d.) QB01.

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.

Organic matter measured either as TOC or sediment pigments in the nearfield sediments has been variable and although we have observed some higher values in the post-relocation period, through 2003 none had exceeded the range observed during the baseline period. In fact, averages of pre-relocation vs. post-relocation years are not significantly different for either measure.

In 2004, however, seasonal average TOC at one station, Station MB03, did exceed previous observations. At the same time, C/N for these sediments decreased and was well below that of the other two nearfield stations. In addition, sediment total chlorophyll *a* levels were high. The low C/N and high chlorophyll *a* lead us to think the elevated TOC at this station may have resulted from deposition of the large spring *Phaeocystis* bloom. We are uncertain why indications of the bloom would only be present at this station, but it may be related to highest densities of *Phaeocystis* occurring in Boston Harbor and Broad Sound (Libby et al., 2005) and the more southerly ("down-current") position of Station MB03.

Rates of SOD in 2004 were typical of the post-relocation period and in the low end of the baseline range. The average for the May to November sampling period for the nearfield stations was 16.0 mmol m^{-2} d^{-1}, whereas the baseline average was 17.2 mmol m^{-2} d^{-1}. At Stellwagen Station MB05, the seasonal average for 2004 was 10.5 mmol m^{-2} d^{-1}, whereas the baseline average was 11.6 mmol m^{-2} d^{-1}. Although the rates of sediment oxygen demand would be high enough to affect the seasonal drawdown of oxygen in the water column in the nearfield if the water column were stagnant, the rate of water renewal from the Gulf of Maine is sufficient to nearly completely override the effect of local benthic metabolism. The renewal rate of the bottom water, which is determined by wind and other climatological factors, determine the timing and strength of the seasonal oxygen drawdown.

Fluxes of DIN in 2004 were in the mid to low end of the range observed during baseline monitoring. The 2004 seasonal average across the nearfield stations was 0.8 mmol m^{-2} d^{-1} as compared to a baseline average of 0.9 mmol m^{-2} d^{-1}. NO_3^- comprised less of the DIN flux than it had in the previous two years, averaging about 43% of the flux. The most noticeable difference was at Station MB03, where in 2002 and 2003, NO_3^- had comprised all of the DIN but in 2004 was 57%. These low DIN fluxes resulted in a contribution of nitrogen amounting to less than 9% of the requirements for nearfield primary production. At station MB05, average DIN flux for 2004 was 0.18 mmol m^{-2} d^{-1} as compared to the baseline average of 0.25 mmol $m^{-2}d^{-1}$, with NO_3^- comprising 56% of the flux.

In 2004, PO_4^- fluxes at the nearfield stations were low compared to the baseline range, averaging 0.02 mmol $m^{-2}d^{-1}$ as compared to 0.06 mmol $m^{-2}d^{-1}$ and resulting in a potential contribution to primary production of only 3% of requirements. At MB05, the 2004 average PO_4^- flux was slightly negative, whereas the baseline average was 0.04 mmol $m^{-2}d^{-1}$. Nearfield Si fluxes were low compared to baseline, 3.5 mmol $m^{-2}d^{-1}$ compared to 5.1 mmol $m^{-2}d^{-1}$, respectively, but accounting for nearly 40% of 2004

primary production requirements. At MB05, Si fluxes in 2004 were 3.5 mmol $m^{-2}d^{-1}$ as compared to the baseline average of 4.3 mmol $m^{-2}d^{-1}$.

The average denitrification rate for 2004 at the two nearfield stations where it has traditionally been measured was 1.8 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 2004 may have been partly due to the use of an improved analytical method, which tends to yield lower rate estimates than the previous method. The new method allowed denitrification to be measured for the first time at Stations MB01 and MB05 in 2004. The seasonal average rate of 1.8 at MB01 compared well with the other two Nearfield stations, and the rate at Stellwagen station MB05 was only slightly lower, 1.6 mmol N $m^{-2}d^{-1}$. In 2004, denitrification accounted for 69% and 89% of the total inorganic nitrogen (DIN + N_2) flux at the nearfield and Stellwagen stations, respectively.

There was no indication of decreased sediment oxidation in any of our measurements. Respiratory quotients were very close to 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 1. shows a summary of pre- (1993-2000) and post- (2001-2004) relocation fluxes. There has been no discernable change in SOD, NO_3^- fluxes, or denitrification, and for all other fluxes there has been a decrease. Change was not assessed for PO_4^- fluxes because these fluxes vary from positive to negative and are often negligible.

Table 1. Average fluxes for all nearfield stations over the pre-diversion (1993 through 2000) or post-diversion (2001-2004) 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	17.2	0.7	0.2	0.9	0.1	5.1	2.6
Flux Post-Diversion	16.4	0.3	0.2	0.6	0	3.6	2.6
%Reduction	4	43	0	33	nc	29	0

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.

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring, including the four years since diversion. A comparison of averages pre-and post - diversion show that 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 five years (2000-2004).

For the second year, we have observed increased chlorophyll *a* content in surface sediments of two of the four harbor stations, BH02 and QB01. Inventories over the top 5 cm of sediment at these two stations for 2004 were the highest yet observed. Observations of benthic diatoms and sediment profiles of chlorophyll suggest that *in situ* production is important at these sites. Similar increases at the other two sites, BH03 and BH08A, have not been seen, presumably prevented by grazing pressure.

Sediment oxygen demand in 2004 was low compared to previous years; only 2002 rates were lower. The average across the four stations was 28.3 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, which had decreased somewhat from the high rates observed in 2003. Fluxes of DIN and PO_4^- were the lowest to date, although only slightly lower than 2002 observations. Fluxes of dissolved silica decreased from high values observed in 2003, and were also the lowest reported. Fluxes of DIN, PO_4^- and Si in 2004 averaged across the four stations were 2.4, 0.1, and 3.9 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.

Using rates of primary production at the mouth of the harbor and seasonal averages of DIN and PO_4^- fluxes, we calculate that these fluxes could have supplied about 21% and 18% of phytoplankton N and P requirements, respectively, for 2004. Silica fluxes from the sediment were large enough in 2004 to support 34% of primary production, down from a possible 100% contribution in 2003. With the reduction in nutrient inputs to the harbor after the relocation of the outfall, these contributions may become significant, however oceanic and remaining terrestrial inputs still exceed the needs of primary production.

In 2004, 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 2004 was 1.9 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 implementation of a new analytical method. This method enables us to measure denitrification at the other two harbor stations, BH08A and QB01 for the first time. BH08A had somewhat higher rates and QB01 lower, resulting in an overall average of 2.2 mmol N $m^{-2}d^{-1}$, essentially equivalent to the average DIN flux.

Patterns in redox measurements varied across stations. At BH02, respiratory quotients were elevated throughout the 2004 season. Further evidence of reducing conditions was supplied by Eh measurements that indicated sulfate reduction beginning within the top 10 cm of sediments from this station. These conditions are not atypical for this station, but they indicate the relative importance of anaerobic process at this site continues to vary from year to year. Respiratory quotients at BH08A and QB01 were somewhat elevated, but not unusually so for these stations. At BH03, the RQ averaged the theoretical 1.0 in 2004. Eh profiles at these stations were generally more positive than at BH02, but at certain times reached low enough values to suggest the presence of sulfides at depths of 15 cm or greater.

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 status of those benthic communities will no doubt continue to mediate changes in benthic nutrient cycling.

Table 2 is a summary of the flux data for the pre- (1992-1995 through 2000) and post-(2001 through 2004) diversion years. For most of the fluxes, we have observed between a 40% and 60% reduction between the two time periods. For instance, we have observed a reduction of 45% in SOD and 50% 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 2. Average fluxes for all harbor stations over the pre-diversion (1992-1995 through 2000) or post-diversion (2001-2004) 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	37.7	2.0	0.9	2.9	0.2	6.0	4.0
%Reduction	46	43	69	50	62	24	28

4.3 Cross-System Overview

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

First, in all cases, all fluxes in Boston Harbor are much larger than those in Massachusetts Bay and Stellwagen Basin, and often those from Massachusetts Bay are larger than those in Stellwagen. This pattern follows that of increasing water column depth, which is often used as a proxy for organic matter content. Indeed, organic matter content is nearly twice as high in Boston Harbor as in Massachusetts Bay (2.6% TOC, n=45, range 1.3%-4.1%, and 1.3%, n=32, range 0.9-2.3% for the harbor and bay, respectively). However, our Stellwagen Basin station typically has a slightly higher organic carbon content (1.5%, n=10, range (1.2-1.7) than do those in Massachusetts Bay. It may be that the carbon in Stellwagen Basin is of poorer quality than that in the shallower bay stations, having been exposed to water column processing during a longer settling time. Alternately, year-round lower temperatures in the deeper bottom waters of Stellwagen Basin may simply slow biological processes. In the cases where fluxes in Massachusetts Bay and Stellwagen are equivalent (i.e. PO_4^- and DSi), chemical and physical processes may be as important as biological processes in determining fluxes, and therefore not as sensitive to temperature.

It is also obvious that inter-annual variability in the harbor fluxes has been much greater than in the bay and basin. Intra-year variability has also been larger in the harbor as compared to the bay (cannot assess this for Stellwagen given the single station). This variability in the harbor is not surprising given that station characteristics have been much more variable than for bay stations. These characteristics include

1.) organic carbon content, which varied across stations and time, especially in the early years of monitoring, and resulted in wide ranges in fluxes and redox conditions; 2.) presence or absence of infauna, especially the amphipod mats, which in 1993 resulted in some of the highest S.O.D. ever reported; 3.) and proximity to various types of sewage inputs, which underwent substantial treatment improvements during the 1990s. Of course, all of these are inter-related.

Rates and variability in the harbor have decreased over time, in some cases nearing bay rates. 2004 marked a continuation in this decline after an increase between 2002 and 2003. We attribute the general decrease to reductions in sewage inputs to the harbor. Now that effluent discharge has been relocated offshore, we are beginning to see variability in the harbor driven by other, large scale processes such as climatology. For example the very low fluxes observed during 2002 may be attributable to an anomalously dry year that caused low freshwater (and therefore land-derived nutrient) discharge to the harbor. However, this argument does not hold for the low 2004 rates. In contrast, we have observed no indication of increased fluxes or variability in the bay since the relocation of the effluent discharge.

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. 23). Our data are seasonal averages (May-October) whereas Nixon's data are referred to as "summer". 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. During the pre-diversion years, Boston Harbor had among the highest rates of SOD, whereas it is now in the middle of the range. The change is even more dramatic if only the early part of the pre-diversion period (1993-1995) is considered; during those years, the average SOD in Boston Harbor (93 mmol m^{-2} d^{-1}) was equivalent to that of the Pawtuxent River. 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.

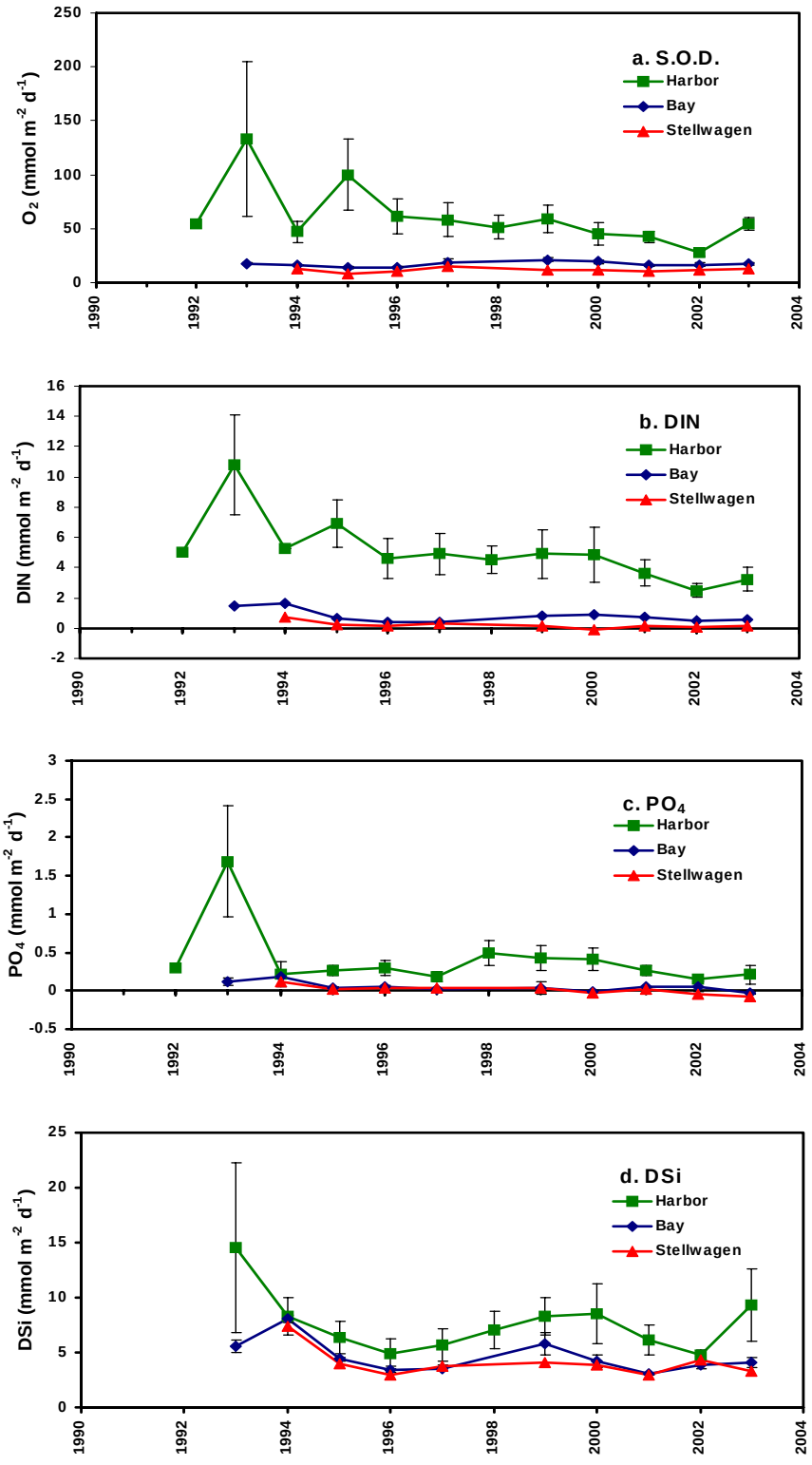

Figure 28. Survey averages of a.) S.O.D., b.) DIN flux, c.) PO4 flux, and d.) DSi flux for Boston Harbor (■), Massachusetts Bay (♦), and Stellwagen Basin (▲) . Error bars represent the standard error of the mean.

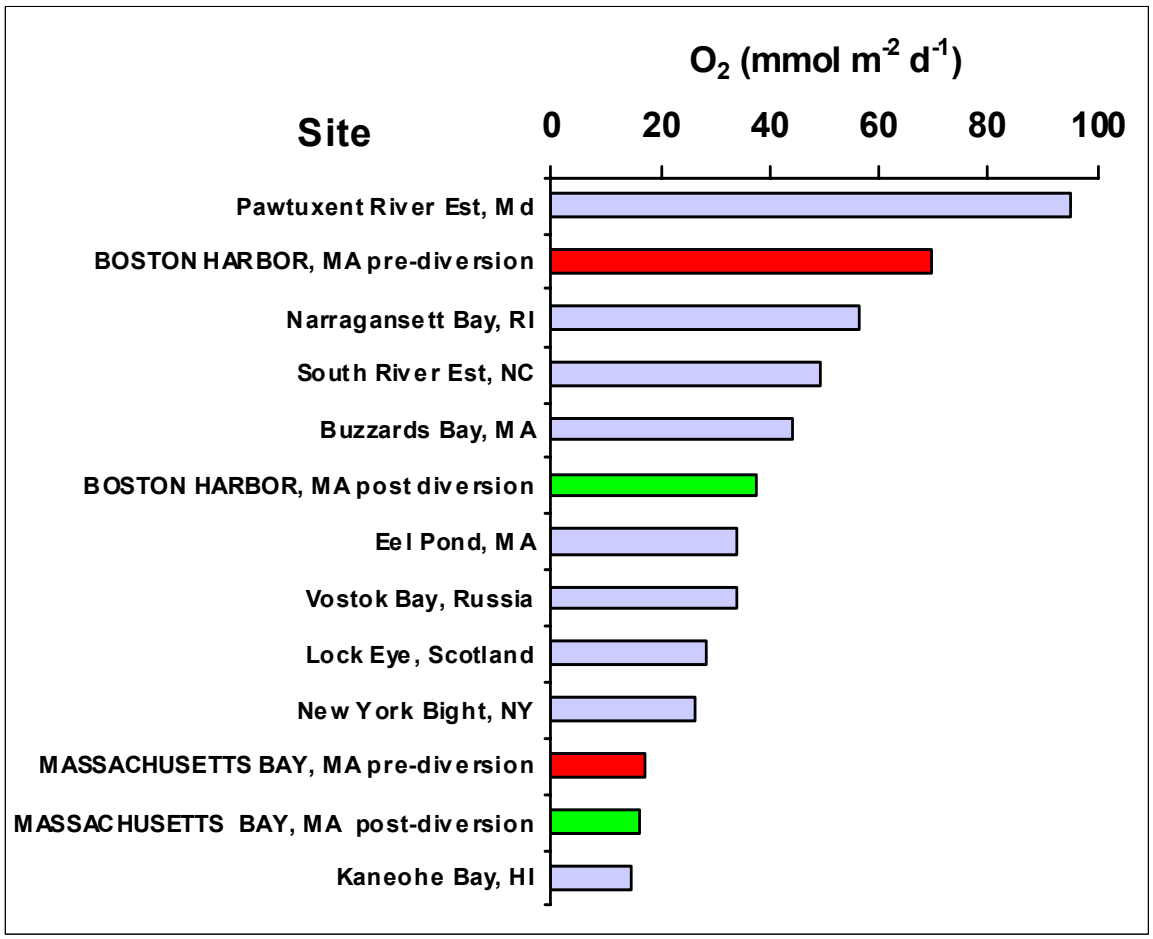

Figure 29. Sediment oxygen demand in Boston Harbor and the nearfield of Massachusetts Bay during pre- and post diversion periods compared to other coastal ecosystems (Nixon 1981). Data for Boston Harbor and Massachusetts Bay are May-October averages. Data for the other systems are summer rates.

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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 2004.

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 2004.

Station	Survey ID	Date	Latitude	Longitude	Depth (m)	Temp (oC)	D.O. ($mg.L^{-1}$)	Salinity (psu)
BH02	NC041	05/11/04	42.34387	-71.00233	9.0	7.8	10.03	33.4
	NC042	07/12/04	42.34357	-71.00218	11.1	15.2	9.08	31.8
	NC043	08/10/04	42.34370	-71.00201	11.0	16.6	8.4	32.2
	NC044	11/02/04	42.34372	-71.00250	9.2	11.1	8.47	30.0
BH03	NC041	05/11/04	42.33072	-70.96180	8.6	7.7	9.86	33.6
	NC042	07/12/04	42.33064	-70.96187	9.0	15.0	8.87	31.8
	NC043	08/10/04	42.33045	-70.96180	8.6	16.2	8.37	32.0
	NC044	11/02/04	42.33070	-70.96198	9.2	11.1	8.61	30.0
BH08A	NC041	05/11/04	42.29100	-70.92202	9.0	8.5	9.73	33.4
	NC042	07/12/04	42.29125	-70.92202	9.4	16.1	8.67	31.6
	NC043	08/10/04	42.29103	-70.92233	9.3	17.6	7.92	32.0
	NC044	11/02/04	42.29117	-70.92226	10.0	11.0	8.42	29.4
QB01	NC041	05/11/04	42.29348	-70.98775	3.3	9.1	9.52	32.8
	NC042	07/12/04	42.29348	-70.98808	4.7	16.5	8.29	32.0
	NC043	08/10/04	42.29335	-70.98782	4.6	18.1	8.3	32.0
	NC044	11/02/04	42.29343	-70.98797	4.8	10.9	8.67	30.0
MB01	NC041	05/10/04	42.40310	-70.83765	29.0	4.1	9.43	34.3
	NC042	07/13/04	42.40280	-70.83767	30.8	6.8	8.47	32.1
	NC043	08/09/04	42.40295	-70.83708	31.3	7.3	9.0	32.8
	NC044	11/07/04	42.40318	-70.83718	30.4	10.4	8.34	32.6
MB02	NC041	05/10/04	42.39240	-70.83415	32.0	4.2	9.30	34.3
	NC042	07/13/04	42.39277	-70.83450	31.8	6.9	8.61	33.0
	NC043	08/09/04	42.39258	-70.83418	32.5	7.7	8.67	32.4
	NC044	11/07/04	42.39273	-70.83395	28.5	10.5	8.49	32.4
MB03	NC041	05/10/04	42.34780	-70.81582	33.5	4.2	9.6	34.7
	NC042	07/13/04	42.34790	-70.81603	34.4	6.8	8.61	33.2
	NC043	08/09/04	42.34778	-70.81599	32.8	7.5	8.74	32.4
	NC044	11/07/04	42.34785	-70.81599	33.4	10.3	8.50	32.6
MB05	NC041	05/10/04	42.41633	-70.65190	45.0	3.5	9.92	34.1
	NC042	07/13/04	42.41658	-70.65224	40.8	5.8	8.76	33.9
	NC043	08/09/04	42.41647	-70.65190	46.7	6.0	9.37	33.2
	NC044	11/07/04	42.41670	-70.65180	44.6	10.1	8.42	32.4

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