2002 Annual benthic nutrient flux monitoring report

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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.

During 2001 and 2002, the two years since the ocean outfall became operational, we have seen small but inconsistent changes in measures of sediment organic matter, and rates of benthic respiration and nutrient fluxes have been well within or lower than typical baseline observations.

Organic matter content of surface sediments in the nearfield had increased somewhat in last two years compared to the previous two or three years, but was still within baseline observations. Small increases in TOC were also observed at farfield station MB05, suggesting these trends may be region-wide.

Nearfield C/N ratios of sediment organic matter were high in 2002 compared to baseline and followed unusually low values observed in 2001. Low values may have been related to the large 1999-2000 phytoplankton blooms. The high values are as yet unexplained

Sediment chlorophyll at nearfield stations in 2002 was typical of baseline, following elevated levels observed during some surveys in 2001. As mentioned above, 2001 was noted for low sediment C/N as well as these incidents of high chlorophyll, but in 2002, typical chlorophyll values did not seem to correspond to high C/N.

In 2002, there was no indication of increased SOD or increased nutrient fluxes from nearfield sediments. In fact, fluxes were in general in the low end of baseline observations or were lower.

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 2002 were in the low end or even lower than the range observed during baseline monitoring. Rates were at times characterized as uptake rather than release. These low DIN fluxes result in a contribution of nitrogen amounting to less than 3% of the requirements for nearfield primary production. At station MB05, we observed very low effluxes of NO_3^- from and moderate uptake of NH_4^+ into the sediments in 2002.

In 2002, PO_4^- fluxes were low compared to the baseline range and often negative, particularly at station MB05. Silica fluxes were low compared to baseline in the nearfield, and typical at MB05.

Denitrification rates at two nearfield stations were typical of baseline observations. Due to the low DIN flux, denitrification accounted for between 83% and 100% of the total nitrogen flux at these stations.

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

BOSTON HARBOR

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

Reduction in organic matter loading has been reflected in sediment TOC measurements throughout baseline monitoring and in the two years since diversion. Decreases in TOC have been most pronounced at Stations BH03, BH08A, and QB01 whereas TOC content at station BH02 has varied. The large range of values observed across the four stations early in the monitoring program has narrowed in the past three years (2000-2002).

Sediment chlorophyll decreased somewhat at two of the harbor stations in 2002, stations BH03 and BH08A, where the amphipods mats have typically been present. At the other two stations, BH02 and QB01, sediment chlorophyll levels were among the higher levels observed during baseline monitoring. Observations of benthic diatoms and sediment profiles of chlorophyll suggest that *in situ* production is important at these sites.

Sediment oxygen demand and all nutrient fluxes in 2002 were lower than at any previous time during monitoring at Stations BH02, BH03, and BH08A. Little change has been observed over the years at QB01. At this point, the large variability between stations and years has largely disappeared.

DIN and PO_4 fluxes may are sufficient to meet up to 15% of phytoplankton N and P requirements. 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.

Although denitrification rates are equivalent to the remaining terrestrial loading, oceanic inputs remain the overwhelming source to the system, and decrease the N sink provided by denitrification to less than 10% of total inputs.

Patterns in redox measurements varied across stations. At BH02, conditions were more reducing than in the previous year, demonstrating that the relative importance of anaerobic process continues to vary from year to year at this site. Less oxic conditions than typical were observed this year at Station BH08A, which may be related to the disappearance of amphipods from this site. At the remaining two sites, conditions were more oxic and typical of the several preceding years.

The decrease in the magnitude of benthic fluxes, of oxygen as well as nutrients, in addition to the dramatic decrease in variability in fluxes across stations suggests that the harbor benthic environment has progressed significantly along the path of “recovery”. However, we still see variability in redox parameters, especially at station BH02 but in 2002 also at station BH08A. The role that infauna has played has been significant in areas like BH08A and BH03, and the status of those benthic communities will no doubt continue to mediate changes in benthic nutrient cycling.

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1.0 INTRODUCTION

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

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

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

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

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

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

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

II. Have the rates of these processes changed?

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

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

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

2.0 MASSACHUSETTS BAY

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

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

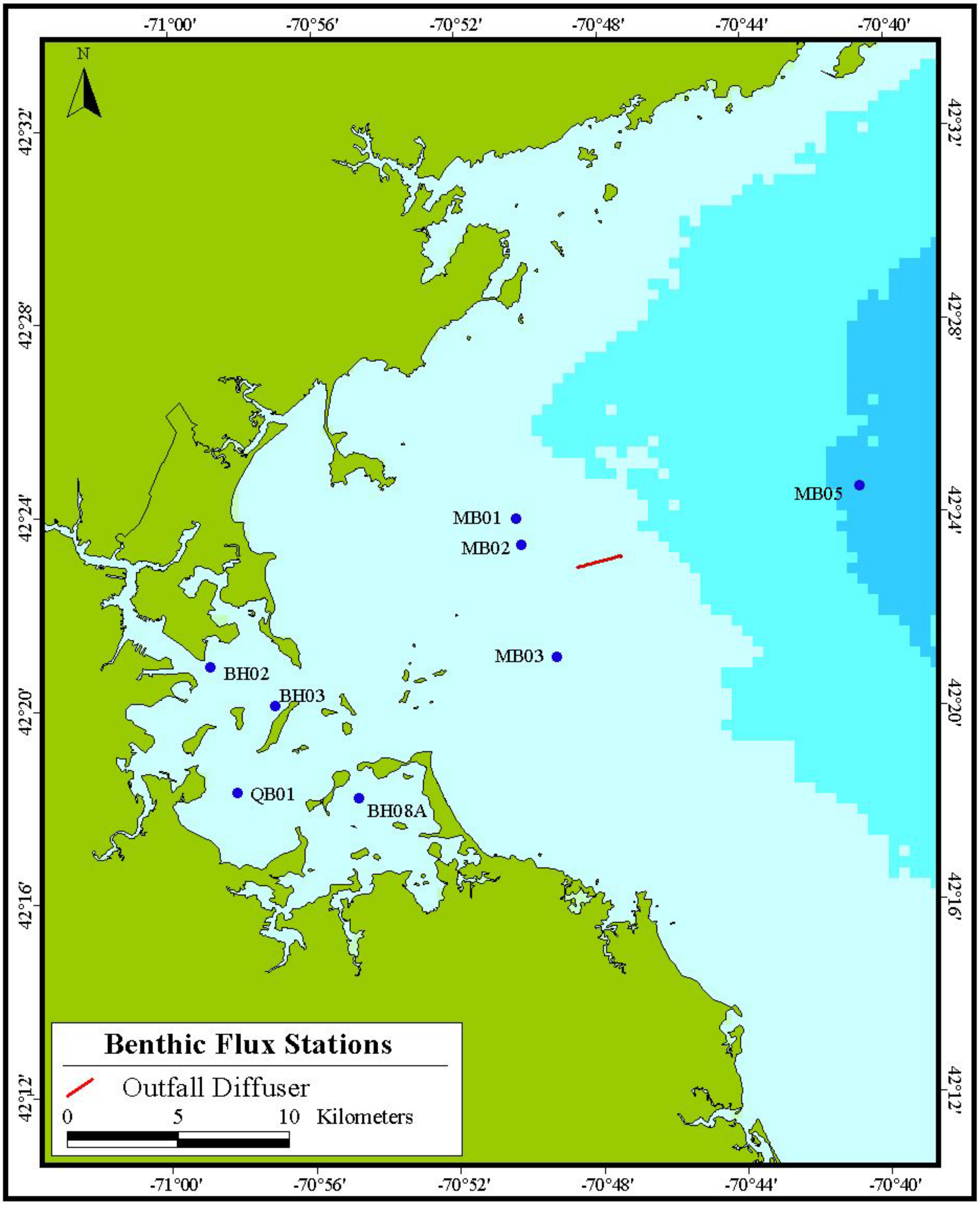


Figure 1. Benthic nutrient cycling stations in Massachusetts Bay and Boston Harbor.

2.1 Organic Matter Loading

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

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

2.1.1 Total Organic Carbon

During baseline monitoring, organic carbon (OC) content in the sediments of the four Massachusetts Bay stations ranged from 0.4% to 4.3%, but with values more typically between 1.0% and 2.9%. Peaks in organic carbon content did not usually correspond to periods of phytoplankton blooms, but very high values observed in 1993 did seem to correspond to the effects of a late 1992 storm that redistributed sediments in the Bay (Bothner *et al*. 2002). In 2002, sediment TOC from all four stations fell in a narrow range from 1.2% to 1.8 %. Seasonal averages for the three nearfield stations were quite similar, about 1.4 %, whereas the seasonal average at Farfield station MB05 was higher, 1.6%. This higher value at MB05 continues a trend of slowly increasing carbon content in sediments at this deepwater site. It also continues the pattern observed since 1997 that average TOC content at MB05 has been greater than that at the nearfield stations.

Using seasonal averages (May-October) we previously noted a decrease in TOC at Nearfield stations MB01 and MB03 over the baseline period, a trend that was only very weak at MB05 and not apparent at MB02.(Fig. 2). In 2001 and 2002, however, we have observed an increasing trend in TOC compared to the proceeding two or three years, although values remain within the baseline range. The striking break with the baseline pattern was observed at MB03, the station to the southwest of the outfall diffusers.

At the three nearfield stations, carbon to nitrogen ratios (C/N) in surface sediments showed a sharp increase in 2002 following low ratios observed in 2001. At MB05, there was little change in C/N. At station MB01, seasonal average C/N was 14.6, the highest for all stations over all years. At MB02, the average was 13.8, the highest observed at this station although a similarly high value was observed in 1995. At MB03 as well, the ratio of 12.2 was a station high (Fig. 3).

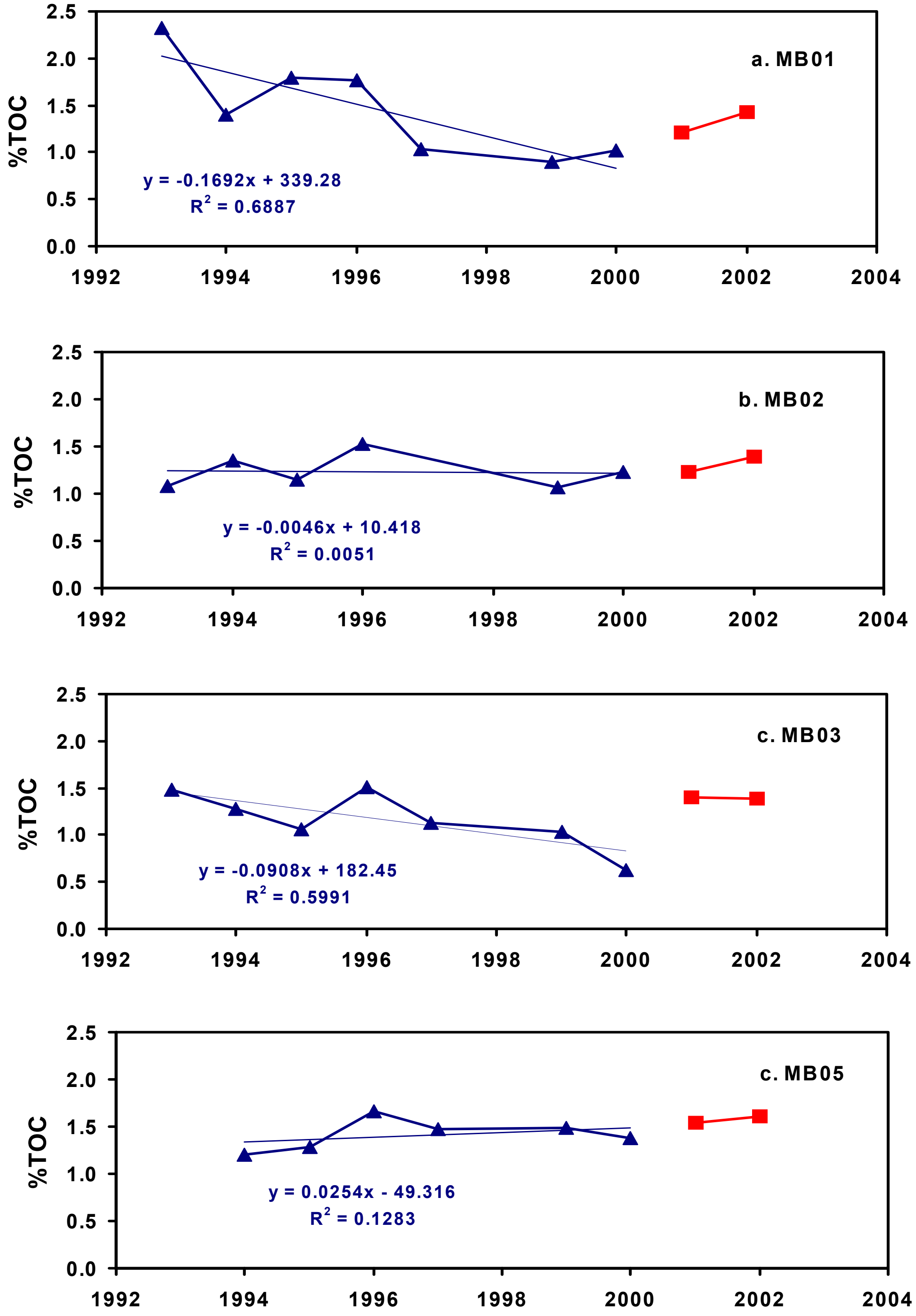


Figure 2. Organic carbon content of top 2 cm of sediment at Nearfield stations a.) MB01, b.) MB02, and c.) MB03 and Farfield station d.)MB05. Baseline data are blue triangles(▲), post-relocation are red squares(■). Regression lines show trend of decreasing TOC during baseline at MB01 and MB03.

Ratios of C/N provide insight into the "quality" or lability of organic matter, with higher values (relatively lower nitrogen content) indicative of lower quality. In these terms, our results would suggest that relatively low quality carbon was present in the nearfield sediments in 2002, after relatively high quality in 2001. If the higher quality carbon were derived from phytoplankton, a lag in deposition is suggested because very high levels of chlorophyll were observed in the water column of the nearfield from late 1999 through 2000, but more typical levels in 2001-2002. The high values are unexplained, but may be related to increased sediment drape observed on nearby hardgrounds in 2002 (Hecker, pers. com), which in turn may be related to the quiet winter season of 2001-2002. The origin of this drape is as yet undetermined.

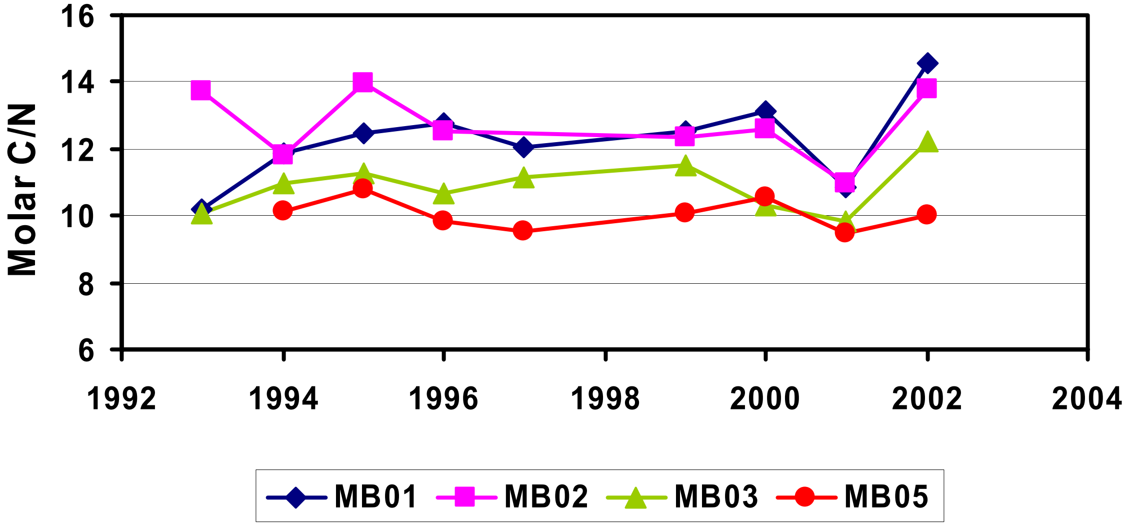


Figure 3. Molar TOC/TON for top 2 cm of sediment.

2.1.2 Sediment Pigments

In 2002, chlorophyll *a* content, measured as inventories over the top 5 cm of sediment, was well within the monitoring baseline (Fig 4.). Inventories were fairly uniform across the three nearfield stations as well as at the Farfield station and also consistent across surveys. Highest inventories in the nearfield , 7.9 µg cm^{-2}, were observed at MB03 in May, and lowest, 3.9µg cm^{-2}, were observed at MB01 in August and MB03 in October. At MB05, the high was 8.1 µg cm^{-2} in July and the low was 3.5µg cm^{-2} in October.

This evenness across stations and surveys contrasts with 2001, the first full year of outfall operation, when there were several instances of elevated concentrations in chlorophyll at the nearfield stations. Seasonal averages for the three nearfield stations were higher in 2001 compared to 2002 (8.3 µg cm^{-2} compared to 5.4 µg cm^{-2}), however this was driven largely by the few elevated values. For instance, at MB01, chlorophyll levels were generally low in 2001 until October, when we observed concentrations much higher than seen before at this station, although not higher than observed during the monitoring program (An inventory of 25.6 µg cm^{-2} was observed at MB02 in October, 1994.). These high concentrations were not observed at MB05, and at MB05, the 2001 seasonal average was lower than in 2002, 3.8 vs 6.1 µg cm^{-2}.

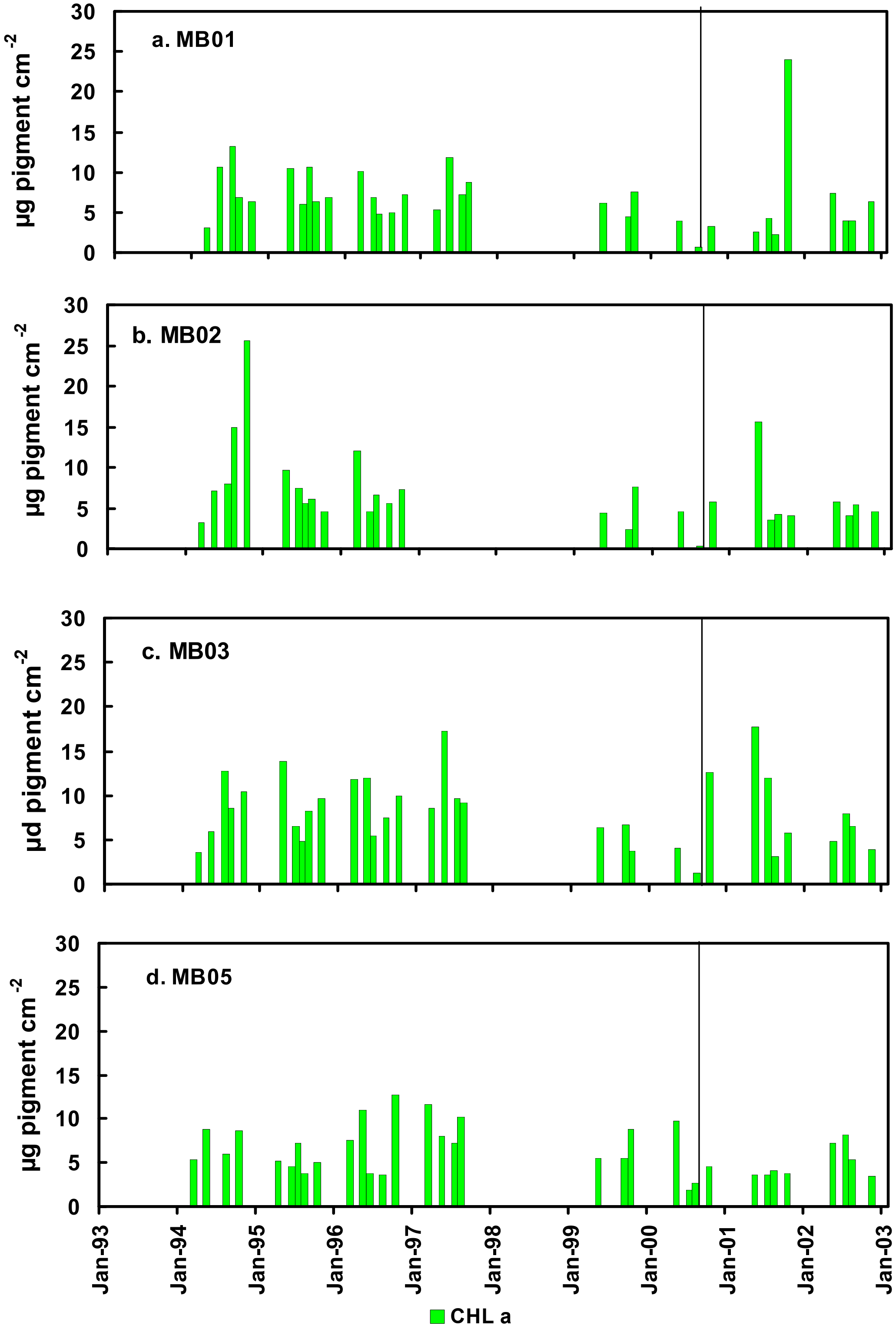


Figure 4. Chlorophyll *a* inventory for top 5 cm of sediment at Nearfield stations a.) MB01, b.) MB02,and c). MB03, and Farfield station c). MB05. Vertical lines mark the transition from baseline to post-relocation observations.

High sediment chlorophyll content in 2001 versus 2002 seemed to be consistent with trends in C/N, with both parameters suggesting more phytoplankton deposition in 2001. In 2002, chlorophyll content and carbon quality were lower, but TOC was higher. It is unclear what relationship these contrasting patterns have to regional versus potential outfall influences. In 2001, high sediment chlorophyll concentrations in the nearfield but not in the farfield might suggest an outfall influence. However, water column chlorophyll levels in 2001 were not particularly high, whereas they were quite high the previous year, before the outfall became operational. As suggested above, it is likely that the high sediment chlorophyll originated with this 1999-2000 bloom. In contrast, in 2002, sediment chlorophyll concentrations were lower and more typical of baseline, and did not indicate unusual inputs of fresh material, which corresponds to typical levels of water column chlorophyll in 2001-2002. In addition, sediment chlorophyll was similar across the region from the nearfield to Stellwagen, belying a local, outfall effect on this parameter.

2.2 Sediment Oxygen Demand

The baseline range for the seasonal average sediment oxygen demand for our three nearfield stations was 12.4 to 24.7 mmol m^{-2} d^{-1} with a grand mean across stations and years of 17.0 mmol m^{-2} d^{-1} (Fig. 5a). In 2002, seasonal average SOD ranged from 14.9 mmol m^{-2} d^{-1} at MB03 to 19.3 at MB01, and the average across the three stations was 16.7 mmol m^{-2} d^{-1}. Clearly observations in 2002 were well within baseline.

Highest rates for 2002 were observed at Station MB01. In fact, in May, sediment respiration of 21.3 mmol m^{-2} d^{-1} exceeded the baseline range for that month at that station, but did not exceed the entire range (Fig. 6a). A relatively high, but within baseline, rate was also observed at this station in August. This rate was influenced by the fact that one of our two experimental cores produced very high fluxes of oxygen and nutrients, whereas the other was quite typical. There were unidentified small tunicate-like organisms on the surface of this core that we believe were responsible for the high rates. In contrast to the high August rates, July rates were at the low end of the range for that month and in October were about average.

At MB02 and MB03, SOD was similar to that observed in 2001, with rates about average the baseline range in May and July, and at the low end of the range in August and October (Fig. 6b and c).

At farfield station MB05, seasonal average SOD was very typical of baseline (Fig 6d). 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 2002 rates ranged from 10.2 in October to 13.7 in July, and the seasonal average was 12.1 mmol m^{-2} d^{-1}.

Multiple factors influence SOD. The primary control in the nearfield continues to be temperature, which explains about 30% of the variability in rates of sediment respiration we observe. In Stellwagen basin, however, where bottom water temperatures vary much less over the season, temperature explains only about 10% of the variability in SOD. At this station, correlations between seasonal average sediment chlorophyll inventory over the top 5 cm of sediment and seasonal average SOD accounts for over 30% of the variability, whereas this correlation is insignificant for the nearfield stations.

Attempts to correlate SOD with parameters measured by other programs within the monitoring effort yielded variable results. These analyses should be considered as "rough" in the sense that we have compared variables measured at different frequencies, or at different but nearby stations, or have used averages over time or space. However, we did so in hopes of gaining some insight into the relative importance of various influences on SOD at individual stations.

We used infaunal abundance data for 1994-2001 from benthic stations close to our flux stations (NF21 for MB01, the average of NF10 and NF12 for MB02, and NF22 for MB03; data were obtained from the MWRA database) to compare to respiration rates. These data are collected in August of each year. When abundance, as number of individuals per grab, was compared to August rates of SOD, we found a strong correlation at only one of the three nearfield stations, Station MB01 ($r^2 = 0.78$). When SOD was averaged over the May-October season, the correlation at MB01 remained strong ($r^2= 0.75$), and became important at MB02 ($r^2=0.39$), but remained insignificant at Station MB03.

We also explored the relationship between annual average water column chlorophyll for the nearfield or the offshore area and SOD measured at our stations in those regions. For the nearfield, a strong relationship existed with seasonal average SOD at MB02 ($r^2 = 0.78$) and a weaker relationship existed at MB01 ($r^2 = 0.37$) but there was no correlation between the two parameters at either Station MB03 or MB05.

2.2.1 Contribution to Oxygen Drawdown in Bottom Water

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

However, the contribution of the biological consumption should not be discounted. The temperature effect noted above was most likely explained by the fact that oxygen consumption (respiration) in both the bottom water and the sediments is temperature-dependent. 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). In 2002, the May-Oct average SOD of 16.7 mmol m^{-2} d^{-1} (also a reasonable average for the baseline) translates to 0.05-0.1 mg L^{-1} d^{-1}, depending on the depth of the stratified layer used (5-10 meters).

2.3 Nutrient Flux

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

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

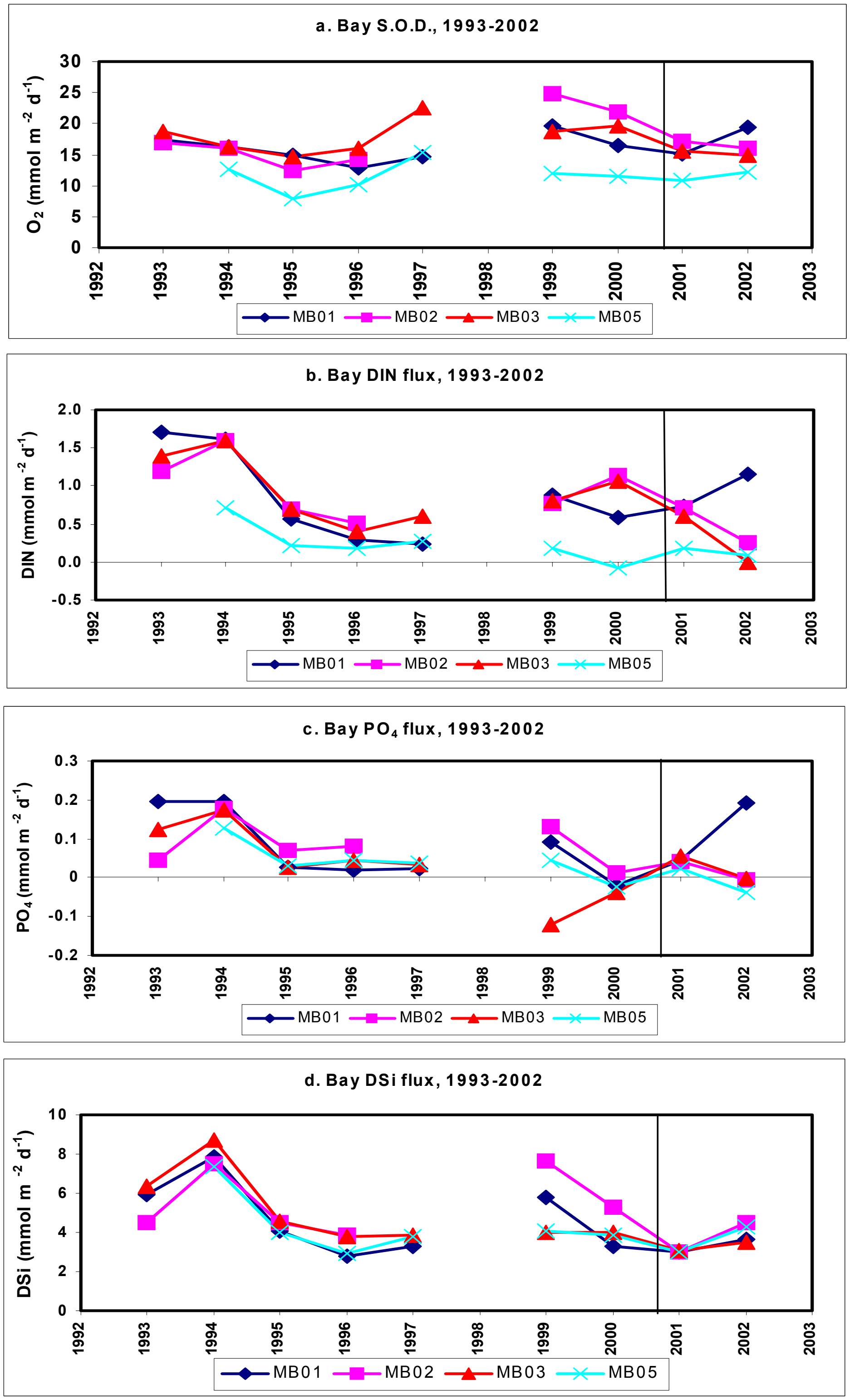


Figure 5. Seasonal (May-October) averages of a.) sediment oxygen demand (S.O.D.), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Massachusetts Bay stations in 1993-2002. The vertical lines mark the transition between baseline and post-relocation measurements.

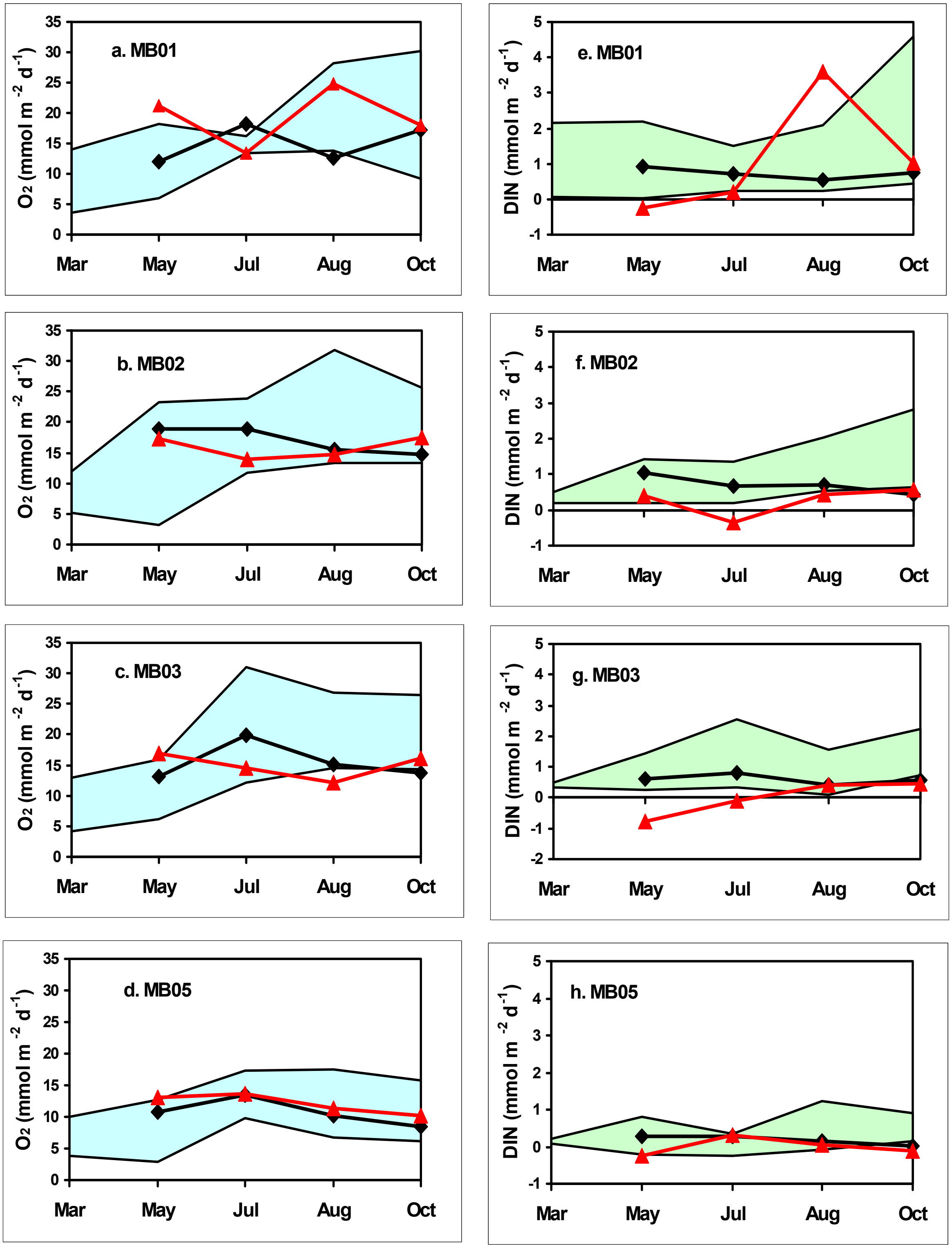


Figure 6. Sediment oxygen demand (O_2flux) and DIN flux for 2001 (black diamonds) and 2002 (red triangles) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations MB01, MB02, MB03, and MB05, respectively.

2.3.1 DIN

In 2002, rates of dissolved inorganic nitrogen (DIN) flux from nearfield sediments were in the low end of or lower than the baseline range (Fig 5b and 6e-h), and also lower than the previous (post-relocation) year (with one exception; see below). There were more frequent observations of DIN uptake than typical of the baseline period, and most often the uptake was of ammonium (NH_4^+) rather than nitrate (NO_3^-). In May at MB03, the DIN uptake rate was 0.8 mmol m^{-2} d^{-1}, resulting from an NH_4 uptake of 1.0 mmol m^{-2} d^{-1}. This was the highest uptake rate yet observed at these stations. At this time we also observed high rates of NH_4^+ uptake at MB01 (0.4 mmol m^{-2} d^{-1}) and virtually no flux of NH_4^+ at MB02.

The exception to the generally low fluxes of DIN noted above was a high rate of 3.4 mmol m^{-2} d^{-1} that was observed at MB01 in August (Fig. 6e). However, as noted for SOD, this was the result of a single experimental core having unusually high fluxes of all parameters; without it, the nearfield high was 1.0 mmol m^{-2} d^{-1} at MB01 in October.

The other somewhat anomalous observation for 2002 was that at MB02, most of the DIN flux, whether uptake or release, was comprised of NO_3. Nitrate also comprised a large part of the flux at MB03 in August and October. More typically, the larger component of the flux is NH_4^+.

As seasonal averages (Fig. 7), DIN fluxes at MB02 and MB03 were the lowest we have observed at these stations. Seasonal averages also illustrate the large amount of NH_4^+ uptake that occurred at Station MB03 during this year. Average rates at MB01 appear high, again due to the single anomalous core.

At MB05, DIN fluxes were among the lowest observed during baseline (Fig. 6h). During all surveys, some portion of the flux was characterized by uptake rather than release. In May and July, NH_4^+ was taken up by these sediments while NO_3^- was released. In August, the reverse was true: NO_3^- was taken up and NH_4^+ was released. In October, both NH_4^+ and NO_3^- were taken up. We must note, however, that these fluxes were weak and not very linear, with the highest rate being an uptake of 0.3 mmol NH_4^+ m^{-2} d^{-1} in May. Largest fluxes out of the sediment, occurring in July and August, were less than 0.1 mmol m^{-2} d^{-1}. The seasonal average was an uptake of about 0.1 mmol m^{-2} d^{-1} (Fig. 7d)

2.3.2 DIN Flux Contribution to Primary Productivity

Average annual primary production in the nearfield area in 2001 was about 477 g C m^{-2} y^{-1} (Oviatt, pers. com.), or 109 mmol C m^{-2} d^{-1}. Following Redfield considerations, this amount of production would require 16.4 mmol N m^{-2} d^{-1}. Using the seasonal average DIN flux from our three nearfield stations of 0.45 mmol m^{-2} d^{-1}, which would be an overestimate of the DIN flux because it does not include winter rates nor fluxes from other, less active sediment types, we find that benthic DIN flux represented less than 3% of phytoplankton requirements.

2.3.3 2.3.3 Phosphorus, Silica, and Urea

Like DIN fluxes, phosphorus and silica fluxes in the nearfield from 2002 were typical or lower than observed during baseline monitoring (Fig 8a-c for PO_4^-, e-g for DSi). Urea fluxes continued to be quite low and variable (data not shown).

For most of the season, we observed either very small fluxes of phosphate out of the sediments, or very low rates of uptake by the sediments. Again there was the one exception of an anomalously high efflux at MB01 in August, as noted for SOD and DIN fluxes. Rates ranged from an uptake of 0.06 mmol m^{-2} d^{-1} in July at MB01 to an efflux of 0.08 mmol m^{-2} d^{-1} in October, also at MB01 (omitting the high August value). It was not until October that we observed reasonable fluxes *out* of the sediments across all stations.

Overall for the year, again discounting the single high flux, phosphate fluxes were characterized by uptake rather than efflux. The only other year we have observed negative fluxes of phosphate at the majority of our stations was in 2000, before the bay outfall became operational.

Phosphate fluxes at the farfield station MB05 were also low compared to baseline (Fig. 8 d), with a very low value, or high uptake rate, of -0.12 mmol m^{-2} d^{-1} in July. As observed for the nearfield, fluxes were directed into the sediments from May through August, and only in October did we observe positive fluxes. Although an overall negative flux was also noted in 2000 at this station, the 2002 values were larger.

Nearfield dissolved silica fluxes in 2002 were intermediate to high as compared to baseline in May, but thereafter were in the low end of the range except at MB01, which had intermediate rates in October (Fig 8. e-g). Larger fluxes in the spring may have been the result of deposition of the 2001 fall or the 2002 winter-spring phytoplankton bloom. Fluxes ranged from a high of 6.1 mmol m^{-2} d^{-1} at MB02 in May to a low of 2.2 mmol $m^{-2}d^{-1}$ at MB01 in July. The anomalously high fluxes noted for other nutrients at MB01 in August were curiously not apparent in the silica fluxes. Silica fluxes at Station MB05 were typical of the station, and varied little over the season (Fig. 8h). Rates ranged from 3.6 mmol m^{-2} d^{-1} in October to 4.7 mmol m^{-2} d^{-1} in July. As was true throughout the entire baseline period, ratios of silica to nitrogen continued to be greater than the 1:1 ratio required by diatoms, implying that benthic fluxes of nutrients favor diatom growth.

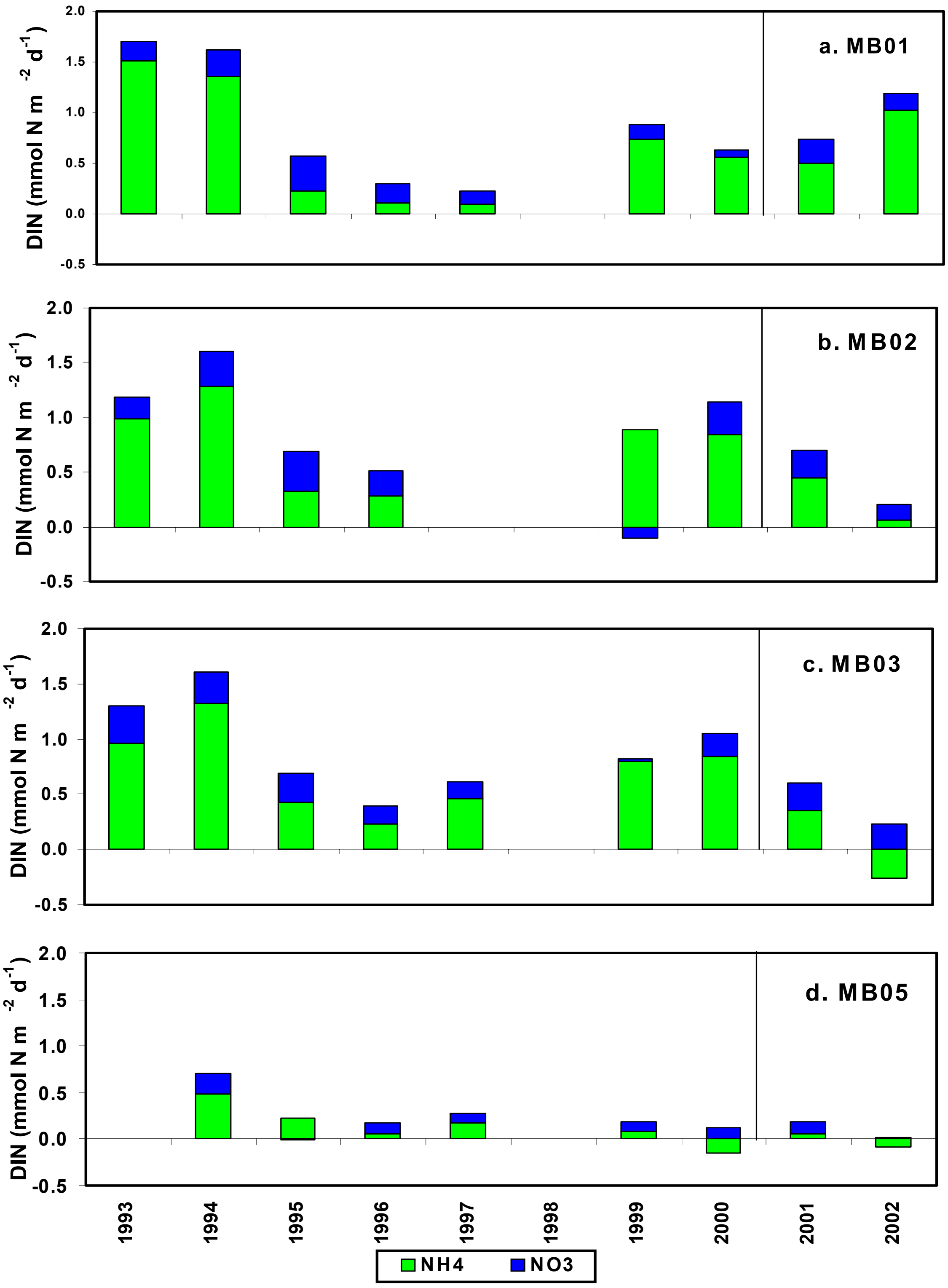


Figure 7. May-October seasonal average DIN flux from 1993-2002 at bay stations a.) MB01, b.) MB02, c.) MB03, d.) MB05. The vertical line marks the transition from baseline to post-relocation observations.

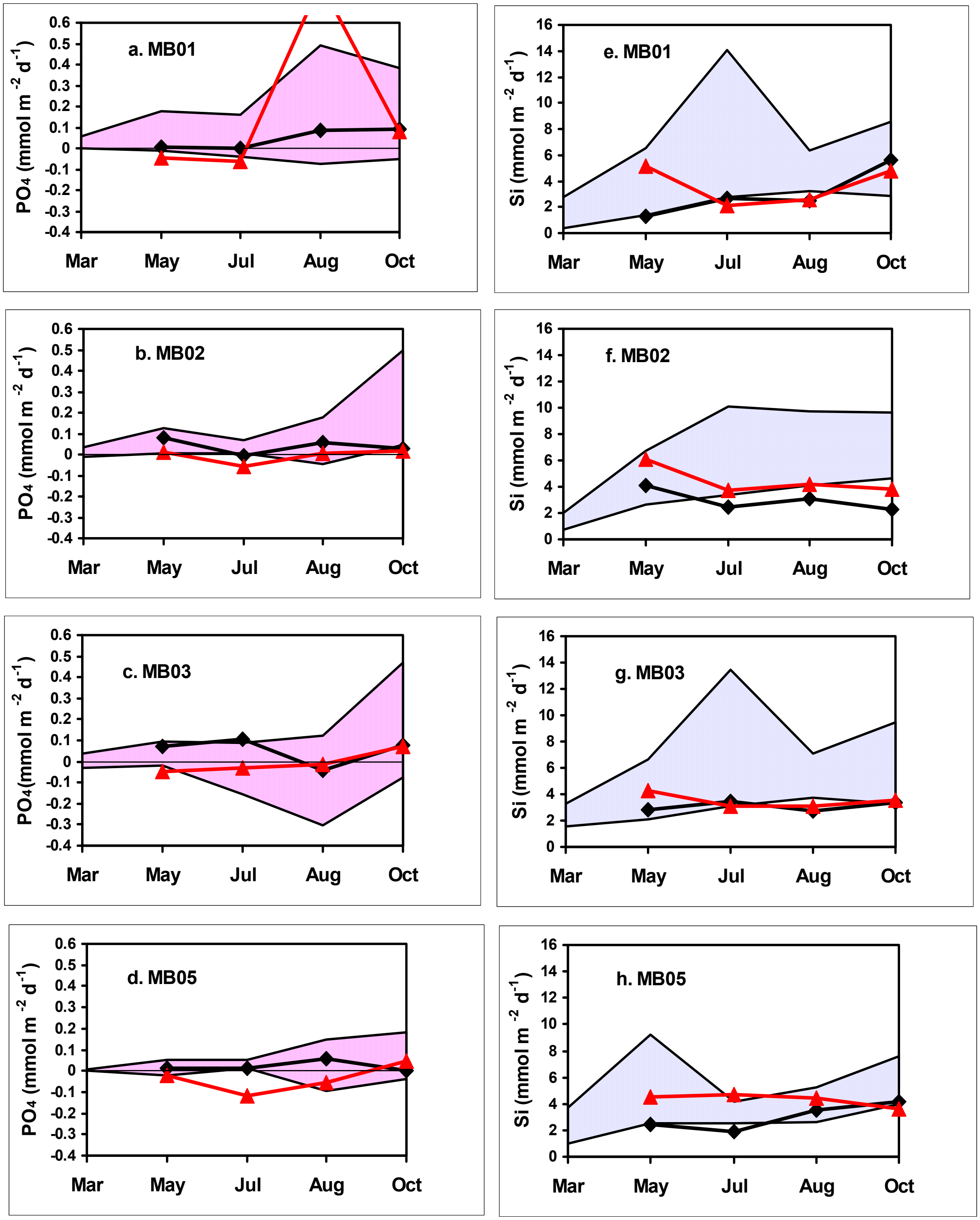


Figure 8. Phosphate and dissolved silica flux 2001 (black diamonds) and 2002 (red triangles) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO_4 flux and panels e-h depict DSi flux for stations MB01, MB02, MB03, and MB05, respectively.

2.4 Denitrification

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

Denitrification rates in 2002 were within baseline ranges (Fig. 9). A high rate of 5.6 mmol N m^{-2} d^{-1} was observed at MB02 in May, which was the second highest rate ever measured at either of these two stations, and the low rate for this year was 2.9 mmol N m^{-2} d^{-1}, also at MB02, in October. Denitrification rates at MB03 were almost identical in May and October at 3.2 mmol N m^{-2} d^{-1}.

We have previously noted that denitrification rates at these two nearfield stations are often of similar and sometimes greater magnitude than the DIN fluxes. For the baseline period, we calculated that denitrification accounted for about 65% of the total N flux in the soft sediments of Massachusetts Bay. In 2001, that percentage was higher, about 80% of total N flux. In 2002, denitrification rates, as given above, were considerably higher than DIN fluxes, which were 0.4 and 0.6 mmol m^{-2} d^{-1} at MB02, and –0.8 mmol m^{-2} d^{-1} and 0.46 mmol m^{-2} d^{-1} at MB03 in May and October, respectively. Denitrification, therefore, accounted for between 83% and 100% of the total nitrogen flux from the sediments (at these two stations) in 2002. The increase in the relative importance in denitrification as compared to DIN flux that we have observed recently is driven by decreases in DIN flux rather than any change in denitrification.

2.5 Redox

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

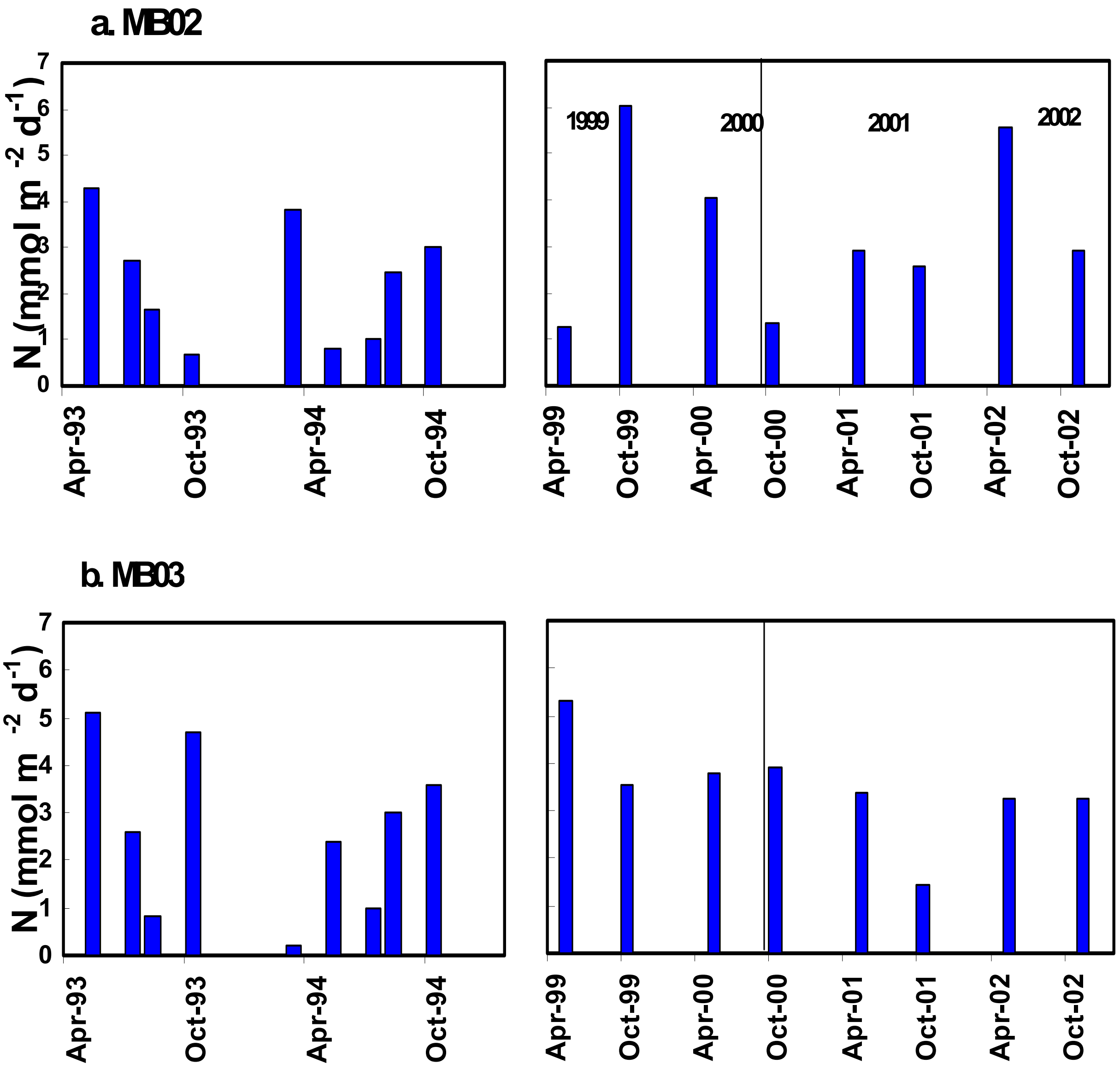


Figure 9. Denitrification at two nearfield stations, a.) MB02, and b.) MB03. Denitrification measurements were not conducted in Massachusetts Bay in 1995-1998. The vertical line marks the transition between baseline and post-relocation of the outfall.

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 endproducts of anaerobic process are stored in the sediments and not reoxidized. However, when these endproducts 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 10). 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.

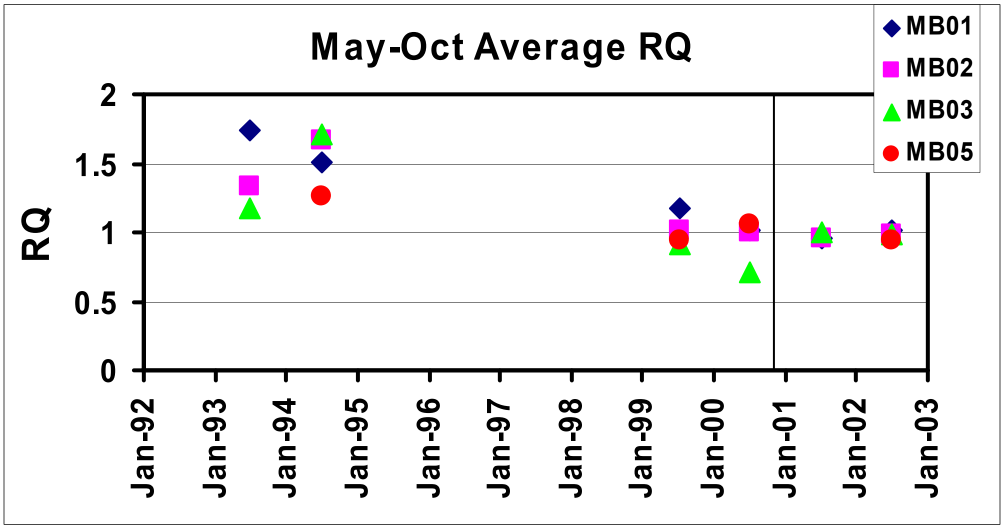


Figure 10. Seasonal (May-October) average respiratory quotients for Nearfield stations MB01, BM02, MB03, and Farfield station MB05 from 1993-2002. The vertical line marks the transition from baseline to post-relocation observations.

2002 was typical of the period that began in 1999. Seasonal averages at all four stations were very close to 1.0. There was a tendency for RQs to be less than 1.0 in May and July; in fact, a very low RQ of 0.5 was observed at Station MB02 in July. In August and October, RQs were greater than 1.0, with a high value of 1.5 at MB02 in October.

2.5.2 Eh profiles

Oxidation-reduction potential measured as Eh in 2002 continued to be indicative of highly oxic conditions in sediment cores from Massachusetts Bay in 2002. We have not observed any tendency towards decreased oxygen levels in these sediments in the two years post-relocation of the outfall. Values continue to be well above those that would indicate the presence of dissolved sulfides (-100 to –200 mV), and in fact we did not detect sulfides in these cores in July or August during our porewater measurements (data not shown).

Profiles of Eh in 2002 were very similar to those from the previous year, although highest and lowest values occurred at different times. In 2001, all three nearfield stations showed highest Eh values in July.

Lowest values occurred in August, and this was true for Station MB05 as well. In 2002, there was less consistency in the seasonal pattern across stations (Fig. 11). Lowest values for the season occurred in August only at Station MB05; for the nearfield stations they tended to occur in October. Highest values occurred in May at Stations MB02 and MB05, in August at MB01, and July for MB03.

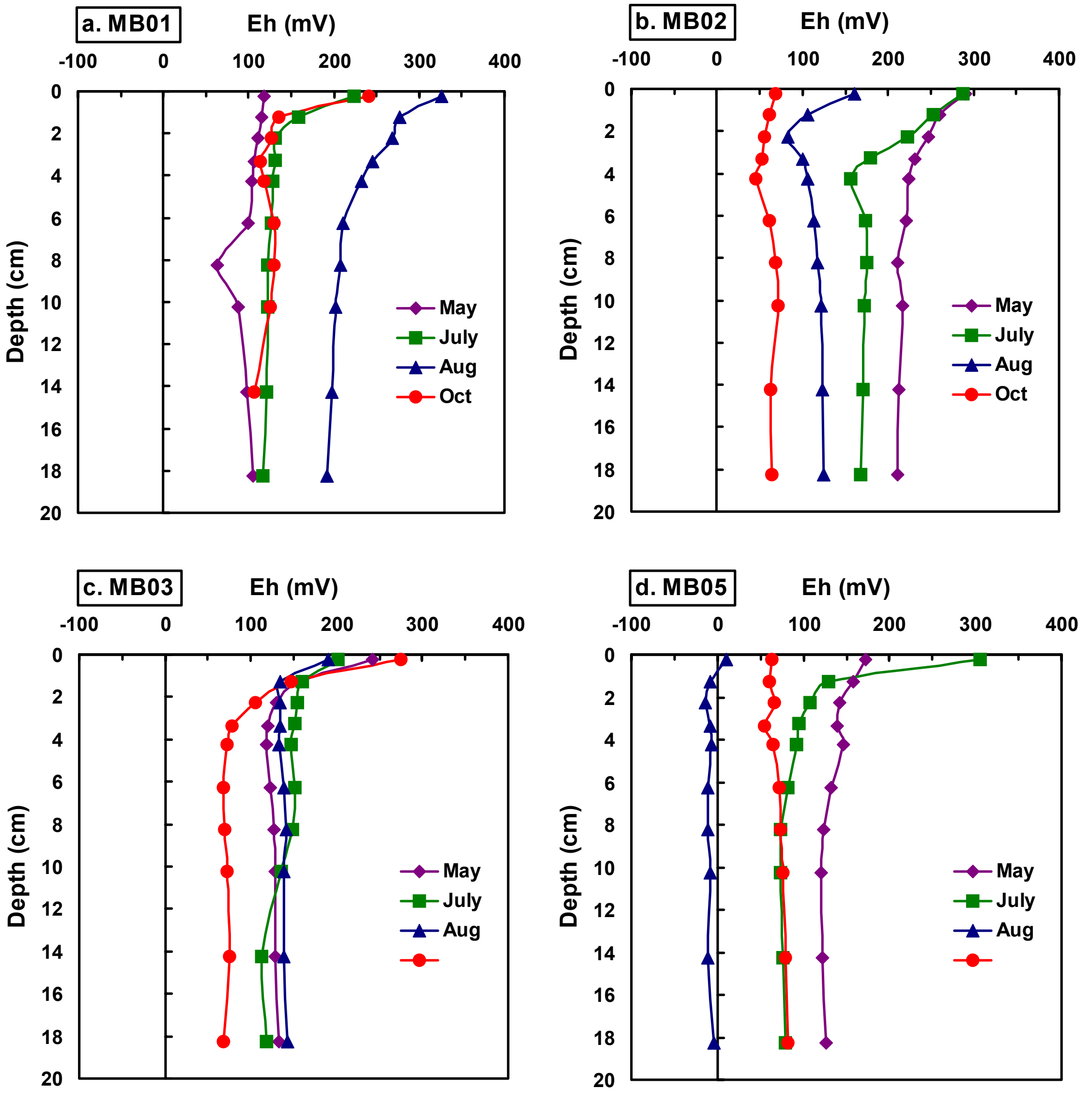


Figure 11. Eh profiles for May through October, 2002, from Nearfield stations a.) MB01, b.) MB02, c.) MB03, and Farfield station d.) MB05.

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 suggested that oceanic inputs of nutrients exceeded those from the land (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. In the second year, similar reductions were reported, resulting in an overall reduction of 63% for the two year period (Taylor, 2003). Within the DIN pool, the largest change was in the proportion contributed by NH_4^+, which decreased from 20% during baseline to 5% two years post diversion. Large reductions were also observed in phosphorus concentrations (31% in DIP for both the one and the two year period). For some parameters, large changes in the first year were not repeated at all locations in the harbor in the second year. 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 two year period, the decrease in chlorophyll *a* was 19%, in particulate carbon was 29% , and the increase in water clarity was 5%.

Four harbor stations have been repeatedly sampled throughout the monitoring period (Figure 12). Two stations, BH02 and BH03, are located in the northern section of Boston Harbor and have been sampled routinely since September, 1991. The other two stations, BH08A and QB01, are in the southern harbor, and have been visited since 1995. Through 1997, these stations were visited in March, May, July, August, and October. After that time, the March surveys were discontinued.

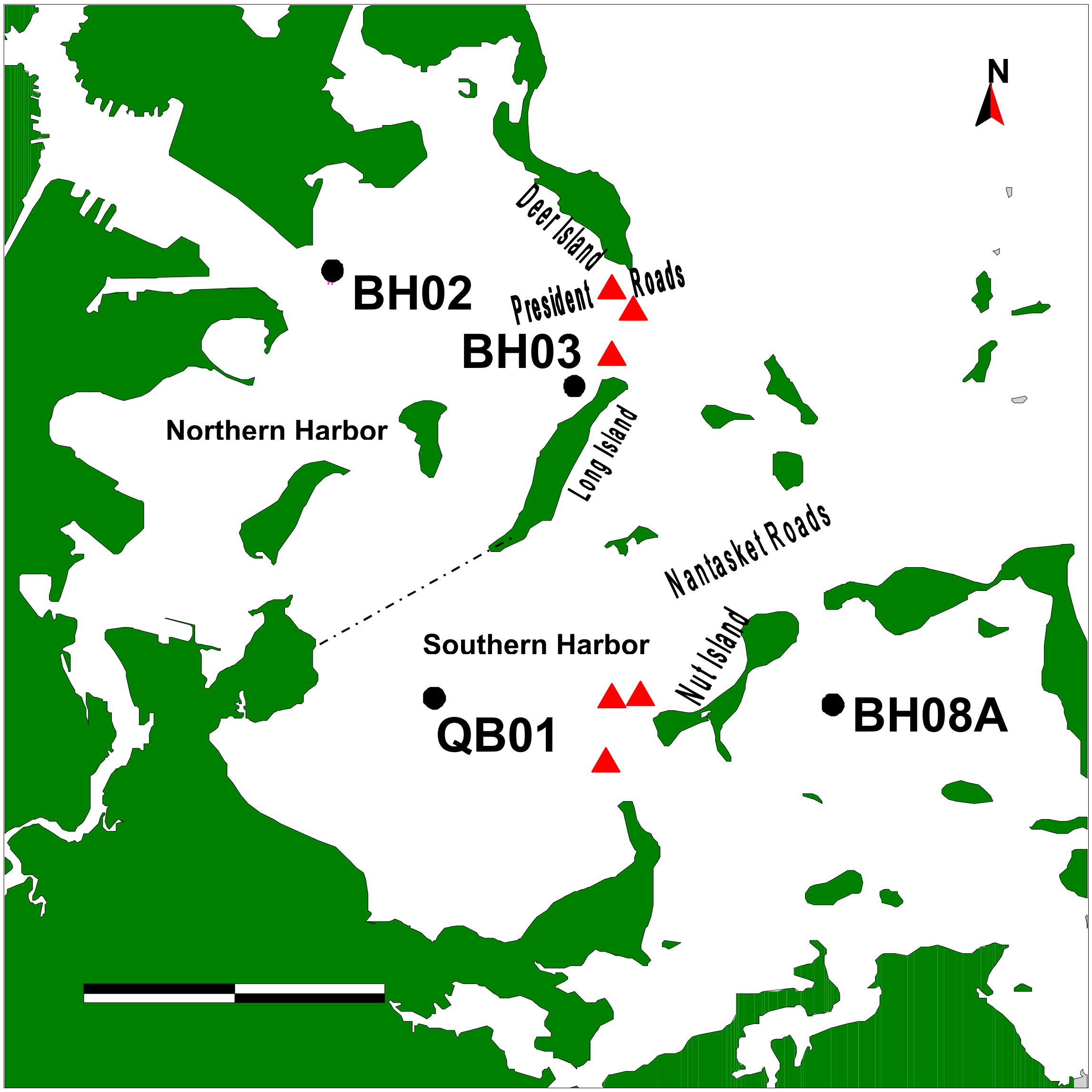


Figure 12. Locations of four Boston Harbor stations. Harbor outfalls, no longer in use, are marked by triangles (▲).

3.1 Organic Matter Loading

3.1.1 Total Organic Carbon

Organic matter loading to Boston Harbor decreased significantly over the baseline monitoring period due to the cessation in late 1991 of sludge disposal in the harbor and with subsequent improvements in sewage treatment. Accordingly, we observed a decrease in the organic matter content of sediments in the Harbor over the baseline period as these direct inputs decreased and carbon stores were metabolized. After the MWRA outfall was relocated offshore, we have continued to observe a decline in sediment TOC as stores continue to be mined. Further reductions in organic matter loading resulting from lower primary production in the harbor post-relocation may also contribute to declining sediment TOC.

In 2002, seasonal averages of total organic carbon (TOC) continued to decrease at all four harbor stations, although by a relatively small increment. After 1999, decreases in TOC have slowed, and variability between and among stations has decreased. The very high percentages (over 4%) that were observed at various times and stations in the harbor before 1999 have not recurred. It appears that the harbor sediments are “winding down”. In 2002, seasonal means ranged from 1.8% at BH02 to 2.5% at BH03, down from 2.0% and 2.6% respectively in 2001 (Fig. 13). Both the high and the low value were observed in July; the low was 1.6% at BH02 and the high was 2.4 at BH08A.

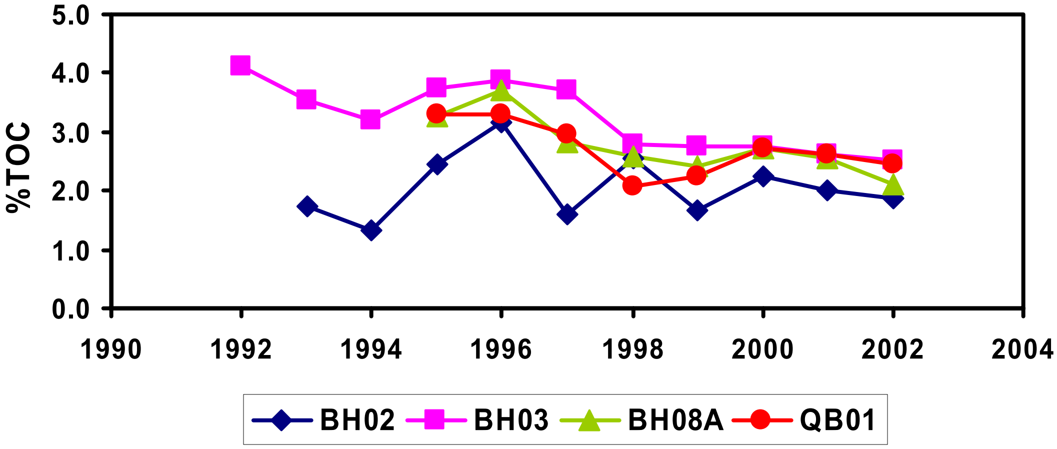


Figure 13. Seasonal average TOC (% dry weight) for top 2 cm of sediment.

3.1.2 Sediment Pigments

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

In 2002, inventories of chlorophyll and its breakdown pigment phaeophytin were well within baseline ranges. For chlorophyll *a* alone, inventories for the top 5 cm of sediment ranged from 7.0 µg cm^{-2} at BH08A in July to 36.4 µg cm^{-2} at BH02 in May. In terms of seasonal averages, BH02 had the highest inventory of 28.9 µg cm^{-2}. Lowest inventories were observed at Station BH03, which had a seasonal average of 9.3 µg cm^{-2}.

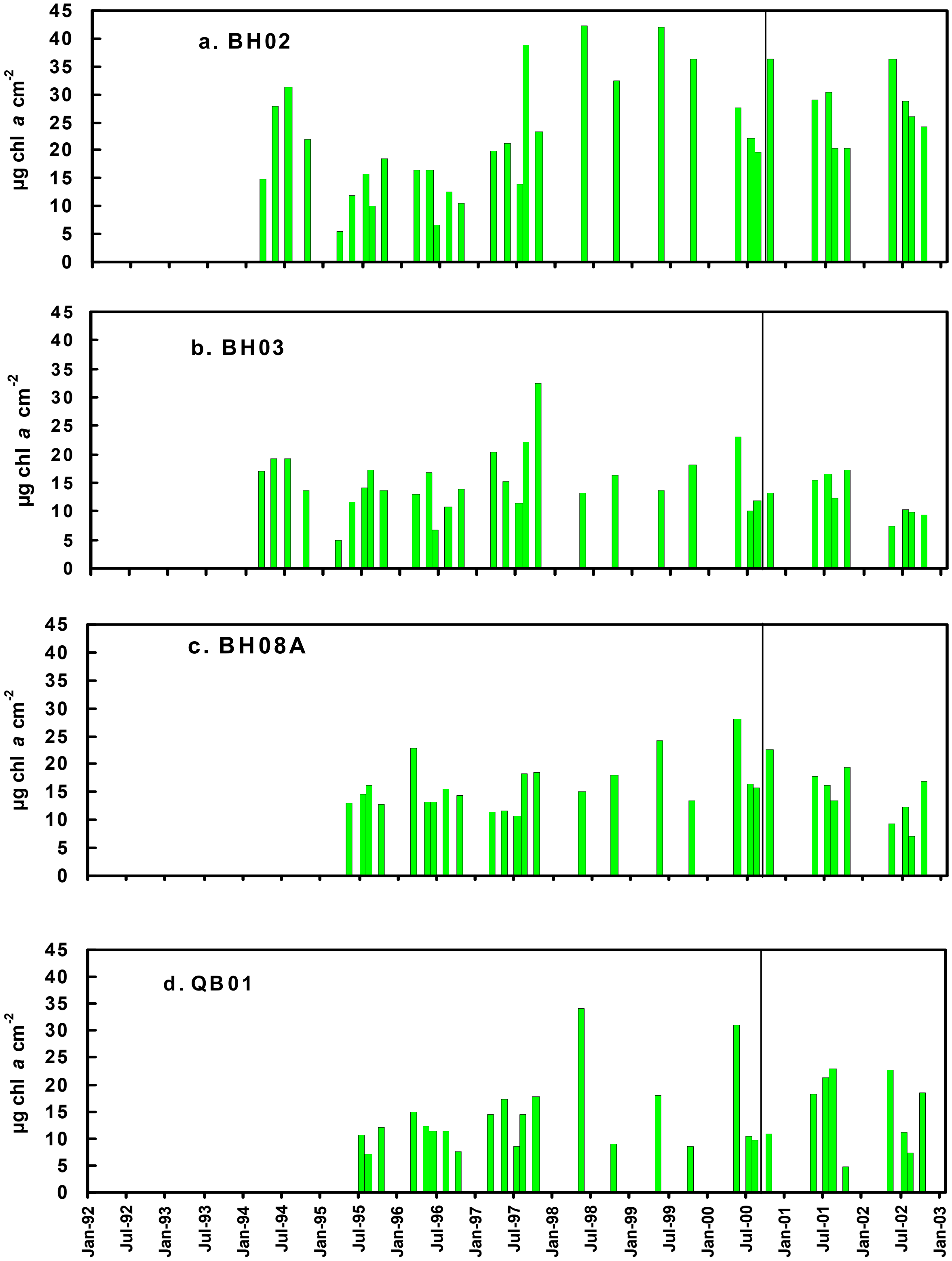


Figure 14. Chlorophyll *a* inventory for top 5 cm of sediment at northern harbor stations a.) BH02, b.) BH03, and southern harbor stations c.) BH08A, d.) QB01. The vertical line marks the transition from baseline to post -relocation observations.

The high values for Station BH02 in the northern harbor were consistent with levels observed at this station since 1997 (Fig. 14a). For 2002, peak values at this station were observed in May, when profiles (Fig. 15a) revealed elevated levels of chlorophyll through the top 4 cm of sediment. It is unclear whether this pattern reflected recent deposition or *in situ* production.

In contrast, chlorophyll inventories at the other northern harbor station, BH03, were among the lowest for the station (Fig 14b), and the May-October seasonal average of 9.3 µg cm^{-2} was the lowest observed at this station. Inventories were similar across the sampling season, and profiles were flat (Fig 15b) as compared to those at BH02. Peak levels at this station were only 10.3 µg cm^{-2}.

At the southern harbor station BH08A (Fig. 14c) the range of chlorophyll content we observed over the 2002 season was larger than at BH03, but the seasonal average of only 11.4µg cm^{-2} was the lowest seen at this station as well. At QB01, the seasonal average of 15 µg cm^{-2} was typical for the station, with peaks in sediment chlorophyll levels in May and October and relatively low values in July and August (Fig 14d). The peaks showed up well in the profiles, with concentrations above 5µg cm^{-3} through 3 cm sediment depth in May, and a large surface peak of over 11 µg cm^{-3} in October (Fig. 15d).

It is interesting to note the contrast between patterns and levels of sediment chlorophyll between BH03 and BH08A, the two stations that have typically been characterized by the presence of amphipod mats, with BH02 and QB01, the two stations without mats. The shapes of the chlorophyll profiles from Stations BH02 and QB01, which show near-surface peaks in chlorophyll (Fig 15a and 15d), as well as direct observations of benthic diatoms on the sediment surface, suggest that some of the chlorophyll we observe at these two stations is due to *in situ* production. Lower levels at the other two stations are most likely the result of grazing. Profiles here show little evidence of near-surface peaks in pigment (Fig. 15b and 15c). Reduced chlorophyll at these two stations in 2002, however, is curious because we have noticed a decline in the amphipod mats during this year and the previous one, which we would expect to lessen grazing pressure. Lower chlorophyll in 2002 could alternately be related to less *in situ* production, caused by higher turbidity (Taylor, pers. com.) in the absence of water column filtration by the benthos.

3.2 Sediment Oxygen Demand

The decreasing trend we have observed in sediment oxygen demand (SOD) in Boston Harbor continued in 2002 (Fig. 16a and 17a-d). Three of the four harbor stations, BH02, BH03, and BH08A showed clear decreases whereas the fourth station, QB01 showed no change. At the three stations where a decrease was observed, the seasonal average rates were the lowest ever observed, and were similar, ranging only from 23 mmol m^{-2} d^{-1} at BH03 to 27 mmol m^{-2} d^{-1} at BH08A. For the first time, the lowest SOD was observed at Station BH03, a remarkable change in the station that had by far the highest SOD in the early years of the monitoring period. In another “first”, the highest SOD was observed at the Quincy Bay station QB01, where the average seasonal rate was 35 mmol m^{-2} d^{-1}.

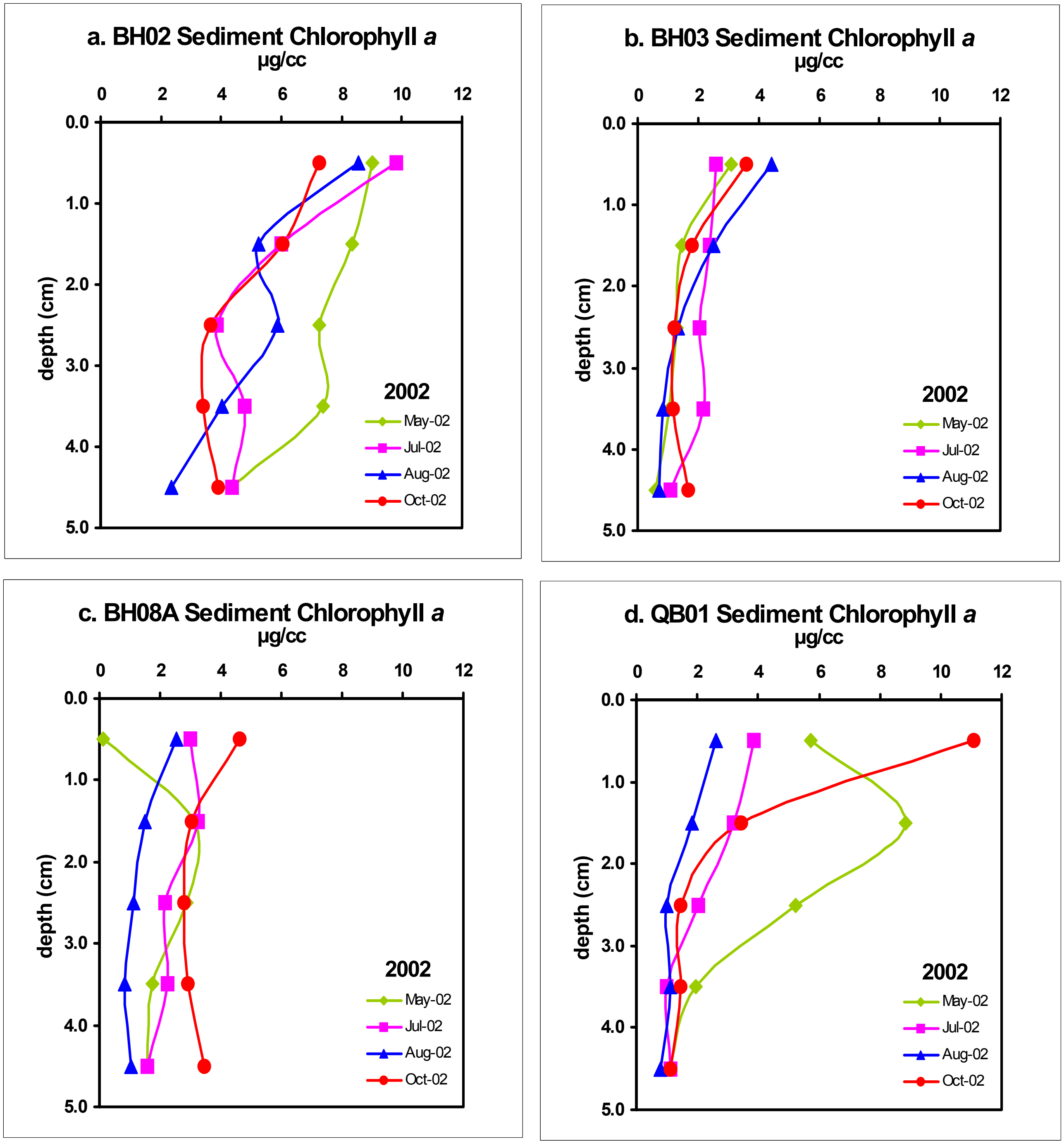


Figure 15. Profiles of chlorophyll *a* in top 5 cm of sediment at Boston Harbor stations a.) BH02, b.) Bh03, C.) Bh08A, and d.) QB01 showing differences between Stations BH02 and QB01 compared to BH03 and BH08A.

The largest drop was observed at Station BH08A. SOD at all four sampling times was well below the baseline range, and the seasonal average represented a drop of over 50% from the previous year. This change is most likely related to the apparent decline of the amphipod mat, as we have noted in recent years at BH03.

Very strong seasonal patterns in SOD were present at Stations BH02 and QB01 in 2002, with temperature explaining 67% and 77% of the variability at these stations, respectively. When all years are combined, the relationship with temperature explains just under 30% of the variability at each of these two stations. A strong relationship with temperature was also observed at Station BH08A in 2002, where it accounted for nearly 40% of the variability. However the long term relationship at this station was much weaker, explaining only 15%. At BH03 the temperature relationship in 2002 was weak, only 16%, whereas the long-term relationship was 32%. Again we see similarities in the patterns observed at Stations BH02 and QB01, whereas BH03 and BH08, where biology plays a key role, patterns are less consistent.

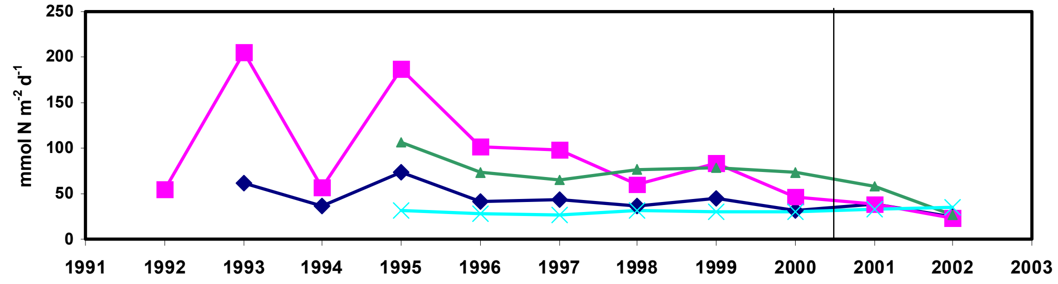
Except in restricted embayments, the harbor is well flushed by tidal mixing, such that even during years that experienced extremely high levels of SOD (i.e. 1993 or 1995), we did not observe hypoxia at any of our stations. The decreasing rates of sediment respiration we have observed would result in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

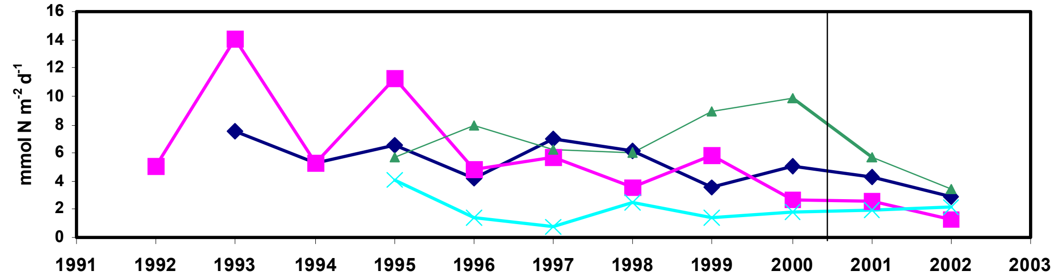
3.3 Nutrient Fluxes

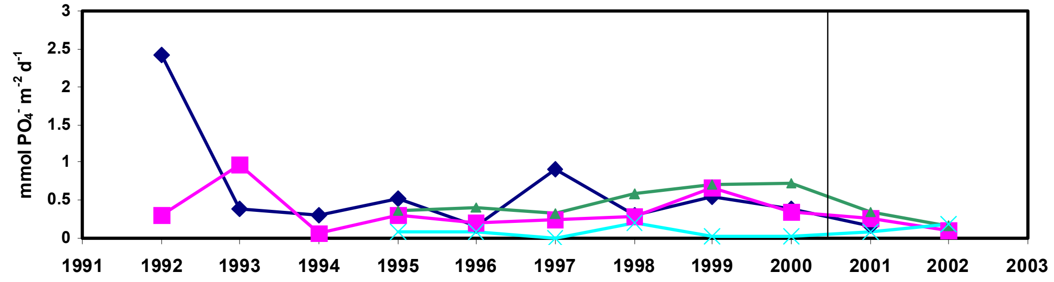
Like sediment respiration, benthic fluxes of DIN, phosphate and silica (Fig 16 b-d) have all decreased at stations BH02, BH03, and BH08A. In contrast, there has been little change at Station QB01. The large variability we observed from station to station and year to year early in the monitoring program has quieted, 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

Trends in DIN fluxes have followed those for SOD throughout the monitoring program, and 2002 was no exception. Seasonal average DIN fluxes in 2002 were the lowest ever observed at the same three stations where SOD was also the lowest: BH02, BH03, BH08A (Fig 16b). At QB01, there was little change from previous years. Seasonal averages ranged from a low of 1.3 mmol m^{-2} d^{-1} at BH03 to a high of 3.4 mmol m^{-2} d^{-1} at BH08. 2002 marks the first year that DIN fluxes at Station BH03 were the lowest of the four stations, again illustrating the dramatic changes that have occurred at this site over the monitoring period.


a. Harbor SOD, 1992-2002


b. Harbor DIN flux, 1992-2002


c. Harbor PO₄ flux, 1992-2002

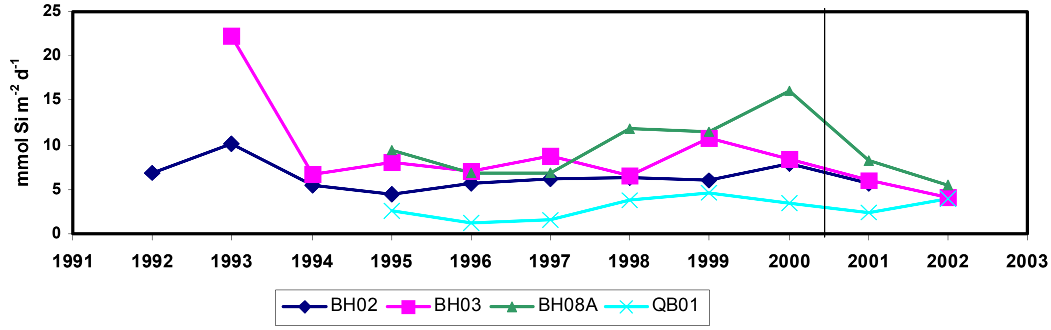

d. Harbor DSi flux, 1993-2002

Figure 16. Seasonal (May-October) averages of a.) sediment oxygen demand (SOD), b.) DIN flux, c.) PO4 flux, and d.) dissolved silica flux for Boston Harbor stations in 1993-2002. The vertical lines mark the transition between baseline and post-relocation observations.

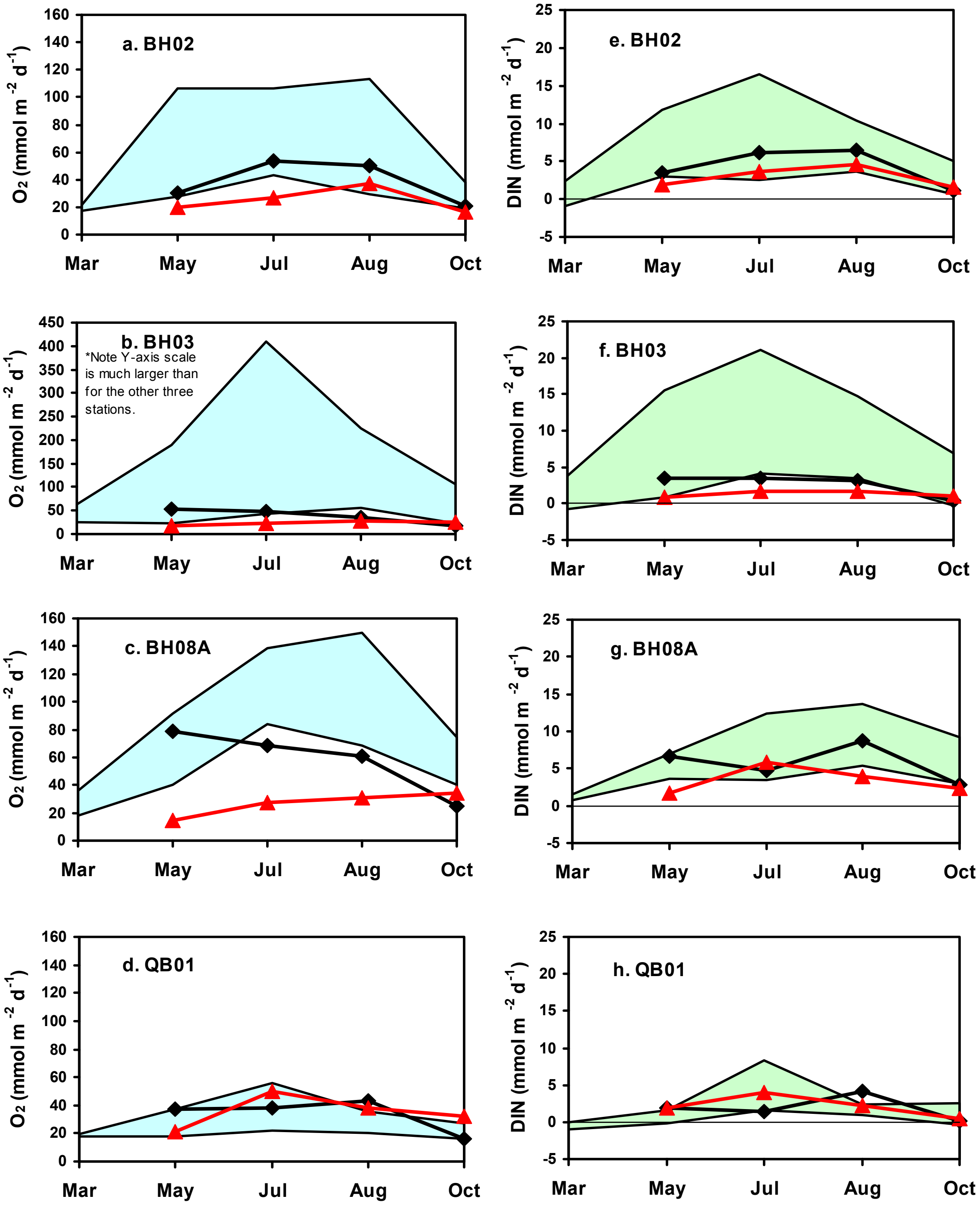


Figure 17. Sediment oxygen demand (O_2flux) and DIN flux for 2001 (♦) and 2002 (▲) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D. and panels e-h depict DIN flux for stations BH02, BH03, BH08A, and QB01, respectively.

Highest rates were observed in July and August, peaking at 5.9 mmol m^{-2} d^{-1} at BH08A in July (Fig 17 e-h). Lower rates were observed in May and October, with a low of 0.5 mmol m^{-2} d^{-1} occurring at QB01 in October. This seasonal pattern is typical for the harbor and in this year produced very strong relationships with temperature at all four station. Temperature explained over 59% at QB01 up to nearly 100% at BH03, with the other two stations both at about 85%. When viewed over all years, this relationship explains between 30 and 55% of the variation.

The major component of the DIN flux in 2002 was NH_4^+. On only one occurrence was NO_3^- the major component, making up 72% of the flux at Station BH03 in October. For the rest of the stations and surveys, NO_3^- comprised less than 40% of the flux. For station BH03 at least, this marks a departure from the very high NO_3^- contribution to the fluxes observed while the amphipod mat was present and is another indication of its decline.

3.3.2 DIN 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 450 g C m^{-2} y^{-1} (Oviatt, pers. com.). This rate equates to 103 mmol C m^{-2} d^{-1}, which by Redfield considerations, would require about 16 mmol N m^{-2} d^{-1}. Seasonal average DIN flux for 2002 across our four stations was 2.5 mmol N m^{-2} d^{-1}, which would meet about 15% of phytoplankton requirements. A similar calculation shows that about 15% of P requirements would also be met by benthic recycling. There are several caveats on this calculation, including the difference in years and annual versus seasonal averages of rates. However, errors around this estimate are of little consequence because, even though the direct input of sewage nutrients to the harbor has ceased, oceanic inputs, including some sewage influence from the new disposal location, together with remaining terrestrial inputs, still exceed the needs of primary production.

3.3.3 Phosphate and Silica

Fluxes of phosphate in 2002 were mostly within the low end of the baseline range, and similar across all stations (Fig. 18 a-d). Highest and lowest rates during the year were observed at Station BH02, ranging from 0.6 mmol m^{-2} d^{-1} in July to an uptake of less than 0.1 mmol m^{-2} d^{-1} in October. Seasonal averages were quite similar across all stations, ranging from only 0.10 mmol m^{-2} d^{-1} at BH03 to 0.18 mmol m^{-2} d^{-1} at QB01 (Fig. 16 c). These averages were among the lowest observed for Stations BH02, BH03, and BH08A, but among the highest for QB01.

PO_4 fluxes are controlled by a combination of biological and chemical factors, and therefore do not always correlate well with temperature. For example, at BH02, which often has quite reducing sediments, the regression with temperature for all years yields an r^2 of only 0.01. Taking 2002 alone, however, a much stronger seasonal pattern was apparent, such that temperature explained nearly 70% of the variability in observed PO_4 fluxes. This relationship also varies with station, but was in general stronger in 2002 than for all years combined. In 2002, temperature explained from 34% at QB01 to over 90% at BH08A of the variability in PO_4 fluxes.

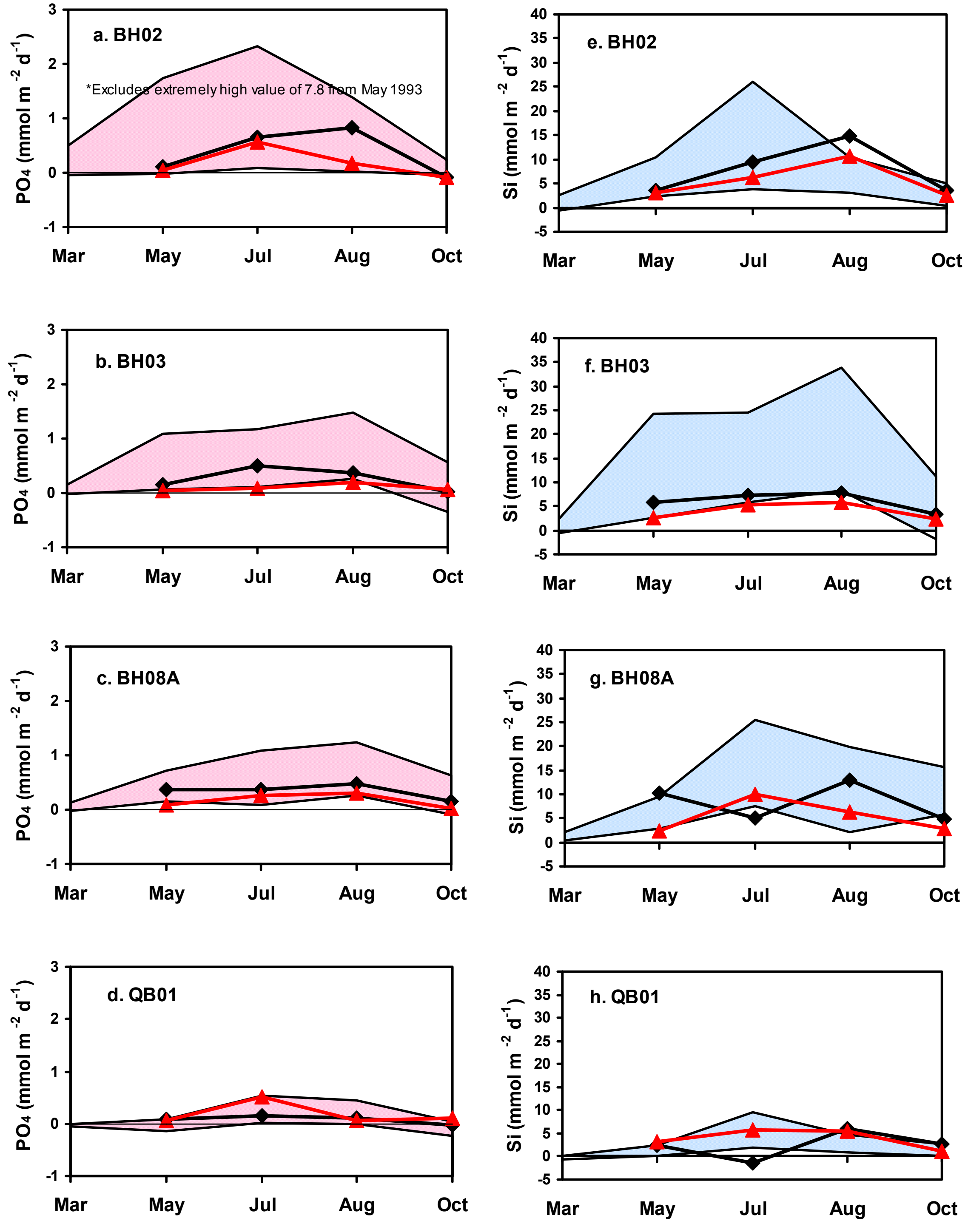


Figure 18. Phosphate (PO4) and dissolved silica (DSi) flux for 2001 (♦) and 2002 (▲) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO4 and panels e-h depict DSi flux for stations BH02, BH03, BH08A, and QB01, respectively.

Silica fluxes followed a similar pattern to that for the other nutrient fluxes in 2002. Fluxes at BH02, BH03, and BH08A were in the low end of the baseline range (Fig 18 e-g), resulting in seasonal averages among the lowest for these stations . Seasonal averages ranged from 4.1 mmol m^{-2} d^{-1} at BH03 to 5.6 mmol m^{-2} d^{-1} at BH02, and included individual measurements as low as 2.4 mmol m^{-2} d^{-1} at BH03 in October and BH08A in May and as high as 10.6 mmol m^{-2} d^{-1} at BH02 in August (Fig 16d). Fluxes at BH02 and BH03 were remarkably similar to those of the previous year. At QB01 Si fluxes were near the high end of the baseline range, with a low of 3.2 mmol m^{-2} d^{-1} in May and high of 5.8 mmol m^{-2} d^{-1} in July. The seasonal average at this station, though similar to the other harbor stations, was among the higher rates observed here. Si fluxes often show a seasonal pattern, and in 2002, as we have noted for the other nutrients, it was strong. In this year, temperature could account for between 70% and 95% of the variability in Si fluxes.

3.4 Denitrification

In 2002, rates of denitrification at the two harbor stations where it is measured, BH02 and BH03, were within the ranges observed during baseline monitoring, and continued the trend in these measurements that we have seen over the last four years (Fig. 19) At BH03, denitrification continued to decrease from the very high rates observed during baseline, with a station high rate this year of 3.5 mmol m^{-2} d^{-1} in May to essentially no flux at this site in August. The seasonal average was 1.9 mmol m^{-2} d^{-1}, which was about half the rate of the previous year and continued the trend of a steep decrease from very high rates observed in 1999. At BH02, the seasonal average of 5.0 mmol m^{-2} d^{-1} was similar to rates observed consistently at this site since 1999, although slightly lower. It included a relatively high flux in May of 9.0 mmol m^{-2} d^{-1} and a low of 1.9 mmol m^{-2} d^{-1} in October. As observed for the first time in 2001, denitrification rates at BH02 exceeded those at BH03.

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 2002 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, oceanic inputs remain the overwhelming input to the system, and decrease the N sink provided by denitrification to less than 10% of total nitrogen inputs.

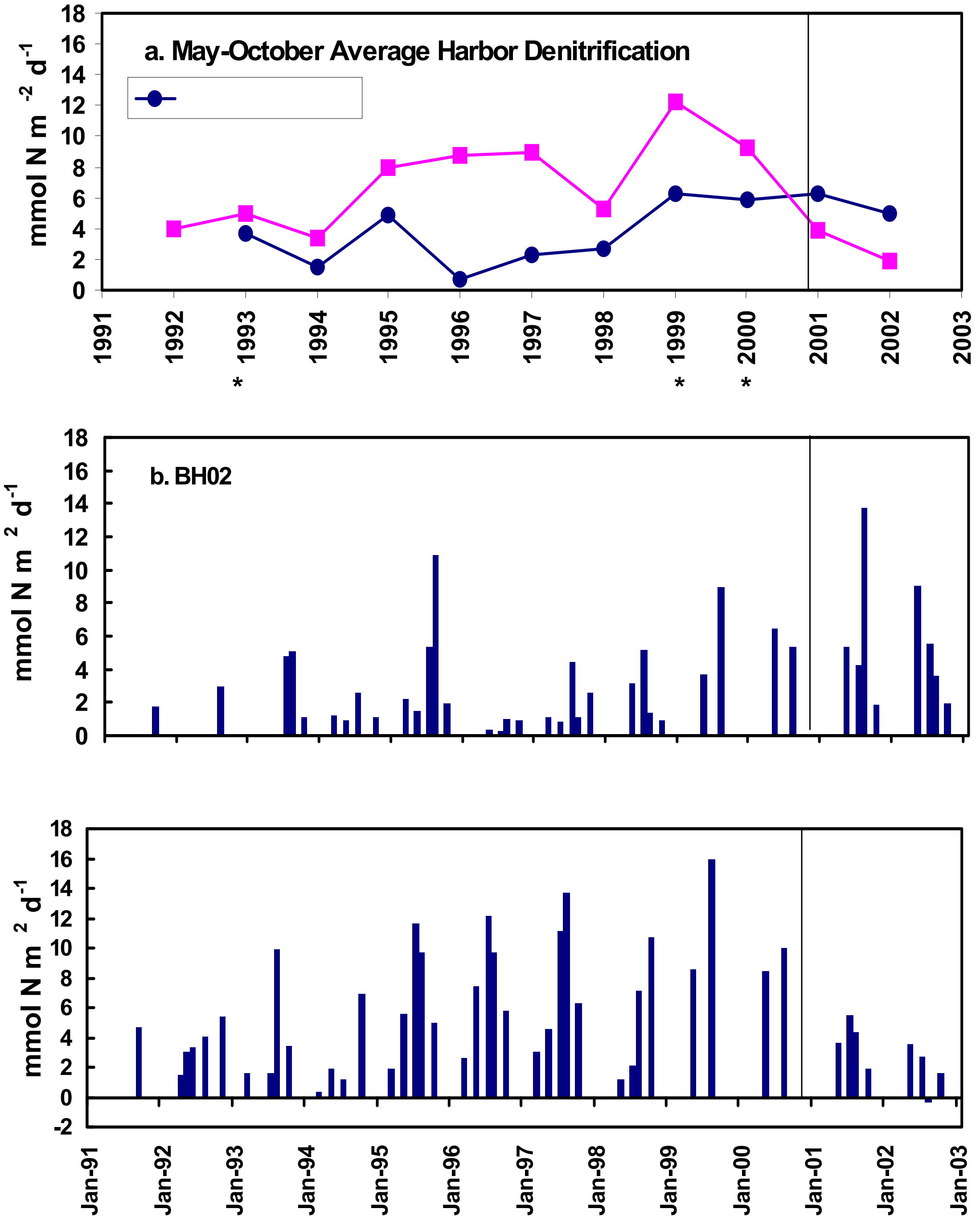


Figure 19. Denitrification in Boston Harbor: a.) May-October seasonal averages for Station BH02 and BH03 from 1992-2002.; * marks years when averages were of three rather than four surveys.; b.) survey means for BH02 and c.) BH03 from 1991-2002. Vertical line marks transition from baseline to post-relocation observations.

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

3.5.1 Respiratory Quotients

In 2002, RQs at Station BH03 were consistent with the trends we have observed over the past several years (Fig. 20b). Values were close to or somewhat lower than 1.0. At the other three stations, however, there were small changes from recent trends. At Station BH02, RQs were elevated, with a high value of 1.9 in October and low value (still well above 1.0) of 1.4 in August (Fig. 20a). These values are not atypical for this station, but they indicate that the relative importance of anaerobic processes at this site continues to vary from year to year. At Station BH08A, a July value of 1.6 was the highest RQ ever observed at this site (Fig 20c). This indication of less oxic conditions was supported by Eh profiles and the presence of dissolved sulfides (see below), and may be related to the decline of the amphipod mat. At QB01, values were close to 1.0 as is typical for this site, but over all were the lowest ever observed at this site (Fig 20d). No single value exceeded 1.0, which also was atypical for the station; values ranged from 0.8 in October to 1.0 in May.

3.5.2 Eh Profiles

Profiles of reduction potential (Eh) taken from within sediment cores during 2002 showed highest or most oxidizing conditions in May, followed by more negative values through the season to October . These profiles were typical of baseline at Stations BH02, BH03, and QB01 (Fig. 21 a, b, d). For BH08A, however, August and October profiles were more negative at depth in the core (> 8cm) than typical for this station (Fig. 21c), and more typical of Station BH02, which traditionally has been characterized by the most reducing conditions of the four stations. Dissolved sulfides were measured at concentrations greater than 0.5 mM in the deeper porewaters of both of these stations in July and August, consistent with Eh values of –150 or lower. At Stations BH03 and QB01, sulfides were detectable at only very low levels (<0.07 mM) when measured in July and August. Although we do not measure sulfide concentrations in May and October, the Eh profiles suggest that sulfides would have been present in the porewaters of Stations BH02, BH08A, and QB01 in October.

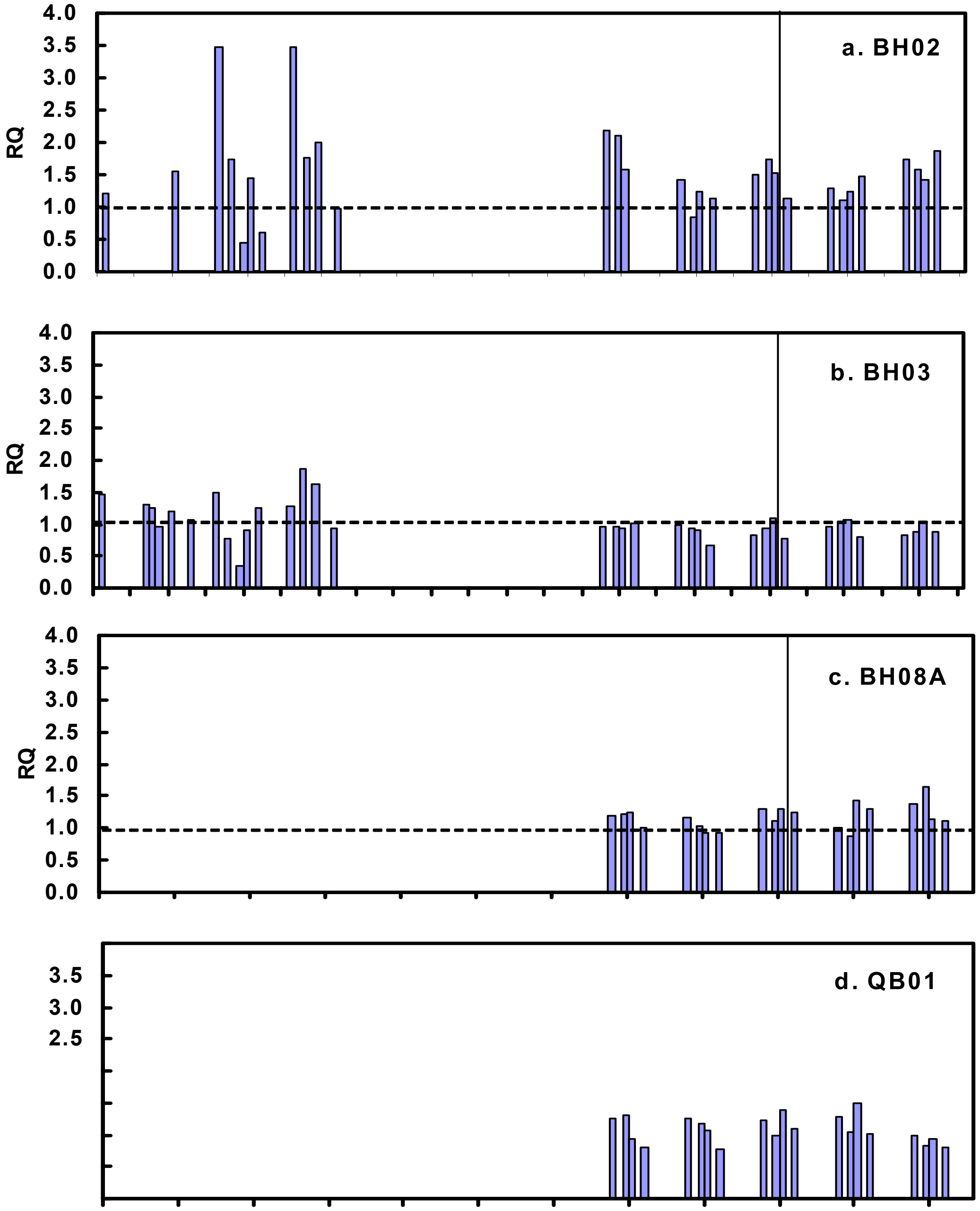


Figure 20. Changes in respiratory quotient over time at Boston Harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01. The horizontal dashed line marks the ratio at 1:1. The vertical solid line marks the transition from baseline to post-relocation observations.

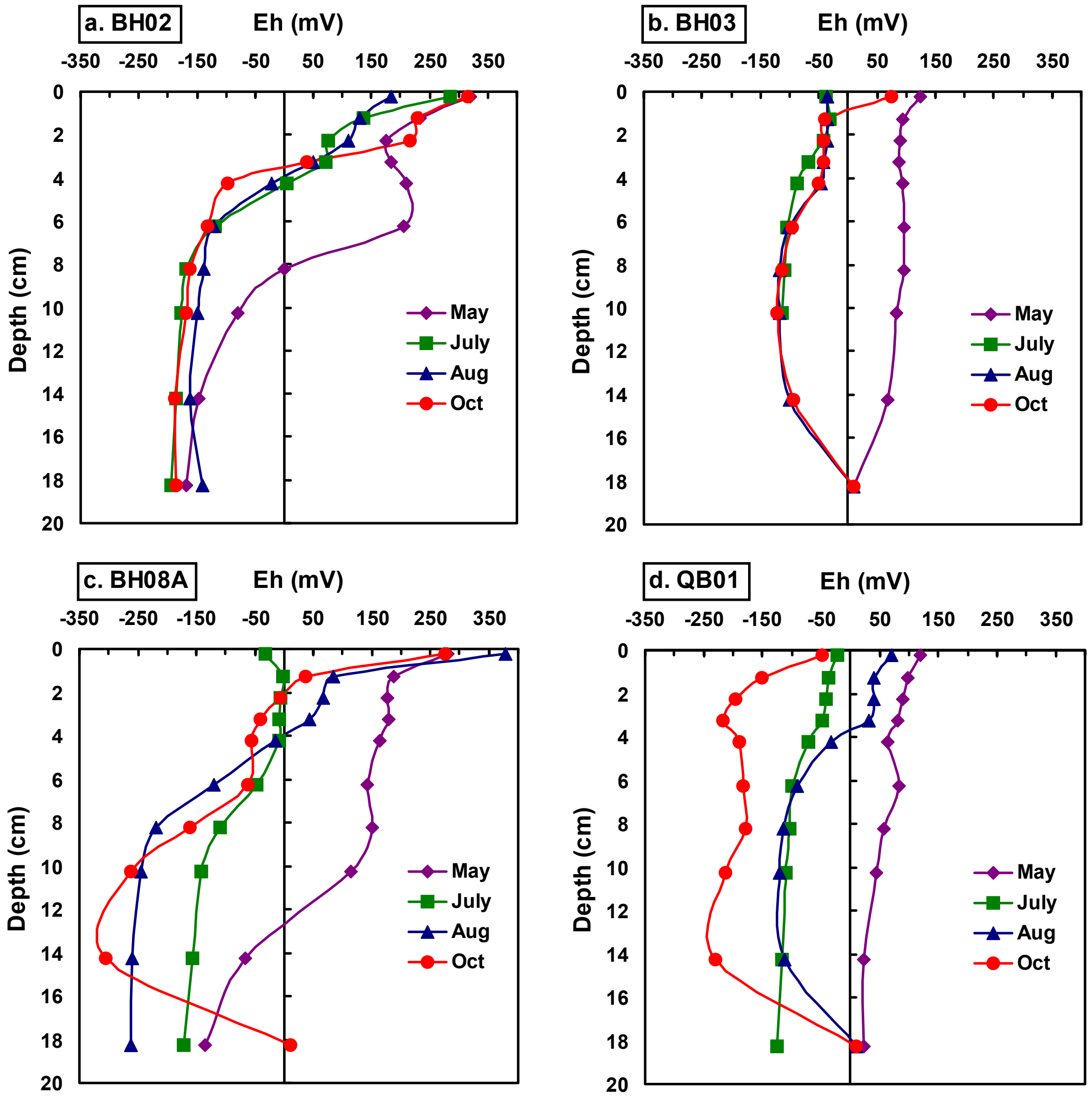


Figure 21. Eh profiles for May through October, 2002, from Harbor stations a.) BH02, b.)BH03, c.) BH08A, and d.) QB01.

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.

During 2001 and 2002, the two years since the ocean outfall became operational, we have seen small but inconsistent changes in measures of sediment organic matter, and rates of benthic respiration and nutrient fluxes have been well within or lower than typical baseline observations.

Organic matter content of surface sediments in the nearfield had increased somewhat in last two years compared to the previous 2-3 years, but was still within baseline observations. The most significant break with the baseline pattern was at MB03, the station southwest of the outfall diffusers, where seasonal average TOC had declined from about 1.5% to 0.6% during baseline, but was back up to about 1.4% in 2001 and 2002. Increases at the other two stations seemed to be following a change in trend that may have started in 2000. Small increases in TOC were also observed at farfield station MB05, suggesting these trends may be region-wide.

Nearfield C/N ratios of sediment organic matter were high in 2002 compared to baseline, following unusually low values observed in 2001. Low values may have been related to the large 1999-2000 phytoplankton blooms. The high values are as yet unexplained, but may be related to increased sediment drape noted on nearby hardgrounds (Hecker, pers. com.), the origin of which has not been determined.

Sediment chlorophyll at nearfield stations in 2002 was typical of baseline, following elevated levels observed during some surveys in 2001. As mentioned above, 2001 was noted for low sediment C/N as well as these incidents of high chlorophyll, both of which may be related to the previous years' blooms. In 2002, typical chlorophyll values did not seem to correspond to high C/N.

In 2002, there was no indication of increased SOD or increased nutrient fluxes from nearfield sediments. In fact, fluxes were generally in the low end of baseline observations or were lower. Temperature continued to be the primary control on these fluxes, with infaunal abundance also important at some stations. Fluxes at station MB05 were quite typical, and at this station, where the range in temperature is small, sediment chlorophyll content is important in regulating fluxes.

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

Fluxes of DIN in 2002 were in the low end or even lower than the range observed during baseline monitoring. Rates were at times characterized as uptake rather than release. At Station MB03 we observed unusual and high uptake rates primarily of NH_4^+, such that the seasonal average efflux was comprised entirely of NO_3^-, also an anomalous observation. At MB02 the efflux was also largely but not entirely comprised of NO_3^-. These low DIN fluxes result in a contribution of nitrogen amounting to less than 3% of the requirements for Nearfield primary production. At station MB05, we observed very low effluxes of NO_3^- from and moderate uptake of NH_4^+ into the sediments in 2002.

In 2002, PO_4^- fluxes were low compared to the baseline range and often negative, particularly at station MB05. Silica fluxes were low compared to baseline in the Nearfield, and typical at MB05.

Denitrification rates at two Nearfield stations were typical of baseline observations. Due to the low DIN flux, denitrification accounted for between 83% and 100% of the total nitrogen flux at these stations.

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

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 and in the two years since diversion. Decreases in TOC have been most pronounced at Stations BH03, BH08A, and QB01 whereas TOC content at station BH02 has varied. The large range of values observed across the four stations early in the monitoring program has narrowed in the past three years (2000-2002).

Another measure of organic matter, sediment chlorophyll, had decreased somewhat at two of the harbor stations in 2002. These were stations BH03 and BH08A, where the amphipod mats have typically been present. Decreases might be attributed to grazing, but in 2002 we noted far fewer amphipods than typical. Instead, or possibly in addition, increased turbidity caused by the absence of filtering by the benthos may have played a role in reducing *in situ* production at these sites. At the other two stations, BH02 and QB01, sediment chlorophyll levels were among the higher levels observed during baseline monitoring. Observations of benthic diatoms and sediment profiles of chlorophyll suggest that *in situ* production is important at these sites.

Sediment oxygen demand and all nutrient fluxes in 2002 were lower than at any previous time during monitoring at Stations BH02, BH03, and BH08A. Little change has been observed over the years at QB01, where fluxes have traditionally been the lowest of the four stations. In 2002, fluxes were very similar across all four stations, and for the first time, seasonal average S.O.D. was highest, though by a very small measure, at QB01. At this point, the large variability between stations and years has largely disappeared. The absence of extremely high rates observed early in the monitoring program is related to the apparent decline of the amphipod mats. Overall reductions, however, are most likely due to the decrease in organic matter loading.

Using post-relocation rates of primary production at the mouth of the harbor and seasonal averages of DIN and PO_4 fluxes, we calculate that these fluxes could each contribute as much as 15% of phytoplankton N and P requirements. With the reduction in nutrient inputs to the harbor after the relocation of the outfall, these contributions may become significant, however oceanic and remaining terrestrial inputs still exceed the needs of primary production.

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

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

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

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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 2002.

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 2002.

Station	Survey ID	Date	Latitude	Longitude	Depth (m)	Temp (oC)	D.O. (mg.L^{-1})	Salinity (psu)
BH02	NC021	05/21/02	42.34362	-71.00204	9.0	10.1	8.47	29.9
	NC022	07/17/02	42.34369	-71.00228	8.8	16.0	8.51	32.4
	NC023	08/06/02	42.34352	-71.00228	9.0	17.5	7.28	32.4
	NC024	10/28/02	42.34355	-71.00228	8.6	11.3	8.06	30.6
BH03	NC021	05/21/02	42.96149	-70.96149	8.2	10.1	9.23	29.6
	NC022	07/17/02	42.33087	-70.96194	8.0	15.5	8.06	32.2
	NC023	08/06/02	42.33065	-70.96105	8.3	17.2	7.58	33.1
	NC024	10/28/02	42.33076	-70.96156	8.0	10.8	8.65	30.4
BH08A	NC021	05/21/02	42.29120	-70.92212	8.0	10.6	10.23	30.2
	NC022	07/17/02	42.29117	-70.92232	6.3	17.1	7.69	17.1
	NC023	08/06/02	42.29100	-70.92178	9.0	18.8	7.97	32.8
	NC024	10/28/02	42.29090	-70.92205	7.5	10.7	8.90	31.4
QB01	NC021	05/21/02	42.29370	-70.98740	4.1	11.0	9.88	29.6
	NC022	07/17/02	42.29345	-70.98760	3.1	17.9	7.54	31.4
	NC023	08/06/02	42.29352	-70.98783	4.1	20.0	7.33	33.1
	NC024	10/28/02	42.29345	-70.98797	3.2	10.5	9.28	30.5
MB01	NC021	05/20/02	42.40298	-70.83725	30.7	7.5	8.54	31.7
	NC022	07/16/02	42.40303	-70.83728	30.5	7.7	8.19	33.6
	NC023	08/05/02	42.40310	-70.83743	31.0	8.0	7.30	32.5
	NC024	11/01/02	42.40312	-70.83723	33.5	11.2	na	32
MB02	NC021	05/20/02	42.39248	-70.83434	31.7	7.5	8.87	30.7
	NC022	07/16/02	42.39252	-70.83425	30.6	7.9	8.32	33.6
	NC023	08/05/02	42.39255	-70.83427	33.0	8.3	7.12	33.2
	NC024	11/01/02	42.39243	-70.83445	34.3	11.3	na	31
MB03	NC021	05/20/02	42.34777	-70.81610	31.6	7.3	8.75	31.8
	NC022	07/16/02	42.34789	-70.81618	26.7	8.0	7.77	33.2
	NC023	08/05/02	42.34782	-70.81617	33.8	8.6	7.81	33.5
	NC024	11/01/02	42.34785	-70.81605	34.1	11.6	8.60	32
MB05	NC021	05/20/02	42.41632	-70.65218	43.8	6.4	9.35	31.7
	NC022	07/16/02	42.41656	-70.65193	43.3	7.0	8.58	33.9
	NC023	08/05/02	42.41650	-70.65185	46.2	8.4	8.42	33.2
	NC024	11/01/02	42.41652	-70.65193	44.8	11.5	8.23	33

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