Benthic metabolism and nutrient cycling in Boston Harbor and Massachusetts Bay: Summary of baseline data and observations after one year of harbor-to-bay diversion of sewage effluent

Massachusetts Water Resources Authority

Environmental Quality Department
Report ENQUAD 2002-13

Citation:

Tucker J, Kelsey S, Giblin A, and Hopkinson C. 2002. **Benthic Metabolism and Nutrient Cycling in Boston Harbor and Massachusetts Bay: Summary of Baseline Data and Observations after One Year of Harbor-to-Bay Diversion of Sewage Effluent.** Boston: Massachusetts Water Resources Authority. Report ENQUAD 2002-13. 83 p.

Benthic Metabolism and Nutrient Cycling in Boston Harbor and Massachusetts Bay: Summary of Baseline Data and Observations after One Year of Harbor-to-Bay Diversion of Sewage Effluent

Submitted to

Massachusetts Water Resources Authority
Environmental Quality Department
100 First Avenue
Charleston Navy yard
Boston, Ma 02129

Prepared by

Jane Tucker
Sam Kelsey
Anne Giblin
and
Chuck Hopkinson

The Ecosystem Center
Marine Biological Laboratory
7 MBL Street
Woods Hole, MA 02543

September 2002

Report No. 2002-13

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 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 been studied. 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. Delays in the construction of the outfall allowed for a much longer baseline period than originally planned (9 years instead of 3), during which we were better able to assess the natural variability in Massachusetts Bay. In September 2000, the final phase of harbor cleanup was realized when all sewage effluent was diverted from Boston Harbor to the bay outfall. 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.

No large changes in benthic nutrient cycling were observed after only one year of diversion of effluent out of Boston Harbor and into Massachusetts Bay in either the harbor or the bay. These results are not surprising, as sediment processes are integrative, and typically have a slow response time. In Boston Harbor, where the water column response to the diversion was dramatic, we expect that resulting reductions in organic matter deposition will become apparent with time in the benthos. In Massachusetts Bay, where the projected impact of the outfall was small (Hydroqual, 1995) but the observed natural variability was large, a substantial and sustained change may be necessary before an outfall influence is detectable.

BOSTON HARBOR

Boston Harbor has seen large reductions in solids and contaminants loading resulting from improvements in sewage treatment and disposal practices that began in the late 1980s. In December 1991, a major change, especially with respect to benthic processes, occurred when the disposal of sludge within the harbor was discontinued. Benthic metabolism and nutrient fluxes from the silty sediments of the harbor, monitored since late1991, decreased over this, the baseline monitoring, period. Most of this decrease resulted from a return to typical fluxes at the two north harbor stations, BH02 and BH03, from quite high rates observed early in the program (1993 and 1995). Very high rates were associated with increases in benthic infaunal abundances, particularly with the presence or absence of the ampeliscid amphipod mat, which spread throughout the harbor during the monitoring period. The "bloom" of amphipods observed at Station BH03 was thought to be triggered by the cessation of sludge disposal, which had until that point prevented colonization. Large fluxes at Station BH02 have also at times been associated with the presence of amphipods (1995), but more typically this station has had low abundances of infauna.

[Many of the large fluctuations we observed in the harbor were associated with the presence of the amphipod community, which affects biogeochemical processes in several ways. The dense mat of tubes built by the amphipods penetrates 5 –10 cm into the sediments. Through ventilation of the tubes, the amphipods increase advective flux and they enhance microbial activity by oxygenating the sediments and increasing access to substances stored in the sediments. Effects are manifested in magnitude of fluxes and in changes in redox processes.]

At the two southern harbor stations, BH08A and QB01, where no such dramatic change in organic matter loading occurred, we observed much less change in SOD or nutrient fluxes; however, monitoring of these stations did not begin until 1995. The amphipod mat is present at BH08A, but it, and therefore benthic fluxes, have been relatively stable. At the end of baseline monitoring, fluxes at Station BH03 and BH08A had become very similar in magnitude. At station QB01, SOD and nutrient fluxes were consistent throughout monitoring, and were the lowest of the four harbor stations.

Before effluent diversion offshore, sewage treatment improvements other than the cessation of sludge disposal were subtle from the perspective of the sediments and changes in fluxes directly related to those changes were not readily apparent. Because nutrient loading was decreased only slightly, primary productivity, which fuels the benthos, remained high. Station BH02 in the north harbor served as an indicator station for changes that might be attributable to improvements such as increasing levels of secondary treatment, but changes there were inconsistent. In 1998 and 1999 we began to see some indications of improvement, for instance the surface oxidized layer of sediments was deeper. However this trend did not continue into 2000.

Decreasing trends in SOD and nutrient fluxes continued in 2001, the first year after all sewage effluent was diverted out of the harbor. At Station BH03, some fluxes were the lowest ever observed. There were a few atypical findings in 2001, most of them at Station BH02.

Sediment oxygen demand in general decreased over the baseline monitoring period in the north harbor, but less so in the south harbor. In particular, the extremely high rates of benthic respiration observed in 1993 and 1995 at the sludge-enriched Station BH03 moderated as stores of organic matter were depleted, and rates became more similar to the other three harbor stations. This trend continued in 2001.

DIN fluxes also decreased over the baseline period in the north harbor, especially at BH03. In 2001, DIN flux was the lowest ever observed at Station BH03. In the south harbor, however, a decreasing trend was not apparent. Nitrate was an important part of the flux at Stations BH03 and BH08A, where amphipods oxygenate the sediments, and occasionally at BH02 when amphipods or other infauna were present. In 2001, the fraction of the DIN flux represented by nitrate at BH02 was higher than it had been since 1995.

Denitrification rates were typically quite high at Station BH03 and quite variable at Station BH02 during baseline. High rates at BH03 were attributable to highly oxygenated sediments, whereas low rates at BH02 were consistent with much more reducing conditions typically present there. In 2001, denitrification rates were atypically low at Station BH03, and high at BH02. Increased denitrification (as well as the increase in the NO_3^- fraction of the DIN flux) at BH02 indicated the presence of more highly oxygenated sediments, consistent with increases in infauna. During baseline, denitrification was estimated to provide a sink of only about 10% of the terrestrial nitrogen inputs to the harbor. After diversion, denitrification became of equal magnitude to the remaining terrestrial inputs. Including oceanic inputs, however, reduces the sink back to about 10%.

Phosphate fluxes were variable over the baseline period and subject to physical, chemical, and biological factors. Again, the presence or absence of amphipods played a role by influencing advection and oxic/anoxic conditions. Phosphate fluxes in 2001 were typical of lower rates observed during monitoring.

Respiratory quotients in much of the harbor where sediments are oxygenated were close to 1.0 for most of baseline. However, values much higher than1.0 were more typical of conditions at Station BH02. In 1999 and 2001, RQs at this station became much closer to 1.0, offering another indication of less reducing conditions in sediment conditions here. Profiles of Eh and sulfide concentration also suggested changes towards more oxic conditions.

Organic carbon content of harbor sediments in 2001 seemed to continue the decreasing trend we have noted during baseline. Sediment chlorophyll *a* inventories were typical of baseline, although at Station BH02 they had declined from very high levels in 1998-2000. Although we have often observed benthic diatoms at Station QB01, May 2001 was the first time we had noted them at Station BH02. It may be that increased water clarity in the harbor, among other improvements noted after diversion will permit more benthic primary production.

MASSACHUSETTS BAY

Massachusetts Bay is part of the much larger Gulf of Maine system, and therefore processes in the bay, including benthic processes, are influenced by large-scale, often region-wide phenomenon. One such phenomenon was a very large storm in December, 1992, that resuspended sediments in Boston Harbor and Massachusetts Bay and redistributed them such that bay sediments received significant inputs from the harbor. Another region-wide event began in the fall of 1999, when a series of large phytoplankton blooms began that lasted through the fall of 2000. Chlorophyll levels during these blooms were much higher than previously observed. Both of these events had impacts in the benthos. The operation of the new bay outfall, which began in September, 2000, represents a new phenomenon with region-wide and long-term implications.

In general, patterns of benthic metabolism and nutrient fluxes measured in depositional sediments in the bay from 1992 to 2001 were fairly consistent across stations, probably due to similar inputs, although differences among stations were apparent at times. Trends in SOD and nutrient fluxes were not similar however. Maximum rates of benthic respiration were observed from 1997-2000, whereas maximum rates of nutrient release occurred in 1993-1994.

Sediment oxygen demand (SOD) at the three nearfield stations in Massachusetts Bay was remarkably similar from 1993-1996, and decreased slightly over that time. Strong seasonal patterns were apparent such that temperature explained over 40% of the variability in flux measurements. In 1997, trends at each station seemed to diverge and were less similar to each other through 2000, and in 1999-2000, the seasonal pattern was not observed. SOD increased at this time as well. Respiration rates were lower at Station MB05 in Stellwagen Basin, but followed a pattern similar to that at Station MB03. Higher rates beginning in 1997 may be related to increases in infaunal abundances that began then and peaked in 1999. In 1999 and 2000 the deposition of the series of large phytoplankton blooms likely augmented the increased rates. The persistence of those blooms, producing a relatively continuous rain of organic matter to the benthos, may help explain the absence of seasonal patterns during that time. In 2001, water column chlorophyll concentrations were typical of baseline and infaunal numbers had decreased for the second year. SOD decreased from the previous two years, and the nearfield station fluxes were once again quite similar.

Highest DIN fluxes of the baseline period occurred in late 1992 (when we first sampled) through 1994, likely the result, in the first part of this period, of large infaunal abundances and then by the redistribution of sediments caused by the December, 1992 storm. Rates were somewhat elevated in 1999-2000, again likely related to the high water column production during this time. Sediments in the bay are well oxygenated, and NO_3^- typically comprises 25%-50% of the DIN flux. DIN fluxes in 2001 were about average those observed during baseline.

Denitrification has varied over the baseline period, and a seasonal pattern has not been apparent. It often represents 60%-80% of the total N mineralized in the depositional sediments of the bay. Denitrification in 2001 was typical of previous years.

Phosphate fluxes in the bay have varied widely in magnitude and direction. Similar to DIN fluxes, highest rates occurred in 1993 and 1994, again probably related to sediment redistribution. In 1999 and 2000, phosphate fluxes were often directed into the sediments. In 2001, PO_4 fluxes were about average for baseline and were directed out of the sediments.

Patterns of silica fluxes in the bay resembled O_2 fluxes in seasonal pattern and DIN fluxes in periods of maxima and minima. From 1993-1997, a seasonal pattern was usually apparent, but was not observed in 1999-2000. Largest fluxes occurred in 1993-1994. The 1994 peak followed the fall 1993 diatom (*Asterionellopsis)* bloom. Somewhat elevated rates in 1999 and 2000 were probably related to the mixed diatom bloom, the persistence of which may help explain the absence of seasonal patterns.

Respiratory quotients in the bay were often greater than 1.0 in the early part of the monitoring program, consistent with organic matter input (from sediment redistribution) and low infaunal abundance. By 1999 and through 2001, RQs were much closer and often lower than 1.0, another indicator of active bioturbation. Redox conditions as measured by Eh profiles also showed improvement over time.

Organic matter content of sediments at Stations MB01 and MB03 showed significant decreases over the baseline period. There was no such trend at Station MB02. It appears that the redistribution of sediments that occurred at the end of 1992 deposited significant amounts of organic matter at these stations, as is evident in TOC concentrations in 1993. Elevated concentrations were not observed and station MB02, and there was no trend with time at this site. Apparently the effects of the storm did not did reach station MB02. TOC content in 2001 was typical of baseline, with the exception of a high value at MB01 in October and at MB03 in July. There has been little change in TOC at station MB05.

Ratios of TOC to TON were consistent within stations from 1994 to 2000, but C/N at MB03 (~11) was lower than at MB01 and MB02 (~12.5), and was lower still at MB05 (~10). Although the differences are small, the implication is that a range of organic matter quality reaches the sediments of Massachusetts Bay that may reflect varying proportions of phytoplankton and Boston Harbor derived particulate matter.

Inventories of total sediment pigments varied over the baseline in the nearfield, but corresponded roughly to concentrations of water column chlorophyll, sometimes with a lag (fall blooms might be apparent as spring high concentrations in sediments). Inventories were elevated in 1994, after the fall, 1993 bloom, and in 1999-2001, during and after the 1999-2000 blooms. High chlorophyll *a* inventories in 2001, after a season when water column chlorophyll was not particularly high, suggested the possibility of *in situ* production.

TABLE OF CONTENTS

TABLE OF FIGURES

APPENDICES

1.0 INTRODUCTION

Boston Harbor and the Massachusetts Bays have undergone major shifts and reductions in sewage inputs over the last ten 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 nitrogen in the effluent stream have decreased only a small amount, as secondary treatment has little effect on nutrients. The culminating event in the series of treatment changes 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 September, 2000, the final phase of harbor cleanup was realized when all sewage effluent was diverted from Boston Harbor to the bay outfall. 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.

The first part of this report describes the understanding we have gained of the sediment biogeochemical processes in the two systems, Boston Harbor and Massachusetts Bay. The second part of the report will discuss our observations during 2001, after effluent discharge had been removed from Boston Harbor and introduced to the deep waters of Massachusetts Bay. Because completion of the Bay outfall was delayed from its scheduled completion date in 1995, we were afforded a nine-year pre-diversion monitoring period, from late 1991 through 2000. In Boston Harbor, these were years of observing recovery in the system as direct inputs to it were drastically changed. In Massachusetts Bay, this longer baseline period enabled us to better assess natural variability in the system and the Bay's role in the larger Gulf of Maine, as well as the effects of historical inputs from the Harbor.

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 1998-2001 (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). Dr. Brian Howes and his colleagues were responsible for the data collected during 1995-1997 (Howes, 1998a; Howes, 1998b; Howes, 1998c).

2.0 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 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 north harbor has received the heaviest loading. The Charles River, flowing through some of the most industrial areas of Boston, terminates in the north harbor, and the Deer Island Sewage Treatment Plant is situated on its northeastern shore. Until December, 1991, sewage sludge mixed with effluent from Nut Island was discharged off Long Island in the north harbor, and sludge/effluent from the Deer Island plant was discharged through outfalls near the entrance of the harbor on outgoing tides. Effluent (without sludge) from the Deer Island plant continued to be discharged until September 6, 2000. This effluent varied in its level of treatment from primary or less until 1995, and then with increasing proportions of secondary treatment after 1997, reaching 85% in 2000.

The south harbor is divided into Quincy and Hingham Bays by Nut Island, where a second sewage treatment plant was located. Outfalls from the Nut Island Sewage Treatment Plant discharged effluent into Quincy Bay until 1998, after which discharge was diverted to the Deer Island plant in the north Harbor. The Nut Island plant produced only primary treated effluent.

In addition to the sewage treatment plant outfalls, numerous combined sewer overflows (CSOs) ring the harbor. CSOs are activated when high flows through the sewage system exceed its volume capacity. At these times, raw sewage may be released into the Harbor and the rivers that drain into the harbor. CSO activations have decreased with increases in pumping capacity in the treatment plant, but may still occur during very heavy storm events.

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 effluent 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 in September 2000 was the final phase in efforts to clean up Boston Harbor, and very quickly resulted in dramatic improvements in water quality. Taylor (2002) reported that in the first year after diversion, average DIN concentrations in the harbor were 55% lower than the baseline average. Within this pool, the reduction in NH_4^+ concentrations was over 80%. Large reductions were also observed in phosphorus concentrations (31% in DIP). Water column chlorophyll decreased by nearly 50%, particulate carbon by nearly 40%, and water clarity increased by about 15%. Although there is yet limited evidence of these improvements in sediment biogeochemistry, certainly reductions in organic matter deposition resulting from water quality improvements will become apparent with time.

Four harbor stations have been repeatedly sampled throughout the monitoring period (Figure 1). Two stations, BH02 and BH03, are located in the northern section of Boston Harbor and have been sampled routinely since September, 1991. The other 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.

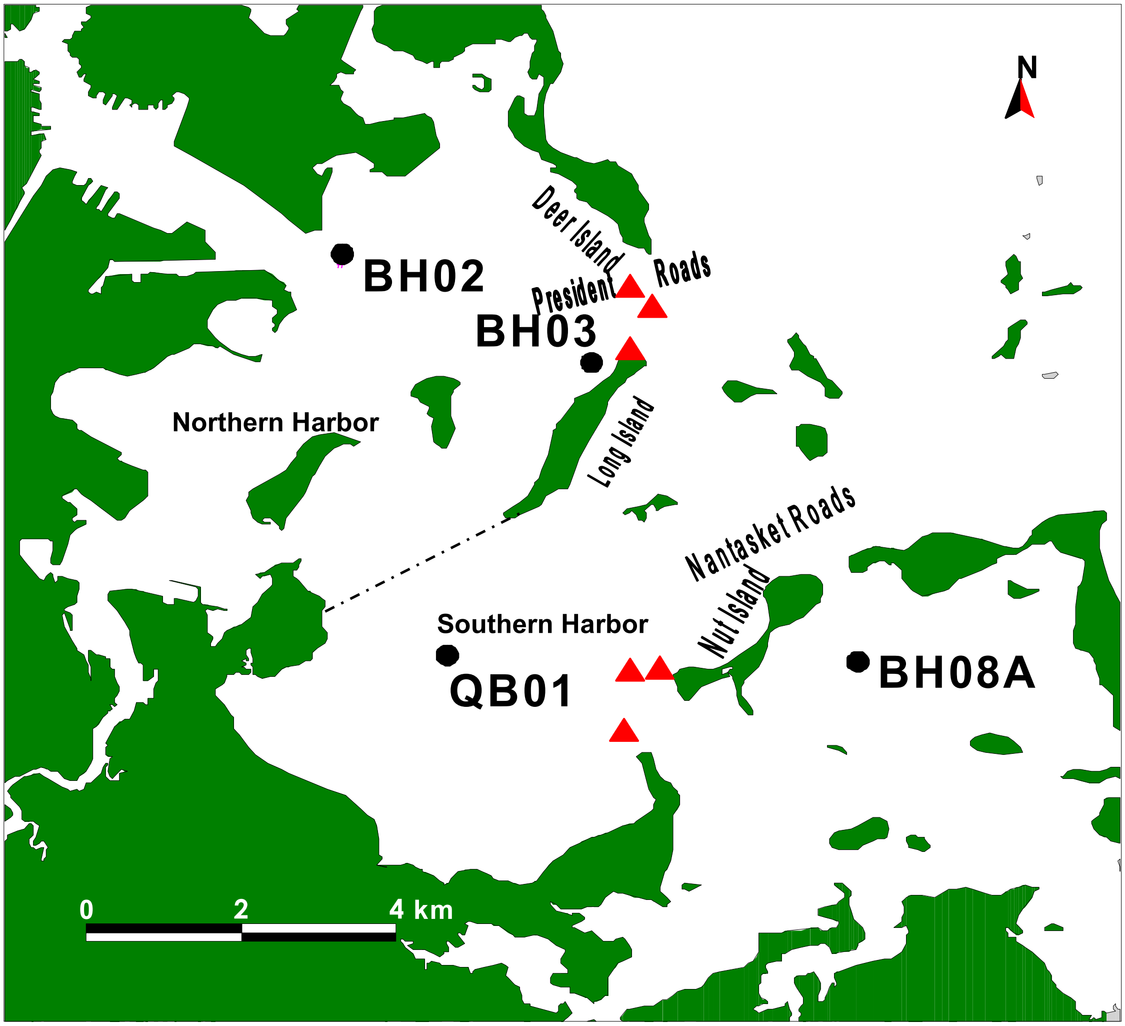


Figure 1. Locations for four harbor stations. Outfalls are marked by triangles (▲).

Station BH02 is near the mouth of the Charles River and inner harbor, and about 4 km from the Deer Island outfall. Station BH03 is just across the harbor from the DITP, is in close proximity (~2km) to the Deer Island outfall, and received substantial inputs of sludge from the Nut Island sludge outfall on Long Island until harbor disposal ceased. Station BH08A is just inside Hingham Bay, in an area well flushed by tidal mixing but also most affected by effluent from the Nut Island outfalls (Rex *et al*., 1992). The fourth harbor station, QB01, is located in shallow water in Quincy Bay, also near the Nut Island outfalls in one of the less-well flushed areas of the Harbor.

The four benthic flux stations have also been studied under the Benthic Monitoring Program. Stations BH02, BH03, BH08A, and QB01 have been studied as T02, T03, R46 and R48. The following summary describing the physical and biological characteristics of the four harbor stations are taken from Kropp *et al*., 2000, and Kropp *et al*., 2001.

Sediments at BH02 (T02) and QB01 (R48) are shaped by physical processes to a higher degree than are those at BH03 (T03) and BH08A (R46). Sediment texture at BH02 (T02) has varied considerably over time, from 70% sand and gravel in 1994 to 84% fines in 1998. BH02 (T02) was classified as a reworking sedimentary environment by Knebel (1993). Other similarities between these two stations were found in their biological characteristics. Both were classified as having infaunal communities in successional stage I/II, or a mix between the pioneering and transitional seres. Typically neither station supported *Ampelisca* mats, although by1999 amphipod mats had begun to appear at Station BH02. Both stations were assigned low organism/sediment indices (OSI), indicating the communities are under some form of moderate stress (Kropp *et al*., 1999). Both stations have shallow redox potential discontinuities (RPD).

In contrast, Stations BH03 (T03) and BH08A (R46) are both dominated by biological processes, with sediments covered by *Ampelisca* mats. Sediments at these two stations are silts, although some variability has been noted at BH03 (T03). Station BH08A (R46) has been classified with a higher successional stage than BH03A (T03), II on III as opposed to II. Both stations have high OSIs (6-8) and deep RPDs (2-10 cm).

3.0 HARBOR MONITORING PRE-DIVERSION, 1991-2000

3.1 Trends in Benthic Respiration and Nutrient Fluxes

In this report, we have presented much of the data as seasonal averages (May, July, August, October) in order to condense the data and examine long-term trends in benthic respiration and nutrient fluxes. We have not presented annual averages because winter data are not available for all years. The years covered for each station are 1993-2001 for BH02, 1992-2001 for BH03, and 1995-2001 for BH08A and QB01. We also note that there were no August data in 1994, so the seasonal average for this year at BH02 and BH03 may be biased low. However, rates measured in the other three months of 1994 were in general low compared to 1993 and 1995. Data from May, 1995, are also missing from the southern harbor station QB01 because sampling had not yet begun at that station.

The typical seasonal pattern in fluxes that we have observed in Harbor sediments is that rates peak in the summer, primarily in response to temperature. For example, regression models of benthic respiration rates against temperature suggest that 20-50 % of the variability in rates may be explained by temperature. Deviations from the typical pattern may be the result of other factors such as the deposition of the spring phytoplankton bloom or increases in bioturbation. Seasonal details for the years 1991-2000 may be found in previous reports (refer to list at end of Section 1.0).

3.1.1 Sediment Oxygen Demand

Responses in sediment respiration and nutrient fluxes related to loading changes have been most noticeable at Station BH03. Trends in fluxes at this site generally follow trends in infaunal abundances. However, peaks years of fluxes have not always corresponded to peak years in abundances. The amphipod mats are patchy, and our core samples may capture different densities than the samples taken for abundance measurements. Also, the effect of the animals may be to enhance microbial metabolism such that the effects of infaunal abundance are indirect.

Respiration rates, or sediment oxygen demand (SOD) at BH03 in 1993 and 1995, the second and fourth years after sludge disposal ceased, were among the highest observed in coastal estuaries (Giblin *et al*., 1997), with seasonal averages of 205 and 187 mmol O_2 m^{-2} d^{-1}, respectively (Figures 2a and 3b). During this period, the site became heavily colonized by the mat-building amphipod community that had presumably been excluded from the site by the continuous disposal of sludge. The first peak in infaunal abundance was observed here in 1993 (Kropp *et al*., 2001); at the same time we observed very high rates of sediment respiration. The very highest rates we measured, however, occurred in 1995, and although the amphipod mat was present, infaunal abundances were not unusually high. Since then, rates have declined steadily. By 2000, rates had decreased to 46 mmol O_2 m^{-2} d^{-1}. A linear regression of seasonally averaged rates over time since 1996 indicates that SOD at this site has declined by nearly 13 mmol m^{-2} d^{-1} each year (r^2 of 0.79, $P < .02$). The implication is that the large stores of organic carbon present at BH03 at the beginning of monitoring are being depleted.

Peak respiration rates at Station BH02 also occurred in 1993 and 1995, with seasonal averages of 62 and 74 mmol O_2 m^{-2} d^{-1} (Figures 2a and 3a). The 1995 high rates coincided with peak in infaunal abundance, but that was not the case in 1993. In fact, higher abundances were observed in 1994, but SOD was not elevated. Since 1995, rates have been lower but have not shown a significant change with time, hovering around 40 mmol O_2 m^{-2} d^{-1}. Similarly, there are no temporal trends in S.O.D at Stations BH08A (Figures 2a and 3c). A peak seasonal average of 106 measured in 1995 was followed by five years of rates around 70 mmol O_2 m^{-2} d^{-1}. In 2000, rates at this station were the highest of the four harbor stations; through 1999, highest rates had been observed at Station BH03. Respiration rates at Station QB01 have been low and stable throughout monitoring, with a seasonal average of about 30 mmol O_2 m^{-2} d^{-1} (Figures 2a and 3d).

3.1.2 DIN Flux

Trends in DIN fluxes are similar to those in SOD (Figure 2b). Again, we have observed the largest changes over time at Station BH03. Similar to the pattern we observed for SOD, the years with the highest DIN fluxes at BH03 were 1993 and 1995, after sludge disposal was discontinued and the amphipod community established. After 1995, DIN flux was about 5 mmol m^{-2} d^{-1} (May-October average), declining to about half that rate by 2000 (Figure 4b). Regression of seasonal average DIN by year since 1996 showed a significant trend with time, as it did for SOD, with rates decreasing by 0.6 mmol m^{-2} d^{-1} each year (r^2 0.69, $P = 0.04$). At Station BH02, we have seen little change since 1993 in DIN flux, although there is a small decreasing trend in the data (r^2 of 0.35 and $P = 0.09$; slope 0.3) (Figure 4a).

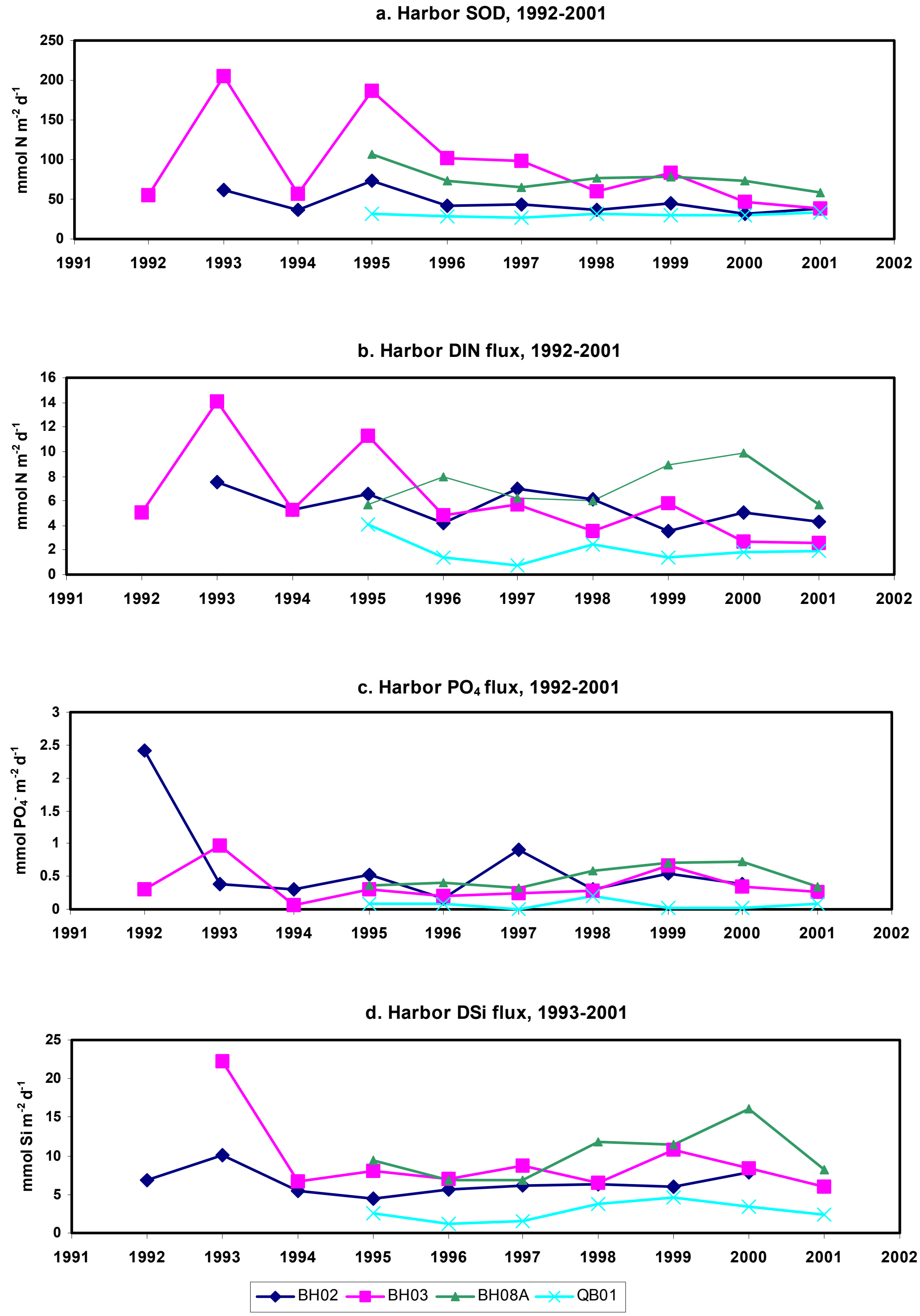


Figure 2. May-October seasonal averages at all four harbor stations for a. SOD, b. DIN flux, c. PO_4^- flux, and d. DSi flux.

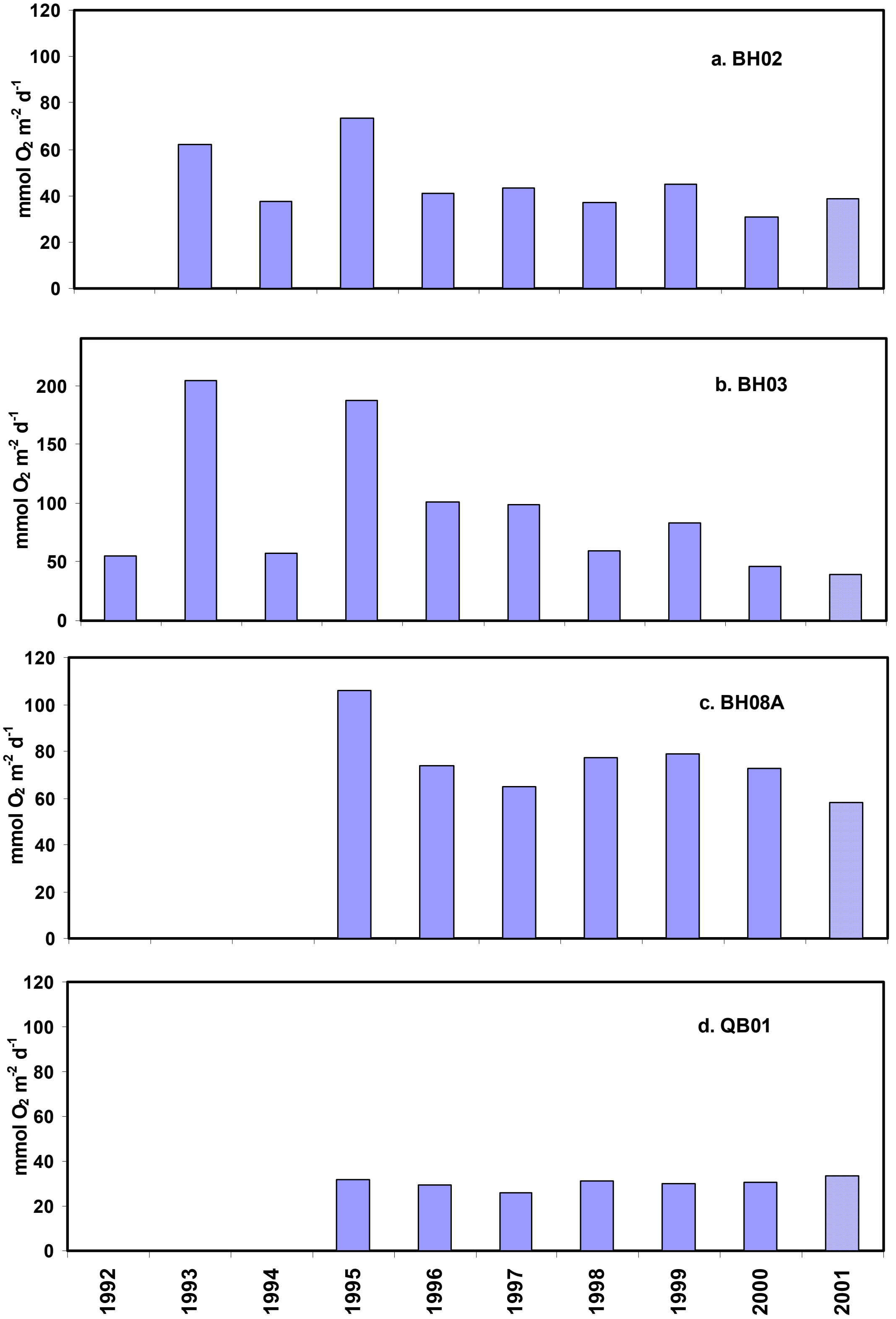


Figure 3. May-October seasonal average sediment oxygen demand from 1992-2001 at harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01. The stippled bar designates post-diversion data (2001). Note that the scale on the y-axis for Station BH03 is twice that for the other stations.

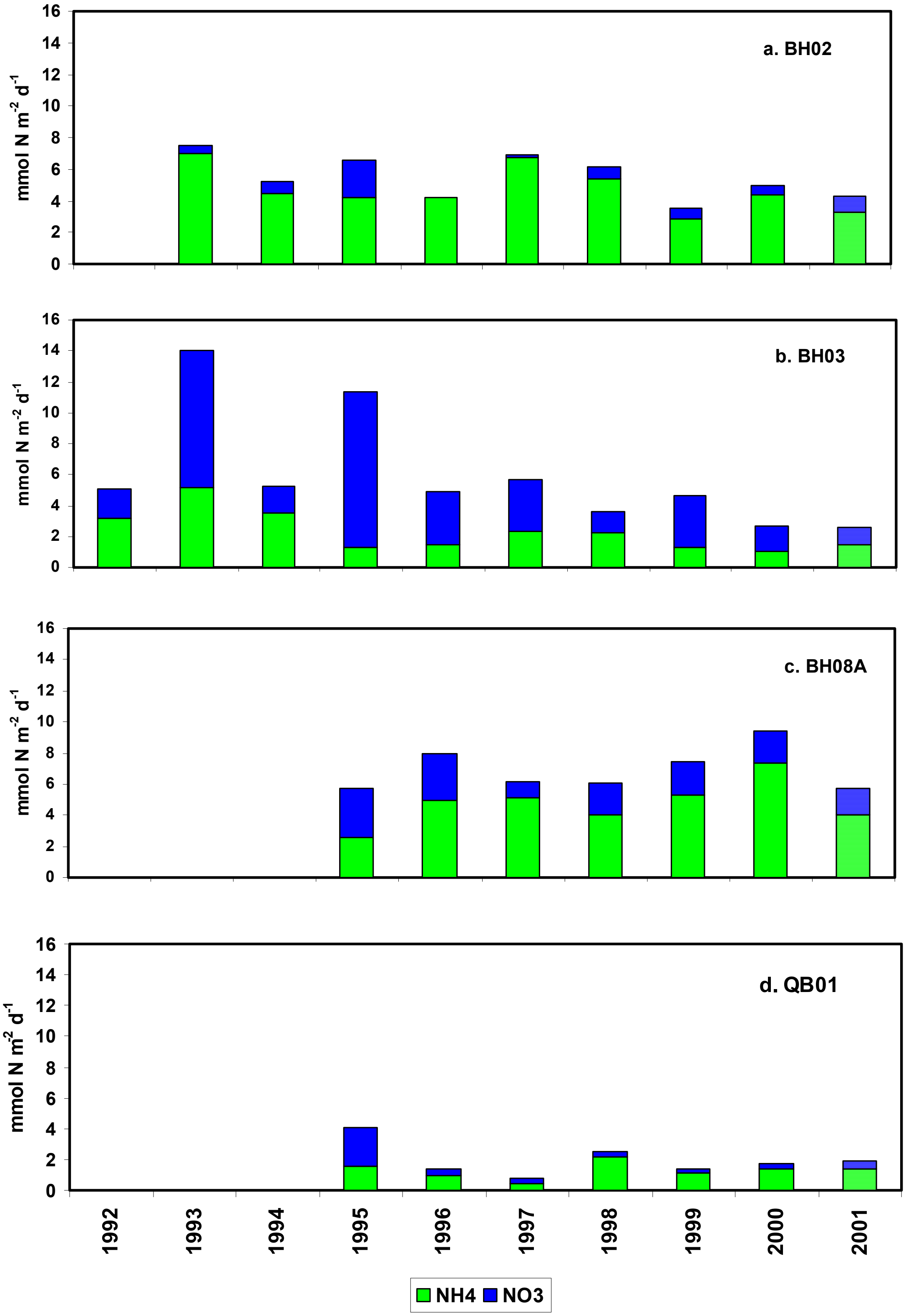


Figure 4. May-October seasonal average DIN flux, separated in NH_4^+ and NO_3^-+NO_2^- fractions from 1992-2001 at harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01. The stippled bar designates post-diversion data (2001).

In the southern harbor, we have observed no temporal trends (Figures 2b, 3c, 3d). DIN fluxes at Station BH08A have been similar from year to year, with no extremely high rates as have been noted at BH03, even though there is a thriving amphipod community present at this site. Interestingly, from 1996-1999, after the years with extremely high rates at BH03, DIN fluxes at these two amphipod-dominated stations were similar in seasonal pattern and magnitude. In 2000, however, rates at BH08A did not decrease as they did at BH03. The stability of the fluxes at Station BH08A most likely reflects the stability of the benthic community there. At Station QB01, rates are typically low and vary little from year to year.

The presence of amphipods, through bioturbation, influenced not only the magnitude of DIN fluxes but also the nitrogen species that comprises the flux. Burrows and burrowing increase the penetration of O_2 into the sediments, thereby enhancing nitrification. At BH03 and BH08A, large percentages of the DIN flux have been comprised of NO_3 (Figures 4b and 4c), whereas at Station BH02 and QB01, DIN fluxes are primarily of NH_4 (Figures 4a and 4d). At Station BH03, NO_3 has comprised over 50% of the flux in 6 out of 10 years, (maximum of 88% in 1995, as seasonal average) and over 30% for the remaining 4 years.

3.1.3 Denitrification

Oxidation of the sediments with its resulting increase in NO_3^- production also increases coupled nitrification-denitrification. Therefore it is not surprising that we have consistently observed quite high rates of denitrification at Station BH03 (Figure 5). Likewise, high rates at Station BH02 have generally coincided with peaks in infaunal abundance (e.g. in 1995). Rates typically peak in mid to late summer; summer rates at BH03 reached a maximum of 15.9 mmol N m^{-2} d^{-1} in August, 1999, which was a very high rate(Figure 5c). During baseline monitoring there was an increasing trend in denitrification rates at both stations. At station BH03, this trend was apparent from 1994 through 1999, with average rates ranging from 3.3 to 12.2 mmol N m^{-2} d^{-1}, but a return to lower rates may have begun in 2000. At BH02, the increasing trend began two years later (Figure 5b). Seasonal average rates increased from a low of 0.7 in 1996 to 6.3 and 5.9 mmol N m^{-2} d^{-1} in 1999 and 2000, respectively (Figure 5a). We do not have direct measurements of N_2 flux from Stations BH08A or QB01.

In some estuaries, denitrification is a major sink for nitrogen. In nearby Delaware and Narragansett Bays for example, denitrification removes 44% and around 23% of total terrestrial N inputs (Seitzinger, 2000). In the Choptank Estuary in Chesapeake Bay, denitrification removes 89% of inputs. In contrast, Kelly (1997, using data from 1991-1994) calculated that denitrification accounted for less than 10% of the total N loading to Boston Harbor. Even with the apparent increase in denitrification rates since Kelly's estimate, we calculate that denitrification removed only about 13% of total inputs to the harbor during the period before outfall diversion (through 2000). The low percentage removal was a consequence of both the very high loading and the short residence time of the water within the harbor. (This rough estimate was made using all data from all years for Stations BH03, representing depositional areas, and Station BH02, representing reworking areas of the harbor. Data from Station BH08, sampled from 1991-1994, were used to represent erosional areas. Each month of the year was assigned a daily rate, using average rates for a given month and interpolating when data for a given month was not available. Average March rates were used as wintertime rates, i.e. Dec-Mar. Using this method, we calculate a removal of N by denitrification of over 1000 mmol m^{-2} yr^{-1}, which is at the upper end of Kelly's 1997 estimates. Inputs to the Harbor were assumed to be the same as used by Kelly, 1997.)

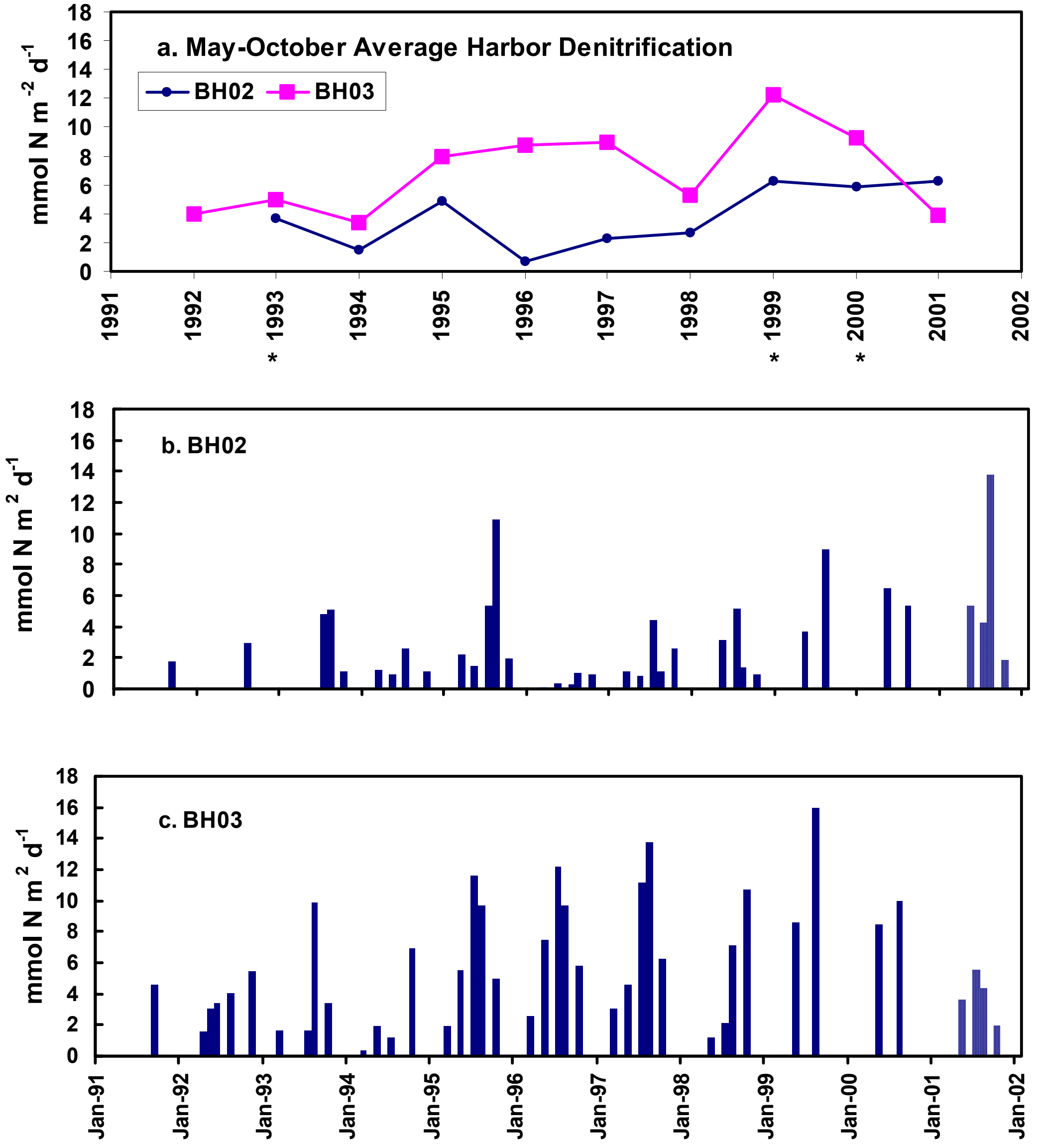


Figure 5. Denitrification at Stations BH02 and BH03. a.) May-October seasonal averages for 1992-2001. Asterisks indicate years with missing sampling dates. b. and c.) Individual survey results for BH02 and BH03, respectively. Stippled bars indicate post-diversion data (2001).

3.1.4 Phosphate Fluxes

Seasonally averaged fluxes of dissolved inorganic phosphorus (DIP), in general, have not followed the same long term trends as respiration and DIN flux, although like these other measures, 1993 was the peak year for phosphate fluxes at stations BH02 and BH03 (Figures 6a and 6b). Phosphate dynamics are regulated by both biological and chemical processes, and are therefore often decoupled from DIN fluxes. High PO_4 flux may correspond to anoxic sediments, conditions under which ferric hydroxides become soluble and release their bound phosphate. Phosphate efflux is also influenced by bioturbation, but the effects of bioturbation may be to diminish *or* enhance the flux. By increasing oxidation of the sediments, the binding of PO_4 to ferric hydroxides is enhanced and effluxes reduced. By irrigation of the sediments, bioturbation changes the mechanism of transport from diffusion to advection, thereby increasing the flux. The complex nature of phosphate dynamics means that a number of mechanisms, some of them competing, can combine to produce the fluxes we measure.

Phosphate fluxes at Station BH02 have in general been more variable than at the other three Harbor stations and at times have been very large. The 1993 seasonal average was 2.4 mmol m^{-2} d^{-1}, over twice as high as any other time at this or the other three harbor stations. Porewater profiles revealed a large pool of phosphate had accumulated in the sediments at a depth of about 5 cm by May, when concentrations at that depth exceeded 1100 µM, the highest we have measured (Figure 7a). Throughout the summer, concentrations declined to around 200 µM at that depth by August. In this same year, porewater parameters revealed strongly reducing conditions. Summer HS^- profiles (Aug) showed high concentrations of HS^-, up to 5mM at 18 cm depth, and Eh profiles were the most negative we have observed (see Figures 11 a and e). The very large phosphate fluxes in this year, therefore, were fully consistent with phosphate release from anoxic sediments. In contrast, phosphate efflux was high again in 1998 (seasonal average of ~0.95), although HS^- levels were not unusually high nor redox conditions unusually low for this station. Infaunal numbers showed only a very small increase over the previous year. Porewater profiles of phosphate did, however, show strong diffusional gradients in both July and August (Figure 7b).

For most years at Station BH03, phosphate fluxes have shown little interannual variability, fluctuating around 0.3 mmol m^{-2} d^{-1}(May-Oct average) (Figure 6b). Two years, however, had exceptionally high rates. The 1993 peak rates (May to October average = 1.0 mmol m^{-2} d^{-1}) were most likely associated with high infaunal abundances recorded that year, with active bioturbation serving to flush (advect) porewater phosphate out of the sediment. In addition to the high numbers of infauna, the timing of the development of the amphipod community seems to be important for explaining at least the early season part of the pattern we have observed. Porewater concentrations of PO_4 in May 1992 and 1994 (Figures 7a and 7c, respectively), when fluxes were average or low, described strong diffusional profiles over the top 3-4 cm, indicating an absence of bioturbation or other sediment flushing. Indeed, our field notes support the idea that the amphipod community had not yet developed. In contrast, field notes indicate a very dense community was present by spring, 1993. Phosphate profiles in May, 1993 (Figure 8b) were indicative of advective processes, with porewater concentrations low and changing little over the first 5 cm. This type of profile persisted through the summer, as did large fluxes. These differences in porewater profiles are consistent with the differences we observed in fluxes, as advective transport can exceed molecular diffusion by orders of magnitude (Huettel and Webster, 2001).

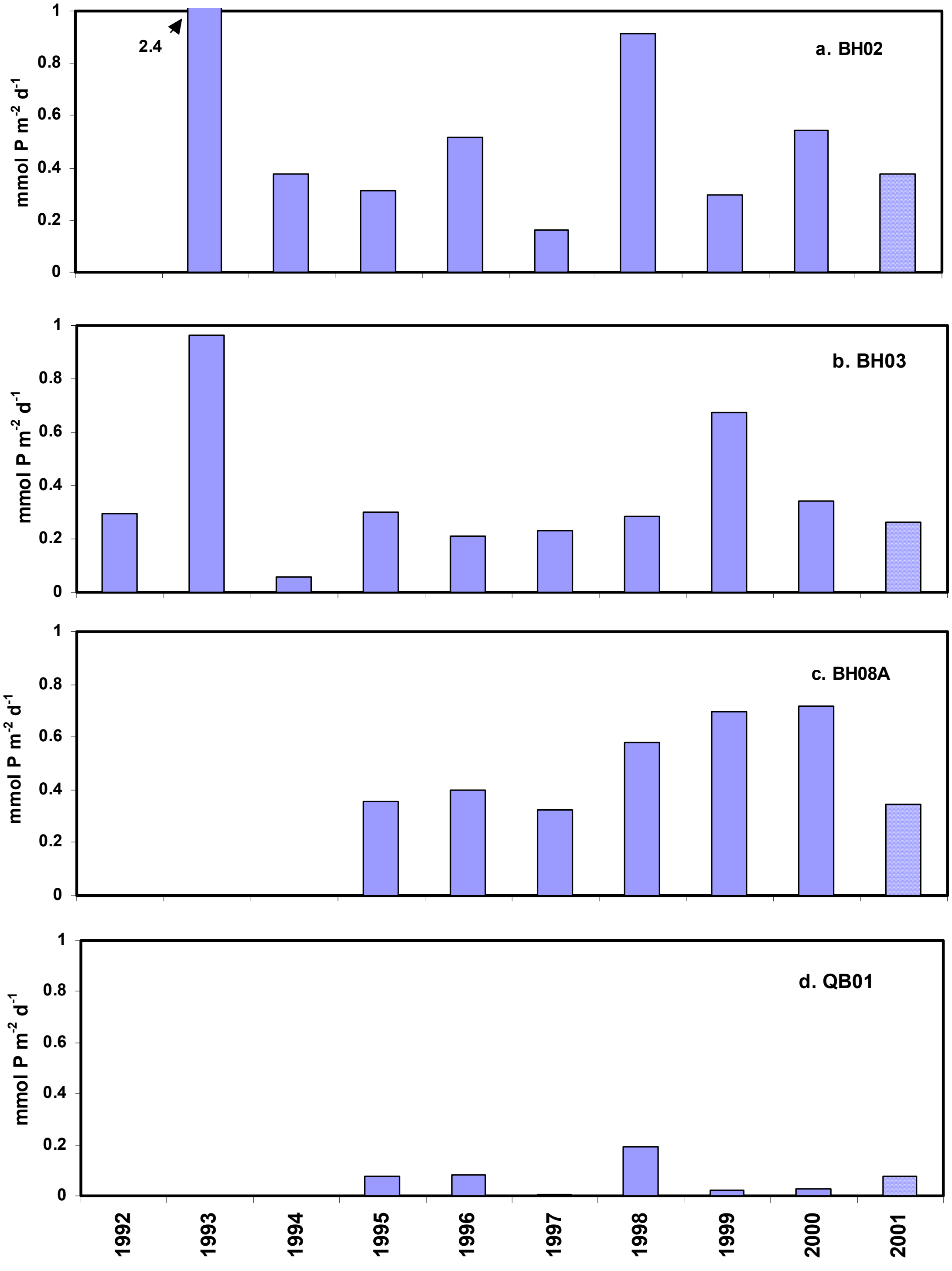
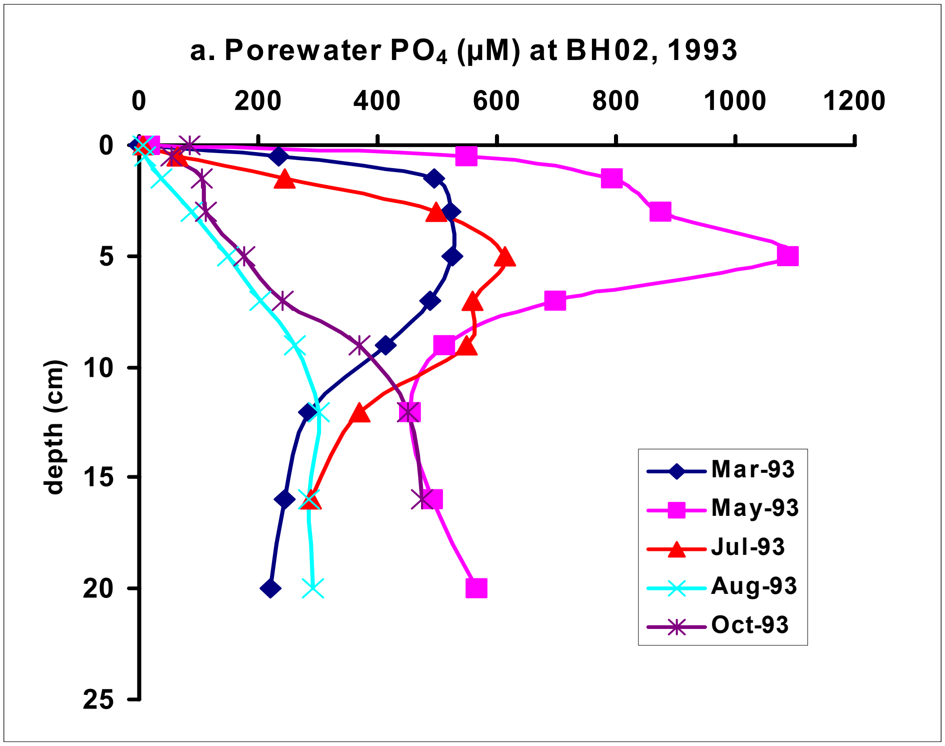


Figure 6. May-October seasonal average ortho-phosphate flux from 1992-2001 at harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01. The stippled bar designates post-diversion data (2001).



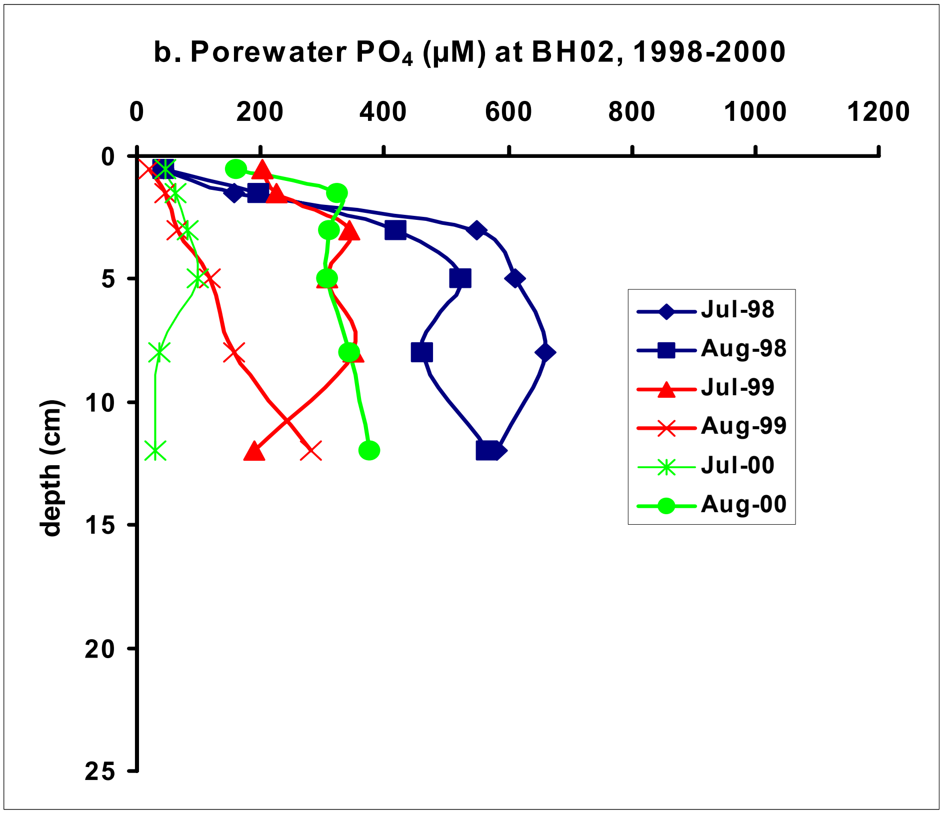


Figure 7. Porewater phosphate concentrations at BH02 in a.) 1993, and b.) July and August of 1998-2000.

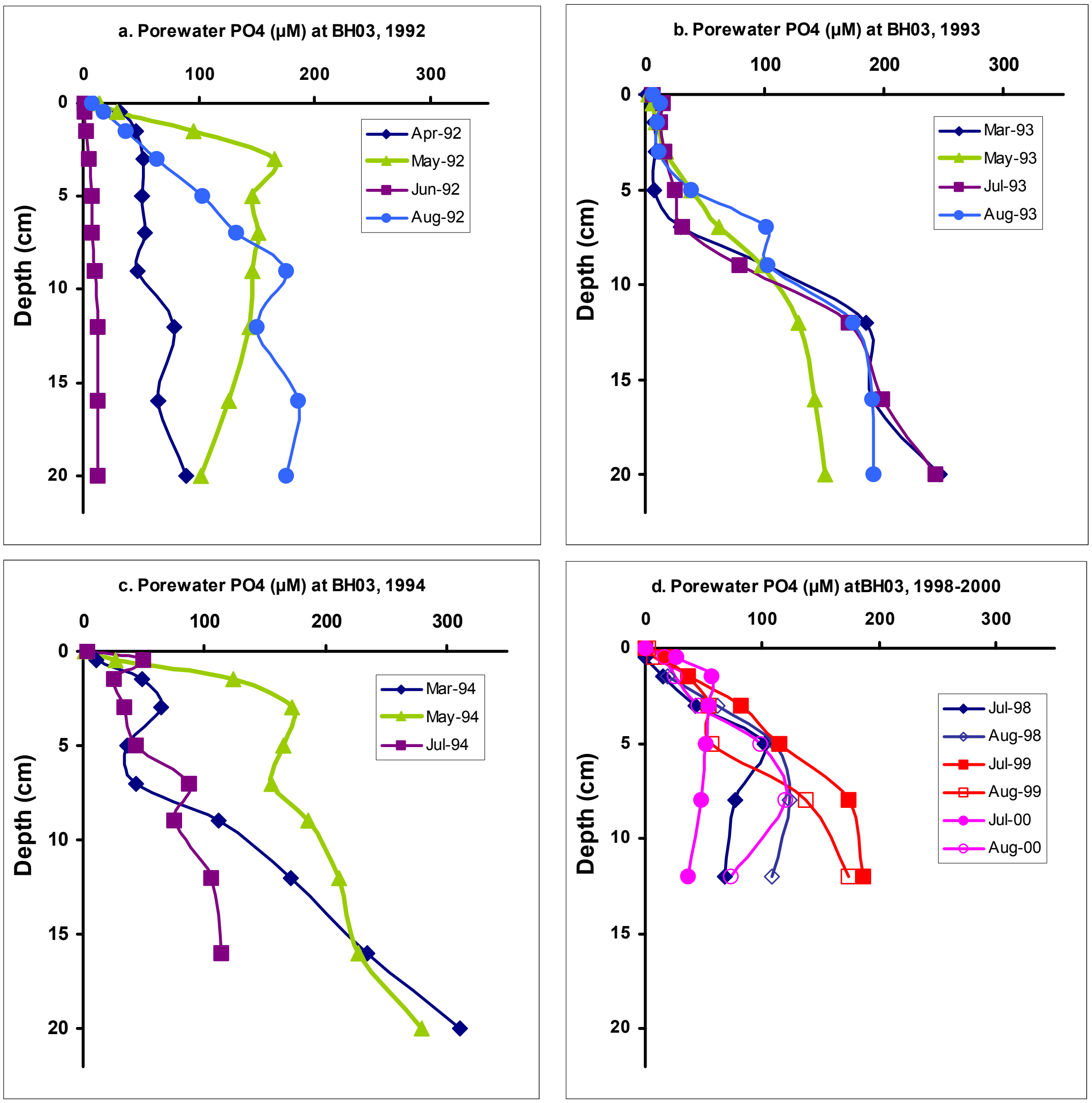


Figure 8. Porewater PO_4 concentrations in a.) spring-summer 1992, b.) spring-summer 1993, c.) spring-summer 1994, highlighting differences in May profiles, and d.) summer 1998-2000.

The second year with large PO_4 release at BH03 (May to October average = 0.7 mmol m^{-2} d^{-1}) occurred in 1999 (Figure 6b). We are not able to explain the high 1999 rate as easily as the 1993 peak. Summer infaunal abundance was high in 1999, but not as high as in 1997 or 1998, when PO_4 fluxes were low. May porewater profiles are not available, but summer (July and Aug) PO_4 profiles from 1999 were not substantially different from 1998 or 2000 (Figure 8d), when fluxes were much smaller. Field notes from May indicate that the amphipod community had not "set up" for the season, which would discount an early spring, large advective flux as an explanation. Although we did not measure porewater profiles in May 1999, Eh profiles may provide some insight. These profiles indicated that moderately reducing conditions were present below 6cm sediment depth in May, conditions reducing enough for ferric hydroxide dissolution and the release of phosphorus. As the high average flux rate was driven largely by May rates, we speculate that a large spring diffusive pulse, enhanced by a concentration gradient created by reducing conditions, was the cause.

In the Southern Harbor, phosphate fluxes have varied over narrower ranges, although the ranges are quite different for the two stations. At Station BH08A (Figure 6c), May-October rates have varied from 0.32 to 0.72 mmol m^{-2} d^{-1}. From 1995 to 1997, phosphate fluxes were relatively stable around 0.36. Rates increased from 1998 to 2000 to the maximum of 0.72, but returned to the 1995-1997 levels in 2001. PO_4 fluxes at Station BH08A, like Station BH03, are largely influenced by the very dense infaunal community.

At QB01, phosphate fluxes have been quite low, with seasonal averages typically less than 0.1 mmol m^{-2} d^{-1}(Figure 6d). On occasion we have observed PO_4 uptake by sediments at this site. The highest seasonal average rate at this station, 0.2 mmol m^{-2} d^{-1} occurred in 1998. As invoked for respiration and other nutrient fluxes, the sandier sediments, depauperate infauna (pers obs), and frequent presence of benthic diatoms combine to produce small fluxes from sediments at this site.

3.1.5 Dissolved Silica Fluxes

Patterns in fluxes of dissolved silicates resemble those for phosphate at Stations BH03 and BH08A, where the amphipod mats are present, but have shown little variability at Stations BH02 and QB01 (Figures 2d and 9). Rates of Si flux are known to increase with increasing bioturbation (Aller, 1982). In 1993, in the early stages of colonization of these sediments by the mat community, we measured very high rates of DSi flux at BH03, resulting in a seasonal average of 22 mmol m^{-2} d^{-1} (Figure 9b) . Rates at this station since that time have ranged from about 6 to 11 mmol m^{-2} d^{-1}, with the lowest seasonal average occurring in 2001. At Station BH08A, DSi flux was typically in the same range as for BH03 (Figure 9c) with the exception of a higher flux of just over 16 mmol m^{-2} d^{-1} in 2000. Seasonal average rates at BH02 have ranged from 4 to 10 mmol m^{-2} d^{-1} , with the highest rates in 1994 (Figure 9a). At QB01, average rates have never exceeded 5 mmol m^{-2} d^{-1} (Figure 9d). The highest rates at this station were measured in 1999; the lowest in 1996.

3.2 Sediment Redox Conditions

3.2.1 Respiratory Quotients

Sediment effluxes of CO_2 provide a second measure of sediment respiration in addition to O_2 influxes (S.O.D) discussed above. Comparison of the two fluxes provides insight into the relative importance of aerobic versus anaerobic respiratory processes. A ratio of CO_2 release to O_2 uptake, called the respiratory quotient, or RQ, is used to express this relationship. When aerobic processes dominate sediment metabolism, the flux ratio is close to 1.0 because aerobic respiration produces CO_2 equal to, on a molar

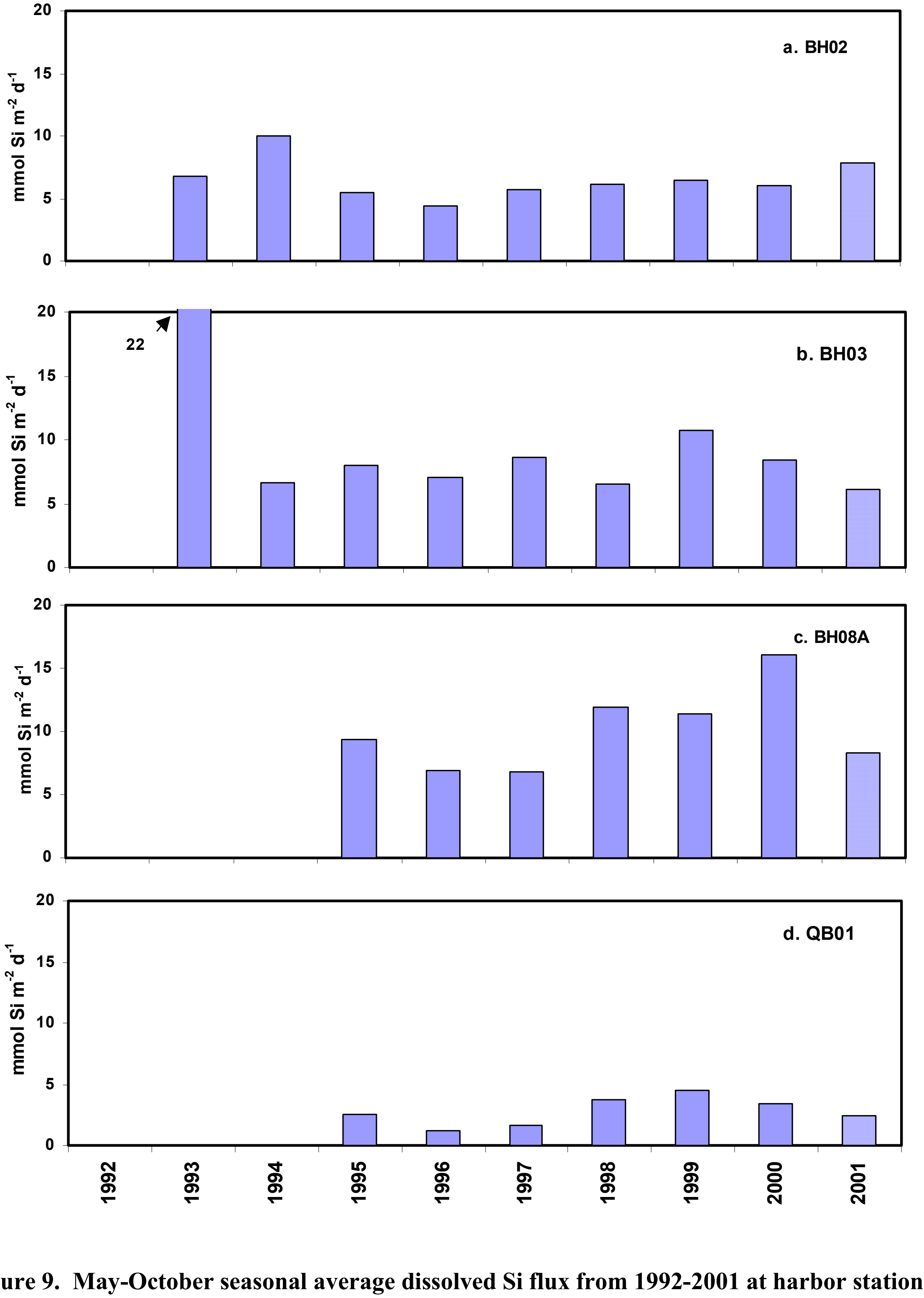


Figure 9. May-October seasonal average dissolved Si flux from 1992-2001 at harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01. The stippled bar designates post-diversion data (2001).

basis, the O_2 it consumes. During anaerobic respiration, CO_2 is produced but, because oxygen is not the terminal electron acceptor, O_2 is not consumed, unless or until the stored endproducts of anaerobic respiration are reoxidized. If the endproducts of anaerobic respiration are stored or released to the water column before they are reoxidized, the resulting RQ from the gas fluxes is greater than 1.0. If the endproducts are reoxidized, for example by winter storms resuspending bottom sediments, the RQ may fall below 1.0. Alternating periods of storage and reoxidation may result in an overall RQ approaching 1.0.

Throughout much of the monitoring period, respiratory quotients at Station BH02 were much greater than 1.0, often nearing and sometimes exceeding 2.0 (Figure 10a). In March of 1993 and 1994, RQs at this station were 3.4, by far the highest values of the monitoring period. Within the monitoring period, 1999 stands out for having RQ values close to 1.0, indicating increased oxidation of the sediments at this site. In 2000, however, RQs were once again well over 1.0 for three out of the four sampling events.

After the cessation of sludge disposal at Station BH03 in 1991, RQs have been close to 1.0 in most years (Figure 10b). With the colonization by the amphipod community, oxic decomposition was enhanced. In 1993, when the amphipod mat had become established and SOD was very high, we observed RQs less than 1.0 from May through August, suggesting that bioturbation was resulting in the reoxidation of some of the large stores of organic matter present at this site. Annual average RQ was only 0.65. In the following year, when respiration was lower and infaunal numbers were down, RQs were higher, with an average of 1.2 for the year. In 1998-2000, RQs averaged very close to 1.0 or slightly lower. It appeared that by 2000, most of the stored anaerobic endproducts at this site had been reoxidized.

At Station BH08A, also heavily colonized by the amphipod community, RQs have been close to 1.0 or somewhat higher (Figure10c). At QB01, where amphipods are not present but sandy sediments may permit oxygen penetration into the sediments, RQs are also near or just above 1.0 (Figure 10d).

3.2.2 Porewater Indicators

Other indicators of the oxic versus anoxic status of the sediments are provided by sediment profiles of sulfide concentrations and redox potential (Eh) (Figure 11). At Station BH03, prior to 1994, free sulfides in the sediment porewaters were detectable within the top 3 cm and sometimes reached very high concentrations, as much as 3mM, deeper in the core (Figure 11f). Since then, concentrations have been low and typical of coastal marine sediments, usually undetectable at sediments depths above 10 cm and less than 50 µM below that depth. Profiles of redox potential have also been more positive since that time, with Eh values greater than -100mV (sulfate reduction does not occur until Eh values of approximately -200 are reached) (Figure 11b). Taken together with the RQ values approximating 1.0, mentioned above, these parameters indicate that endproducts of anaerobic processes are being reoxidized on times scales equal to their production, and are no longer being stored in these sediments.

In contrast, at Station BH02 we regularly measured quite high levels of hydrogen sulfide in the sediments, with detectable levels reached within the top 2 cm of sediment and increasing to well over 1 mM at depth in the core (Figure 11e). This condition changed little over the baseline period. Eh profiles from BH02 also showed reducing conditions that began within the top 1-4 cm of the surface (Figure 11a). However, data from 1998 and 1999 in August, the time of the year when we might expect to see highest HS^- concentrations and lowest Eh values for the season, revealed much less reducing conditions in the top several centimeters of sediment. This pattern was broken by the Eh profile measured in August 2000, which was quite negative. The combination of RQ values larger than 1.0 and sediment profiles of high

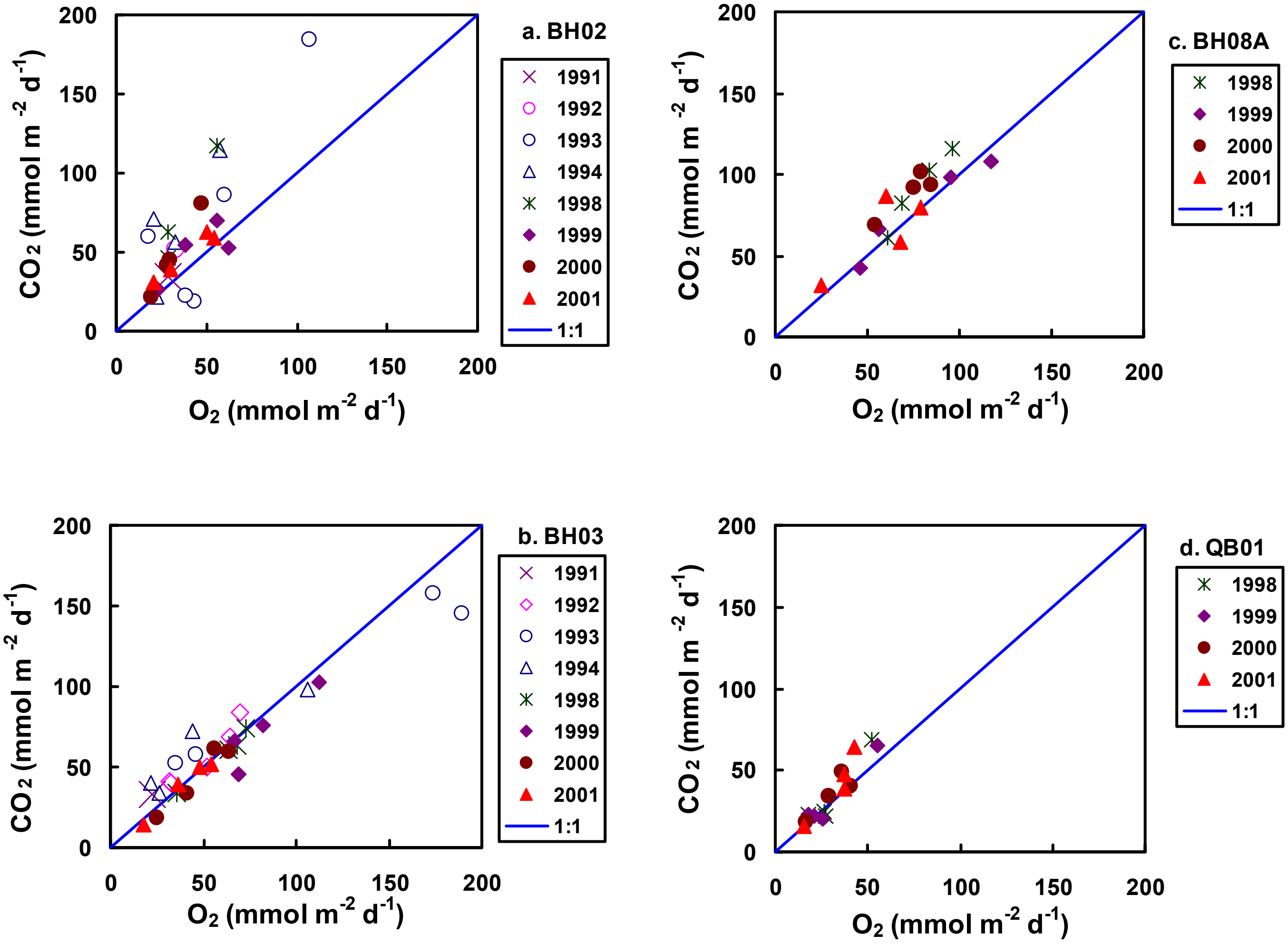


Figure 10. Respiratory quotients (CO_2 flux/O_2 flux) for harbor stations throughout monitoring and including 2001. a.) BH02, B.) BH03, c.) BH08A, d.) QB01.

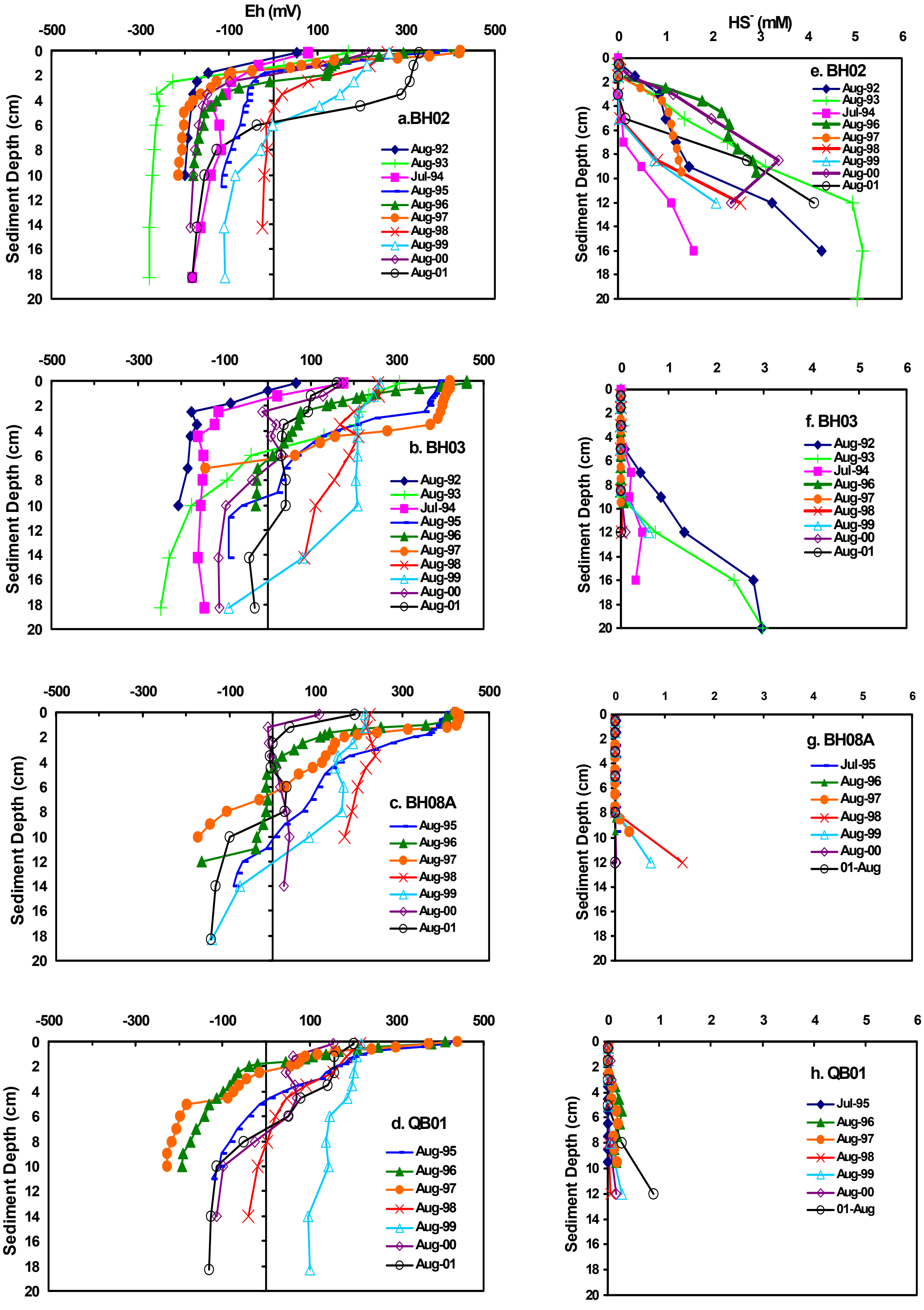


Figure 11. Summer redox (Eh) and dissolved sulfide (HS⁻) profiles for harbor stations, 1992-2001. a-d). Eh profiles, and e-f) HS⁻ profiles for stations BH02, BH03, BH08A, and QB01, respectively.

HS^- and low Eh demonstrate that although two out of the last three years of monitoring indicated improvement, anaerobic processes continue to be important at Station BH02, and that large concentrations of reduced endproducts remain “trapped” in these sediments.

In the southern harbor, we have not observed severely anoxic sediments since we began monitoring these sites in 1995. At Station BH08A free sulfide levels are usually at or below detection (Figure 11g). On the occasions when we have measured sulfides, concentrations have been in the range considered typical for “normal” marine sediments, and have only occurred at depth in the sediment core. Similarly, Eh values rarely drop below –100mV (Figure 11c). At QB01, hydrogen sulfides are often present in porewaters, but at low concentrations, typically less than about 0.3 mM (Figure 11h), contrasting with up to 5 mM at Station BH02. Variable redox conditions (Figure 11d) at this site may be related to a number of factors. Sediments at this site contain smaller percentages of fines than those at the other stations, often including shell fragments, which allows easier movement of water and materials through interstitial spaces. In addition, the benthic diatoms often present at this site can complicate sediment biogeochemistry by consuming nutrients and producing oxygen.

3.3 Sediment Parameters

3.3.1 Total Organic Carbon

Total organic carbon (TOC) content of harbor sediments at the four Benthic Flux stations has ranged from 0.5 % to 4.9% over the course of the monitoring period (Figure12). The station with the highest grand mean value, 3.4%, was Station BH03 whereas the station with the lowest mean, 2.1%, was Station BH02. The two southern harbor stations were similar and intermediate in mean values.

High organic carbon content in the sediments of Station BH03 is the result of the accumulation of sludge deposits at that site. It appears that since the cessation of dumping, and with the colonization of the site by amphipods and associated infauna, the stores of carbon are slowly decreasing. The benthic community has both utilized the organic matter directly and has enhanced microbial decomposition through active bioturbation. Seasonal means of percent carbon were 4.1% in 1992 and had decreased to 2.8% in 2000 (Figure 12b).

A similar downward trend has not been apparent at the other north harbor site. From 1992 to 1998, Station BH02 exhibited large variability in sediment TOC, within and among years. Highest organic carbon content was observed at this site in 1996. From 1999-2000, TOC content was more stable (Figure 12a).

Sediment characteristics at the two southern harbor stations, Stations BH08A and QB01, are quite different. Station BH08A has much siltier sediments than does QB01, and is colonized by the amphipod mat community. Even so, trends in TOC content of the sediments have been similar (Figures 12c and 12d). Higher carbon content was observed in 1995 and 1996 than for the rest of the monitoring period, with values decreasing through 1999, then increasing again somewhat in 2000. Average TOC is similar between the two stations, but BH08A has experienced much higher values and QB01 much lower. Sediments at QB01 tend to show more interannual variability.

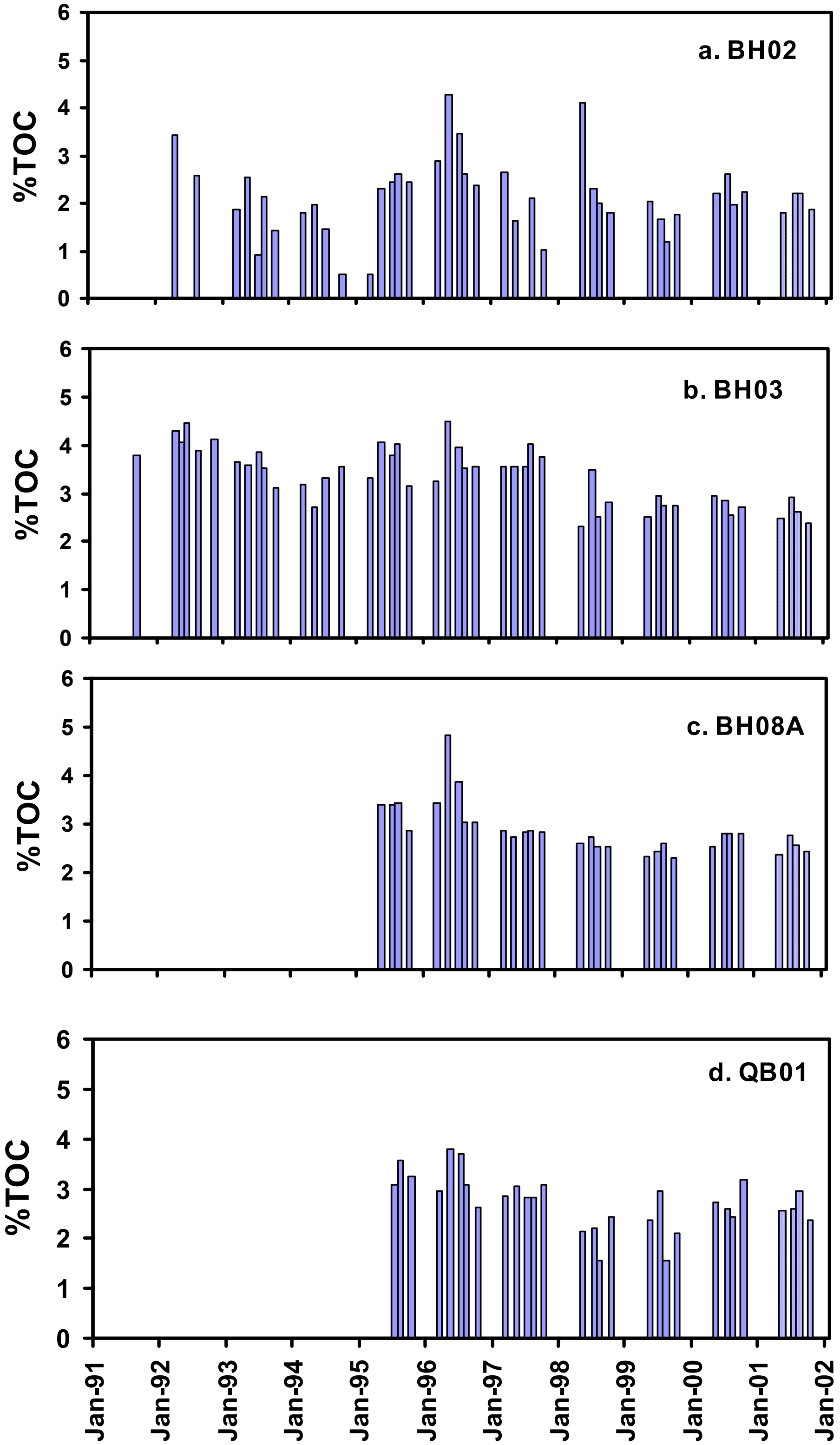


Figure 12. %TOC in top 2 cm of sediment for harbor stations a.) BH02, b.) BH03, c.) BH08A, d.) QB01. Stippled bars denote post-diversion data (2001).

3.3.2 Sediment Pigments

Pigment content of Boston Harbor sediments has been measured since 1994 at BH02 and BH03 and since 1995 at BH08A and QB01. Benthic pigments may be derived from phytoplankton production or from *in situ* growth where sufficient light reaches the bottom. At times, benthic diatoms are visible on the sediment surface. Most frequently, we have observed benthic diatoms at Station QB01, which, due to its shallow depth, has good light penetration to the bottom. The station is also characterized by low infaunal abundances, therefore grazing pressure is low. We have less frequently noticed benthic diatoms at the other stations.

Chlorophyll *a* and phaeopigment content have varied widely over the monitoring period, with the full range of values (from 90 to 233 µg pigment/ cm^{-2} integrated over the top 5 cm of sediment) occurring at Station BH02. Total pigment levels appeared lower at all stations in 1995-1997, years that also corresponded to a change in contract. Much of the difference is in the phaeopigment fraction, and is likely due to differences in pigment extraction procedures, as we have discussed before (Tucker *et al.*, 1999 and 2000). This difference is not apparent in the chlorophyll fraction.

At station BH02, chlorophyll *a* inventories from late 1997 through the end of the monitoring period were larger than they had been in 1995-early 1997, and were more similar to inventories measured in 1994 (13a). This increase may in part be due to high water column chlorophyll present in 1998-2000 (Werme and Hunt, 2001). At QB01, background levels were stable, but there was often a large peak in early spring, when we typically have noted benthic diatoms (Figure 13d). An especially large peak was measured in May, 1998, when integrated chlorophyll levels were nearly 35 µg cm^{-2}. Chlorophyll concentration in the sediments at BH03 and BH08 have been variable, but the variability seems damped compared to the other two stations, likely an effect of grazing and mixing by the amphipod community present at both sites (Figures 13b and 13c).

Sediment profiles of chlorophyll *a* have also been variable, but some trends emerge. Station QB01 has the most consistent seasonal pattern of chlorophyll content (Figure 14 j-k). Concentrations are typically highest in May, sometimes showing a very high surface concentration, consistent with our observations of benthic diatoms. By October, concentrations reach their lowest and the profile is flat. Profiles from BH03 and BH08A, where the amphipod community is present, show less change with depth or season as compared to QB01 (Figures 14 d-e and g-h). There is a tendency for the May and October profiles at these stations to be similar, and exhibit higher concentrations than in mid-summer, but not as high as at QB01. Higher concentrations at early and late season may be related to lower grazing pressure by the benthos; we have at times noted that the amphipod mat is not yet well developed in early spring, and has declined by mid autumn. Station BH02 has typically had high sediment chlorophyll *a* concentrations, similar to those at QB01, but has shown less seasonal definition in the profile (Figures 14 a-b).

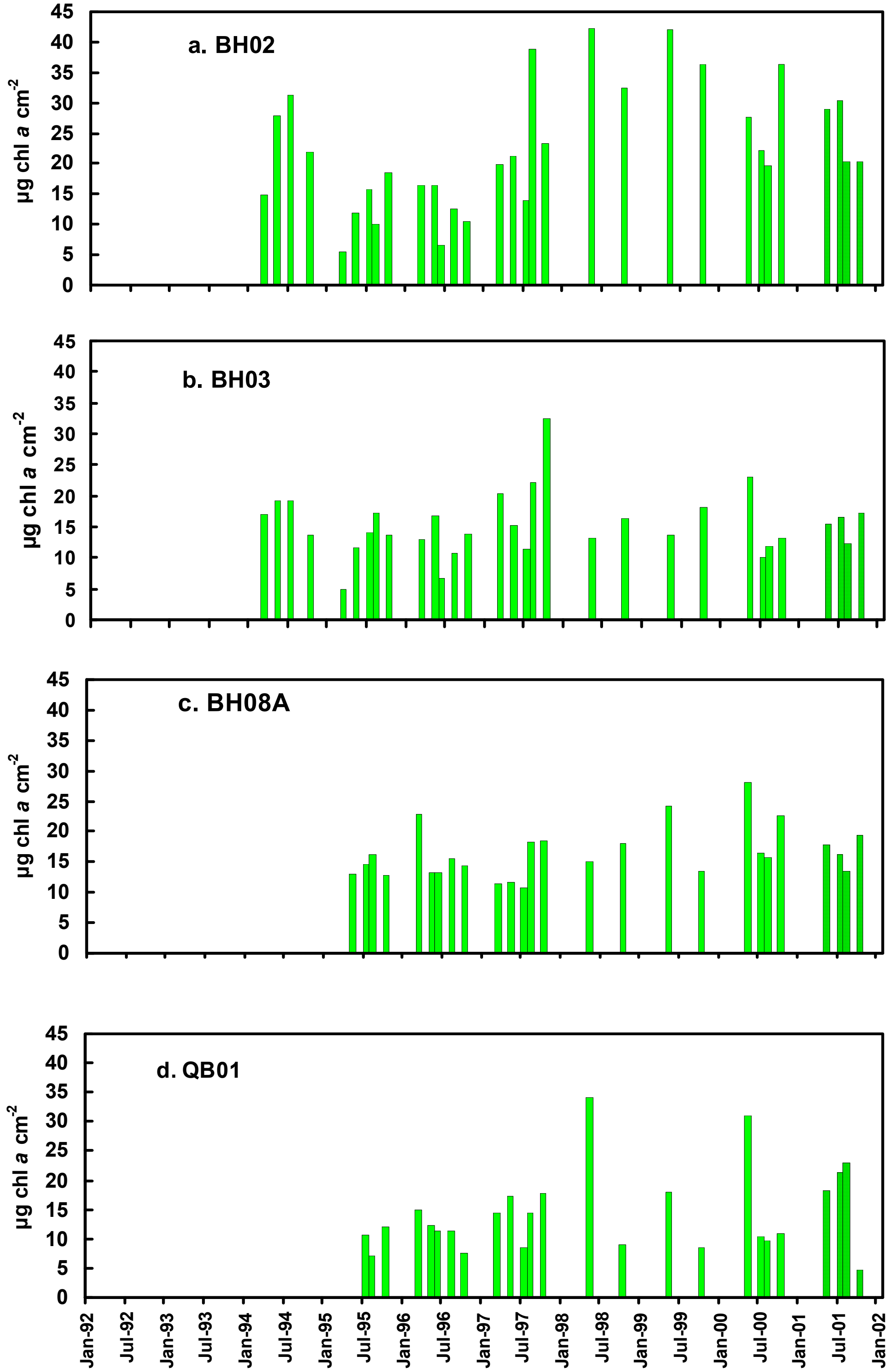


Figure 13. Chlorophyll a inventory in the top 5 cm of sediment from 1994-2001 at harbor stations a.) BH02 and b.) BH03, and from 1995-2001 at stations c.) BH08A and d.) QB01. Stippled bars denote post-diversion data (2001).

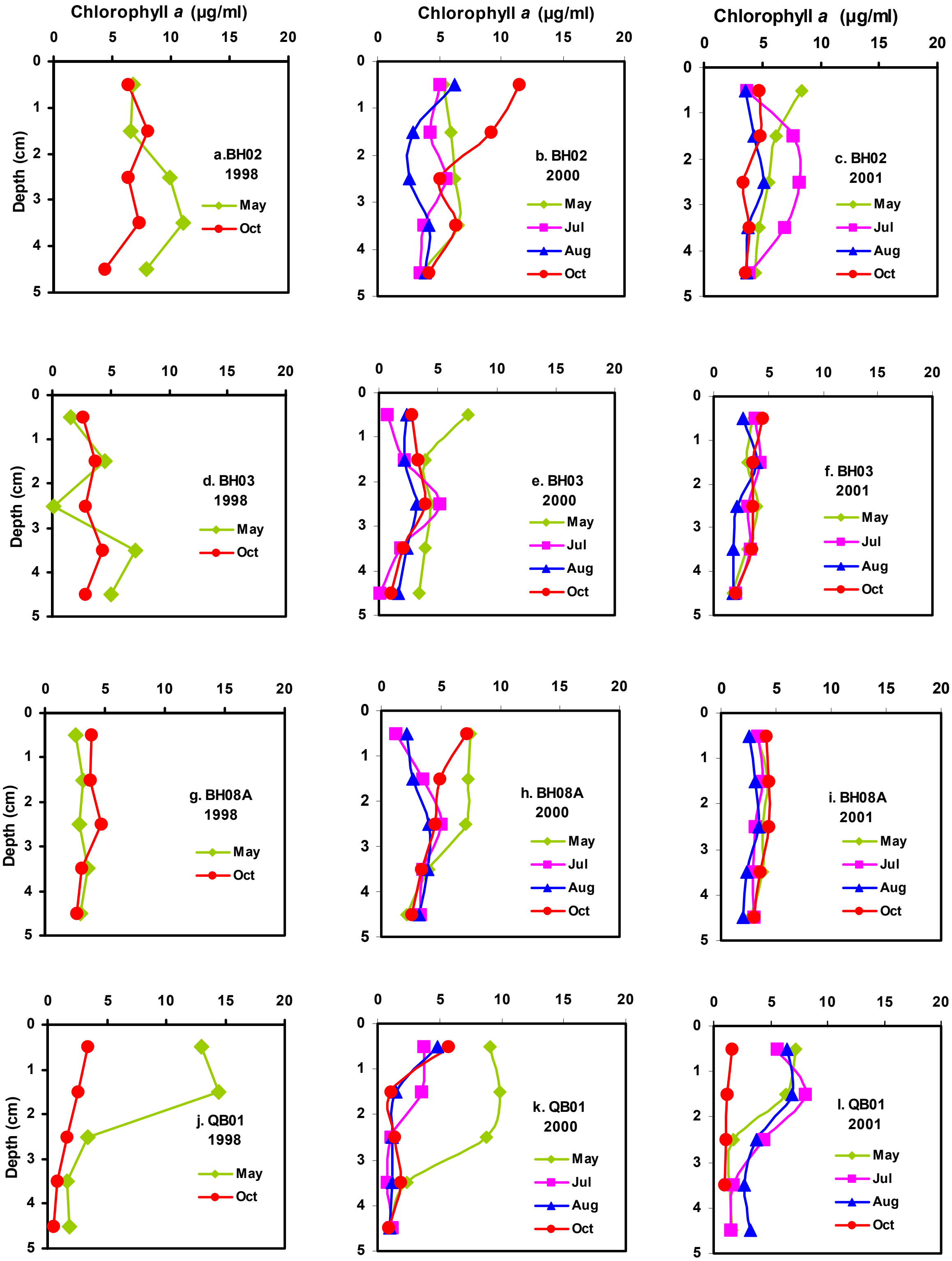


Figure 14. Representative profiles of chlorophyll *a* concentrations (µg chl *a*/ml sediment) from 1998, 2000, and 2001 in the top 5 cm of sediment at harbor stations a-c). BH02, d-f) BH03, g-i) BH08A, and j-l). QB01.

4.0 HARBOR OBSERVATIONS ONE YEAR POST-DIVERSION; 2001

4.1 Trends in Benthic Respiration and Nutrient Fluxes

In 2001, the first full year of effluent diversion out of Boston Harbor, benthic metabolism and nutrient fluxes at Stations BH02, BH03, and BH08A were in the low end of the range observed during the monitoring period. At Station QB01, fluxes were in general in the middle of the range.

4.1.1 Sediment Oxygen Demand

At the two northern harbor stations, BH02 and BH03, sediment oxygen demand in 2001 was in the low end of the range established during monitoring (Figures. 15 a and b). At Station BH02, early and late season (May and October, respectively), rates were among the lowest observed during monitoring. At BH03, SOD in August was lower than the range for that month, and the seasonal average rate of 39 mmol m^{-2} d^{-1} was the lowest yet observed, continuing the decreasing trend we have observed at this station since 1996 (refer back to Figure 3b). Highest SOD for the year among the four harbor stations was measured at Station BH08A in Hingham Bay, where rates peaked at nearly 80 mmol m^{-2} d^{-1} in May, and decreased through the season to 25 mmol m^{-2} d^{-1} in October (Figure 15c). 2001 was the second sequential year that highest sediment respiration was recorded at Station BH08A rather than BH03. Even so, SOD at this station was below the baseline range from July through October and the seasonal average, 58 mmol m^{-2} d^{-1}, was lower than observed in all previous years (Figure 3c). At Quincy Bay station QB01, SOD was typical for the monitoring period, albeit with slightly elevated August rates (Figure 15d).

4.1.2 DIN Fluxes

DIN flux in 2001 in the northern harbor seemed to continue the decreasing trend we have observed in the last several years. At station BH02, DIN fluxes in May and October were among the lowest observed (Figure 15e). July and August rates were low to moderate. The seasonal average of 4.3 mmol m^{-2} d^{-1} was typical, but somewhat atypical was that NO_3 comprised a relatively large portion, 23%, of the flux (Figure 4a). In only two other years during monitoring, 1995 and 1999, had nitrate been greater than 15% of the DIN flux at this station. An increase in NO_3 efflux probably correlates with increased infaunal colonization, and is an indicator of less reducing conditions in these sediments. At station BH03, DIN flux was also among the lowest observed during monitoring (Figure 15f). Seasonal average DIN fluxes matched the baseline low rate of 2.6 mmol m-2 d-1, which was recorded in 2000 (Figure 4b). Nitrate continued to comprise a large portion of the DIN flux, 44%. However, NO_3^- flux at this station, especially during years of peak infaunal numbers and health, has at times comprised as much as 88% of the DIN flux (1995). A relative decrease in NO_3^- flux together with lower overall DIN and O_2 fluxes may reflect a decreasing influence on benthic fluxes by infauna. Such a decrease might result from the depletion of stored organic matter, or may be the result of degradation of or patchiness within the amphipod mat.

At station BH08A, rates of DIN flux were higher than at the northern harbor stations, but somewhat lower than the previous two years and in the mid- to low end of the baseline range (Figure 15c). The seasonal average of 5.7 mmol m^{-2} d^{-1} was quite typical (Figure 4c). Nitrate flux was 31% of the total DIN flux at this station, where the contribution of nitrate has ranged from 16% to 55%. At station QB01, 2001 fluxes were at the upper end of the range in May, the lower end in July, somewhat higher than the range in August, and low again in October (Figure 15d). Seasonal average DIN flux was 1.9 mmol m^{-2} d^{-1}, with 27% of the flux made up by NO_3^-, quite typical for this station (Figure 4d).

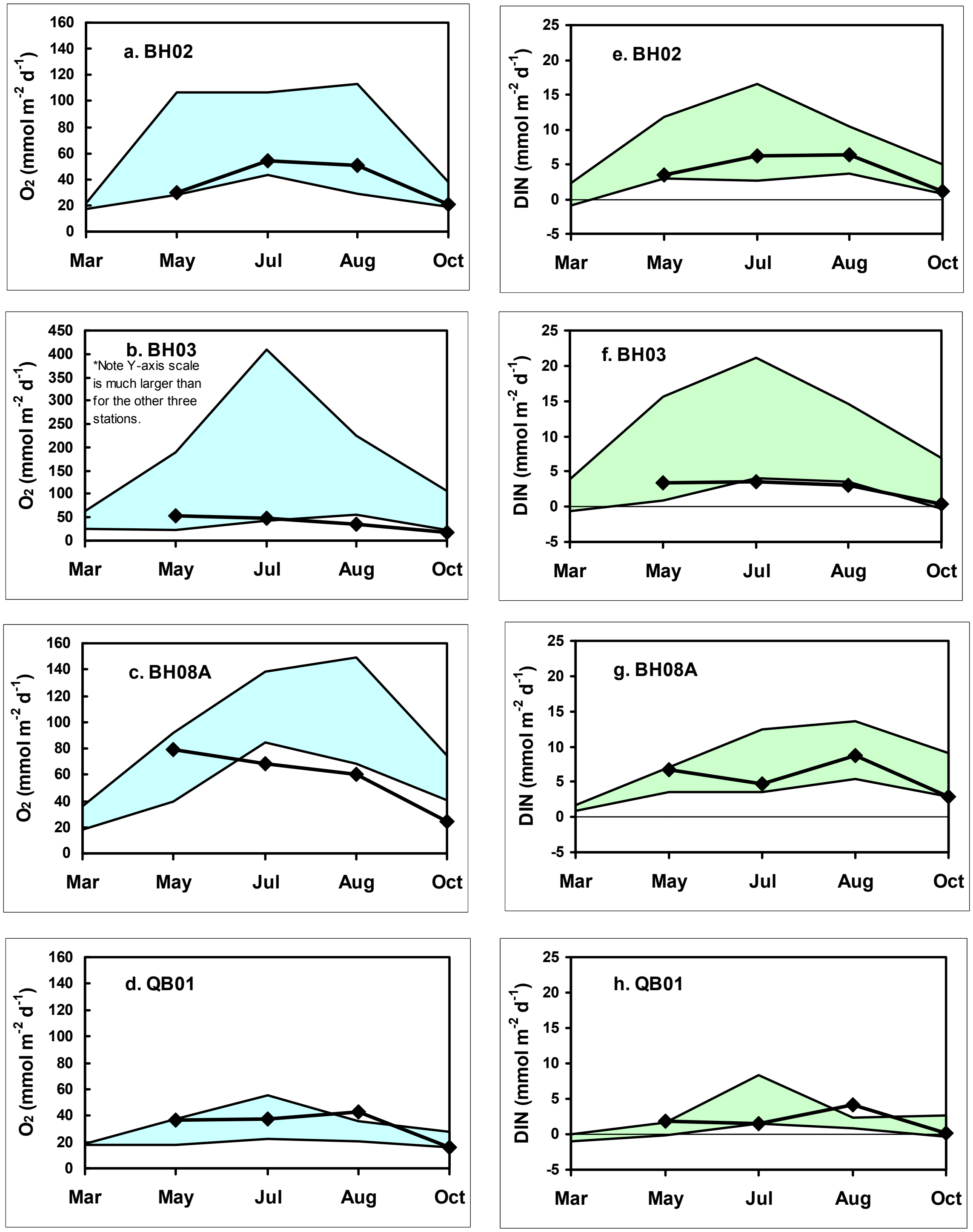


Figure 15. Sediment oxygen demand (O_2 flux) and DIN flux for 2001 (solid lines) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O. D. and panels e-h depict DIN flux for stations BH02, BH03, BH08A, and QB01, respectively.

4.1.3 Denitrification

In 2001, rates of denitrification at the two harbor stations where it is measured revealed some differences compared to previous years. At Station BH02, denitrification was typical of baseline in May, July, and October, but August rates of 13.8 mmol N m^{-2} d^{-1} were the highest observed at this site (Figure 5b). A seasonal average of 6.3 mmol N m^{-2} d^{-1} was at the high end of the range encountered during monitoring., and was also higher for the first time than rates measured at Station BH03 (Figure 5a). At BH03, denitrification in 2001 was lower than all previous years except 1994, and continued what appears to be a return to lower rates at this site since the very high rates observed in 1999 (Figures 5a and 5c).

With the removal of sewage-derived nitrogen loading from the harbor, high rates of denitrification like those we measure at these two stations may become a significant sink for excess nitrogen. Kelly (1997) calculated that the MWRA contribution to harbor N-loading accounted for 89% of the total. Assuming this amount of nitrogen was removed by diversion, the remaining loading from terrestrial sources is 930 mmol N m^{-2} yr^{-1}. Under this post diversion scenario, the denitrification estimate used above (Section 2.1.3) of more than 1000 mmol m^{-2} yr^{-1} becomes a sink equivalent to inputs.

However, terrestrial inputs, even when including the sewage contribution, are dwarfed by oceanic inputs, which are more than two times greater (Kelly, 1998). Although oceanic inputs are predicted to decrease somewhat after diversion, their relative contribution to the harbor N budget will be much larger. Including oceanic inputs (taken from Kelly, 1998), the percent removal of TN by denitrification, pre-diversion, drops to about 5%. After diversion, calculations suggest that denitrification will remove only about 7% of total TN inputs, not the entire amount suggested by comparison to terrestrial loading alone.

4.1.4 Phosphate Fluxes

Phosphate fluxes in 2001 were in general moderate to low compared to baseline, and quite similar across three of the four stations, BH02, BH03, BH08A (Figure 16 a-c). At Station BH02, fluxes in May and October were among the lowest rates observed during monitoring, in a similar pattern to oxygen and DIN. July and August fluxes were moderate, leading to an intermediate seasonal average of 0.4 mmol m^{-2} d^{-1}(Figure 6a). At BH03, the seasonal average flux of 0.3 mmol m^{-2} d^{-1} was quite typical of most of baseline observations (Figure 6b), which fall in the lower end of the full range observed. At BH08A, phosphate fluxes had decreased from large fluxes during 1998-2000 back to lower rates of 1995-1997. The seasonal average was 0.3 mmol m-2 d-1 (Figure 6c). Phosphate fluxes at QB01, with a seasonal average of less than 0.1 mmol m-2 d-1 (Figure 6d), were, typically, much smaller than at the other three stations, but intermediate the range established at this site (Figure 16d).

4.1.5 Dissolved Silica Fluxes

Dissolved silica fluxes were also within the ranges observed during monitoring (Figures 16 e-h). At BH02, Si fluxes were somewhat higher than the previous few years, and in August were higher than the range previously seen for that month. The seasonal average flux for 2001 of 7.8 mmol m^{-2} d^{-1} was the largest since the baseline high of 10 mmol m^{-2} d^{-1} in 1994 (Figure 9a); however variability around seasonal average fluxes at this station has been small, with the total range only 4.4 to 10.0 mmol m^{-2} d^{-1}. In contrast, DSi fluxes at BH03 were the smallest observed at this station, but again, with the exception of very high rates in 1993, the range in DSi fluxes has been narrow, from 6.1 (2001) to 8.7 mmol m^{-2} d^{-1}(seasonal average)(Figure 9b). DSi fluxes at Station BH08A have exhibited more variability from year to year than the northern harbor stations (again, with the exception of the high fluxes at BH03 in 1993),

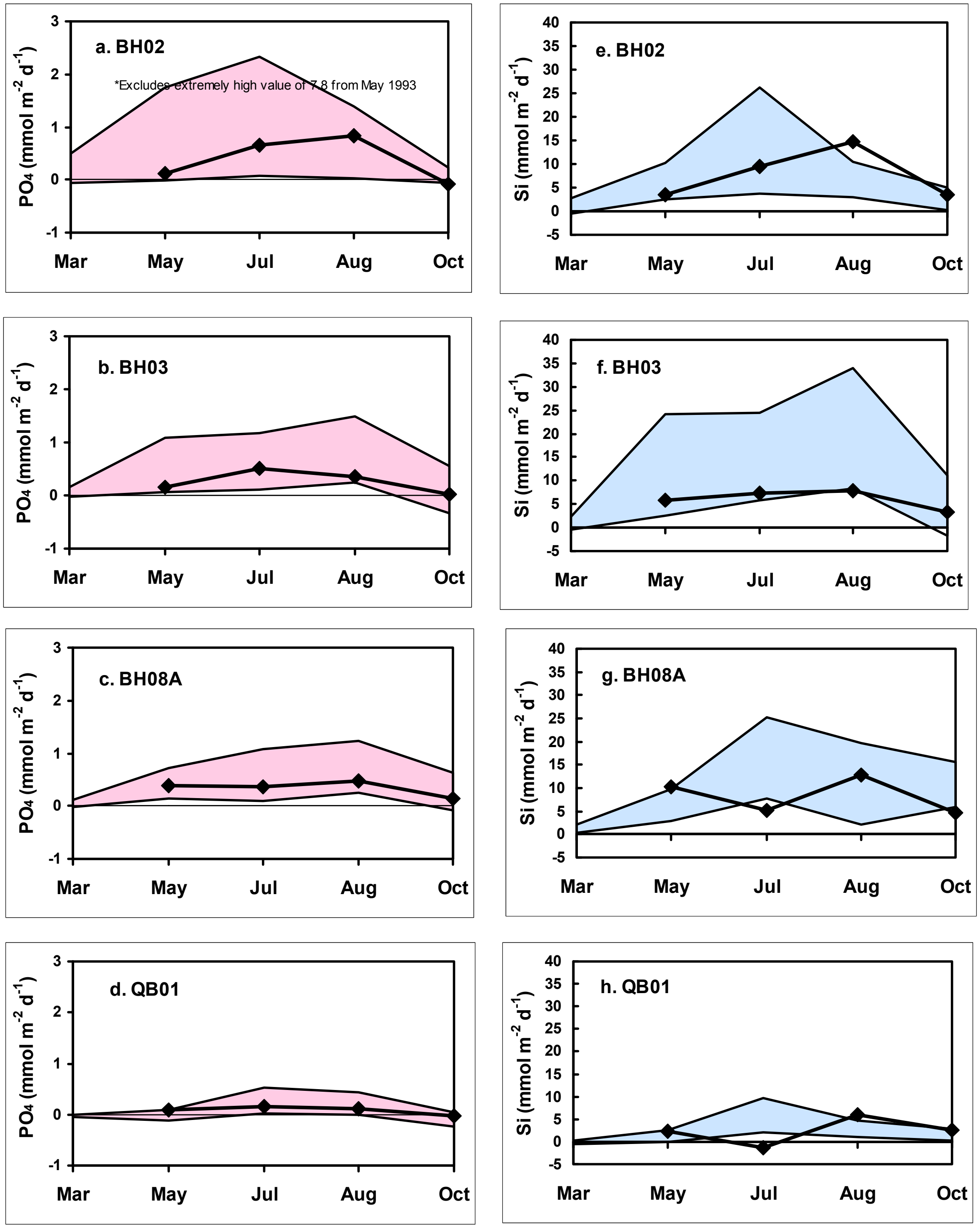


Figure 16. Phosphate and dissolved silica for 2001 (solid lines) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO_4 flux. and panels e-h depict DSi flux for stations BH02, BH03, BH08A, and QB01, respectively.

but in 2001 were about average for the station at 8.3 mmol m^{-2} d^{-1} (Figure 9c). July fluxes were lower than previously observed in that month (Figure16c). Average DSi fluxes of 2.4 mmol m^{-2} d^{-1} at Station QB01 were also typical for that site (Figure 9d), but included the more atypical event of Si influx in July (Figure 16d). Benthic diatoms are often noted at this site and may have been responsible for the uptake.

4.2 Sediment Redox Conditions

4.2.1 Respiratory Quotients and Porewater Indicators

Indicators of sediment redox conditions at the amphipod dominated sites BH03 and BH08A revealed that strongly oxidizing conditions in sediments persisted at those sites in 2001. The continued presence of the amphipod community and the bioturbation of the sediments caused by its activities have maintained these conditions. After an imbalance in oxygen versus carbon dioxide fluxes observed early in the monitoring program at BH03, respiratory quotients (RQs) at these two sites have been very close to 1.0 (Figures 10b and c). Likewise, Eh profiles in 2001 were not strongly reducing (Figures 17 b and c), and HS^- was not detected (Figure 11f). There was a similar seasonal pattern in Eh profiles between the two stations, with more reducing conditions present in May and August, and more oxidizing conditions present in July and October. Decomposition processes enhanced by a spring phytoplankton bloom in May and increased temperature in August may account for lower Eh values in those months.

At Station BH02, RQs were also very close to 1.0 in 2001 (Figure 10a). At this station, a reducing sediment environment has been typical and the infaunal community has been sparse. Often only a thin oxidized surface layer of sediments is present and concentrations of hydrogen sulfide in the porewaters are appreciable. RQs have at times been well over 1.0. Patterns in 2001 have now repeated the encouraging signs of improved sediment conditions that we observed in 1999. In addition to RQs near 1.0, Eh profiles indicated a deeper (4 cm or deeper, depending on season) oxidized layer than typical (Figure 17a), and measurable HS- were encountered deeper in the sediment profile. (In August, HS^- was not detectable until deeper than 5 cm in the sediment profile; Figure 11e.). Redox conditions were most reducing in May, then became progressively less so through the season to October.

Respiratory quotients at Station QB01 have typically been close to 1.0, as they were in 2001 (Figure 10d). The seasonal pattern we observed in Eh at Station BH03 and BH08A was more pronounced at Station QB01 (Figure 17d). May and August profiles were very similar, becoming negative between 8 and 10 cm depth and reaching values around –130 mV at 18 cm. In August, sulfide became detectable below 5 cm, and increased to 0.9 mM by 18 cm, the highest concentrations measured at this site (Figure 11h). (We do not measure porewater constituents in May; however the similarity in Eh profiles suggests sulfides would have been present in May). The August Eh profile, however, was not extraordinary in any way, plotting in the middle of August profiles measured since 1995 (Figure 11d).

4.3 Sediment Parameters

4.3.1 Total Organic Carbon

Organic carbon content of harbor sediments in 2001 was very similar to that observed in the previous two to three years (Figure 12). Concentrations were consistent throughout the year at all four sites, showing no significant highs or lows. Stations BH03, BH08A, and QB01 had very similar average %TOC, 2.6% (S.D.= 0.05), and for all three stations these values continued the pattern of decreased organic matter since 1997. Lowest average organic carbon content, 2.1% TOC, was found at Station BH02.

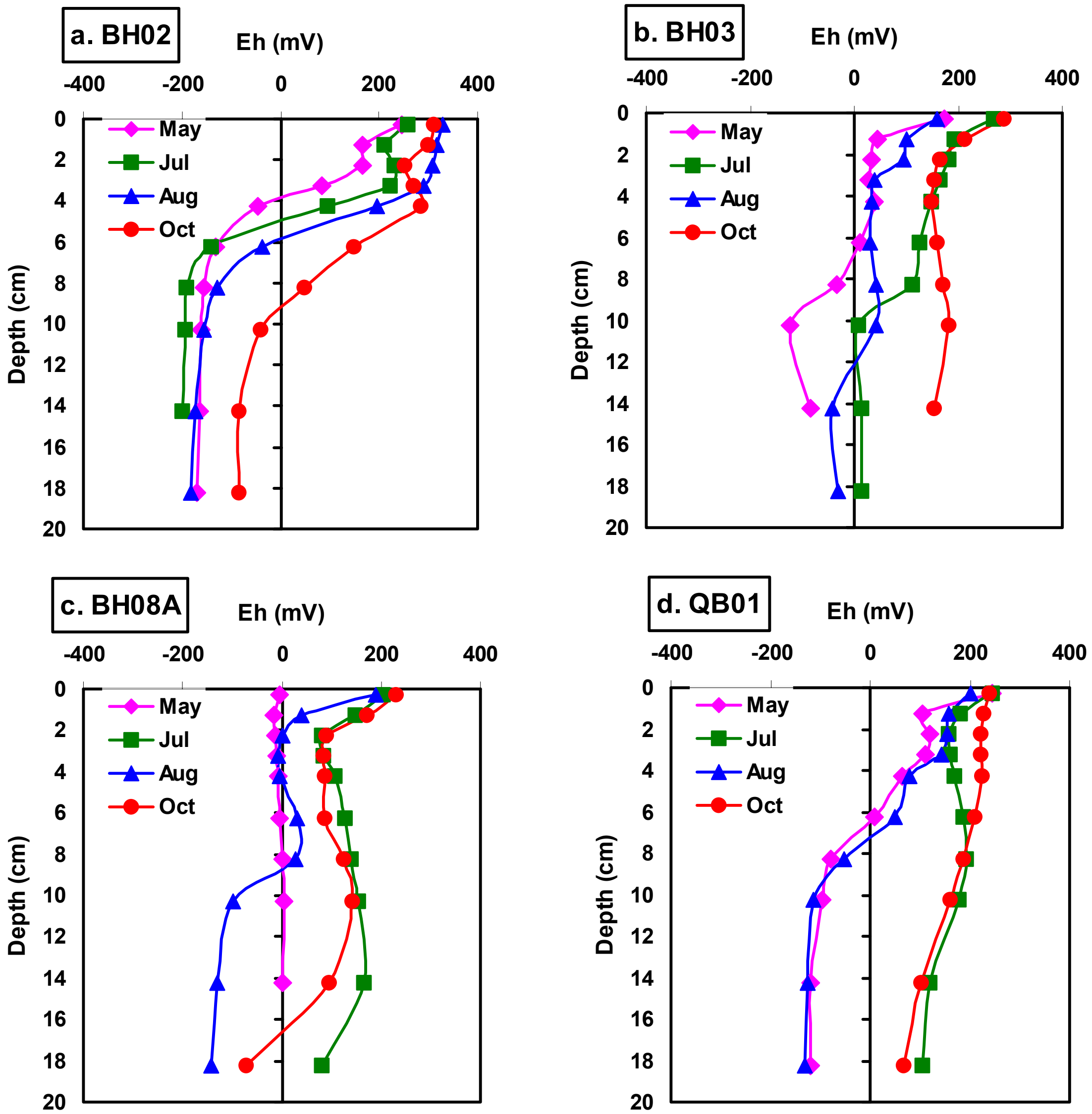


Figure 17. Redox (Eh) profiles in 2001 from harbor stations a.) BH02, b.) BH03, c.) BH08A, and d.) QB01.

4.3.2 Sediment Pigments

Total photosynthetic pigment inventories were in the high end of the baseline range in 2001, but lower, in general, than the large amounts observed in 1998-2000. As noted in previous reports (Tucker *et al*., 1999; Tucker *et al*., 2000, Tucker *et al*., 2001), anomalously low phaeophytin values in 1995-1997 make up most of the difference in total pigment concentrations between those and later years. In the chlorophyll fraction alone, 2001 was unremarkable (Figure 13) except for very low chlorophyll *a* inventories at Station QB01 in October.

Profiles of chlorophyll *a* through the top 5 cm of sediment at Stations BH02 and QB01 were interesting in 2001. The early spring (May) profile at BH02 showed elevated surface concentrations (Figure 14c). At this time, we observed red-brown benthic diatoms (unidentified), at Station BH02 in May. This is the first time we have noticed benthic diatoms at this station. In July, surface chlorophyll *a* concentrations were depleted, but higher concentrations were apparent in a bulge in the profile between 1 and 4 cm depth, the chlorophyll having apparently been mixed down into the top few centimeters of sediment. By August and in October, the profile indicated a well-mixed top 5 cm of sediment. Total chlorophyll inventories in May and July were similar, and larger than in August and October.

Chlorophyll profiles from Station QB01 (Figure 14 l) showed high surface concentrations from May through August. The profiles indicate high concentrations through the first 2 cm of sediment in all three months, so although we did not see a surface layer of diatoms, it is likely they were present within the sediments. By October, chlorophyll *a* and total pigments were much reduced, with the profile showing well-mixed conditions in the top 5 cm.

Profiles of chlorophyll *a* at stations BH03 and BH08A revealed well-mixed sediments, consistent with bioturbation and with previous years observations (Figures 14f and i).

5.0 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. Concentrations of dissolved oxygen present in GOM water at the onset of stratification in the spring contribute directly to the degree of seasonal O_2 depletion in the bottom waters of the bay (Geyer, pers. com). In addition, nutrients are delivered to the bay in GOM water.

Another major source of nutrients and other materials to Massachusetts Bay has been Boston Harbor. Estimates suggest that as much as 90% of nitrogen loading to the harbor was exported to the bay by tidal flushing (Kelly, 1997). Concentration gradients dominated by DIN in the winter and TN in the summer extended 20 km into the bay. In addition, chlorophyll was also exported from the harbor in the summer, adding another organic component to the “fertilization” effect. Evidence of particulate matter export from the harbor has also been noted in the chemistry of bay sediments. Concentrations of silver, used in processing film and shown to be a sewage indicator, and *Clostridium perfringens* spores, from a benign bacterium found in sewage, document the presence of sewage particulates in the sediments (Bothner, 2001). Similarly, ^{15}N natural isotopes demonstrated a sewage component in bay sediments (Tucker *et al*. 1999b). In recent years, indicators of sewage inputs of particulates, metals, and *Clostridium* spores to Massachusetts Bay declined with treatment improvements, consistent with reductions noted in the harbor.

With the bay outfall operational, all effluent is now being delivered to bottom waters of Massachusetts Bay. Although organic matter and contaminants loading have been greatly reduced in the MWRA effluent by secondary treatment and source reduction, they remain a concern. Because nutrient concentrations are not greatly reduced by secondary treatment, there also exists the possibility of enhanced phytoplankton blooms. We would expect sediment biogeochemistry to be affected by each of these issues, should they occur. The depositional sites that we study are likely repositories for organic matter or contaminants delivered in the effluent, or deposited as phytoplankton blooms senesce. Resulting potential increases in SOD could contribute to bottom water depletion of oxygen. However, sediment processes act as integrators of water column processes with relatively slow response times, and therefore changes may only be detectable over time.

We have monitored three stations, MB01, MB02, MB03, in the nearfield region of Massachusetts Bay and one station, MB05, in the farfield (Stellwagen Basin) (Figure 18). 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.

In order to examine long-term trends, we have calculated seasonal averages (May-October) of metabolism and nutrient flux rates for all years sampled. We have excluded winter data because they were not available for all years. Details of the years before 2001 may be found in previous reports (refer to list at end of Section 1.0).

6.0 BAY MONITORING PRE-DIVERSION, 1992-2000

6.1 Trends in Benthic Respiration and Nutrient Fluxes

The temporal pattern in all the fluxes during the baseline period was similar although somewhat more pronounced in the nutrient fluxes as compared to sediment respiration. In general, fluxes were high in the first two to three years, declined during the middle of baseline, and were high or intermediate in 1999-2000 (Figure 19).

That these patterns were roughly parallel across stations, especially in the nearfield, and across analyte, suggests region-wide mechanisms at work and remind us that Massachusetts Bay is part of the larger Gulf of Maine system. Flux patterns in the bay may be related to region-wide phenomena such as water column chlorophyll and/or benthic infaunal abundances. In addition, episodic events such as large storms which resuspend and redistribute sediments (Bothner, 2001) may have major effects on benthic processes.

6.1.1 Sediment Oxygen Demand

Sediment respiration in nearfield sediments of Massachusetts Bay is much lower and rates are less variable than we observe for Boston Harbor sediments. Seasonal average rates have ranged from 12.4 (1995) to 24.7 (1999) mmol m-2 d-1 during the baseline monitoring period, with both the high and the low values observed at Station MB02 (Figure 20b). A grand seasonal mean across the three nearfield stations is 17 mmol m^{-2} d^{-1}. At Station MB05, SOD is lower still, with seasonal averages ranging from 7.8 (1995) to 15.3 mmol m^{-2} d^{-1} (1997) (Figure 20d). (Data from 1992 are not included in the seasonal

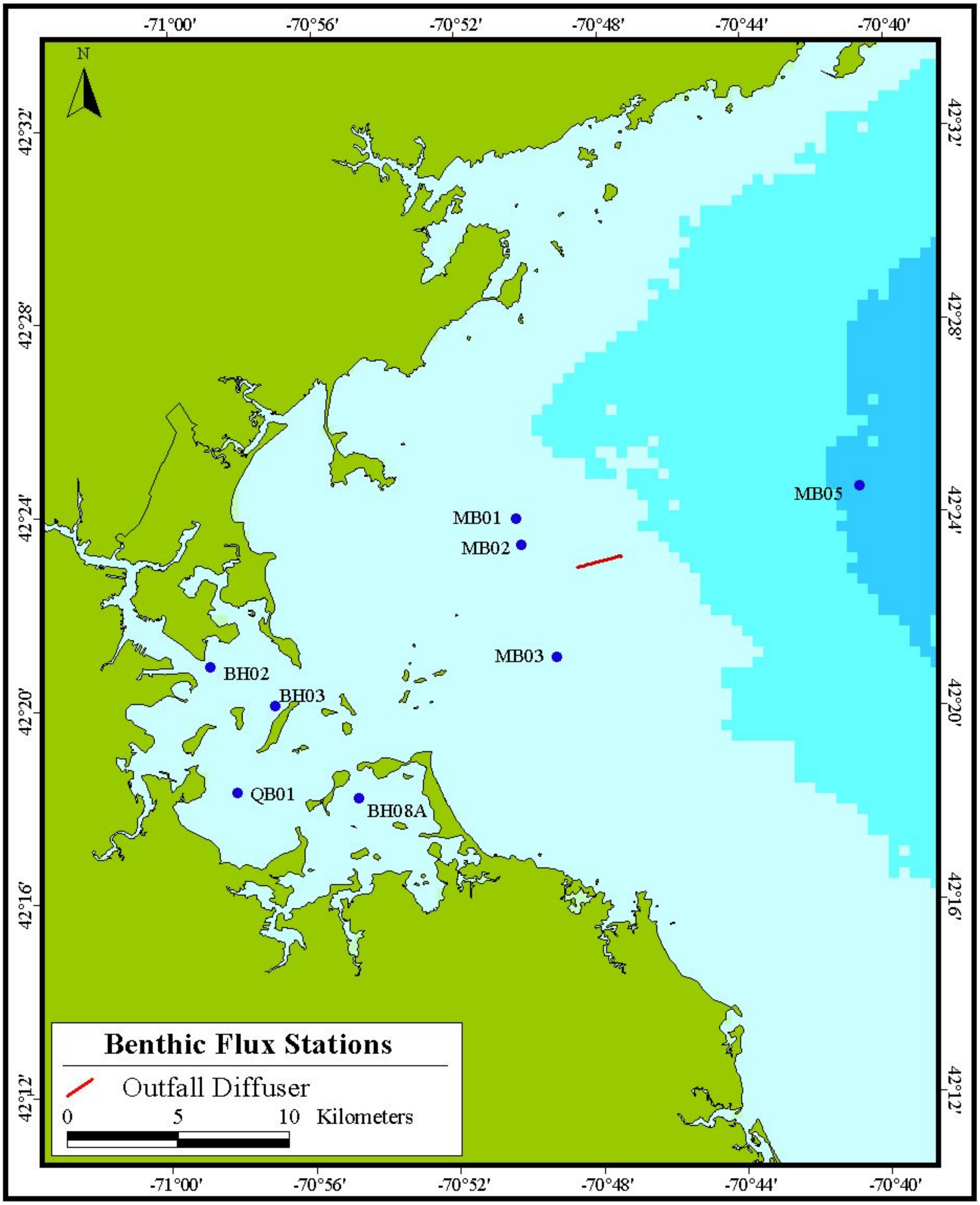


Figure 18. Benthic nutrient cycling stations in Massachusetts Bay.

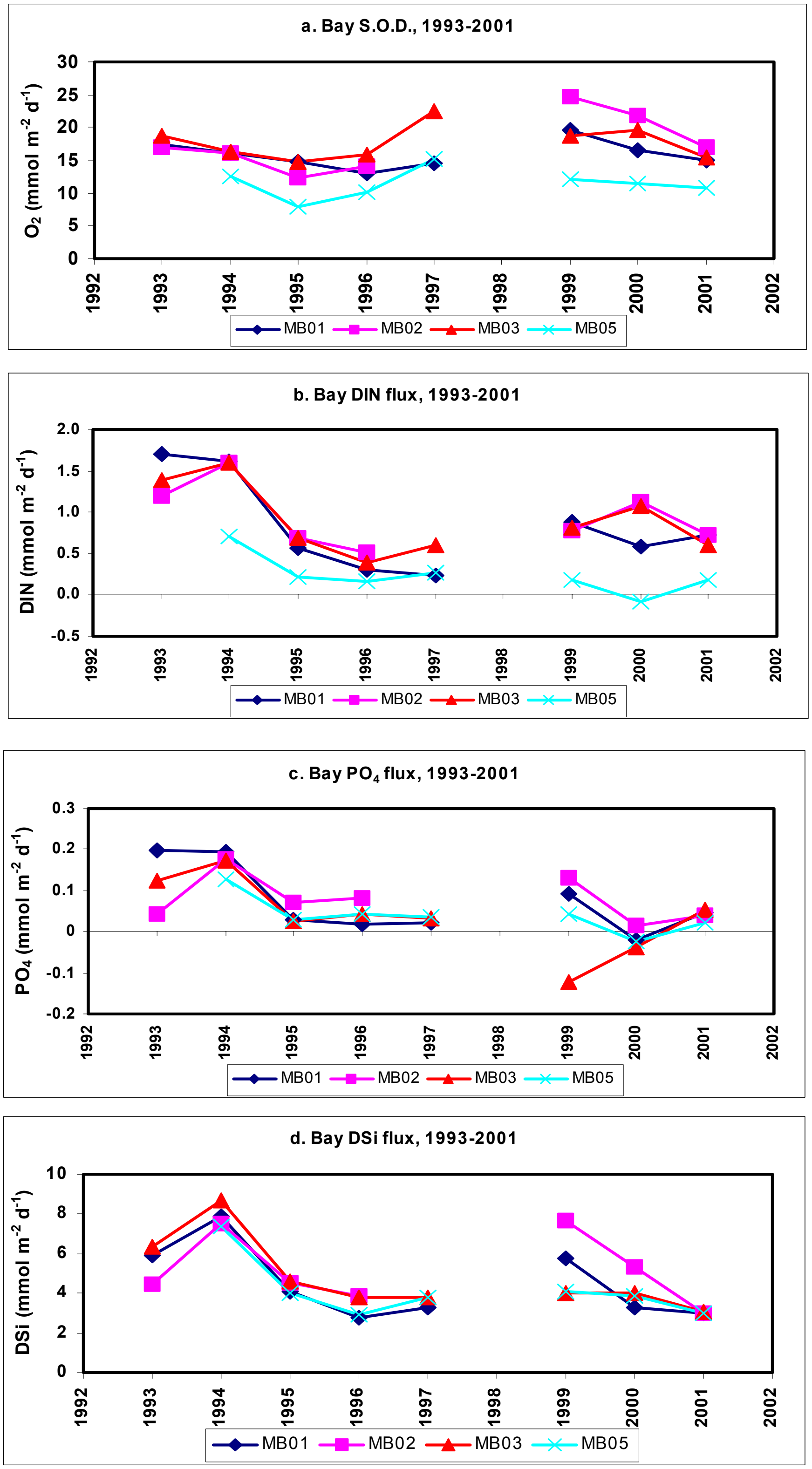


Figure 19. May-October seasonal averages for all four Massachusetts Bay stations for a.)S.O.D., b.) DIN flux, c.)PO_4 flux, d.) DSi flux.

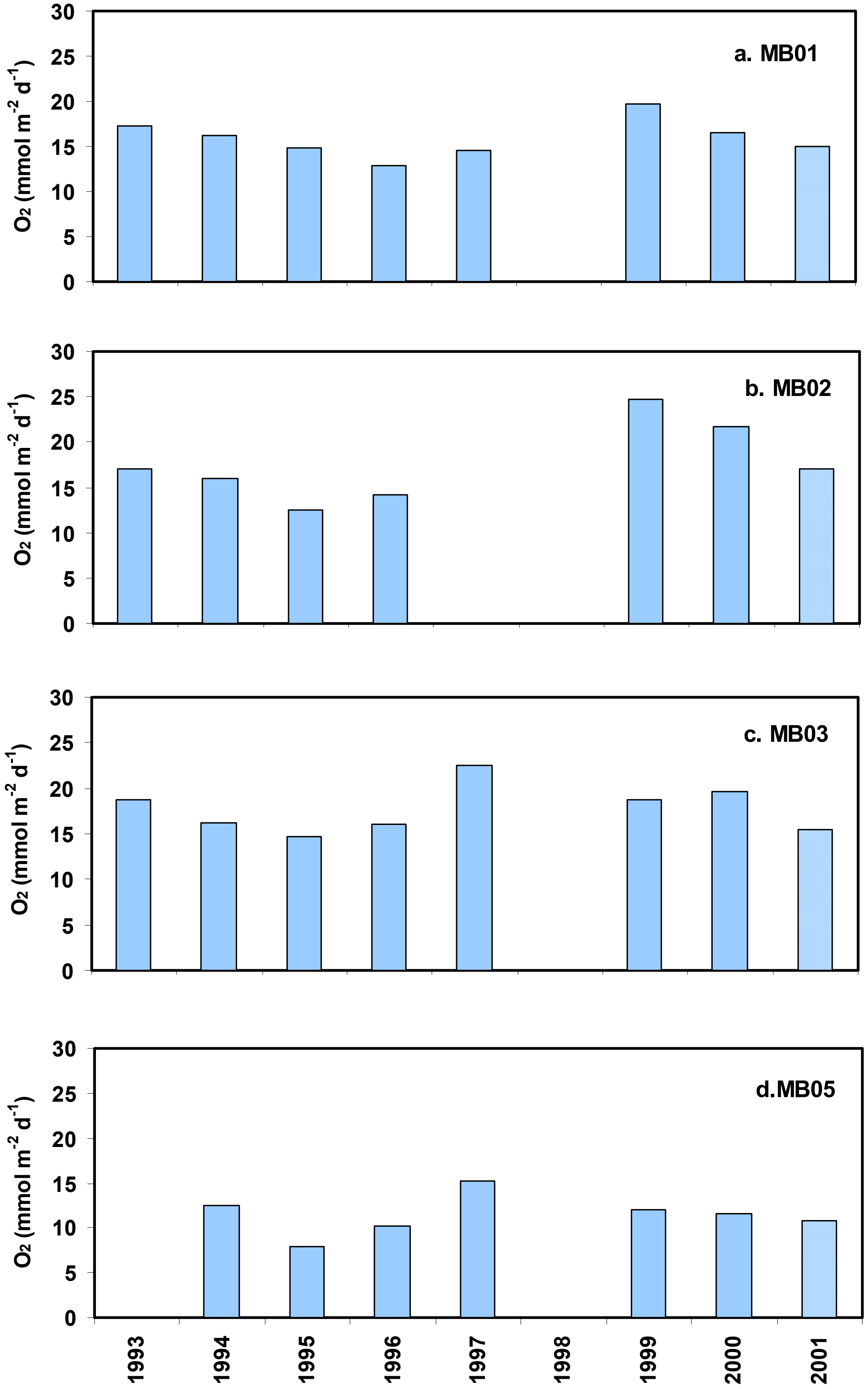


Figure 20. May- October seasonal average sediment oxygen demand from 1993-2001 at bay stations a.) MB01, b.) MB02, c.) MB03, and d.) MB05. The stippled bar designates post-diversion data (2001).

means comparisons for the nearfield stations because only October and November data are available. However, it is noteworthy that SOD in October of 1993 at Station MB01 was the highest recorded during baseline monitoring.)

In the early years of monitoring, interannual variability within and between the nearfield stations appeared to be low. From late 1992 through 1996, rates across the three nearfield stations tracked each other remarkably well, with lowest rates for these stations occurring in 1995-1996 (Figure 19a). 1997 seemed to mark a change in the consistency across stations we had come to expect. In 1997, only two nearfield stations were sampled, and at this time SOD was quite different between the two, with MB03 having the highest rates observed to that point (Figures 19a and 20c). When sampling in the Bay resumed in 1999, very high rates (for the bay) were measured at Station MB02 (Figures 19a and 20b), the maximum we have observed in the bay stations, and rates were high at the other two stations as well. High rates continued to be apparent at MB02 and MB03 into 2000 (Figures 19a and 20 b and c). A similar pattern was observed at the farfield station MB05, with lowest values noted in 1995 and highest in 1997 (Figures 19a and 20d).

For most years during the monitoring period (1992-1995 and 1997), a strong seasonal pattern was apparent, with rates typically increasing from early spring through summer and peaking in late summer or fall, when bottom water temperatures were warmest. During this period, temperature accounted for over 40% of the variation we observed in respiration rates. In 1996, a less distinct seasonal pattern was observed, with less variability in rates across the months sampled. In 1999-2000 a seasonal pattern was not apparent; a factor other than temperature appeared to be playing a dominant role in determining sediment respiration.

Although we cannot make direct correlations between the benthic flux data and the benthic infaunal data, there are similarities worth noting in the long-term temporal patterns of both datasets. Kropp notes two contrasting periods during the 9-year monitoring period of benthic infauna: an early period (1992-1996) when abundances were low and variable, and a later period (1997-2000) of relatively high and stable abundance (Kropp *et al*. 2002). A large storm that occurred in late 1992 redistributed sediments (Bothner, 2001) and was thought to be responsible for the low infaunal abundances in the following several years. The later phase represents a recovery from this large disturbance, with abundance peaking in 1997-1999, but beginning to decrease in 2000 (Kropp *et al.*, 2002). In addition to abundance changes, species dominants also changed between the two periods. By 1999 and 2000, stage II communities and even stage III in 2000, were widespread. An increase in bioturbation in areas of fine sediments has been observed since 1995, and especially since 1998. As we have documented for the harbor, bioturbation often enhances benthic fluxes, and may be responsible for recent elevated rates of sediment respiration.

Higher SOD in 1999 and 2000 may also be related to water column productivity. Libby noted an increasing trend in chlorophyll concentration from 1997 to 1999 (Libby *et al.*, 2000) which continued through 2000 (Werme and Hunt, 2001). In fact, annual mean chlorophyll concentrations in 2000 were the maximum reached during baseline monitoring. The resulting increase in available organic matter was cited as the reason for unusually high bottom water respiration in 1999 (Libby *et al.*, 2000). Benthic respiration, too, would be stimulated by deposition of phytodetritus.

6.1.2 DIN Fluxes

Sediment fluxes of nitrogen have shown considerable variability over the monitoring period. May to October average DIN fluxes were highest in the early part of baseline monitoring (1993-1994), ranging from 1.2 to 1.7 mmol m^{-2} d^{-1} (Figure 19b). (Data from 1992 are not included in the seasonal means comparisons because only October and November data are available. However, it is noteworthy that the overall highest single DIN flux, over 4 mmol m^{-2} d^{-1}, was observed in October 1992 at Station MB01. Fluxes continued to be high in the following month.) DIN fluxes at farfield station MB05 were also high in 1993 and 1994. After 1994, DIN fluxes decreased by half or more at all four stations for a period of about three years (Figure 19b and Figures 21a-d). When monitoring resumed in 1999, fluxes at the nearfield stations had increased to intermediate levels between about 0.5 and 1.0 mmol m^{-2} d^{-1}. Fluxes at the Stellwagen station continued to be low and similar to the 1995-1997 period.

The composition of the DIN flux has also varied over the baseline period (Figure 21). In the early years when fluxes were highest, the majority of the flux, 75% or more on a May to October seasonal basis, was comprised of NH_4^+. In the middle years of low flux, NO_3^- was often over 50% of the flux. In 1999-2000, with intermediate rates, NH_4^+ was once again the major component of the DIN flux. In fact, in 1999 at Station MB02, NH_4^+ comprised all of the DIN efflux; that year, NO_3^- was taken up by sediments at this site (Figure 21b). The pattern at Station MB05 was similar to that for the nearfield stations through 1997 (Figure 21d). In 1999 through 2000, however, NO_3^- comprised most or all (2000) of the DIN efflux at this site; in 2000, NH_4^+ flux was directed into the sediments.

The relative importance of NO_3^- flux may be related to the sediment oxygenating effects of bioturbation. In the nearfield, increased bioturbation was noted beginning in 1995, consistent with higher percentages of NO_3^- observed from 1995-1997. However the correspondence fails after that time, when bioturbation became even more important but DIN fluxes became once again dominated by NH_4^+.

In the pattern of DIN fluxes we again see evidence of a region-wide mechanism at work. Large DIN fluxes in 1993 and 1994 may be related to the redistribution of fine sediments caused by the strong storm of December, 1992, which likely deposited organic-rich particles from the harbor as well as silver and *Clostridium* spores (Bothner, 2001). In fact, organic carbon content in the sediments at MB01 and MB03 was elevated in 1993 (see Section 6.3.1.) Highest rates observed in 1992, noted above, however, were probably due to large numbers of infauna that were present before the storm occurred. The intermediate fluxes observed in 1999-2000 were most likely related to deposition of the phytoplankton blooms, although such deposition was not apparent in the organic carbon measurements.

6.1.3 Denitrification

Denitrification rates were measured periodically during the baseline period (1993, 1994, 1999, 2000, 2001) at two nearfield stations, MB02 and MB03. Rates have exhibited considerable variability, ranging from 0.2 mmol N m^{-2} d^{-1} at MB03 in March 1994 to just over 6 mmol N m^{-2} d^{-1} at Station MB02 in October, 1999 (Figure 22). In 1993 and 1994, there was good seasonal coverage in the data, as measurements were made during each survey, however there was not a consistent seasonal trend. In 1999-2001, measurements were made in May and October only, and again there was no consistent trend with respect to spring versus fall rates. Although we cannot discern a temporal or spatial pattern in these fluxes, neither do we detect any anomalous results. We note, however, that denitrification rates at these two nearfield stations are often of similar and sometimes greater magnitude than the DIN fluxes. Using stoichiometric estimates from 1992-1994 data, Hopkinson *et al.* (2001) calculated that denitrification accounts for about 60% of the total N mineralization in the soft sediments of Massachusetts Bay. Using our direct measurements, we calculate a similar average percentage of about 65% for the two stations MB02 and MB03.

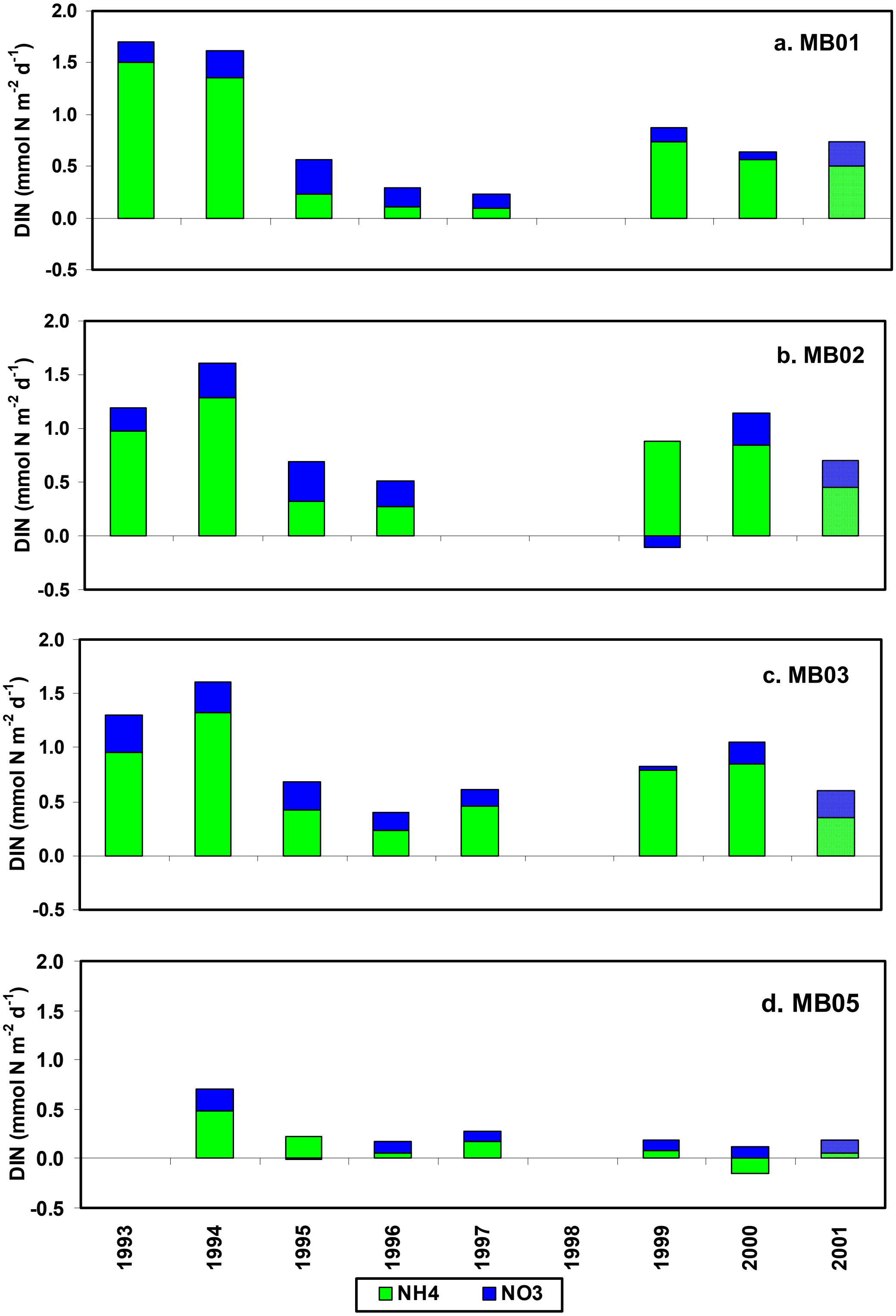


Figure 21. May-October seasonal average DIN flux from 1993-2001 at bay stations a.) MB01, b.) MB02, c.) MB03, d.)MB05. The stippled bar designates post-diversion data (2001).

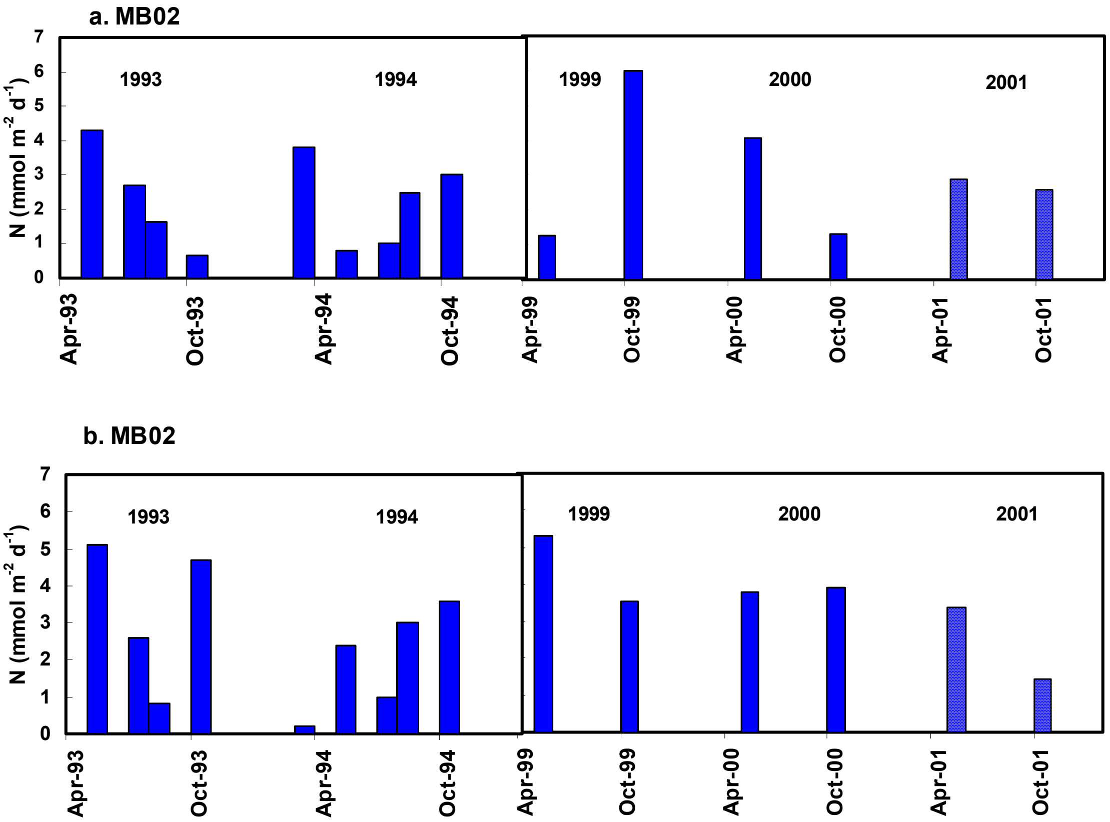


Figure 22. Denitrification at two nearfield stations, a.) MB02, and b.) MB03. Denitrification measurements were not conducted in Massachusetts Bay in 1995-1998. The stippled bar denotes post-diversion data (2001).

6.1.4 Phosphate Fluxes

Fluxes of dissolved inorganic phosphorus followed a similar temporal pattern to that of DIN for the first 5 years of baseline monitoring, with highest seasonal average fluxes early in the monitoring period (1993-1994), followed by lower fluxes in the middle years (1995-1997) (Figure 23). Phosphate flux for the May to October period of 1993 and 1994 averaged across the three nearfield stations was 0.15 mmol m^{-2} d^{-1}, whereas for 1995-1997 the flux decreased to 0.04 mmol m^{-2} d^{-1}. Similar rates and patterns were observed at farfield station MB05. In 1999-2000, we observed variable magnitude and even direction of phosphate fluxes. At Stations MB01 and MB02 (Figures 24 a and b), PO_4 fluxes were intermediate to those of the early and middle years, but at Station MB03 (Figure 23c), fluxes were strongly negative (i.e. influx rather than efflux; -0.12 mmol m^{-2} d^{-1}). In 2000, fluxes at MB03 were weaker but remained negative, and they were also negative at Stations MB01 and MB05.

6.1.5 Dissolved Silica Fluxes

Long term trends in dissolved silica fluxes followed the same general pattern as for fluxes of other nutrients (Figure 19d). May through October fluxes were high in 1993-1994 at all three nearfield stations, with peak rates around 8 mmol m^{-2} d^{-1} occurring in 1994, possibly in response to deposition of the large bloom of *Asterionellopsis* that occurred the previous fall (Libby *et al.*, 2000). DSi fluxes decreased in the 1995-1997 period, but were not especially low compared to later years as was the case for DIN and PO_4. In fact, Si fluxes remained quite consistent at this lower rate of around 4 mmol m^{-2} d^{-1} for the remainder of baseline monitoring at Stations MB03 and MB05 (Figures 24 c and d). At MB01 and MB02, however, fluxes were elevated in 1999 and also in 2000 at MB02 (Figures 24 a and b), likely in response to the large and sustained phytoplankton blooms in those years, which were mixed diatom assemblages (Libby *et al.*, 2000).

6.2 Sediment Redox Conditions

6.2.1 Respiratory Quotients

In the earlier years of monitoring (1992-1994), O_2 and CO_2 fluxes at the nearfield stations often resulted in RQs greater than 1.0 (Figure 25a). That is, CO_2 release was in excess of O_2 uptake, indicating that anaerobic respiration was important. (CO_2 data are not available for 1995-1997.) In 1999 and 2000, however, RQs were much closer to 1.0 or lower (Figure 25b), indicating a change towards a predominance of aerobic respiration and/or more oxygenated sediments, possibly related to increased infaunal abundances and bioturbation noted above.

6.2.2 Porewater Indicators

Oxidation-reduction (redox) potential measured in sediment cores also document changes in the state of the sediments towards more oxidizing conditions over the baseline monitoring period. In early Eh profiles, e.g. 1994, the depth at which Eh values changed from positive to negative was typically within the first 5 cm of sediment (Figure 26a). This depth to 0mV increased to between 5 and 10 cm in 1995-1997 (Figure 26b) and by 1999, had increased beyond the depth we are able to measure (> 18 cm) (Figure 26c). In the benthic monitoring program, sediment profile imaging has likewise documented a deepening of the apparent color RPD since 1997, although deepest RPDs were measured in 1992 (pre-storm) and 1995 (when bioturbation became important) (Kropp *et al.*, 2002).

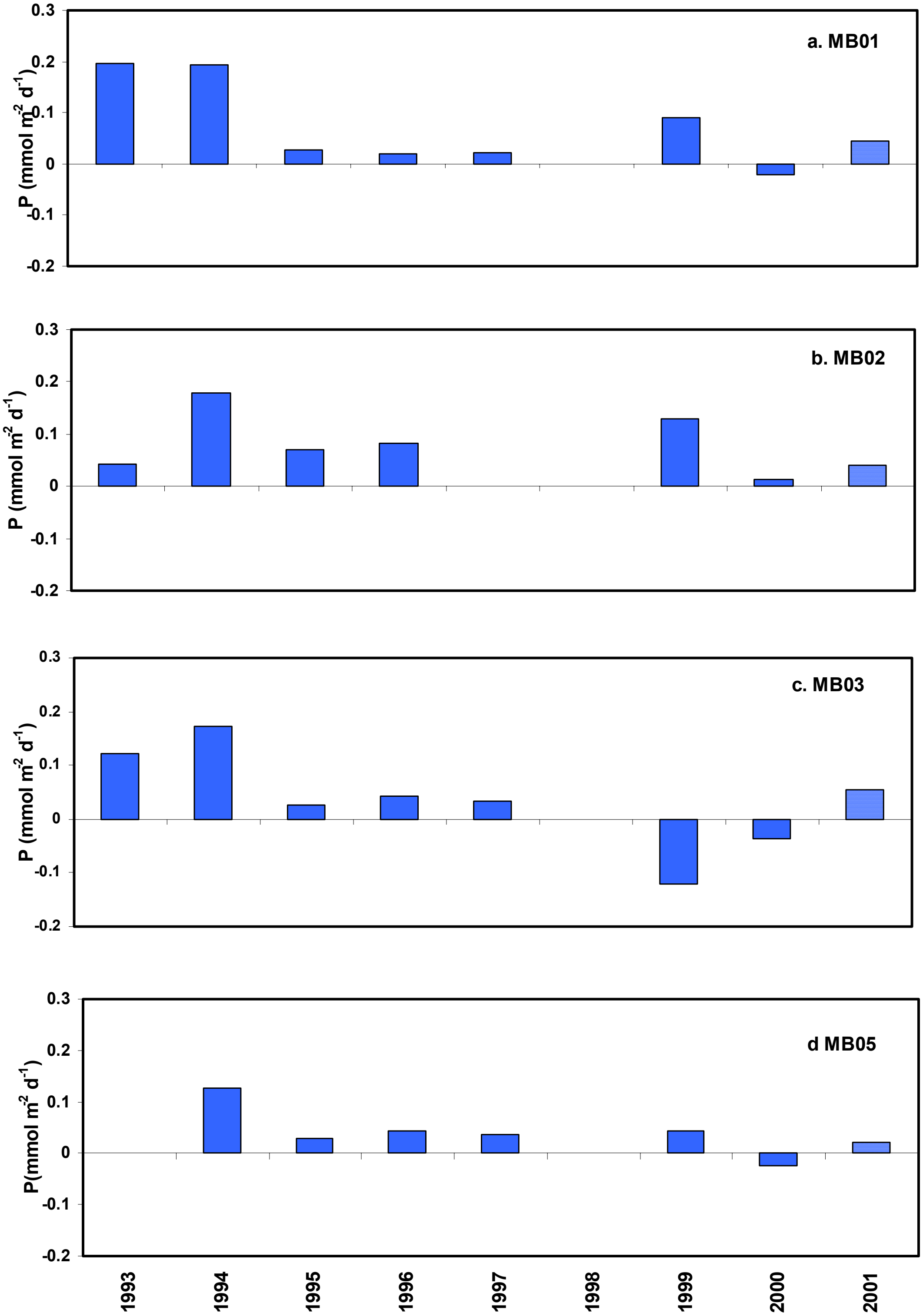


Figure 23. May-October seasonal average phosphate flux from 1993-2001 at bay stations a.) MB01, b.) MB02, c.) MB03, d.)MB05. The stippled bar designates post-diversion data (2001).

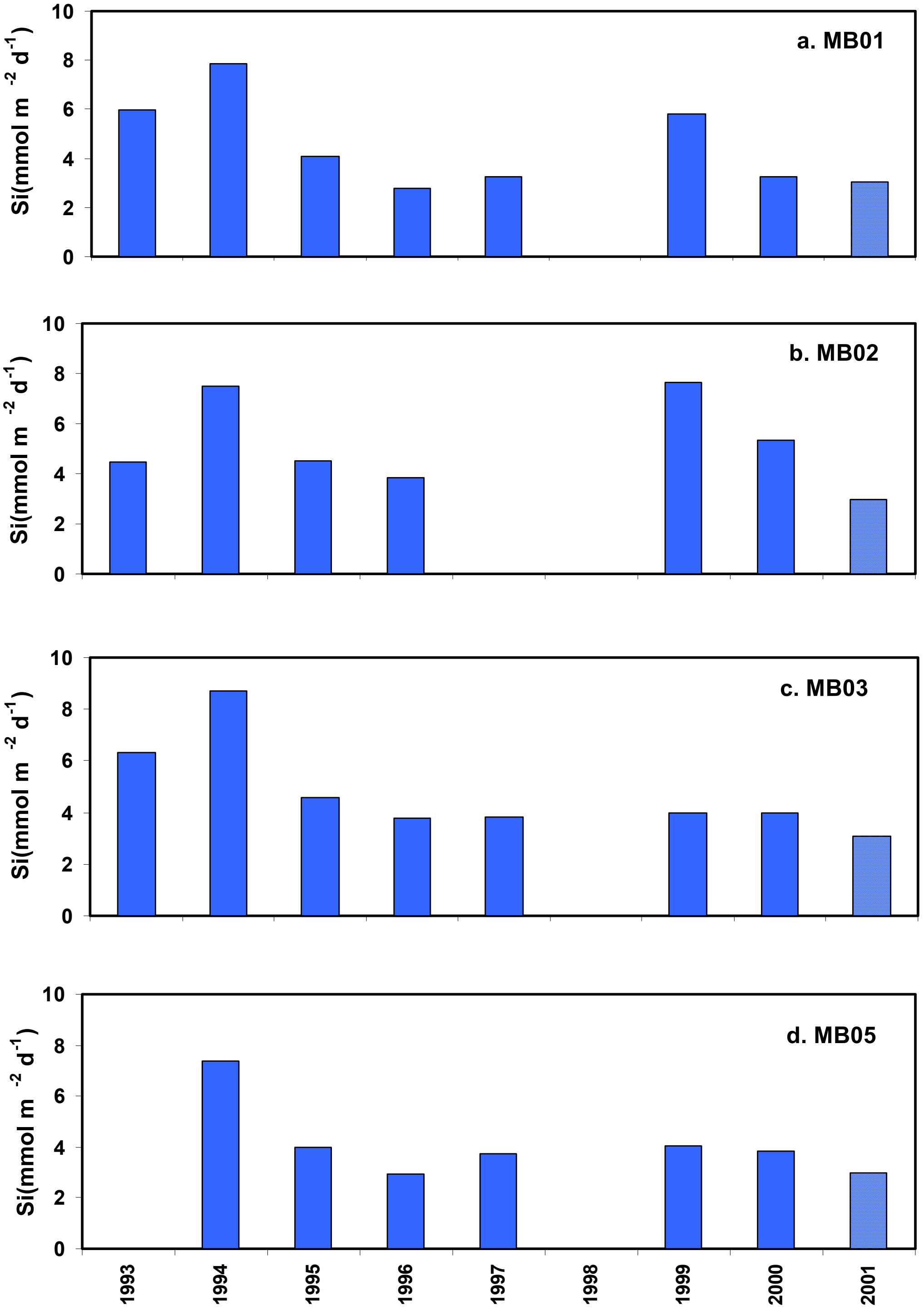


Figure 24. May-October seasonal average dissolved silica flux from 1993-2001 at bay stations a.) MB01, b.) MB02, c.) MB03, d.)MB05. The stippled bar designates post-diversion data (2001).

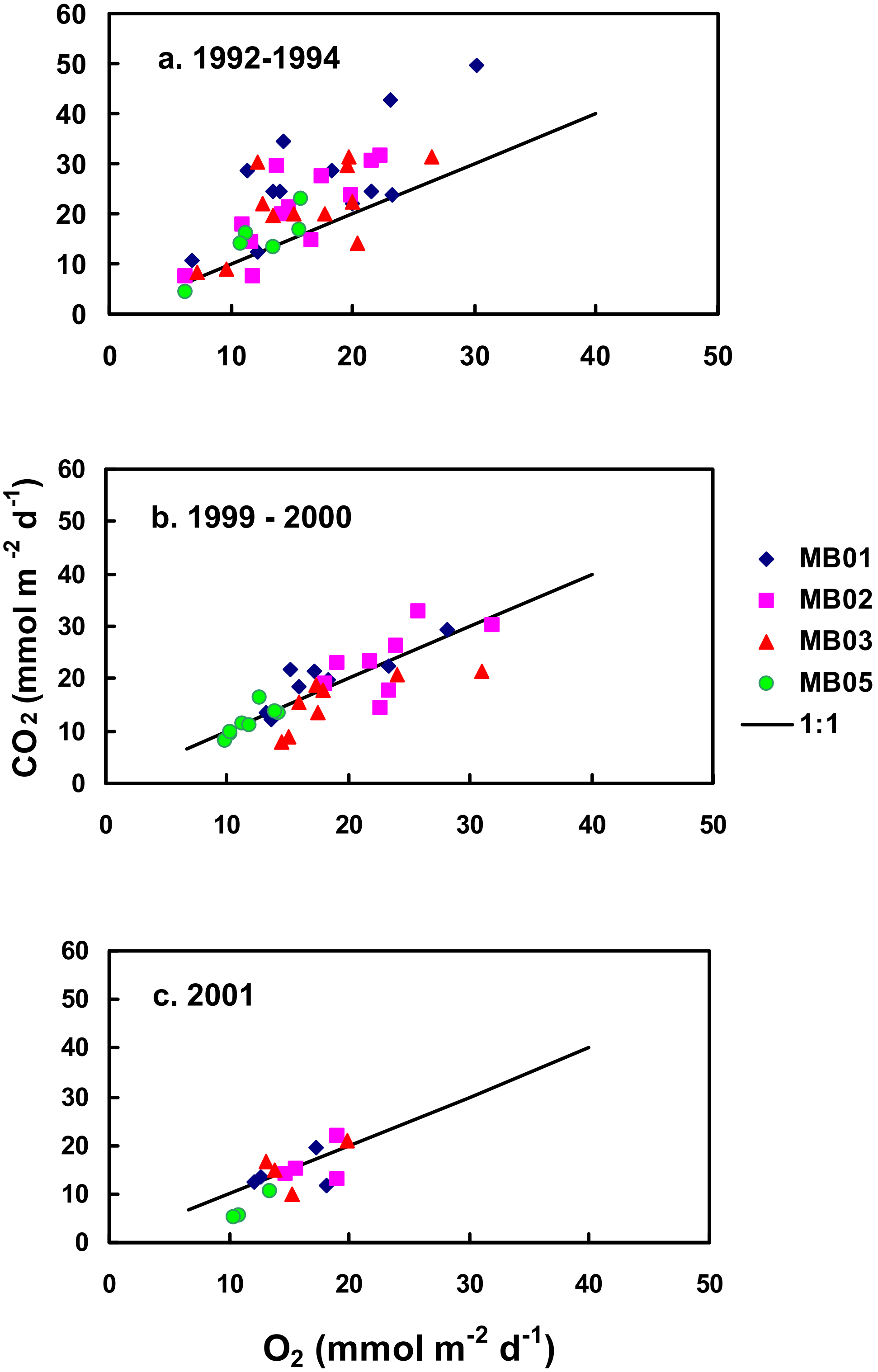


Figure 25. Respiratory quotients (CO_2 flux/O_2 flux) for bay stations in a.)1992-1994, b.) 1999-2000, and c.) 2001 (post-diversion).

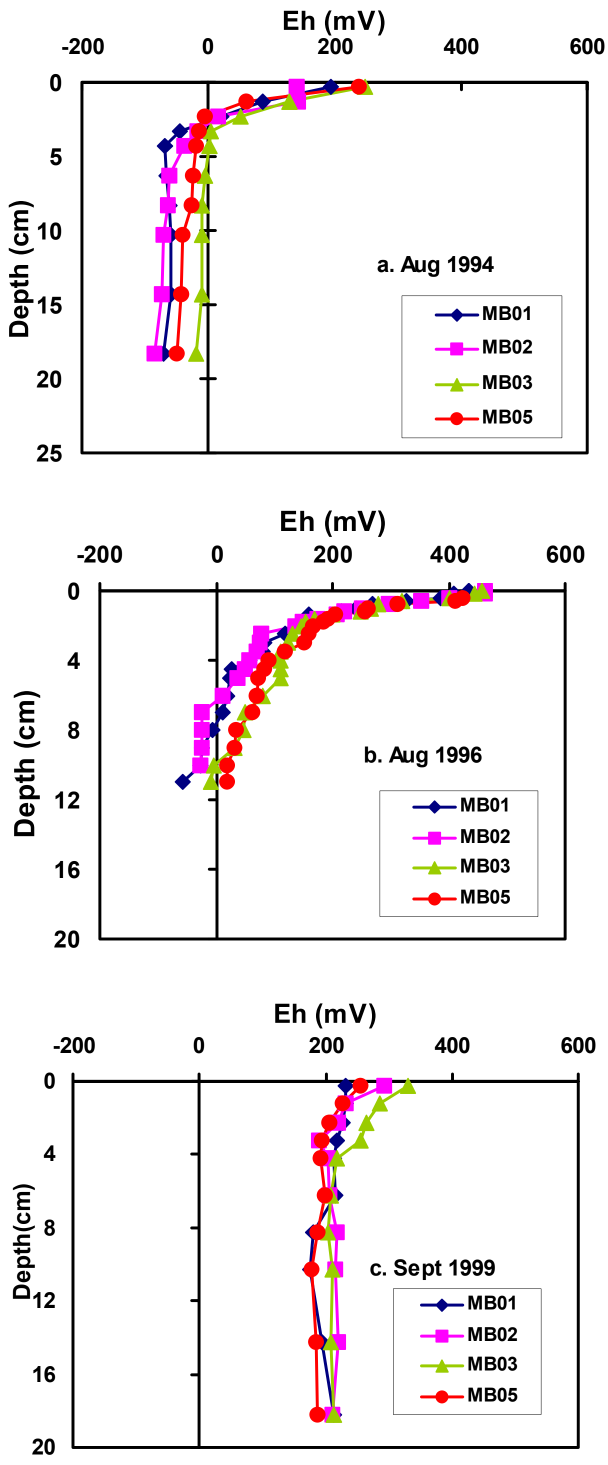


Figure 26. Representative Eh profiles from nearfield stations in late summer, showing increase in depth to reach Eh= 0mV over time: a.) Aug. 1994, b.) Aug. 1996, and c.) early Sept., 1999.

6.3 Sediment parameters

6.3.1

Total organic carbon (TOC) content in the sediments of the four Massachusetts Bay stations varied over the baseline period, ranging from 0.4% to 4.3%, but with values more typically between 1.0% and 2.0 % (dry weight) (Figure 27). Changes in carbon content that might reflect the deposition of phytoplankton blooms were usually not apparent. However, very high TOC content was measured in sediments at Station MB01 in 1993 (Figure 27a), presumably reflecting the sediment redistribution caused by the large Dec., 1992 storm. In March, TOC was greater than 4% at this station, and high levels were also measured in July and October. Levels more typical of this station and the bay overall were measured in May and August. At MB03, levels were also high, ~3.5% in March, 1993, but were more typical for the station the rest of the year (Figure 27c). At station MB02, situated between the other two stations, there was no indication of carbon input during 1993 (Figure 27b). It may be that Station MB02 is somewhat protected from bed-level flows by the drumlins surrounding it.

Using May to October seasonal averages for the baseline years 1993-2000, a regression model suggests a significant reduction in TOC at Station MB01 of nearly 0.2% per year ($P = 0.02$, $r^2 = 0.69$; Figure 28a). A similar, but weaker decreasing trend was noted for MB03, which experienced a decrease of nearly 0.1% per year ($P = 0.04$, $r^2=0.6$; Figure 28c). Similarly, nearfield baseline TOC as reported in the Outfall Benthic Monitoring Program seemed to show a decreasing trend in TOC from 1992 to 1998 (Kropp *et al.*, 2001). At station MB02, TOC content has remained remarkably consistent throughout baseline monitoring, showing no trend with time (Figure 28b). A similar lack of change in TOC has been observed at station MB05 in Stellwagen basin, however it is interesting to note that from 1997-2000, TOC content at that station was greater than it was at the nearfield stations.

Ratios of TOC to total organic nitrogen (TON) may provide an indication of organic matter lability and/or source. At MB01 and MB03, seasonal average C/N in 1993, when TOC levels were high presumably due to sediment redistribution, was curiously low, about 10 (Figure 29). In contrast, at Station MB02, where elevated TOC was not observed, the average C/N was about 12.5. (Unfortunately we did not start collecting sediment pigment data until 1994.) Consistent with little change in %TOC at MBO2 was that C/N ratios at this station also changed very little over the monitoring period. After 1993, C/N at Station MB01 was also about 12.5, and in fact the two stations remained similar to each other from 1994-2000. At Station MB03, however, ratios during this time period were consistently around 11. C/N at Station MB05 was lower than the three nearfield stations, averaging around 10.

C/N ratios, would suggest, therefore, that apart from the anomalous year 1993, organic matter input to MB01 and MB02, which are in close proximity to each other, was somewhat different from that at MB03. The difference would suggest that the material delivered to the sediments at MB03 was enriched in higher quality carbon (phytodetritus) relative to that reaching the bottom at MB01 and MB02. The low C/N at station MB05 suggests that even higher quality carbon was deposited to the sediments in Stellwagen basin, where we expect little evidence of harbor inputs. Although these differences are small, they suggest a gradation within the POM pool reflecting a mixture between material derived from Boston Harbor and that associated with phytoplankton production.

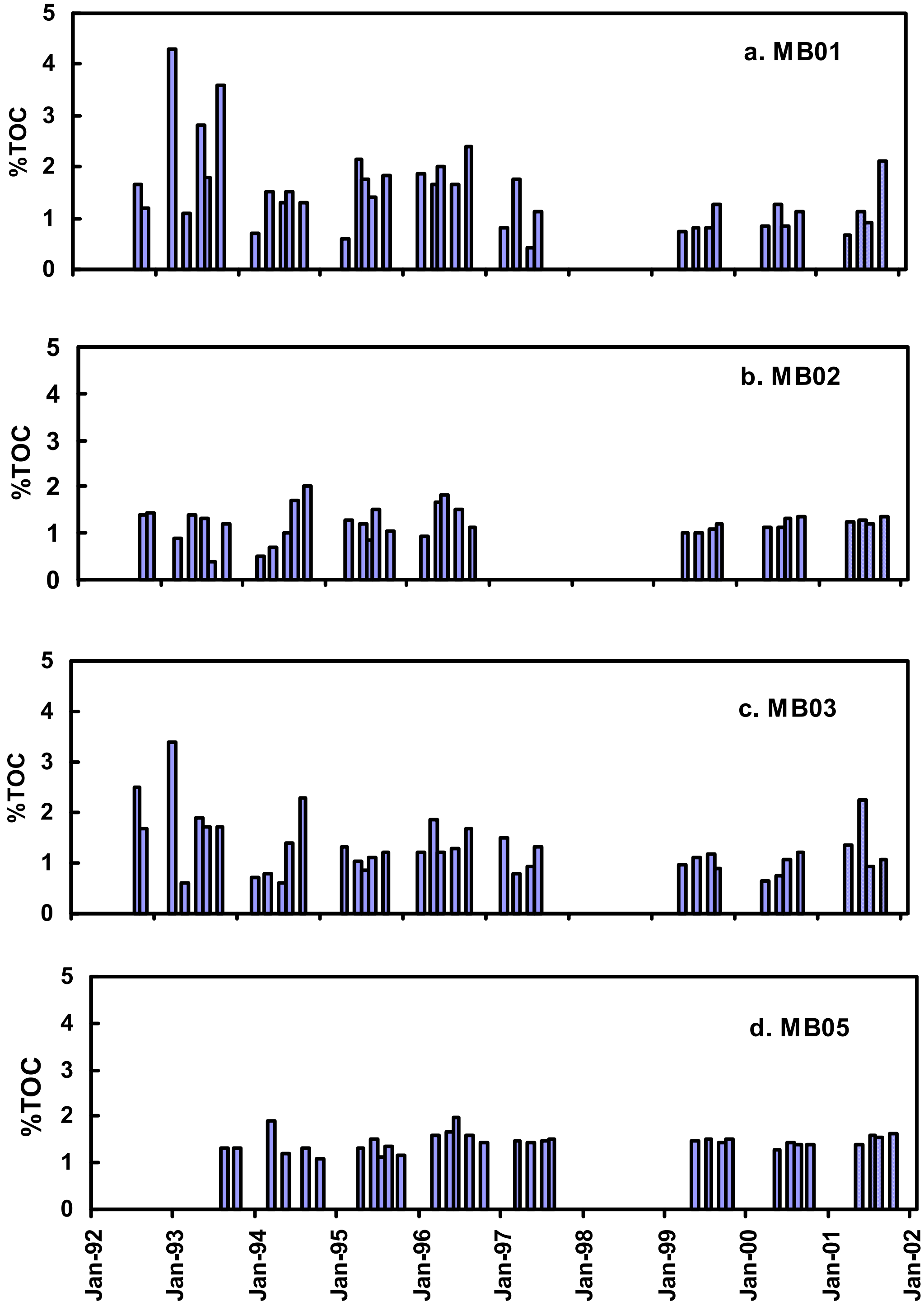


Figure 27. % TOC in top 2 cm of sediment for bay stations a.) MB01, b.) MB02, c.) MB03, and d.) MB05. Stippled bars denote post-diversion data (2001).

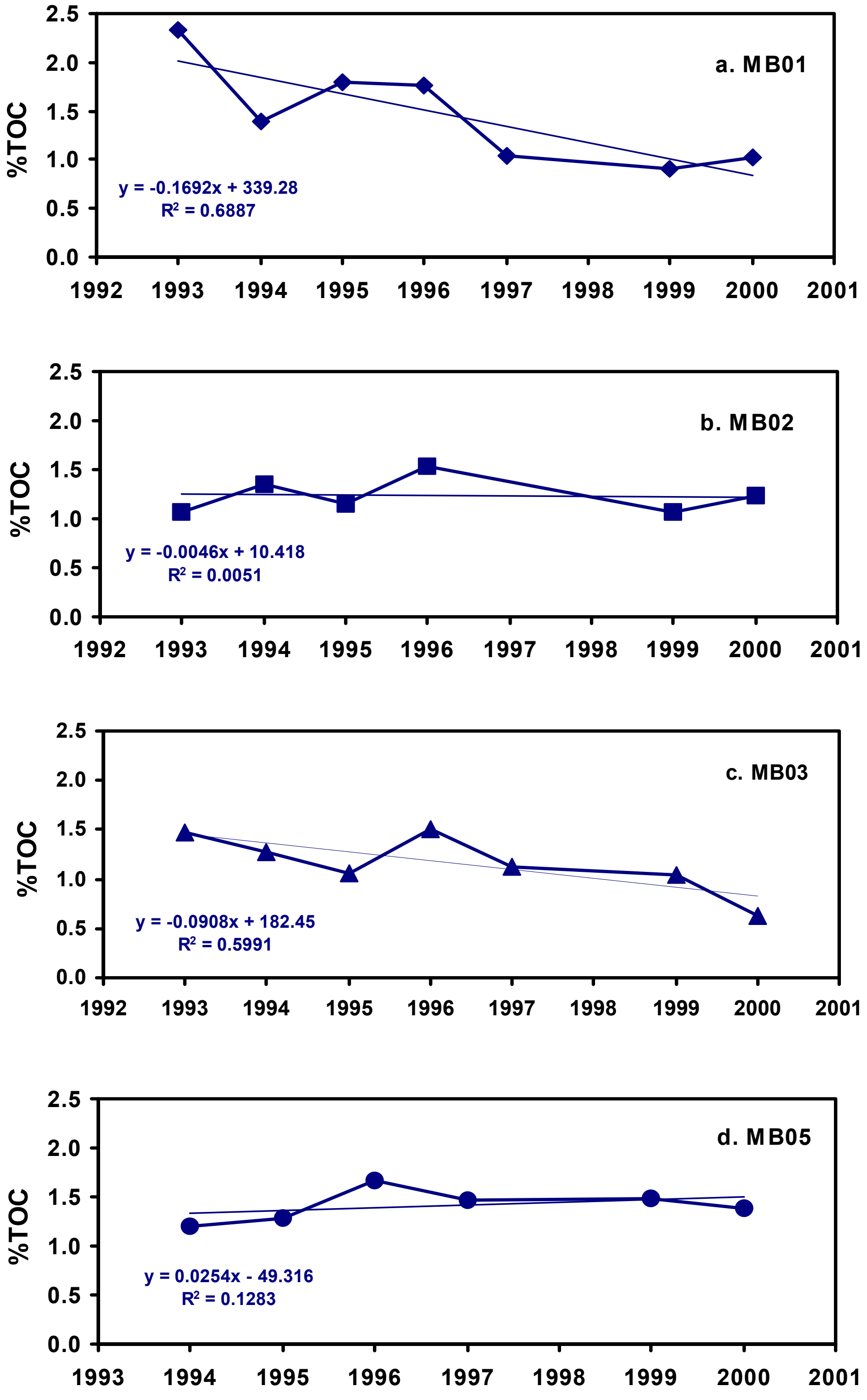


Figure 28. May-October seasonal averages for % TOC, and regressions with time for a.) MB01, b.) MB02, c.) MB03, and d.) MB05. Regressions are significant at $P < 0.05$ for MB01 And MB03.

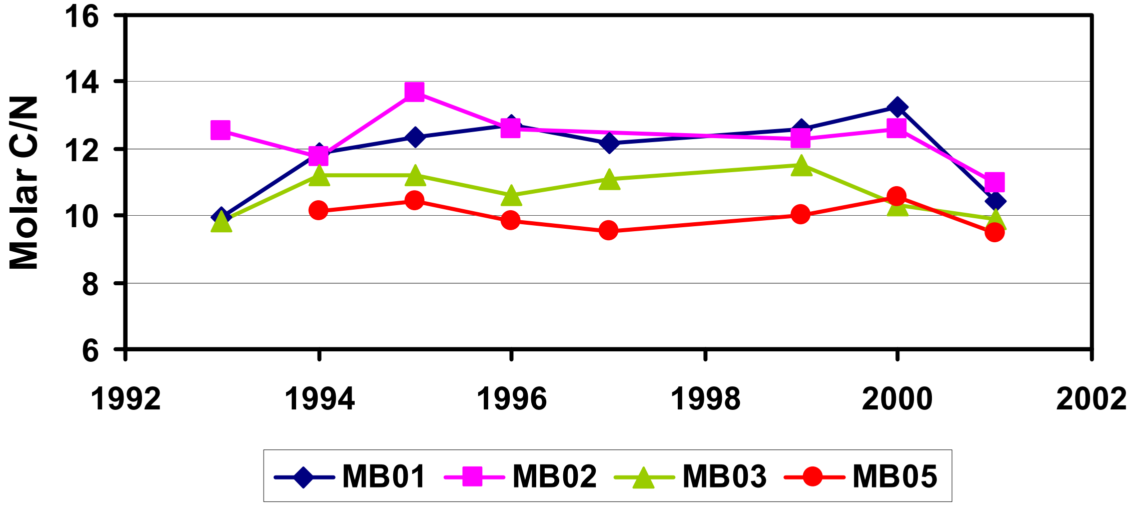


Figure 29. Molar ratios of TOC/TON in sediments from Massachusetts Bay stations.

6.3.2 Sediment Pigments

Sediment chlorophyll *a* and phaeophytin were measured at the four Massachusetts Bay stations starting in 1994. The majority of pigments in sediments were present as phaeophytin, the degraded form of chlorophyll *a*. During baseline monitoring, inventories of total pigments over the top 5 cm of sediment at the three nearfield stations have ranged from as little as 12 ug cm^{-2} (March, 1994, MB01) to over 125 ug cm^{-2} (July, 1994, MB03) (Figures 30 a-c). This large range that occurred within the same year was atypical for the baseline but appeared to be a seasonal pattern present at all three stations, with higher values in the mid-summer or fall. The seasonal pattern was more pronounced in the chlorophyll fraction, particularly at Station MB02. At that station, chlorophyll *a* increased from about 3 to over 25 ug cm^{-2} from March to October. More typically, pigments showed less intra-annual variability.

Years with higher total sediment pigments corresponded roughly, sometimes with a lag, to years with elevated chlorophyll concentrations in the water column (Figure 31). For instance, total pigment inventories were higher in 1994 than were observed for the next three years, and were probably the result of the fall 1993 *Asterionellopsis* bloom. Similar and even higher levels of total sediment pigments in 1999-2000 corresponded to unprecedented high water column chlorophyll concentrations (Werme and Hunt, 2001). In Stellwagen basin, the same pattern emerged, but was damped by the overall lower inventories. Throughout the baseline period, pigment inventories at this station ranged between about 30 to 80 $\mu g\ cm^{-2}$.

Chlorophyll roughly followed the same pattern as total pigments from 1994-1997, and was about 15% (± 5%)of the total pigment inventory. When total pigments increased in 1999-2000, however, the increase was comprised largely of phaeophytin. The relative contribution of chlorophyll had dropped to 5% (±3%). The higher percentage of degraded chlorophyll may be another indication of increased bioturbation.

7.0 BAY OBSERVATIONS ONE YEAR POST-DIVERSION; 2001

7.1 Trends in Benthic Respiration and Nutrient Fluxes

Benthic metabolism and nutrient fluxes in 2001, the first year of bay outfall operation, were well within ranges established during baseline monitoring. In fact, for many of the fluxes, rates were lower in 2001 than in the previous two years. These decreases may be related to lower phytoplankton biomass in 2001 compared to the previous two years (Werme and Hunt, 2001), and may also correspond to a decrease in infaunal abundances.

7.1.1 Sediment Oxygen Demand

Sediment oxygen demand in 2001 at the three nearfield stations ranged from 12 to 20 mmol $m^{-2}\ d^{-1}$, falling in the middle to the lower end of the baseline range (Figure 32a-c). At MB01, the mid- summer (July) and late-summer (August) rates were slightly above and below the ranges for those months, respectively, but well within the overall range. At these nearfield stations, SOD was lower in 2001 than in 1999-2000 and appeared to have returned to values more typical of those observed in the first years of monitoring. At station MB02, in particular, the average rate for 2001 (May-October) had decreased to 17 mmol $m^{-2}\ d^{-1}$, a rate typical of baseline, from a baseline high value of nearly 25 mmol $m^{-2}\ d^{-1}$ in 1999 (Figure 20b). At farfield station MB05, SOD was intermediate the baseline range (Figure 32d). In 2001, like 1999-2000, a seasonal pattern in SOD was not apparent, suggesting that a factor other than temperature was playing a dominant role in determining sediment respiration.

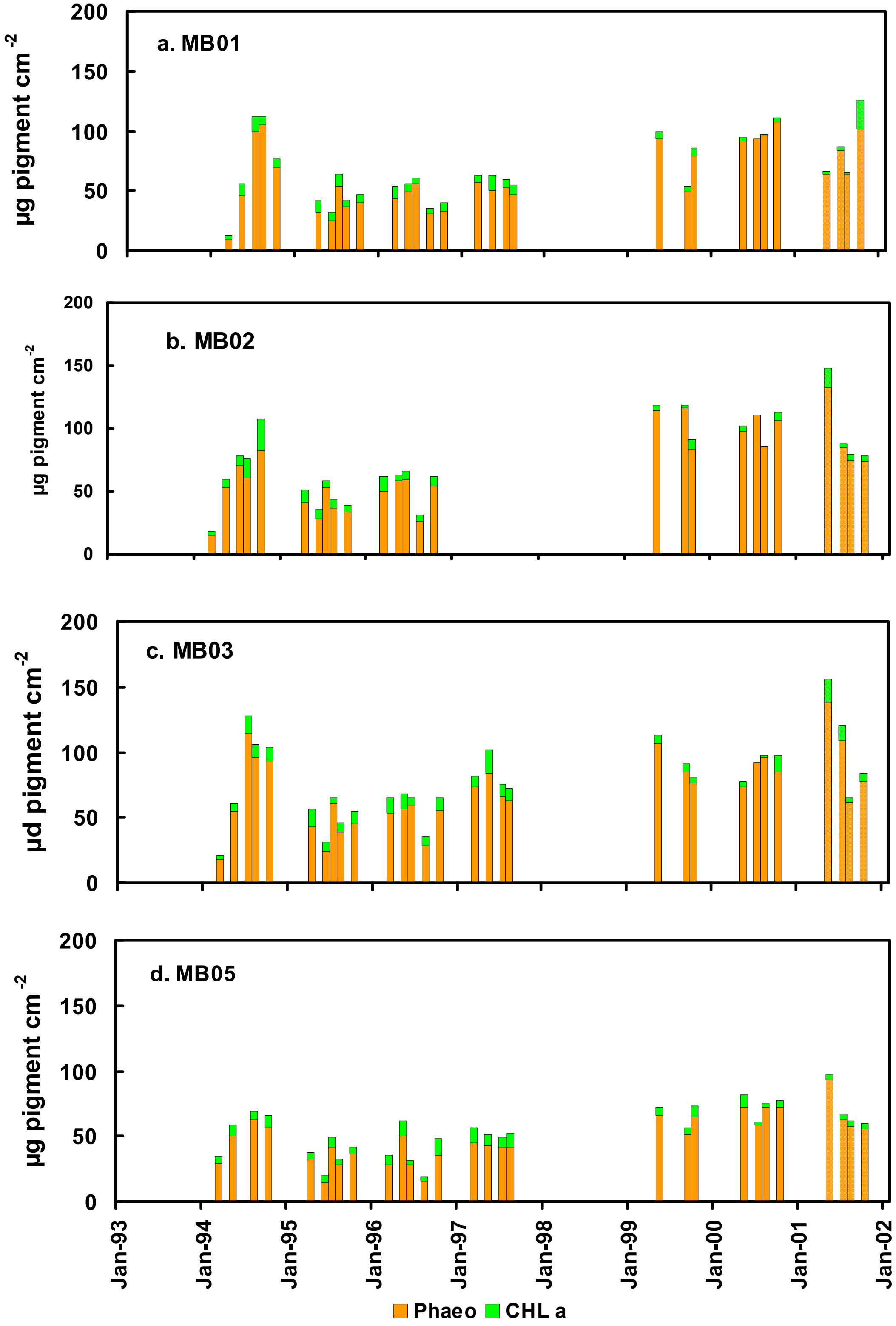


Figure 30. Photopigment inventories for top 5 cm of sediment at nearfield stations a.) MB01, b.) MB02, c.) MB03, d.) MB05. Stippled bars denote post-diversion data (2001).

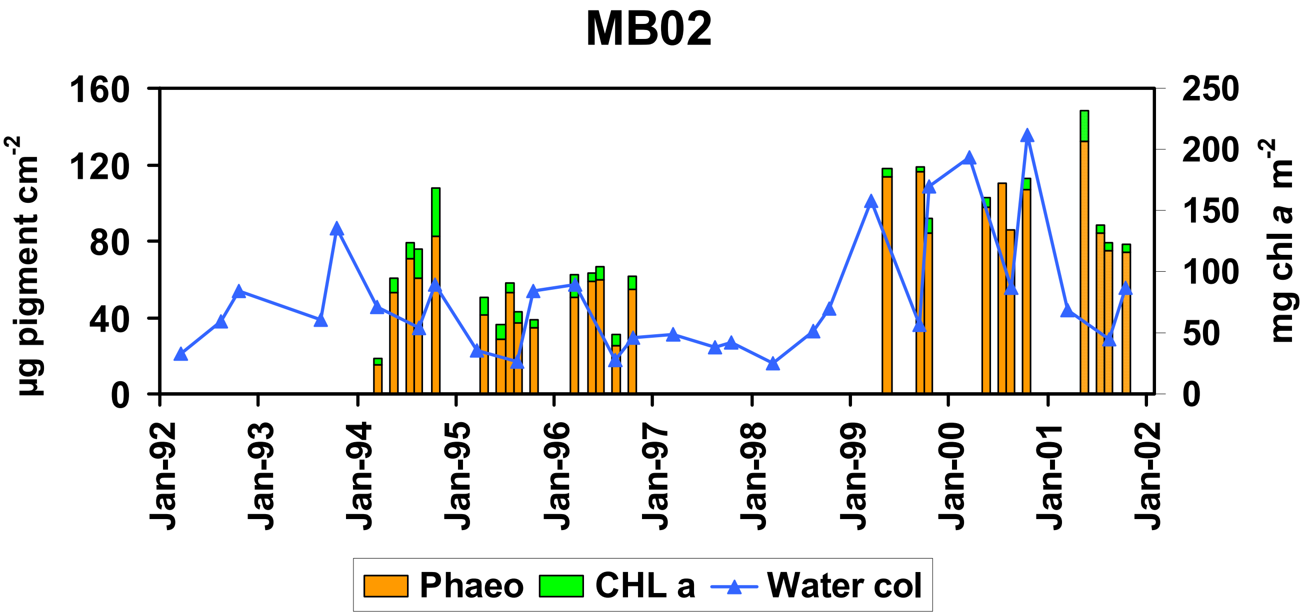


Figure 31. Sediment pigments at representative bay station MB02 (bars) compared to seasonal averages of water column chlorophyll *a* (line) through the baseline monitoring period and one year post diversion (stippled bars).

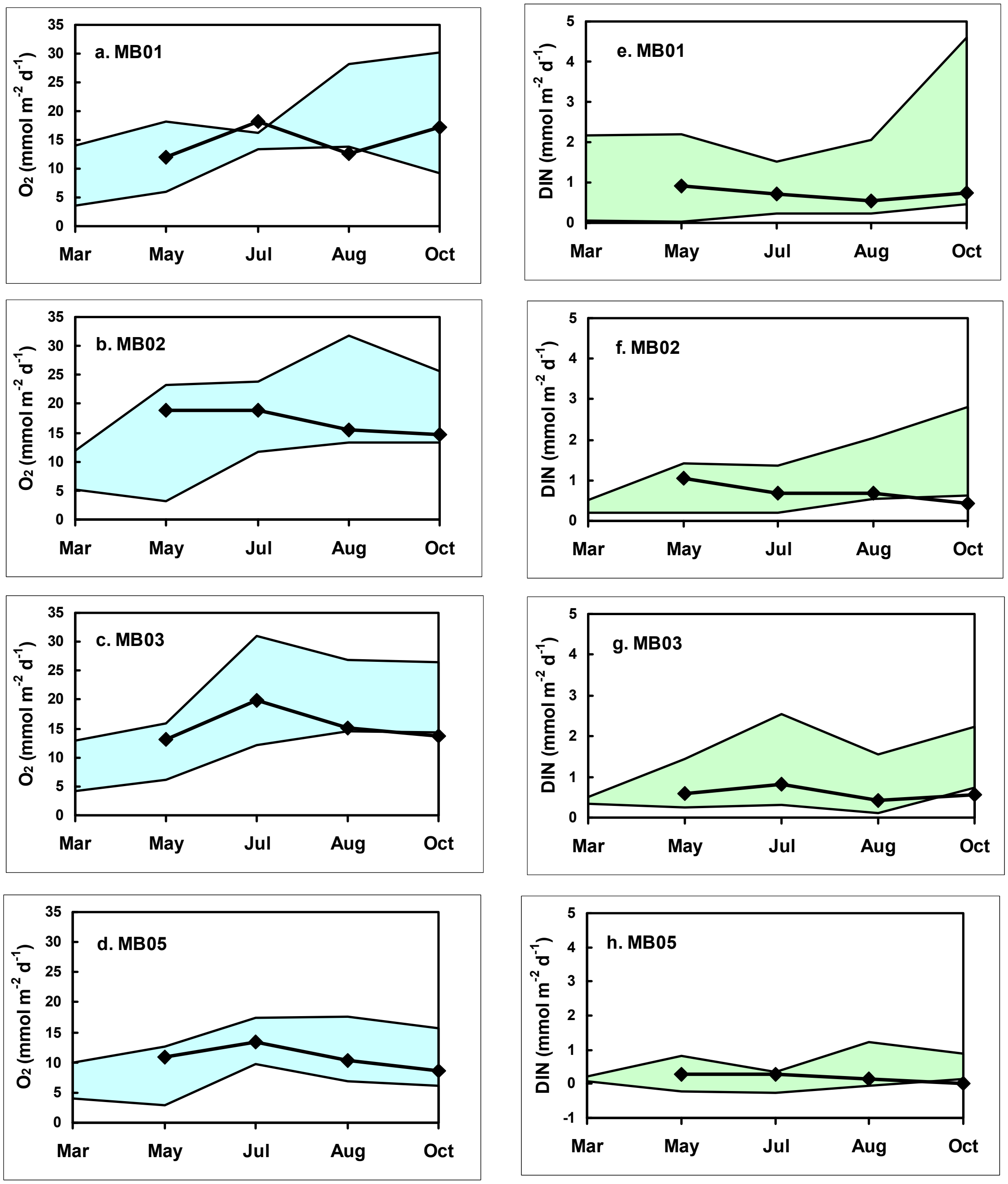


Figure 32. Sediment oxygen demand (O_2 flux) and DIN flux for 2001 (solid lines) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict S.O.D and panels e-h depict DIN flux for stations MB01, MB02, MB03, and MB05, respectively.

7.1.2 DIN Fluxes

Fluxes of dissolved inorganic nitrogen were also typical of baseline values. At the nearfield stations, the 2001 DIN fluxes varied from 0.4 to 1.1 mmol m^{-2} d^{-1}, in the low end of the baseline envelope (Figures 32 e-g). October rates at MB02 and MB03, in fact, fell below the baseline low for that month, but within the overall range. At MB05, DIN flux in 2001 ranged from 0.02 to 0.3 mmol m^{-2} d^{-1}, and were intermediate the baseline range in May, at the high end in July, low in August, and just below the range in October (Figure 32h). It is worth noting that the ranges documented at MB05 are narrower than those for the nearfield stations.

Although DIN fluxes in 2001 were smaller than they had been in 1999-2000, the percent of the DIN flux that was NO_3^- had increased to about 35% from lower percentages in the previous two years (Figure 21). The contribution of NO_3^- to the DIN flux was not as large, however, as it was in 1995-1997, when fluxes at these nearfield stations were lowest.

7.1.3 Denitrification

Denitrification in 2001 was well within ranges and about average those observed during baseline monitoring (Figure 22). At station MB02, rates were similar in May and October, (2.9 and 2.5 mmol N m^{-2} d^{-1}, respectively), whereas at station MB03, rates in May (3.4 mmol m^{-2} d^{-1}) were higher than in October (1.5 mmol m^{-2} d^{-1}). DIN fluxes, in comparison, were less than denitrification fluxes: 1.1 and 0.43 mmol m^{-2} d^{-1} at MB02 in May and October, respectively, and 0.6 at MB03 in May and October. Denitrification, therefore, accounted for nearly 80% of the total nitrogen flux from the sediments (at these two stations) in 2001.

7.1.4 Phosphate Fluxes

Phosphate fluxes in 2001 were also “normal” compared to baseline maxima and minima (Figure 33 a-d). Seasonal averages for the three nearfield stations were quite similar (0.04, 0.04, and 0.05 mmol m^{-2} d^{-1} for MB01, MB02, MB03 respectively; Figures 23 a-c), and at the lower end of the baseline range, resembling rates from the 1995-1997 period. Phosphate was taken up by sediments in only two instances in this year (Figures 33 b and c) and seasonal averages were positive, whereas in 1999, there was a strong average phosphate influx at Station MB03, and in 2000, average fluxes were negative at MB01 and MB03 (Figure 23). Phosphate fluxes in 2001, in fact, appeared to represent a return to the more typical pattern observed during baseline monitoring. Phosphate fluxes at farfield station MB05 were intermediate baseline ranges (Figure 33d).

7.1.5 Dissolved Silica Fluxes

Fluxes of dissolved silica (DSi) in 2001 were at the low end of the baseline range or were somewhat lower (Figures 33 e-h). At station MB02, these lower rates were a continuation of a decrease in fluxes from a station maximum in 1999. At this station, DSi fluxes in July through October, 2001, were lower than all previous measurements made in those months, though not lower than typical for winter (March) rates (Figure 33f). DSi fluxes at MB05 were also on the low end of the range. The absence of a large phytoplankton bloom in 2001, especially in comparison to the very large and sustained blooms that occurred from 1998-2000, may have resulted in less silica deposition to and therefore flux from the benthos.

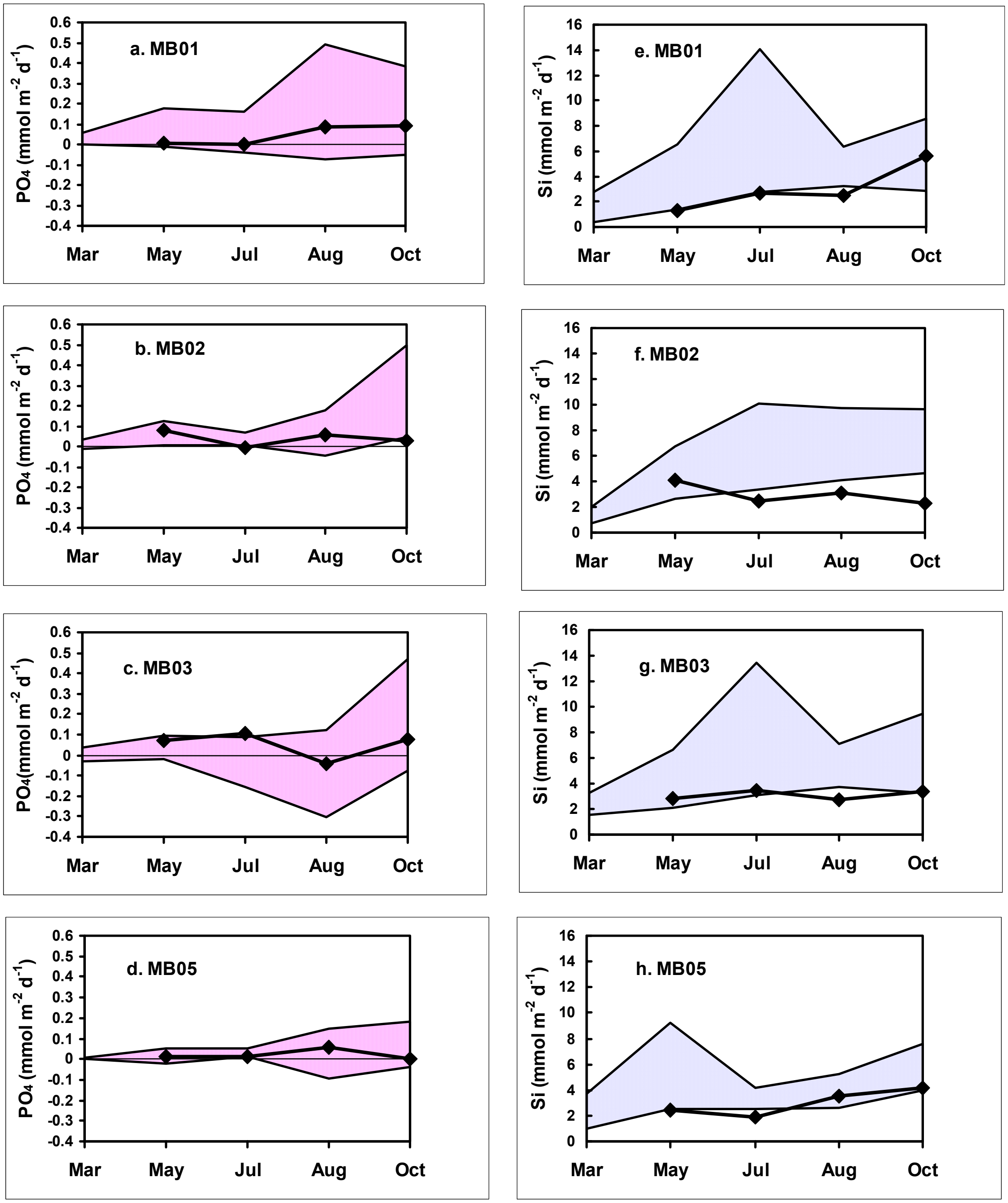


Figure 33. Phosphate and dissolved silica flux for 2001 (solid lines) compared to maximum and minimum values observed during baseline monitoring (shaded area). Panels a-d depict PO_4 flux and panels e-h depict DSi flux for stations MB01, MB02, MB03, and MB05, respectively.

7.2 Sediment Redox Conditions

7.2.1 Respiratory Quotients and Porewater Indicators

Sediment redox conditions in 2001 were similar to those observed in 1999 and 2000, continuing the trend of the latter part of baseline monitoring towards more oxidizing conditions in the sediments. The respiratory quotient (RQ) remained near 1.0 at all stations (Figure 25c), and positive Eh values were measured throughout the sediment profile depth of 18 cm (Figure 34). Lowest Eh values of about 50 to 100 mV were observed in August; these values are well above the initiation point for sulfate reduction (~-200mV); accordingly, dissolved sulfides were not detected.

7.3 Sediment Parameters

7.3.1 Total Organic Carbon

Organic carbon content of the nearfield sediments in 2001 fell well within the range of values observed during baseline monitoring. With two exceptions, sediment TOC most resembled the lower values of the previous two years and seemed to continue the decreasing trend since 1993 noted especially for Stations MB01 and MB03. In 1999-2000, the average TOC for the nearfield was 1.0% (S.D. = 0.2). Most sediment samples from 2001 had similar carbon content, but two contained organic carbon content over twice that average. Sediments taken from Station MB03 in July had 2.3% TOC and from Station MB01 in October had 2.1% TOC. At Station MB02, organic carbon content was slightly higher than the previous two years, but we did not observed any "spikes" in TOC at this station. Sediments at farfield station MB05 had organic carbon content typical of all preceding years of monitoring.

Although TOC concentrations in 2001 were in general in the low end of the baseline range, average molar ratios of TOC/TON at all three stations decreased in 2001 compared to baseline (Figure 29). There was a sharp drop in C/N at Stations MB01 and MB02 from the 1993-2000 average of 12.5 to 10.9 and 10.4, respectively. The average C/N at Station MB03 was 9.9 in 2001, down from the 1994-2000 average of 11.

7.3.2 Sediment Pigments

Photopigment inventories in 2001 were similar to those of the two preceding years, which were characterized by some of the higher values recorded during baseline monitoring (Figure 30). As mentioned above, elevated pigment concentrations are likely related to the deposition of the large phytoplankton blooms that occurred in 1999-2000. In May, 2001, total photopigment inventories of approximately 150 ug cm^{-2} in the top 5 cm of sediment at two of the three nearfield stations, MB02 and MB03, were higher than any observations during baseline monitoring. Both the chlorophyll *a* and the phaeophytin fractions were elevated, and although the chlorophyll fractions were high, 15.6 and 17.8µg cm^{-2}, respectively, they did not exceed previous observations. Curiously, elevated chlorophyll concentrations were not observed at Station MB01 in May, but in October, very high sediment chlorophyll *a* inventories of 24 µg cm^{-2} were measured at this station, representing 20% of the total pigments. Although similarly high percentages of chlorophyll relative to total pigment had been observed early in the monitoring period, in more recent years chlorophyll typically has comprised 10% or less of the total.

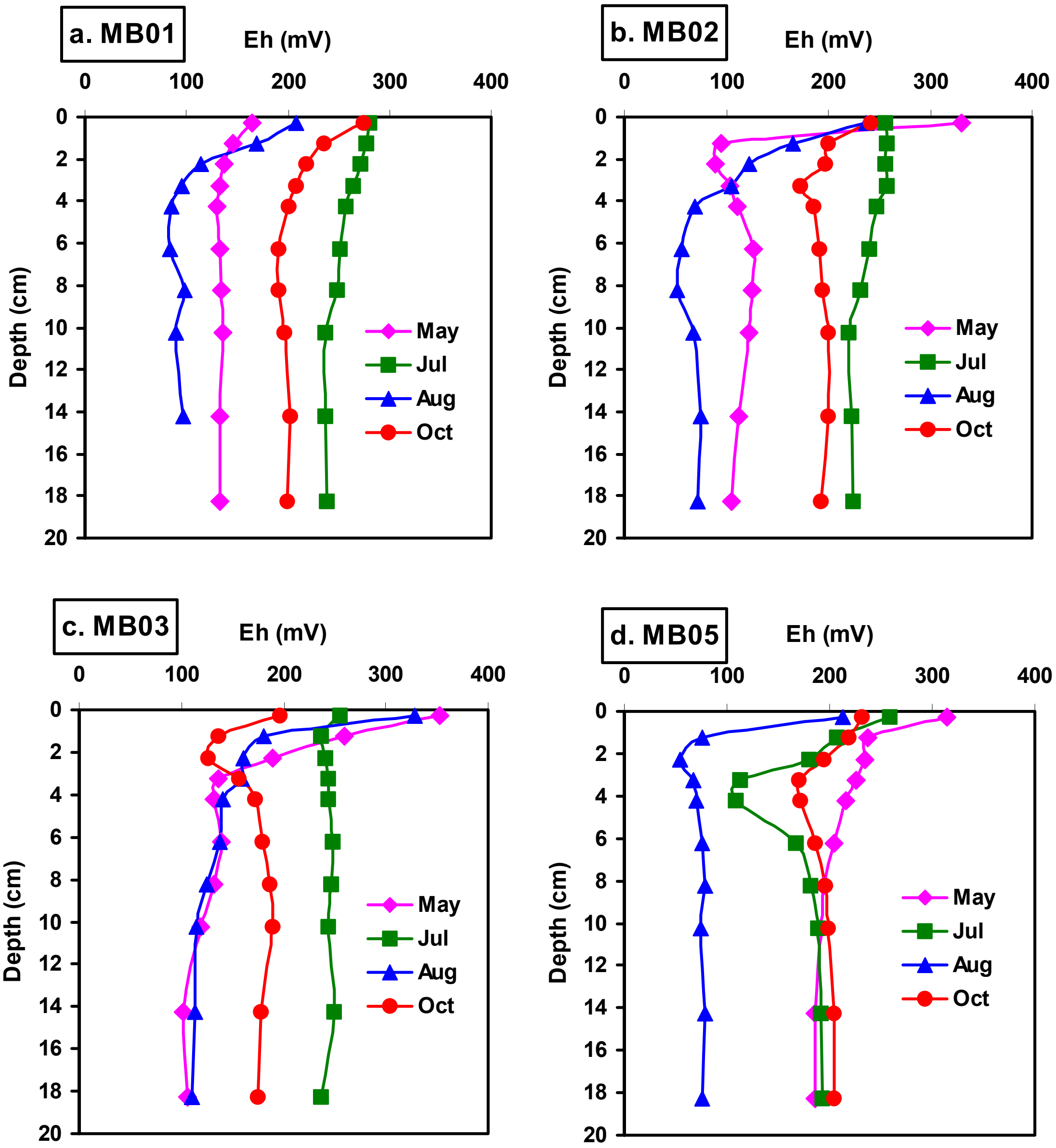


Figure 34. Redox (Eh) profiles in 2001 from bay stations a.) MB01, b.) MB02, c.) MB03, d.) MB05.

High levels of sediment chlorophyll *a* were consistent with generally lower C/N ratios and taken together would suggest that elevated amounts of undegraded phytoplankton debris were present. However, water column chlorophyll concentrations were not particularly high in 2001. Elevated total pigment inventories in the spring of 2001 at MB02 and MB03 may have been caused by the deposition of the fall, 2000 bloom, when water column chlorophyll reached maximum levels for the 1999-2000 series of blooms. However it seems unlikely that high concentrations of undegraded pigment would persist from fall until spring. Also, the chlorophyll peak at Station MB01 in October, 2001, was a curiosity. In this case, elevated chlorophyll inventories did correspond to a spike in TOC and a low C/N (9.4). In the absence of a phytoplankton bloom, another source of chlorophyll must be identified. The data suggest that, whereas total pigments are a reflection of water column blooms, peaks in benthic chlorophyll *a*, even at the depth of these nearfield stations, may be due to *in situ* production.

8.0 SUMMARY

8.1 Boston Harbor

In general, benthic metabolism and nutrient fluxes from the silty sediments of Boston Harbor decreased over the baseline monitoring period. Most of this decrease resulted from a return to typical fluxes at the two north harbor stations, BH02 and BH03, from quite high rates observed early in the program (1993 and 1995). Very high rates were associated with increases in benthic infaunal abundances, particularly with the presence or absence of the *Ampelisca* mat, which spread throughout the harbor during the monitoring period. The "bloom" of amphipods we observed at Station BH03 is thought to have been triggered by the cessation of sludge disposal in December, 1991, which had until that point prevented colonization. Large fluxes at station BH02 have also at times been associated with the presence of amphipods (1995), but more typically this station has had low abundances of infauna.

The presence of the amphipod community affects biogeochemical processes in several ways. The dense mat of tubes built by the amphipods penetrates 5 –10 cm into the sediments. Through ventilation of the tubes, the amphipods increase advective flux and they enhance microbial activity by oxygenating the sediments and increasing access to substances stored in the sediments. Effects are manifested in magnitude of fluxes and in changes in redox processes.

At the two southern harbor stations, BH08A and QB01, where no such dramatic change in organic matter loading occurred, we observed much less change in SOD or nutrient fluxes; however, monitoring of these stations did not begin until 1995. The amphipod mat is present at BH08A, but it, and therefore benthic fluxes, have been relatively stable. At the end of baseline monitoring, fluxes at Station BH03 and BH08A had become very similar in magnitude. At station QB01, SOD and nutrient fluxes were consistent throughout monitoring, and were the lowest of the four harbor stations.

Before effluent diversion offshore, sewage treatment improvements other than the cessation of sludge disposal were subtle from the perspective of the sediments and changes in fluxes directly related to those changes were not apparent. Because nutrient loading was decreased only slightly, primary productivity, which fuels the benthos, remained high. Station BH02 in the north harbor served as an indicator station for changes that might be attributable to improvements such as increasing levels of secondary treatment. In 1998 and 1999 we began to see some indications of improvement, for instance the surface oxidized layer of sediments was deeper. However this trend did not continue into 2000.

Decreasing trends in SOD and nutrient fluxes continued in 2001, the first year after all sewage effluent was diverted out of the harbor. At Station BH03, some fluxes were the lowest ever observed. There were a few atypical findings in 2001, most of them at Station BH02.

Sediment oxygen demand in general decreased over the baseline monitoring period. In particular, the extremely high rates of benthic respiration observed in 1993 and 1995 at the sludge-enriched Station BH03 moderated as stores of organic matter were depleted, and rates became more similar to the other three harbor stations. This trend continued in 2001, and in fact SOD at Station BH03 was the lowest ever observed at that station. Whereas highest SOD was typically measured at BH03 during baseline, in 2000 and 2001 highest rates were at station BH08A.

DIN fluxes decreased over the baseline period in the north harbor, especially at BH03. In the south harbor, however, a decreasing trend was not apparent, and baseline maximum rates for the station were observed at BH08A in 2000. In 2001, DIN flux was the lowest ever observed at Station BH03 and had decreased to typical levels at BH08A. Nitrate was an important part of the flux at Stations BH03 and BH08A, where amphipods oxygenate the sediments, and at BH02 in 1995 when amphipods were present. In 1998, nitrate was again becoming an important fraction of the DIN flux at BH02; in 2001, the fraction represented by nitrate was higher than it had been since 1995.

Denitrification rates were typically quite high at Station BH03 and quite variable at Station BH02 during baseline. High rates at BH03 were attributable to highly oxygenated sediments, whereas low rates at BH02 were consistent with much more reducing conditions typically present there. In 2001, denitrification rates were atypically low at Station BH03, and high at BH02. Increased denitrification (as well as the increase in the NO_3^- fraction of the DIN flux) at BH02 indicates the presence of more highly-oxygenated sediments, consistent with increases in infauna. During baseline, denitrification was estimated to provide a sink of only about 10% of the terrestrial nitrogen inputs to the harbor. After diversion, denitrification became of equal magnitude to the remaining terrestrial inputs. Including oceanic inputs, however, reduces the sink back to about 10%.

Phosphate fluxes were variable over the baseline period and subject to physical, chemical, and biological factors. Again, the presence or absence of amphipods played a role by influencing advection and oxic/anoxic conditions. Phosphate fluxes in 2001 were typical of lower rates observed during monitoring.

Respiratory quotients in much of the harbor where sediments are oxygenated were close to 1.0. Values much higher that 1.0 were more typical of conditions at Station BH02. In 1999 and 2001, RQs at this station became much closer to 1.0, again indicating less reducing conditions in sediments here. Profiles of Eh and sulfide concentration also suggested more oxic conditions.

Organic carbon content of harbor sediments in 2001 seemed to continue the decreasing trend we have noted during baseline. Sediment chlorophyll *a* inventories were typical of baseline, although at Station BH02 they had declined from very high levels in 1998-2000. Although we have often observed benthic diatoms at Station QB01, May 2001 was the first time we had noted them at Station BH02. It may be that increased water clarity in the harbor, among other improvements noted after diversion will permit more benthic primary production.

8.2 Massachusetts Bay

Massachusetts Bay is part of the much larger Gulf of Maine system, and therefore processes in the bay, including benthic processes, are influenced by large-scale, often region-wide phenomenon. One such phenomenon was a very large storm in December, 1992, that resuspended sediments in Boston Harbor and Massachusetts Bay and redistributed them such that bay sediments received significant inputs from the harbor. Another region-wide event began in the fall of 1999, when a series of large phytoplankton blooms began that lasted through the fall of 2000. Chlorophyll levels during these blooms were much higher than previously observed. Both of these events had impacts in the benthos. The operation of the new bay outfall, which began in September, 2000, represents a new phenomenon with region-wide and long-term implications.

In general, patterns of benthic metabolism and nutrient fluxes measured in depositional sediments in the bay from 1992 to 2001 were fairly consistent across stations, probably due to similar inputs, although differences among stations were apparent at times. Trends in SOD and nutrient fluxes were not similar however. Maximum rates of benthic respiration were observed from 1997-2000, whereas maximum rates of nutrient release occurred in 1993-1994.

Sediment oxygen demand (SOD) at the three nearfield stations in Massachusetts Bay was remarkably similar from 1993-1996, and decreased slightly over that time. Strong seasonal patterns were apparent such that temperature explained over 40% of the variation in the flux. In 1997, trends at each station seemed to diverge and were less similar to each other through 2000, and in 1999-2000, the seasonal pattern was not observed. SOD increased at this time as well. Respiration rates were lower at Station MB05 in Stellwagen Basin, but followed a pattern most similar to that at station MB03. Higher rates beginning in 1997 may be related to increases in infaunal abundances that began then and peaked in 1999. In 1999 and 2000 the deposition of the series of large phytoplankton blooms likely augmented the increased rates. The persistence of those blooms, producing a relatively continuous rain of organic matter to the benthos, may help explain the absence of seasonal patterns during that time. In 2001, water column chlorophyll concentrations were typical of baseline and infaunal numbers had decreased for the second year. SOD decreased from the previous two years, and the nearfield station fluxes were once again quite similar. This was the first year the bay outfall was operational.

Highest DIN fluxes of the baseline period occurred in late 1992 (when we first sampled) through 1994, likely the result, in the first part of this period, of large infaunal abundance and then by the redistribution of sediments caused by the December, 1992 storm. Rates were somewhat elevated in 1999-2000, again likely related to the high water column production during this time. Sediments in the bay are well oxygenated, and NO_3^- typically comprises 25%-50% of the DIN flux. DIN fluxes in 2001 were about average those observed during baseline.

Denitrification has varied over the baseline period, and a seasonal pattern has not been apparent. It often represents 60%-80% of the total N mineralized in the depositional sediments of the bay. Denitrification in 2001 was typical of previous years.

Phosphate fluxes in the bay have varied widely in magnitude and direction. Similar to DIN fluxes, highest rates occurred in 1993 and 1994, again probably related to sediment redistribution. In 1999 and 2000, phosphate fluxes were often directed into the sediments In 2001, PO_4 fluxes were about average for baseline and were directed out of the sediments.

Patterns of silica fluxes in the bay resembled O_2 fluxes in seasonal pattern and DIN fluxes in periods of maxima and minima. From 1993-1997, a seasonal pattern was usually apparent, but was not observed in

1999-2000. Largest fluxes occurred in 1993-1994. The 1994 peak followed the fall 1993 diatom (*Asterionellopsis)* bloom. Somewhat elevated rates in 1999 and 2000 were probably related to the mixed diatom bloom, the persistence of which may help explain the absence of seasonal patterns.

Respiratory quotients in the bay were often greater than 1.0 in the early part of the monitoring program, consistent with organic matter input (from sediment redistribution) and low infaunal abundance. By 1999 and through 2001, RQs were much closer to and often lower than 1.0, another indicator of active bioturbation. Redox conditions as measured by Eh profiles also showed changes toward more oxic conditions over time.

Organic matter content of sediments at Stations MB01 and MB03 showed significant decreases over the baseline period. There was no such trend at Station MB02. It appears that the redistribution of sediments that occurred at the end of 1992 deposited significant amounts of organic matter at these stations, as is evident in TOC concentrations in 1993. Elevated concentrations were not observed at MB02, and there was no trend with time at this site. Apparently the effects of the storm did not reach this site. TOC content in 2001 was typical of baseline, with the exception of a high value at MB01 in October and at MB03 in July. There has been little change in TOC at Station MB05.

Ratios of TOC to TON were consistent within stations from 1994 to 2000, but C/N at MB03 (~11) was lower than at MB01 and MB02 (~12.5), and was lower still at MB05 (~10). Although the differences are small, the implication is that a range of organic matter quality reaches the sediments of Massachusetts Bay that may reflect varying proportions of phytoplankton and Boston Harbor derived particulate matter.

Inventories of total sediment pigments varied over the baseline in the nearfield, but corresponded roughly to concentrations of water column chlorophyll, sometimes with a lag (fall blooms might be apparent as spring high concentrations in sediments). Inventories were elevated in 1994, after the fall, 1993 bloom, and in 1999-2001, during and after the 1999-2000 blooms. High chlorophyll *a* inventories in 2001, after a season when water column chlorophyll was not particularly high, suggested the possibility of *in situ* production.

8.3 Observations vs Expectations for first year of diversion

No large changes in benthic nutrient cycling were observed after only one year of diversion of effluent out of Boston Harbor and into Massachusetts Bay in either the harbor or the bay. These results are not surprising, as sediment processes are integrative, and typically have a slow response time.

In Boston Harbor, the water column response to the diversion was dramatic. Large reductions in inorganic nutrients and chlorophyll were reported, and water clarity was substantially improved (Taylor, 2002). Although there is yet limited evidence of these changes in sediment biogeochemistry, certainly reductions in organic matter deposition resulting from water quality improvements will become apparent with time.

In particular, we will look for improvements at Station BH02, which up to this point has shown little change. In general, we anticipate further reductions in SOD and ammonium flux, for example, and increases in RPD depths in areas such as BH02 and QB01; all of these parameters may be used as indicators of the status of the benthic environment. However, we expect these changes to occur only gradually. We also will be watching for signs of increases in benthic primary production that may result from improved water clarity.

Any response in Massachusetts Bay sediments will also be apparent only over time, and will have to be quite large or sustained to be detected over the natural variability we observed during the extended baseline. Projections made by the Bays Eutrophication Model (BEM) suggest that a large response is unlikely. They indicated that POC flux to the sediments, including effluent and algal-derived POC, would occur only in a very localized area around the outfall, and the increase would be less than a doubling (Hydroqual, 1995). The limited impact projected by the model was largely attributed to secondary treatment, which produces effluent with low solids and biological oxygen demand. The model projections required five years to achieve a new equilibrium response representative of the full effect of the outfall, a length of time derived from time constants of decay and delivery of particulates to the sediments. In addition, our nutrient flux stations are outside the areas projected to see an increase. It is too early to judge whether the model predictions were accurate.

9.0 REFERENCES

Aller, R.C. 1982. The effects of macrobenthos on chemical properties of marine sediment and overlying water, pp 53-102. In PL McCall and MJS Tevesz, [eds.], Animal-Sediment Relations. New York; Plenum Press.

Alpkem. 1986. Nitrate and nitrite in water and seawater. RFA Method Number A303-S171. Alpkem Corporation, Clackamas, OR.

Armstrong, F.A.J. 1951. The determination of silicate in seawater. J. Mar. Biol. Assoc. U.K. 30:149-1160.

Bohn, H.L. 1971. Redox potentials. Soil Sci. 112:39-45.

Bothner, M.H. 2001. Concentrations of metals and bacterial spores in sediments near the Massachusetts Bay Outfall before and after discharge began. USGS Open-file Report 01-356. 2p.

Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr. 14:454-458.

Dornblaser, M.M., J. Tucker, G.T. Banta, K.H. Foreman, M.C. O'Brien, and A.E. Giblin. 1989. Obtaining undisturbed sediment cores for biogeochemical process studies using SCUBA, pp. 97-104. In M.A. Lang and W.C. Jaap [eds.], Proc. Amer. Acad. Underwater Sciences, 9th Ann. Scientific Diving Symp.

Edmond, J.M. 1970. High precision determination of titration alkalinity and total carbon dioxide content of seawater by potentiometric titration. Deep Sea Res. 17: 737-750.

Giblin, A.E., C.S. Hopkinson, and J. Tucker. 1992. Metabolism and nutrient cycling in Boston Harbor and Massachusetts Bay sediments. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1992-01. 42p.

Giblin, A.G., J. Tucker, and C. Hopkinson. 1993. Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1993-02. 46 pp.

Giblin, A.G., C.S. Hopkinson, J. Tucker, B. Nowicki, and J.R. Kelley. 1994. Metabolism and nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments in 1993. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1994-05. 61 p.

Giblin, A.G., C.S. Hopkinson, J. Tucker, B. Nowicki, and J.R. Kelley. 1995. Metabolism and nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments in 1994. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1995-13. 56 p.

Giblin, A.G., C.S. Hopkinson, and J. Tucker. 1997. Benthic Metabolism and Nutrient Cycling in Boston Harbor, Massachusetts. Estuaries. 20: 346-364.

Hopkinson, C.S., A.E. Giblin, and J. Tucker. 2001. Benthic metabolism and nutrient regeneration on the continental shelf of eastern Massachusetts, USA. Mar. Ecol. Prog. Ser. 224: 1-19.

Howes, B.L. 1998a. Sediment metabolism within Massachusetts Bay and Boston Harbor relating to sediment-water column exchanges of nutrients and oxygen in 1995. Boston: Massachusetts Water Resources Authority. Report ENQUAD. 1998-02. 68 p.

Howes, B. L. 1998b. Sediment metabolism within Massachusetts Bay and Boston Harbor relating to system stability and sediment-water column exchanges of nutrients and oxygen in 1996. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1998-10. 67p.

Howes, B.L. 1998c. Sediment metabolism within Massachusetts Bay and Boston Harbor relating to rates and controls of sediment-water column exchanges of nutrients and oxygen in 1997. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1998-20. 80 p.

Huettel, M. and I.T. Webster. 2001. Porewater flow in permeable sediments, p.144-179. *In* B.P. Boudreau and B.B Jorgensen (eds), The Benthic Boundary Layer, Transport Processes and Biogeochemistry. Oxford University Press, New York.

HydroQual, Inc. and Normandeau Associates. 1995. A water quality model for Massachusetts and Cape Cod Bays: calibration of the Bays Eutrophication Model (BEM). Prepared for the Massachusetts Water Resources Authority. Boston Massachusetts.

Kelly, J.R. and B. L. Nowicki. 1992. Sediment denitrification in Boston Harbor. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1992-02. 56 p.

Kelly, J.R. and B.L. Nowicki. 1993. Direct measurements of denitrification in Boston Harbor. Boston: Massachusetts Water Resources Authority. Report ENQUAD. 1993-3. 39 p.

Kelly, J.R. 1997. Nitrogen flow and the interaction of Boston Harbor with Massachusetts Bay. Estuaries 20: 365-380.

Kelly, J.R. 1998. Quantification and potential role of oceanic nutrient loading to Boston Harbor, Massachusetts (USA). Mar. Ecol. Prog. Ser. 173: 53-65.

Knebel, H.J. 1993. Sedimentary environments within a glaciated estuarine-inner shelf system: Boston Harbor and Massachusetts Bay. Mar. Geol. 110:7-30.

Kropp, R.K., Diaz, R.J., Hecker, B., Dahlen, D., Keay, K.E., Gallagher, E.D., Boyle, J.D. 1999. 1998 outfall benthic monitoring report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1999-15. 320 p.

Kropp, R.K., Diaz, R.J., Dahlen, D., Shull, D.H., Boyle, J.D., Gallagher, E.D. 2000. 1998 Harbor Benthic Monitoring Report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2000-06. 208 p.

Kropp, R.K., Diaz, R.J., Dahlen, D., Boyle, J.D., Hunt, C.D. 2001. 1999 Draft Harbor Benthic Monitoring Report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-03. 94 p.

Kropp, R.K., Diaz, R.J., Hecker, B., Dahlen, D., Boyle, J.D., Abramson, S.L., Emsbo-Mattingly, S. 2002. 2000 outfall benthic monitoring report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-11. 148 p.

Libby, PS, Hunt, CD, Geyer, WR, Keller, AA, Oviatt, CA, Turner, JT. 2000. 1999 Annual water column monitoring report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2000-09. 180 p.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

Nowicki, B.L. 1994. The effect of temperature, oxygen, salinity, and nutrient enrichment on estuarine denitrification rates measured with a modified nitrogen gas flux technique. Estuar. Coast. Shelf. Sci. 38:137-156.

Nowicki, B.L., J.R. Kelly, E. Requintina, and D. Van Keuren. 1997. Nitrogen losses through denitrification in Boston Harbor and Massachusetts Bay. Estuaries 20: 626-639.

Price, N.M. and P.J. Harrison. 1987. Comparison of methods for the analysis of dissolved urea in seawater. Mar. Biol. 94:307-317.

Rex, A.C., Keay, KE, Smith, WM, Cura, JJ, Menzie, CA, Steinhauer, MS, and Conner, MS. 1992. The state of Boston Harbor: 1991. Boston: Massachusetts Water Resource Authority. Report ENQUAD 92-3. 98p.

Seitzinger, S. S. 2000. Scaling up: site specific measurements to global-scale estimates of denitrification, p. 211-240. *In* J. E. Hobbie (ed), Estuarine Science, a Synthetic Approach to Research and Practice. Island Press, Washington, D.C.

Signell, R.P., and B. Butman. 1992. Modeling tidal exchange and dispersions in Boston Harbor. J. Geophy. Res. 97: 15,191-15,606.

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnol. Oceanogr. 14:799-801.

Strickland, J.D.H. and T.R. Parsons. 1972. A practical handbook of seawater analysis. Fish. Res. Board of Canada. Bulletin 167.

Taylor, D. 2001a. Trends in water quality in Boston Harbor during the 8 years before offshore trasfer of Deer Island flows. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-05. 54 p.

Taylor, D. 2001b. Comparison of water quality in Boston Harbor before and after inter-island transfer. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-09. 104 p.

Taylor, D. 2002. Water quality improvements in Boston Harbor during the first year after offshore transfer of Deer Island flows. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2002-04. 61 p. plus appendices.

Tucker, J., Giblin A.E., Hopkinson C.S. 1999. Metabolism, nutrient cycling and denitrification in Boston Harbor sediments in 1998. Boston: Massachusetts Water Resources Authority. Report ENQUAD 1999-08. 33 p.

Tucker, J., Giblin, Sheats, N., Giblin, A.E., Hopkinson, C.S., and Montoya, J.P. 1999b. Using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay. Mar. Environ. Res. 48: 353-375.

Tucker J,. Giblin, A.E, , Hopkinson CS, Vasiliou D. 2000. Benthic Nutrient Cycling in Boston Harbor and Massachusetts Bay: 1999 Annual Report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2000-11. 63 p.

Tucker J, Giblin, AE, , Hopkinson CS, Vasiliou D. 2001. Benthic Nutrient Cycling in Boston Harbor and Massachusetts Bay: 2000 Annual Report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 01-07. 48 p.

Tucker, J. and Giblin, A. 2001b. Combined work/quality assurance plan (CW/QAPP) Revision 1 for benthic nutrient flux studies: 1998-2001. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-051 Revision 1. 36 p.

Werme, C , Hunt, CD. 2001. 2000 Outfall Monitoring Overview. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-10. 92p.

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 2001.

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 2001.

Station	Survey ID	Date	Latitude	Longitude	Depth (m)	Temp (oC)	D.O. (mg.L^{-1})	Salinity (psu)
BH02	NC011	05/14/01	42.34347	-71.00200	9.5	11.9	9.51	30.0
	NC012	07/18/01	42.34380	-71.00216	10.3	13.8	8.75	31.4
	NC013	08/07/01	42.34372	-71.00210	7.9	15.7	8.03	31.2
	NC014	10/29/01	42.34368	-71.00188	11.1	10.2	9.19	30.5
BH03	NC011	05/14/01	42.33100	-70.96217	7.8	11.6	9.20	30.7
	NC012	07/18/01	42.33052	-70.96168	9.4	13.5	9.04	33.0
	NC013	08/07/01	42.33068	-70.96195	7.3	17.3	7.80	32.2
	NC014	10/29/01	42.33077	-70.96160	9.7	10.0	9.31	30.5
BH08A	NC011	05/14/01	42.29143	-70.92162	7.0	12.2	8.99	30.5
	NC012	07/18/01	42.29139	-70.92193	9.4	13.4	9.06	31.1
	NC013	08/07/01	42.29111	-70.92242	6.9	17.4	8.03	32.4
	NC014	10/29/01	42.29090	-70.92218	8.4	10.2	9.40	30.2
QB01	NC011	05/14/01	42.29277	-70.98795	3.9	13.8	8.92	29.8
	NC012	07/18/01	42.29325	-70.98780	5.5	14.8	8.46	31.6
	NC013	08/07/01	42.29333	-70.98769	3.5	19.8	7.75	31.8
	NC014	10/29/01	42.29348	-70.98780	4.2	10.5	9.17	30.1
MB01	NC011	05/24/01	42.40353	-70.83698	30.1	6.0	9.4	32.0
	NC012	07/17/01	42.40298	-70.83736	32.1	6.8	8.59	33.5
	NC013	08/08/01	42.40298	-70.83740	29.4	7.3	9.12	33.3
	NC014	10/30/01	42.40282	-70.83640	32.0	7.9	7.37	30.9
MB02	NC011	05/24/01	42.39253	-70.83385	29.2	6.8	9.20	33.0
	NC012	07/17/01	42.39256	-70.83434	32.1	6.7	8.55	33.5
	NC013	08/08/01	42.39258	-70.83443	31.7	7.2	9.46	32.5
	NC014	10/30/01	42.39260	-70.83401	32.5	8.1	7.56	31.1
MB03	NC011	05/24/01	42.34782	-70.81623	25.5	7.5	9.15	32.8
	NC012	07/17/01	42.34786	-70.81612	33.7	6.84	8.69	32.8
	NC013	08/08/01	42.34785	-70.81560	32.0	7.2	9.09	32.4
	NC014	10/30/01	42.34883	-70.81505	33.0	7.9	7.30	30.5
MB05	NC011	05/24/01	42.41630	-70.65147	42.9	5.0	10.77	33.6
	NC012	07/17/01	42.41636	-70.65202	45.5	5.4	9.80	34.0
	NC013	08/08/01	42.41643	-70.65193	45.4	6.4	8.74	34.8
	NC014	10/31/01	42.41645	-70.65165	43.4	7.5	7.51	31.7

Appendix B

Methods

Appendix B

Methods

The methods used in this study have been described in Giblin *et al*. (1997) and in the CW/QAPP (Tucker and Giblin, 2001b). They will be only briefly described here. Because the monitoring of these stations in 1995-1997 was carried out by other investigators, we have noted any deviations from the CW/QAPP and discussed specific aspects of the methods that may not be obvious from the previous reports.

Field Sampling

For flux measurements, two large, 15-cm. diameter cores were collected per station. Replicate 6.5-cm diameter cores were collected for porewater analysis. Two to three 2.5-cm diameter cores were taken for porosity and solid phase analyses. At BH02 ,BH03, MB02, and MB03, two additional cores, approximately 10.1-cm. in diameter, were taken for direct measurements of N_2 flux. All cores collected from Boston Harbor stations were sampled by SCUBA divers. The Massachusetts Bay cores were obtained using a box corer (50X50 cm). For the nutrient flux cores, core tubes were mounted inside the box corer before deployment. The additional smaller cores were collected from the filled box core after retrieval.

Bottom water temperature, O_2, and salinity were measured in situ with a water quality monitoring sonde unit (Hydrolab Scout 2 Multiparamenter Water Quality Data System). Water depths at Station MB05 (~75m) exceeded the length of our sonde cable (50m); however, by sampling from below the pycnocline we were confident that we collected data representative of bottom water. In these deeper waters, stratification below the pycnocline is weak (R. Geyer, pers.comm.) At each station 15 liters of seawater were collected with a diaphragm pump and immediately filtered through a series of cartridge filters (nominally 20 and 1.0 µm). Water was collected from just above the bottom at all stations except for Station MB05; at this station water was collected from about 33m depth, below the thermocline and equal to the length of our sampling equipment. The collected water was held at in situ temperatures and used to replace the overlying water in cores just prior to flux measurements.

Benthic Respiration and Nutrient Fluxes

Cores were transported to Woods Hole, MA, submerged in water in large insulated containers and maintained at *in situ* temperatures. Before transporting the cores, care was taken to be sure the headspaces of the cores were completely filled with water. This prevented sediment disturbance during handling. Upon arrival, cores were placed in a dark incubator where they were aerated and held overnight at the *in situ* temperature of the station. Flux measurements were begun within 24-48 hours of collection. Prior to initiating flux measurements, the overlying water of each core was replaced with the filtered seawater collected at each station. Two BOD bottles filled with the filtered water obtained from each station were used to correct for respiration in the water overlying the sediments.

Cores were sealed with tops containing magnetic stirrers (Dornblaser *et al*., 1989) and gently mixed. We monitored concentrations of oxygen in the overlying water throughout the incubation period. Incubation duration was determined by the time required for oxygen concentrations to fall by 2 to 5 ppm (generally 6 to 24 hrs). Water samples were taken periodically from each core throughout the incubation period. Benthic respiration was calculated as the slope of oxygen concentration versus time. The values were corrected for the oxygen uptake in the water overlying the cores by using O_2 changes measured in

BOD bottles. Taking measurements over time enabled us to determine whether oxygen consumption was linear.

Concurrent with O_2 measurements, samples of the overlying water were withdrawn for dissolved inorganic nitrogen and phosphorus, urea, and silicate analysis. Ammonium concentrations were determined within 12 hrs. from duplicate 3 ml subsamples by the technique of Solorzano (1969), modified for small sample size. A 3 ml sample was saved for phosphate analysis, acidified to pH 2 with 10 µl of 4.8N HCl and kept at 4°C until analysis by the spectrophotometric method of Murphy & Riley (1962).

Additional sub-samples were frozen for later measurement of nitrate + nitrite, silicate, and urea concentrations. Nitrate + nitrite were determined together using the cadmium reduction method on a rapid flow analyzer (Lachat 8000). DIN was calculated as the sum of ammonium, nitrate, and nitrite. Silicate was analyzed by reduction with stannous chloride using an autoanalyzer (method of Armstrong 1951 as adapted by RFA, Alpkem Corp 1986; Alpkem RFA-300). Urea was analyzed using the method of Price and Harrison (1987).

At the beginning and end of the incubation period, 60 mL samples were also taken for total CO_2 analysis. These samples were stored at 4°C in glass BOD bottles with mercuric chloride (10 µL of a $HgCl_2$ saturated solution) as a preservative. Samples were analyzed with a high precision coulometric CO_2 analyzer capable of measuring total CO_2 with a precision of 0.05% (1 µM).

Porewater Sampling and Analysis

Sediment samples for porewater extraction were taken from all 8 stations in July and August. Cores were sectioned into depth intervals in a glove bag under a nitrogen atmosphere. Sediments were sampled in 1 cm intervals down to 2 cm, 2 cm intervals to 6 cm and then in 4 cm intervals at greater depths (typically to 14 cm). Nutrients, urea, silicate, sulfides (Cline 1969), pH and alkalinity (Edmond 1970) in porewaters were analyzed as previously described in Tucker and Giblin, 2001. Sediment oxidation-reduction potential (Eh) and porewater pH were measured in a separate core. Eh was measured using a platinum electrode (Bohn 1971). The values reported here have been corrected for the potential of the reference electrode. Porewater pH was measured using an *in situ* pH probe.

Porosity and Sediment C and N

Sediments from 2.5-cm diameter cores were sectioned in 1 cm intervals to a depth of 10 cm and then in 2 cm intervals to the bottom of the core. Sediment wet weight was measured immediately and dry weight after a minimum of 72 hrs at 105°C. Porosity was calculated as: (volume of water in the depth interval sampled)/(total volume of water + sediment).

Organic carbon and nitrogen content was measured on the dried sediments after carbonates had been removed by acid fuming. Analyses were performed using a Perkin Elmer 2400 CHN elemental analyzer. The % carbon and nitrogen measured on the sediment was corrected for the weight change due to the acidification procedure which was usually 3-7%.

The depth intervals were measured from the apparent top of the sediment surface. At some stations, especially BH03 and BH08A, a large number of biogenic tubes protruded above the sediment surface. These were included in the sediment sample so reported carbon and nitrogen values include all of the material in the core. Because these tubes had substantial quantities of water in them, they may have increased the apparent porosity of the surface samples.

Chlorophyll *a* and Phaeopigments

Sediment samples for chlorophyll *a* and phaeophytin were collected from all eight stations. Pigments were measured in 1 cm increments down to 5 cm from a 2.5 cm diameter core. Each sediment section was placed in a separate centrifuge tube and frozen. Samples were later extracted with cold acetone in the dark. After extraction, samples were centrifuged and the absorbance of the supernatant was measured at 750 and 665 nm before and after acidification (Strickland and Parsons 1972).

Measurements of Denitrification

Sediment denitrification was measured as the direct flux of N_2 gas from sediment cores in gas-tight N_2-free chambers. These measurements were made in May and August for the Harbor stations, and in May and October for the Bay stations. Two sediment cores were incubated from each site on each sampling date; one was used for measurements of total sediment N_2 flux ("experimental core") and the other as a control for background N_2 de-gassing ("control core"; Nowicki, 1994).

A detailed description of sampling and measurement methods is given in Nowicki *et al*. (1997) and in the CW/QAPP (Tucker and Giblin, 2001b). Briefly, the depth of the sediment in the cores was adjusted to provide equal sediment depths for the experimental core and its anoxic control. Field core stoppers were replaced with gas-tight tops and bottoms so that the core tubes became the incubation chambers. The chambers were filled with ambient seawater and then a gas headspace was created by withdrawing an accurately measured volume of the seawater. The chambers were maintained in the dark, at ambient temperatures, with constant stirring. The overlying seawater and a gas-filled head space in each chamber were sparged with a mixture of helium and oxygen (80 He:20 O_2) to remove nitrogen but to maintain dissolved oxygen concentrations at levels similar to those observed in bottom waters in the field. Control cores were treated in the same manner as the experimental cores, but were maintained without oxygen so that coupled denitrification was prevented. These anoxic control cores were used to monitor and correct for background fluxes of N_2 (due primarily to N_2 in porewater diffusing into the N_2-free headspace) which were not caused by denitrification (Nowicki *et al*., 1997).

Measurements of the concentrations of nitrogen and oxygen in the gas-filled headspace of each chamber were determined from samples (100 µl) withdrawn with a gas-tight syringe from the chamber sampling port. Concentrations of nitrogen and oxygen in the gas samples were measured with a Shimadzu 8A Gas Chromatograph equipped with a thermal conductivity detector. Calibration curves were run with each set of samples using a certified standard gas mixture. Rates of N_2 gas production and O_2 uptake for sediments in the denitrification chambers were calculated from the slopes of 4-point (or more) linear regressions of N_2 or O_2 concentration in the gas phase of each chamber over time.

Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA 02129
(617) 242-6000
http://www.mwra.state.ma.us