Sediment metabolism within Massachusetts Bay and Boston Harbor relating to sediment-water column exchanges of nutrients and oxygen in 1995

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SEDIMENT METABOLISM WITHIN MASSACHUSETTS BAY AND BOSTON HARBOR RELATING TO SEDIMENT-WATER COLUMN EXCHANGES OF NUTRIENTS AND OXYGEN IN 1995

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EXECUTIVE SUMMARY

Sediment Metabolism within Massachusetts Bay and Boston Harbor Relating to Sediment-Water Column Exchanges of Nutrients and Oxygen in 1995

Rates of sediment oxygen uptake were measured throughout 1995 along an organic matter gradient from Boston's Inner Harbor through the outer edge of the nearfield grid to Stellwagen Basin. These data were coupled with seasonal measurements of water column-sediment exchanges of nutrients (primarily nitrogen), sediment oxidation, and porewater chemistry. In addition, parallel measurements of denitrification were conducted at two stations within Boston Harbor (high versus low infaunal density).

Monitoring of sediment carbon and nutrient cycling is currently providing sensitive indicators of changing ecological health of Boston Harbor and key elements for evaluating the oxygen balance of Massachusetts Bay bottom waters. Results from studies of the sediment-infauna complex within Boston Harbor provide an example of the non-linear responses of marine systems to changes in organic matter loading rates and the need for direct measurement.

Boston Harbor: Rates of total sediment community respiration, while showing significant inter-annual variability, appear to be increasing in portions of Boston Harbor. Seasonal measurements of carbon and nitrogen cycling in surficial sediments indicate that rates of organic carbon and nitrogen remineralization and denitrification were higher in 1995 than reported in each of the previous years of monitoring. Concurrent with the measured increases in rates of diagensis has been rapid colonization of Harbor sediments by infauna, particularly the development of dense amphipod mats (*Ampelisca* and *Leptocheirus*).

Ampelisca are deposit feeding amphipods capable of building mats several centimeters thick and reaching densities of over 100,000 individuals m^{-2}. *Ampelisca* are pollution sensitive relative to equilibrium assemblages found in shallow coastal systems. The widespread colonization of Harbor sediments by this infaunal complex has increased both the degree of sediment oxidation and rates of sediment/water column exchange through bioturbation and burrow ventilation. While populations continue to show cyclical variations, the amphipod mats appear to be becoming more persistent over the period from 1989 to 1995. The expanded distribution and reduction of interannual variations in the *Ampelisca* complex are likely related to improving water quality, particularly in the northern region of Boston Harbor, due to cessation of sludge discharges and/or contaminant reduction measures.

Remineralization rates and denitrification were significantly enhanced in areas densely colonized by amphipods (North of Long Island, BH03A > Hull Bay, BH08A > North Harbor, BH02) compared to areas with lower total infaunal densities (Quincy Bay, QB01). Infauna affected carbon mineralization directly through their metabolism and indirectly through their irrigation of the surficial sediments. The result was increasing oxidation of surficial sediments and higher rates of nitrification/denitrification. At the most heavily colonized sites, BHO3A and BH08A, oxidation of sediments resulted in a shift from ammonium to nitrate as the predominant DIN species regenerated. The data suggest that variability in partitioning between ammonium and nitrate observed in previous years was due to the periodic sampling of amphipod mats. Similarly, the increased oxidation of sediments colonized by amphipods showed a shift to DIN flux in "excess" of PO_4 flux (based upon the Redfield Ratio=16), compared to non-colonized sites in 1995 and previous years. This shift in N/P flux ratio was not observed at the Bay stations. It appears that the increased oxidation through irrigation of the surficial sediments within the Harbor is resulting in increased nitrification and nitrate flux, but increased retention of PO_4 through sorption to particles.

Sediments at BH03A and BH08A were heavily colonized by amphipods (*Ampelisca* and *Leptocheirus*) from March through August 1995. The dense amphipod mats began to break-up in August and were virtually gone by the October sampling. The nearly linear increases in community respiration with temperature measured at both stations when the mats were present (Mar-Aug) contrasted strongly with the much lower rates in October when the mats were senescent, but temperatures remained high. The influence of the infaunal community upon organic matter turnover is seen in the five fold (BH03A) and two fold (BHO2) higher rates of oxygen uptake at similar temperatures when the amphipod community was present.

Similarly, interannual comparisons showed large increases in measured rates of sediment oxygen uptake and denitrification in Boston Harbor (1992-1995). In contrast to 1995, the *Ampelisca* complex was only occasionally encountered during previous monitoring. In all cases data from 1992-1994 (SOD: Giblin *et al.* 1995; denitrification: Nowicki *et al.* In Press) showed significantly lower rates than those in 1995, except where amphipod mats were noted by the earlier studies. In contrast, Massachusetts Bay stations were similar in all years. It appears that during 1995, rates of carbon mineralization and denitrification within Boston Harbor were more than two fold higher than in previous years due to the increased area of the Harbor bottom colonized by amphipod mats. The extent to which the higher rates were the result of "mining" of sediment deposits versus increased trapping of water column particles by mats requires further study.

These results suggest that a positive feed-back loop exists whereby improving habitat quality results in increased persistence and abundance of infaunal populations. Increased sediment irrigation by infauna results in accelerated rates of organic matter and nutrient cycling and subsequent removal from Harbor sediments leading to improved habitat. This accelerated nutrient depuration of Harbor sediments suggests that the use of static analysis (which assumes proportional responses) in predicting future rates of change in habitat quality may be inappropriate in the Boston Harbor system.

It appears that nitrogen and carbon cycling within the Harbor and transport to Massachusetts Bay may be very dynamic under changing environmental quality. The temporal nature of these biologically mediated effects and their potential role in accelerating nutrient removal from the Harbor will be elucidated by the continued monitoring of this system.

Massachusetts Bay: Rates of respiration in bottom waters varied over five fold throughout the year at both the nearfield and Stellwagen Basin stations. Rates of metabolism show a gradient from Boston Harbor>nearfield>Stellwagen Basin. Rates were directly related to organic matter availability and temperature. Respiration within Massachusetts Bay was highest during and after the stratified period, declining to a low winter rate after fall turnover. In contrast, bottom water respiration was highest during non-stratified periods and lowest during stratification. The decline in bottom water respiration during stratification appears to be associated with reduction in the transfer of labile organic matter to the hypolimnion. The result is that the relative importance of sediment versus water column respiration shifts with stratification. Estimates of oxygen depletion in bottom waters during stratification were comparable to the measured total oxygen uptake by sediments and water column, each contributing about equally to system respiration. These data suggest that ventilation of bottom waters during stratification was likely small. However, since the monitoring data used in this analysis focus primarily upon depositional sediments, evaluation of oxygen uptake from non-depositional areas is required for a complete oxygen and nutrient balance.

Analysis of sediment nutrient fluxes showed lower rates (about half) during the stratified period than in 1994. Rates of sediment flux in 1995 were equal to observed changes in integrated hypolimnion DIN and PO_4 during stratification. When watercolumn regeneration is included, it appears that the nutrient regeneration rates from non-depositional areas must be slightly lower than depositional sites or that watercolumn respiration is retaining N in microbial biomass. As with bottom water oxygen dynamics, a complete nutrient balance during stratification requires an estimate of flux from the non-depositional areas. However, from the 1995 data it appears that both oxygen uptake and nutrient release from depositional versus non-depositional areas during the stratified period are nearly equivalent to 0.5X, depending upon the constituent.

Rates of sediment oxygen uptake at the long-term monitoring sites were comparable to previous studies (within 15%). Nutrient regeneration rates were similar between years but the source of the observed annual variability is at present unclear. The sediments at all stations were relatively oxidized with undetectable dissolved sulfide within the porewaters (0-10cm). The low rates of oxygen uptake were consistent with the low rates of nutrient release and porewater nutrient pools. The inter-annual stability of these integrative, process level measures indicate that they will be a sensitive tool for detecting relatively small changes in carbon enrichment. In addition, since benthic respiration appears to play a major role in bottom water oxygen depletion particularly during the stratified period, changes in uptake rates may allow prediction of changes in the extent of annual oxygen depletion. Our preliminary carbon budget, based upon measures of carbon production and decomposition within Bay waters and sediments, suggests that organic matter cycling within the nearfield is tightly coupled to water column production. Initial analysis suggests that comparable masses of organic matter are produced and respired within the nearfield region and that respiration does not require large imports of organic matter from inshore sources.

I. Introduction

The overall objective of the Benthic Nutrient Flux Study is to quantify the seasonal flux of selected nutrients and oxygen between the sediments and their overlying waters in Boston Harbor and Massachusetts Bay in the vicinity of the Massachusetts Water Resources Authority (MWRA) effluent outfall. These fluxes relate directly to total annual carbon, nutrient and oxygen dynamics in shallow marine ecosystems. The magnitude of flux can be influenced by many environmental factors including temperature and availability of labile organic carbon. While the partitioning of organic matter degradation between aerobic and anoxic pathways can dampen the magnitude of the seasonal excursion in surface oxygen consumption rates, integration of seasonal measures provides an evaluation of annual organic matter deposition. The goal is to determine, through continued monitoring, changes in sediment organic matter and nutrient cycling related to relocation of effluent discharges and potential secondary effects on the Harbor and Bay environments.

The organic rich nature and relatively shallow waters of coastal systems like Boston Harbor and Western Massachusetts Bay result sediments having a significant role in system biogeochemical cycles. However, the role of benthic processes in the ecological functioning of each of these two closely linked systems can be very different. Organic matter deposition to sediments, hence benthic respiration, tends to decrease with increasing depth of overlying waters due to interception by watercolumn heterotrophic processes (Hargrave 1975). In addition, in Boston Harbor direct organic matter loading (Alber and Chan 1994) and in situ production are significantly higher than to the Bay (Kelly In press, Cibik *et al.* 1996). The result is that in Boston Harbor respiration rates are typically many fold higher than in the adjacent Massachusetts Bay (Giblin *et al.* 1995). However, given the stratification of Bay waters, sediment metabolism still plays a major role in bottomwater oxygen decline, a ecosystem structuring parameter (Cibik *et al.* 1996).

Rates of organic matter remineralization and nutrient regeneration within the Harbor and Bay sediment systems are ultimately controlled by the organic matter inputs. These inputs depend upon external loading and in situ production and the physical and biological processes controlling deposition. In a steady state system, the instantaneous rate of sediment metabolism is controlled mainly by the level of labile organic matter (biologically degradable) and temperature, where increasing either results in increased rates of community metabolism. Infaunal communities also play a role in community metabolism and benthic exchanges. Infauna influence sediment-watercolumn exchanges through physical mixing of sediments, irrigation of burrows and their own metabolic activities. Sediment systems undergoing changes in organic matter inputs can undergo major restructuring of infaunal communities (Rhoads and Germano 1986). The subsequent impact of such infaunal changes on rates of sediment metabolism and system biogeochemical cycling is uncertain and likely system specific.

Another major role of sediment metabolism in coastal systems is as a site for microbial denitrification (Seitzinger 1988, Nowicki In press). Due to the deposition of labile organic matter to sediments at a level supporting oxygen consumption in excess of resupply from overlying water, coastal sediments are typically anoxic below the surface few millimeters to centimeters. The result is that unlike the watercolumn which typically supports only aerobic respiration, the anaerobic sediment layers support a diversity of electron acceptor pathways. Both Boston Harbor and Massachusetts Bay study areas support sediments with aerobic, nitrate and sulfate reducing zones. The result is that nitrogen remineralized within the sediments can be released to the overlying waters or be denitrified after oxidation to nitrate within the surficial sediments or walls of infauna burrows. The rate and distribution of denitrifying activities within the Harbor and Bay represent the major in situ mechanism for decreasing nitrogen related effects on these nitrogen limited systems. Since interactions between organic matter loading and denitrification can result in negative feedbacks, and interactions with infaunal communities positive feedbacks, future nitrogen losses from the Harbor and Bay under altered loadings are at present unclear.

Given the sensitivity of sediment metabolism, nutrient regeneration and infaunal communities to changing organic matter inputs, the infauna/sediment system has been used as a sentinel indicator of environmental constancy in estuarine systems. In addition, when projecting sediment depuration rates of organic matter and improvements in secondary diagenic factors such as porewater inorganic nitrogen/phosphorus and dissolved sulfide and oxygen penetration, it is essential to account for interactions between biogeochemical processes and infaunal activities.

The Benthic Flux Study focusses on the biogeochemical rates and pools within Boston Harbor and Massachusetts Bay sediments which are potentially responsive to changes organic deposition rates. The study includes collection of sediment cores by diver and box core sampler throughout the year, focusing on the periods of greatest microbial activity, with an additional low temperature sampling to provide seasonal data. Cores are collected for oxygen and nutrient flux, with separate parallel cores collected for N_2-denitrification; redox potential and chlorophyll-a; total organic carbon, grain size, and porosity; and for porewater chemical measurements. The Benthic Flux Study is coordinated with the MWRA's Soft-Bottom Benthic Monitoring Study of Boston Harbor and Massachusetts Bay in order to integrate biogeochemical processes with infaunal community structure.

This report details the results of the 1995 benthic flux program. In addition to presenting the 1995 results, comparisons will be made to previous studies to evaluate potential changes associated with decreased organic matter/nutrient loading to Boston Harbor and potential changes to loading to Western Massachusetts Bay. Due to alterations in the major sediment biogeochemical cycles in Boston Harbor detected in 1995, separate discussion will be made of the Harbor and Bay results. However, differences between the Harbor and Bay stations will be evaluated together in order evaluate the sensitivity of benthic processes as indicators of change. Linkages between watercolumn and sediment respiration in Massachusetts Bay relating to (1) carbon balance in the nearfield and (2) controls on Bay bottomwater oxygen levels during stratification is presented elsewhere (Cibik *et al.* 1996).

II. Methods

Sampling protocols and analytical techniques are detailed in the Combined Work/Quality Assurance Project Plan (Cibik and Howes 1995). However, a brief overview of the methodologies is below.

Field Sampling:

Sediment samples were collected from Boston Harbor and Massachusetts Bay on five surveys in 1995. Four sampling events focussed on periods of higher microbial activity: (1) after the deposition of the spring bloom and after onset of stratification, May/June; (2 & 3) during the warmest months of peak activity, July and August; and (4) in the fall after the breakdown of stratification and at about the mean annual temperature, October. There was a single low temperature sampling in March. Locations of the 8 sites sampled during 1995 are shown in Figure 1 with co-ordinates in Table 1. All four of the Bay sites and BH02 within the Harbor

TABLE 1
Locations for Long-Term Monitoring of Benthic Flux

Station I.D.	Depth (m)	Latitude	Longitude
BH08A	10	42°17.46'N	70°55.33'W
BH03A	7	42°19.70'N	70°58.05'W
BH08	12	42°17.18N	70°54.68W
BH03	5	42°19.79N	70°57.69W
BH02	6	42°20.62'N	71°00.13'W
MB05	76	42°25.01'N	70°39.26'W
MB01	35	42°24.16'N	70°50.20'W
MB02	35	42°23.54'N	70°50.02'W
MB03	34	42°20.87'N	70°48.90'W
QB01	3	42°17.614'N	70°59.274'W

Note: Stations followed by "A" are near historic stations with the same numerical prefix.
BH03 & BH08 were only sampled in March Survey

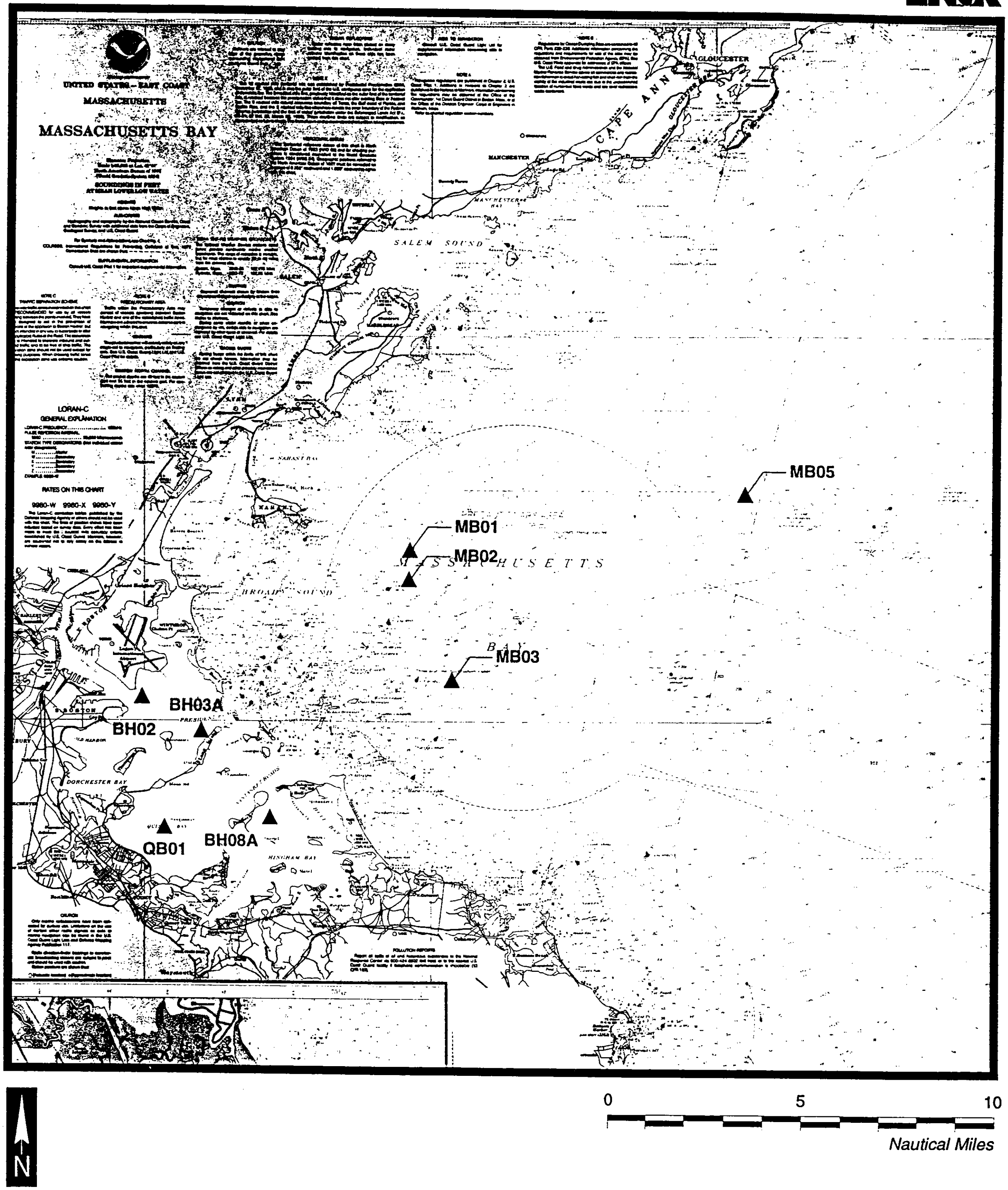


FIGURE 1

Station Locations for Benthic Flux Surveys are part of the long-term outfall monitoring program. The Bay sites, MB01, MB02, and MB03, are depositional sites within the western portion of the Nearfield grid of the high-frequency watercolumn monitoring program. The relocated outfall is within a few km of these sites. MB05 is in the deeper waters of Stellwagen Basin (F19) and is also linked to the watercolumn surveys. BH03 which was sited on a slope was relocated a short distance to BH03A which had similar infauna and sediment characteristics and is comparable to BH03. BH08 was similarly relocated to BH08A, which had sediments of a finer grain-size. The original stations, BH03 and BH08, were sampled during the March Survey. A new station, QB01, located in Quincy Bay was included to enhance areal data coverage and to serve as an infauna reference station as it was uncolonized by amphipods. Vessel positioning was by Northstar 941XD differential Global Positioning System (GPS) with an accuracy of 10 meters.

Sediment cores were collected by SCUBA diver within the Harbor and by box core sampler (40 x 40 x 50 cm) within the Bay. Cores were maintained at *in situ* temperatures on board ship by running seawater or a cooling bath depending upon the temperature conditions. From each sampling location cores for flux incubations (four 15 cm id), redox profiles (one 6.5 cm id), porewater extraction (from flux cores) and solids processing (two 6.5 cm id) were processed at a field laboratory within 0.1 mile of the ship dockage, in order to prevent disturbance to the cores due to transport. To assess core disturbance, bentonite was lightly applied to the surface of two extra cores on each survey to identify any vibrational mixing (as opposed to bioturbation). Cores for N_2-denitrification assay (four 9 cm id) were transported in a temperature controlled bath on a shock absorption anti-vibration system to the Woods Hole laboratory.

Water samples were collected by Niskin sampler from within 1 m, 2 m or 4 m of the bottom at the Boston Harbor, Western Bay and Stellwagen stations, respectively. Water was assayed for dissolved oxygen by Winkler titration with and temperature and salinity measured by electrode. Twenty liters of bottom water were collected and filtered to replace the headspace water of the flux cores prior to incubation.

Incubations:

The flux and porewater measurements follow the methods of Jorgensen (1977), Klump and Martens (1983), and Giblin *et al.* (1995) for nutrients and metabolism, and the methods of Kelly and Nowicki (1993) for denitrification measurements. Cores were maintained in the dark within 2°C of the *in situ* temperature.

<u>Benthic flux</u>: Upon return to the field laboratory the four 15 cm (id) cores per station were transferred to pre-equilibrated temperature baths. The headspace water was replaced, magnetic stirrers emplaced and the headspaces enclosed. Oxygen consumption was determined in time- course incubations up to 24 hrs. Oxygen levels were not allowed to drop below 50% air equilibration during the incubations. Periodic 60 mL water samples were withdrawn (volume replaced with filtered water), filtered into acid leached polyethylene bottles and held on ice for nutrient analysis. Ammonium (Scheiner 1976) and

ortho-phosphate (Murphy and Reilly 1962) assays were conducted within 24 hrs and the remaining sample frozen (-20°C) for assay of urea (RFA Alpchem), nitrate+nitrite (Cd reduction: Lachat Autoanalysis), DON (D'Elia *et al.* 197) and silicate (Parsons *et al.* 1989). DIC samples were injected into gas-tight serum vials and assayed by headspace equilibration and infra-red gas analysis. Alkalinity titrations were performed immediately upon sample collection. All rates were determined from linear regression of analyte concentrations through time.

Denitrification: Two pairs of cores in gas-tight chambers were incubated at in situ temperatures per station. One of each pair was incubated with a helium/oxygen headspace and one control with an anoxic headspace. Measurements followed the procedures of Seitzinger *et al.* (1980) with the modifications noted by Nowicki (1994). However, rather than performing 2 back-to- back incubations on a single pair of cores, analyses were conducted on replicate pairs of cores. The latter approach is supported by the generally small analytical error associated with multiple incubation of the same core material (Kelly and Nowicki 1993) as opposed to spatial variation assessed by replicate cores. Argon was measured at the end of each incubation and the ratio of N_2 to argon used to assess the total mass of denitrified nitrogen associated with the core. This calculation uses argon as a tracer for N_2 whose source was the atmosphere versus denitrification. N_2, O_2 and argon were measured by gas chromatography fitted using a sample loop and thermal conductivity detection.

Sediment Analyses:

Porewater: Porewater was obtained by sectioning the flux cores at 1-cm intervals to a core depth of 10 cm with extraction by anaerobic-refrigerated centrifugation (6000 rpm). Porewater from similar depths in replicate cores was pooled and assayed for ammonium, nitrate + nitrite, urea, ortho-phosphate, silicate, alkalinity and dissolved sulfides. Dissolved sulfides were fixed with Cline's Reagent (Cline 1969) immediately upon recovery of porewater. Measurements by Giblin *et al.* 1993 indicated that the spatial variations in profiles of most porewater constituents were almost always found within the 0-10 cm interval. Nutrient assays were conducted in a similar manner as the flux samples described above.

Eh: Profiles of sediment oxidation-reduction potential (Eh) were measured using small (20 gauge) platinum electrodes (Bagander and Niemisto 1978) inserted using a micromanipulator. Eh was determined by 2 mm intervals to 2 cm, 5 mm intervals to 5 cm and 10 mm intervals to 10 cm or deeper if the RPD was not clearly defined. Separate 6.5 cm cores were used for redox determinations. Visual RPD was measured on each core before the electrode measurements. Cores with anomalous burrow disturbance were not used.

TOC, porosity and chlorophyll: A 6.5 cm core was collected from each location for analysis of TOC and porosity and another for chlorophyll. The TOC core was sectioned at 1 cm intervals to 10 cm and the entire volume dispensed to pre-weighed cups. The samples were dried for 96 hrs at 60°C, and re-weighed to allow determination of porosity. Subsample were collected from the top 2 depths (0-2 cm), ground in a mortar and pestle, acidified to remove carbonates, and assayed for TOC and TN on a Perkin Elmer 2400 CHN Elemental Analyzer.

Sub-samples (15 cm^3) of sediments from 1-cm intervals from the surface to 5-cm depth and the 5-10 cm section were extracted in cold acetone with magnesium carbonate in the dark (-20°C). Pigments were analyzed using a Milton Roy scanning spectrophotometer before and after acidification with HCl. Chlorophyll-a will be separated from pheophytin a by analyzing the extract before and after acidification with HCl (Strickland and Parsons 1972).

III. Results and Discussion

Annual oxygen uptake by benthic sediments is a measure of total community metabolism, the total organic matter turnover within the benthos. Total community metabolism includes the respiration of benthic animals and plants, as well as carbon remineralization by heterotrophic micro-organisms. Sediment respiration is similar to watercolumn respiration in that it is controlled primarily by the availability of decomposable organic matter and in situ temperature. However unlike the watercolumn, sediments can accumulate organic matter over relatively long periods and therefore allow cumulative increases in oxygen uptake as organic matter is deposited over extended periods.

In Boston Harbor and Massachusetts Bay the watercolumn is oxygenated, whereas oxygen availability in sediments is limited usually being depleted at relatively shallow depths (mm to cm; Revsbech et al. 1980). As a result in the sediments a fraction of the organic matter decay is through anaerobic microbial processes, such as denitrification and sulfate reduction. Although at present denitrification does not represent a major pathway for carbon mineralization, it does represent an important potential sink for fixed nitrogen, particularly if concentrations of nitrate in the overlying water increase (Henriksen *et al.* 1993). Within deeper sediments, sulfate reduction produces sulfide as an end-product, some of which is permanently stored within the sediments as metal sulfides, but most of which is re-oxidized to sulfate on an annual basis (Jorgensen 1982).

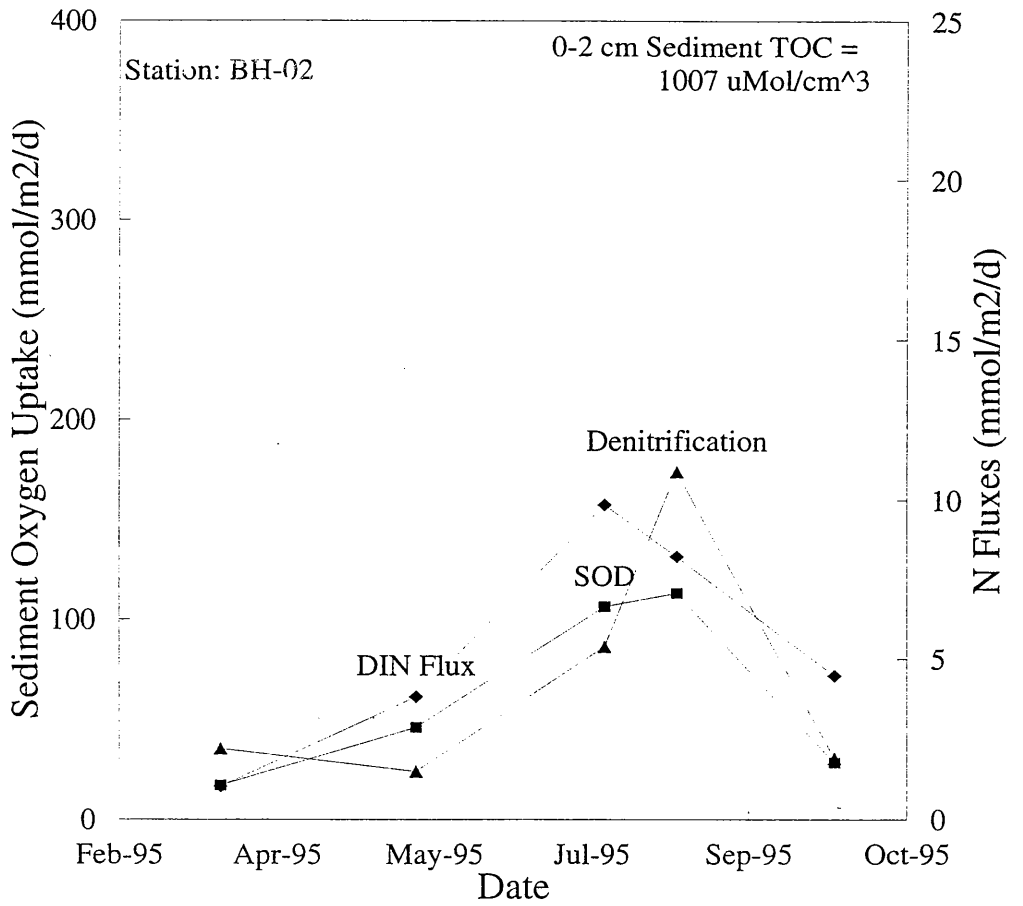
In most systems an amount equivalent to the mass of sulfide produced over the course of a year is oxidized each year (except for the small amount buried); the annual oxygen uptake rate generally reflects the annual carbon remineralization rate. However, due to the time-lag between sulfide formation in the deeper anoxic layer and oxidation by surface exchanged oxygen, single point estimates of the rate of surface oxygen uptake can either over or under estimate the rate of carbon mineralization taking place. It is primarily through reduced sulfur storage that DIC/SOD ratios (Respiratory Quotient: RQ) can exceed the theoretical Redfield organic matter oxidation ratio of 1-1.3 (Redfield 1963). In systems like present Massachusetts Bay, carbon flow through sulfate reduction is almost certainly small relative to aerobic processes (Jorgensen 1982) and therefore errors due to the oxidation time-lag are likely small even on single time-point samples.

Elemental indicators can also be used to gauge increases in organic matter loading to sediment systems. Increases in the mass of total reduced sulfur and/or non-pyritic reduced sulfur over several years has been suggested as an indicator of an increase in the rate of organic matter loading to sediments. While reduced sulfur pools can reflect loading rates, they represent the residue of the much larger reduction-oxidation cycle. In contrast, annual sediment oxygen uptake rates represent the total carbon remineralization rate which should be a direct indicator of the annual loading of decomposable organic matter to the benthos. In addition, sediment oxygen dynamics are important on an ecological basis in that where low oxygen or high sulfide levels occur, infaunal populations, hence food chain dynamics, are effected.

Annual Cycle of Benthic Metabolism: A pronounced seasonality in both rates of sediment oxygen uptake, denitrification and dissolved inorganic nitrogen (DIN) flux to the watercolumn was observed within all of the Boston Harbor stations in 1995 (Figure 2). Rates of metabolism and associated DIN fluxes exhibited increases of almost an order of magnitude from winter lows to summer maxima at most sites (BH03A, BH02, BH08A). The seasonality of these biologically driven processes within each location is controlled by the amount of decomposable organic matter within the sediments and the environmental temperature. In contrast, the large degree of variation between sites is not related to differences in temperature or the average bulk organic content of the surficial sediment (Figure 2), although differences in labile organic matter deposition cannot be ruled out. Instead, differences in sediment metabolism and associated fluxes within the Harbor appeared to be related to the degree of colonization by amphipods (*Ampelisca* and *Leptocheirus*) and the assemblage of other invertebrate species occupying the mats. Amphipod mats were absent at QB01, weakly to moderately developed at BH02 and BH08A and very dense at BH03A.

Oxygen uptake by sediments of the western portion of the nearfield region of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) showed a different temporal pattern than the Harbor. All sites showed increasing oxygen uptake with increasing bottom temperatures (Figure 3). However, the major increase in respiration in Bay sediments appeared to occur between late-May and July which may reflect deposition of the Spring bloom as little temperature increase occurred during this interval. Overall the Bay sediments supported significantly lower rates of respiration then the Harbor sediments most likely as a result of differences in rates and quality of organic matter deposition and environmental temperature (see below).

The deeper water of Massachusetts Bay with its summer stratification results in a delayed temperature maximum compared to the shallower well-mixed waters of Boston Harbor. The effect of the colder waters in the Bay before stratification should be to help to "preserve" freshly deposited spring bloom material until waters warm. This warming occurs post-stratification. Storage and respiration of spring bloom material in the benthos likely plays an important role in bottom water oxygen balance during stratification and the seasonal distribution of rates. In contrast, during deposition of the fall bloom the bottom waters are still near the annual temperature maximum which should promote the degradation of the freshly deposited bloom material. Given the temporal sequence, much of the fall bloom is likely degraded prior to the next years re-stratification. Since mixing occurs at the fall bloom, its effect on bottom water oxygen deficit is small. Therefore, it appears likely that the spring bloom plays a more important role in oxygen deficits than the fall bloom. Factors which increase delivery of organic matter through the pycnocline during stratification should result in increases in the level of annual oxygen depletion in bottom waters of both the nearfield and Stellwagen Basin. Without further analysis of the potential lability (ability to be biologically degraded) of the organic matter thus delivered, it is not possible to determine the proportional increase in oxygen deficit per unit carbon deposited.



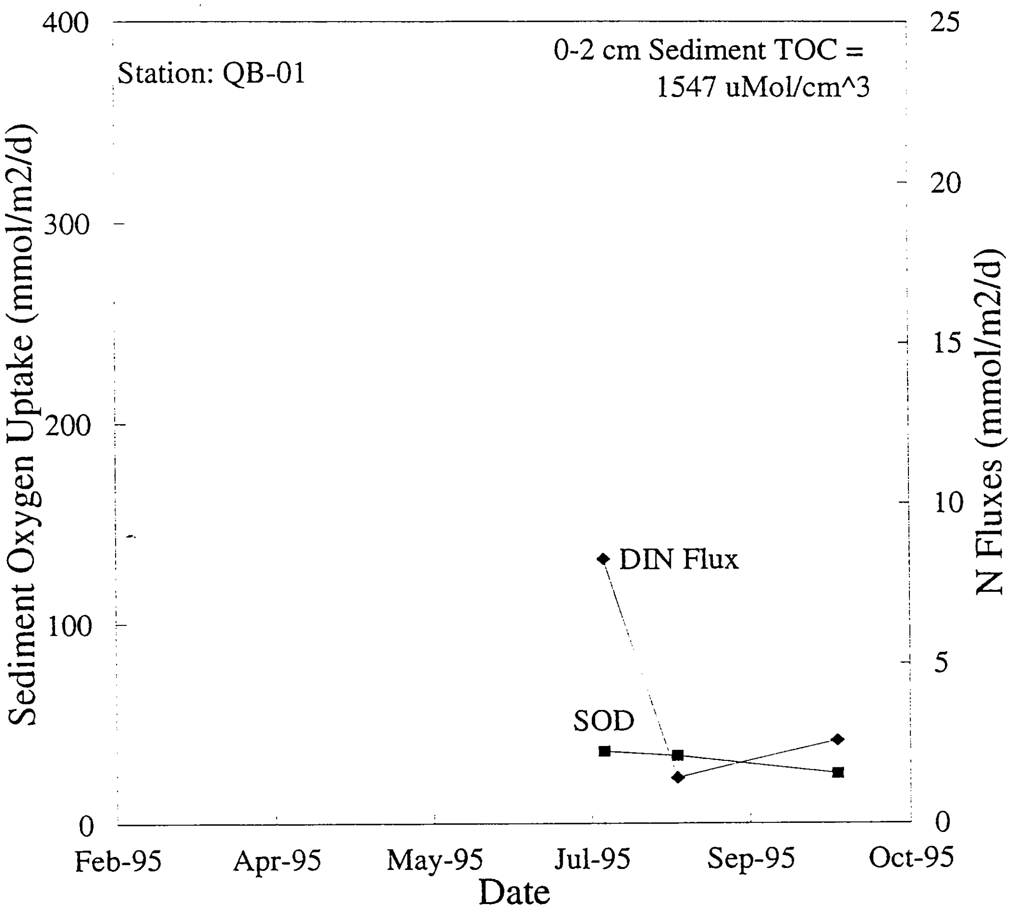


Figure 2. Annual cycle of oxygen uptake, DIN flux and denitrification (BH02 & BH03A only) within the sediments of (A) BH02, (B) QB01, (C) BH03A, (D) BH08A, the four Boston Harbor sites. Amphipod abundance followed BH03A>BH08A>BH02>QB01.

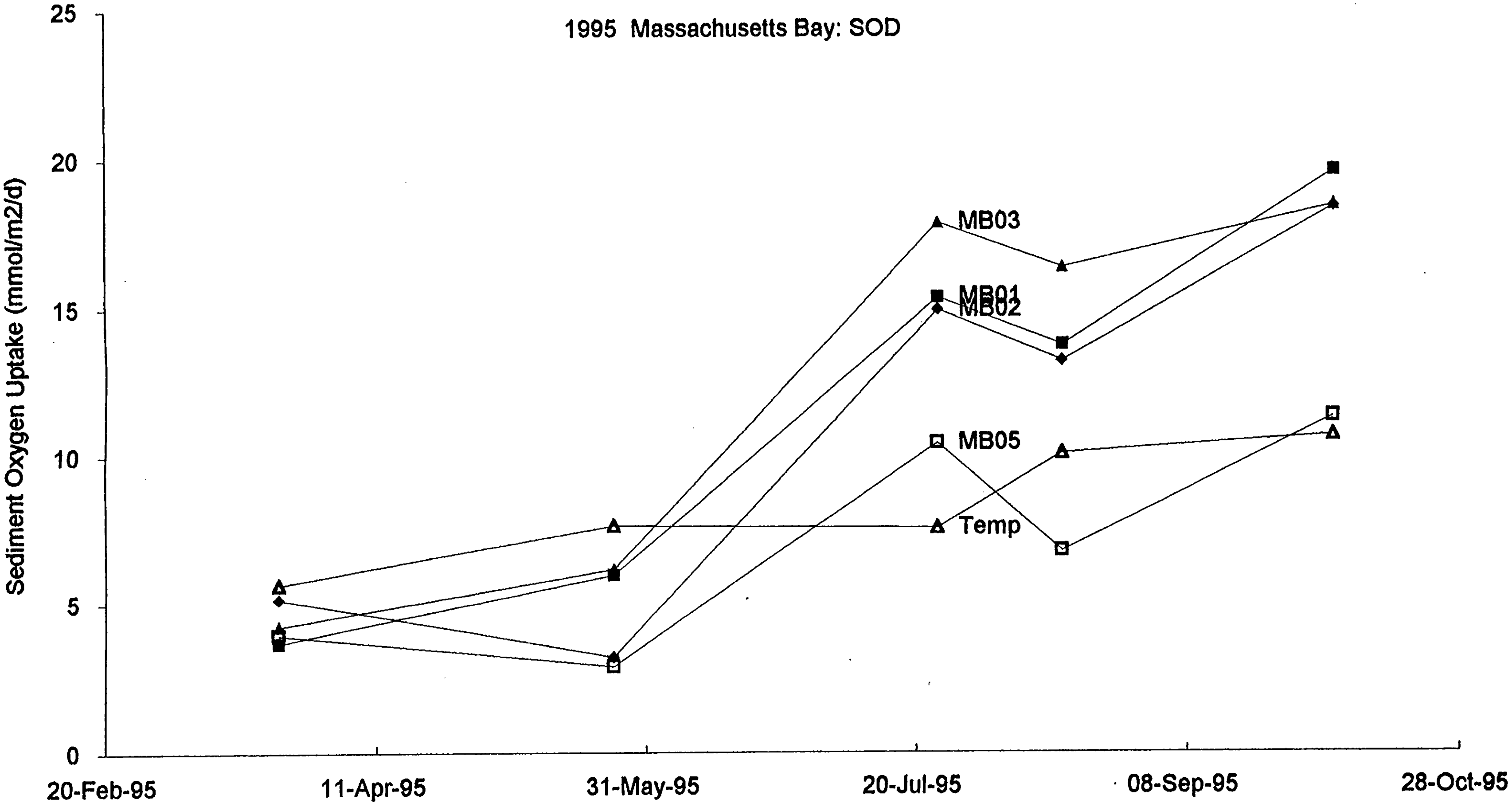


Figure 3. Sediment respiration within the western nearfield (MB01, MB02, MB03) of Massachusetts Bay and Stellwagen Basin (MB05) throughout 1995 and mean bottom water temperature ca. 1 meter above the sediment surface.

Inter-annual comparisons: Given the long-term nature of the Outfall Monitoring Program it is important to evaluate inter-annual variability pre-discharge as a baseline from which to gauge the significance of differences in environmental parameters post-discharge. In addition, comparisons of measurements of relatively stable processes can be evaluated to intercalibrate approaches.

Sediment oxygen uptake during summer in the nearfield region of western Massachusetts Bay and Stellwagen Basin has previously shown a low degree of inter-annual variation (Giblin *et al.* 1995). Similarly, good agreement was found between 1995 and earlier years (Figure 4). While it is not possible to determine if the slightly lower rates in 1995 are "real" or methodological, these data suggest that methodological and inter-annual differences in SOD measurements are small, generally <20%. It appears that measurements of sediment oxygen uptake should be relatively sensitive indicators of potential increases in organic matter deposition during post- discharge.

In strong contrast to the Bay, sediment oxygen uptake within Boston Harbor in 1995 was several fold higher than typically encountered in previous years (Figure 5). As stated above, the spatial variation within the Harbor in 1995 parallelled the intensity of amphipod colonization as gauged by sediment profiling and sorting of core samples. Similarly, the only samples from previous years which approached the 1995 rates were associated with infrequent sampling of amphipod mats (Giblin *et al.* 1994). Additional support for the contention that the observed interannual differences result from infaunal activity stems from the similarity of sediment oxygen uptake at the non-mat station (QB01) with uncolonized sediments, and measurements at analogous sites in previous years (Figure 2 and Giblin In press). Massachusetts Bay stations (MB) showed only small inter-annual differences in SOD. In 1995 two of the stations were moved after the March Survey, BH03 (to BH03A) and BH08 (to BH08A). Station BH08 was moved since it was is a small basin with coarse grained sediments which was not representative of the surrounding bottom. Station BH03 was shifted slightly to the adjacent area of flat bottom (BH03A) which had the same infaunal type, grain-size and was generally undistinguishable except that it was not positioned on a sloping bottom. Regardless of these shifts, evaluation of the impact of colonization by mats could be assessed through both intra and inter-site comparisons. The overall analysis strongly indicates that it is processes associated with the colonization of sediments by amphipod mats which support the several fold higher rates of carbon cycling in sites with versus without mats.

The reason for the shift in infaunal communities likely relates to the cessation of sludge disposal to Harbor waters in December 1991 and the reduction in contaminant loading through CSO's and other sources. These reductions in terrestrial loadings to the Harbor system have been paralleled by a rapid colonization of the harbor benthos by an *Ampelisca* complex (Figure 6; Blake *et al.* 1993, 1996; Kropp & Diaz 1995). *Ampelisca* are deposit feeding amphipods capable of building several centimeter thick mats and reaching densities of over 100,000 individuals m^{-2}. This infaunal complex increases both the degree of sediment oxidation and rates of sediment/watercolumn exchange through bioturbation and burrow ventilation. While populations continue to show cyclical variations, the amphipod

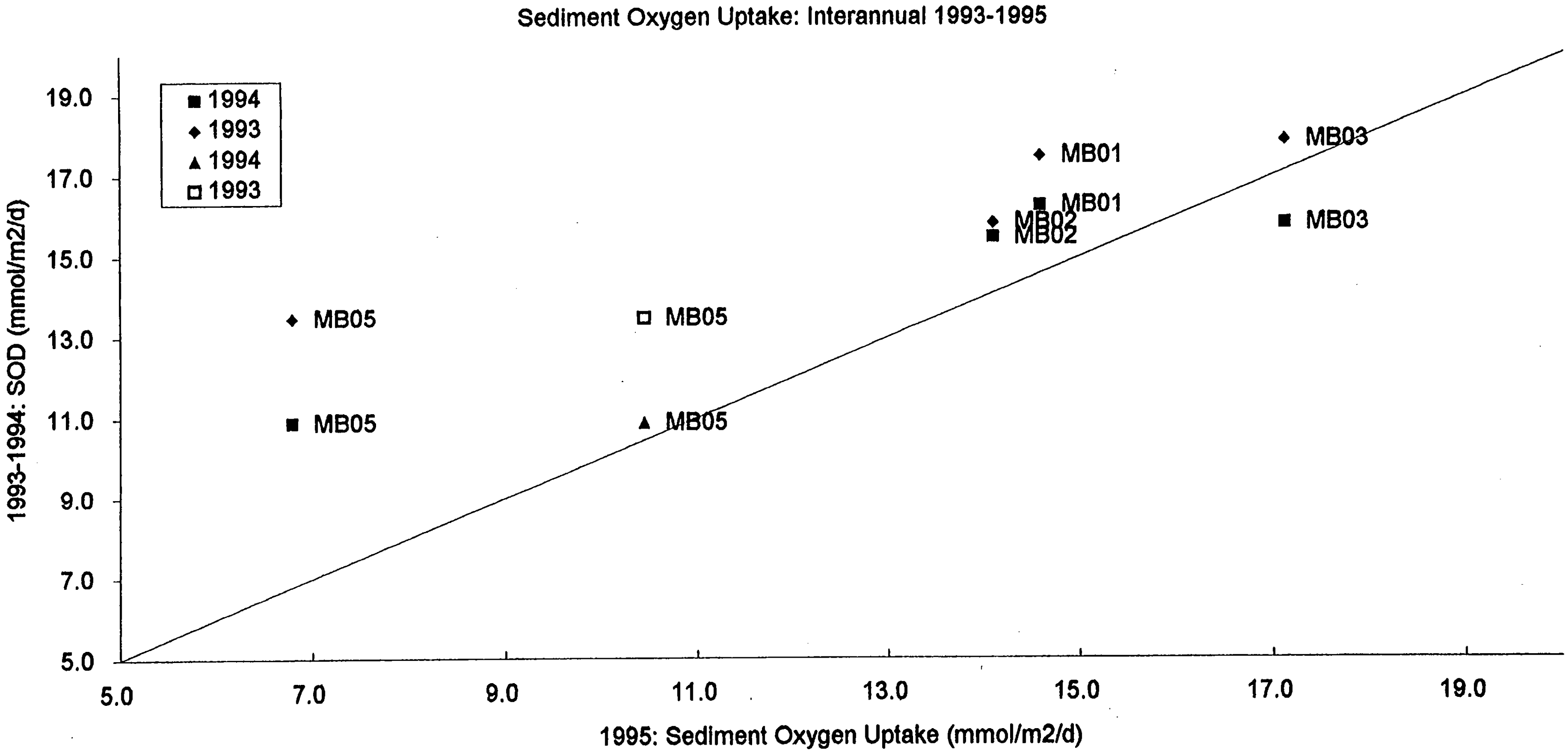


Figure 4. Inter-annual comparison of sediment oxygen uptake from the western nearfield region of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) monitored in 1992-1995. Data from 1993 and 1994 represent average July and August values, except for MB05 where only August data was collected (Giblin et al. 1995). The earlier MB05 August rates are plotted separately against both July (closed diamond, closed box) and August (open box, closed triangle) 1995 data. Values above the line represent rates that are higher than found in 1995.

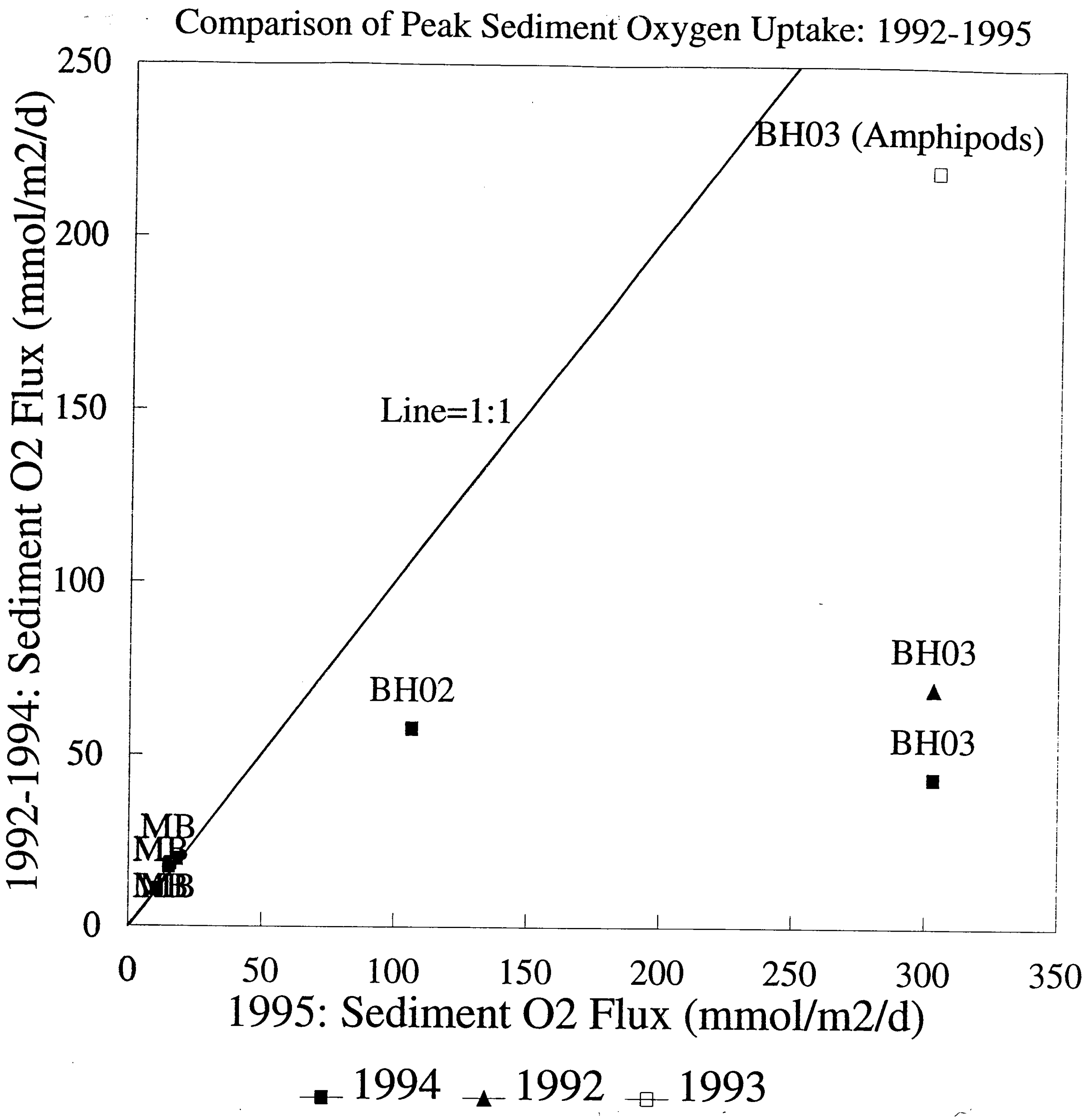


Figure 5. Inter-annual comparison of peak rates of sediment oxygen uptake from stations within Boston Harbor and Massachusetts Bay in 1992-1994 versus 1995. BH03 is compared to the adjacent BH03A site. Note that only during the amphipod event of 1993 did earlier rates approach those of 1995. The similarity in Bay rates between all years suggests that the differences in measured SOD were not methodolgical.

mats appear to be becoming more persistent from year to year (Figure 6). The expanded distribution and reduction of inter- annual variations in the mats appears to be the result of improving water quality, particularly in the northern region of Boston Harbor.
The reduction in external loading to the Harbor may also be enhancing the removal of fixed nitrogen within the Harbor. In conjunction with the high rates of sediment oxygen uptake observed in 1995, the rates of denitrification were similarly enhanced (Figure 7). The high rates of irrigation within the amphipod mats were found to result in significant increases in sediment oxidation, increased porewater nitrate levels and a shift from ammonium to nitrate as the dominant DIN flux constituent (see below). The increased rates of nitrification are likely the proximate cause of the enhanced denitrification within the sediments colonized by the *Ampelisca* complex in 1995.

Infauna and sediment metabolism: Rates of early diagenesis appear to be controlled by the level of organic matter loading and infaunal activities (bioturbation-irrigation) when temperatures are constant. The stations within Boston Harbor and Massachusetts Bay can be categorized by this view with rates highest in the high organic loading/high infauna (BH03A) and lowest at the low loading/low infauna sites.

The significantly higher rates of oxygen uptake and denitrification within sediments colonized by amphipods in 1995 and 1993 compared to uncolonized sites in 1992-1995 is evidence of the effect of infaunal activities on sediment metabolism. For example, in the Harbor sediments where the *Ampelisca* complex was found (BH03, BH02, BH08) the rate of oxygen uptake was 2-5 fold higher than where *Ampelisca* were absent (QB01). In addition, there was a shift from an equal distribution of oxygen uptake between the sediments and overlying watercolumn to a dominance of sediment metabolism as the focus of system carbon remineralization (see below, Figure 10).

Even more direct evidence as to the enhancement of respiration associated with amphipods is available from the seasonal sampling of low (BH02) and high (BH03A) density mats in 1995. Sediments at BH03A and BH02 were colonized by amphipods (*Ampelisca* and *Leptocheirus*) from March through August 1995. The amphipod mats began to break-up in August and were virtually gone by the October sampling. The nearly linear increases in community respiration with temperature measured at both stations when the mats were present (Mar-Aug) contrasted strongly with the much lower rates in October when the mats had senesced but the temperatures remained near July levels. The influence of the infaunal community upon organic matter turnover is seen in the 5 fold (BH03A) and 2 fold (BHO2) higher rates of oxygen uptake at similar temperatures in the presence versus absence of the amphipod community (Figure 8). A similar trend is seen in the rates of denitrification at these sites which showed about 2 fold higher rates before versus after the loss of the mats at similar temperatures (Figure 9).

Harbor versus Bay: Rates of sediment oxygen uptake reflect the level of organic matter loading. Within the marine system, increasing water depth is generally associated with decreasing organic loading and sediment respiration as an increasing percentage of the organic matter is degraded during transport through the watercolumn (Hargrave 1973).

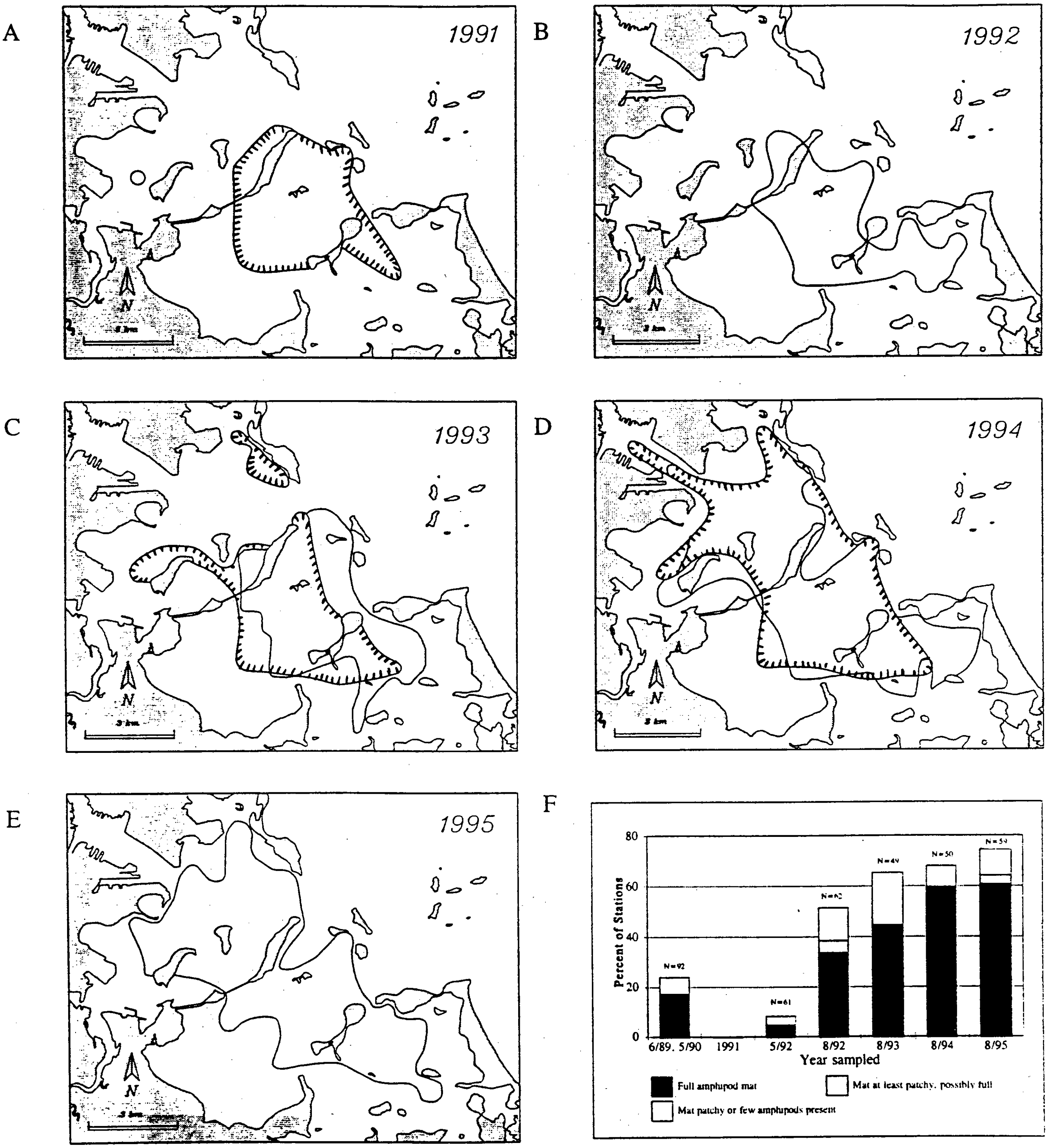


Figure 6. A-E, distribution of amphipod tube mats in Boston Harbor from 1991 through 1995 as determined by sediment profile image analysis (solid lines) and/or *Ampelisca* predominance in grab samples (hatched lines, after Kropp and Diaz, 1995); F, percent of stations with full or patchy mat.

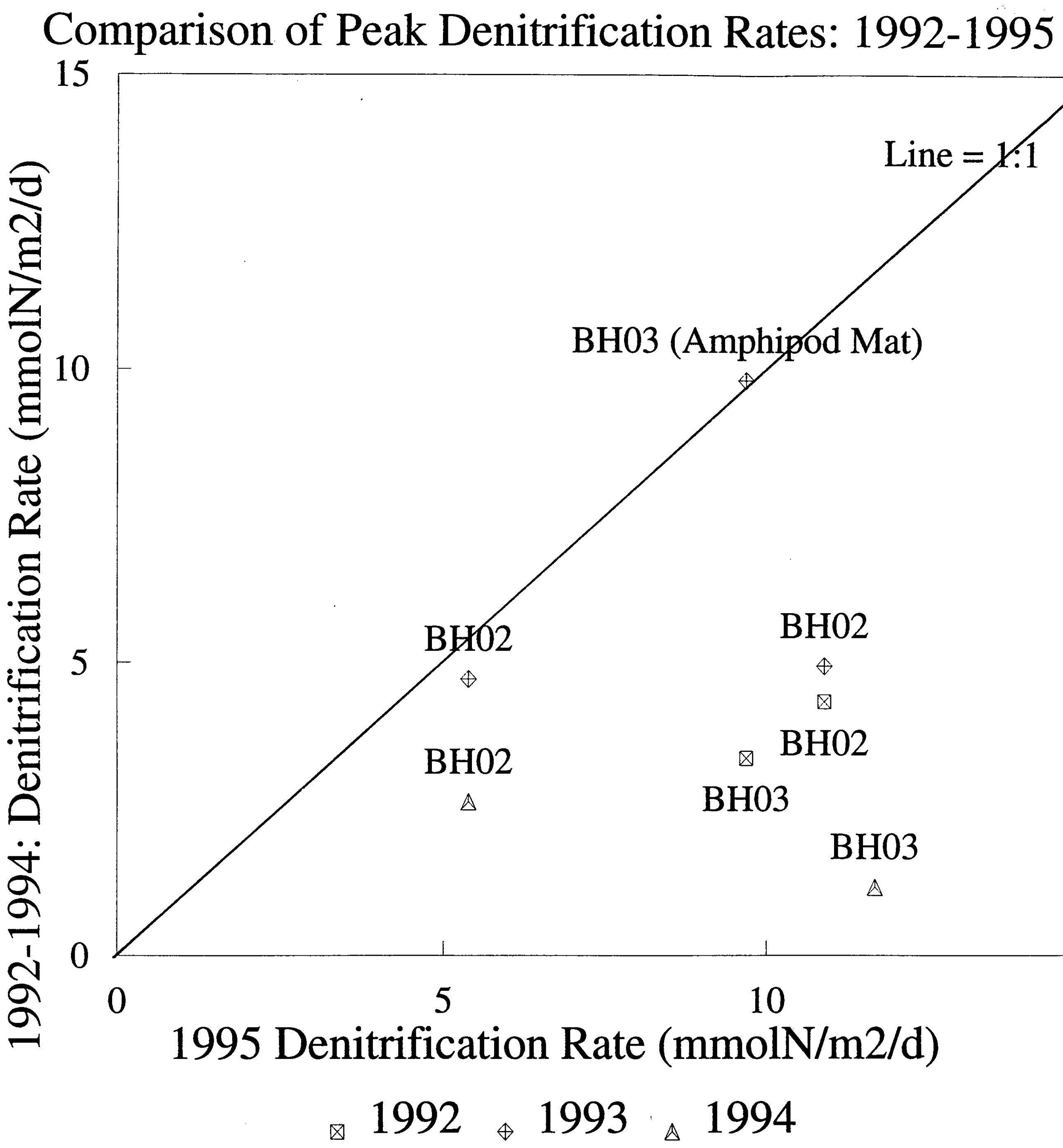


Figure 7. Inter-annual comparison of peak rates of denitrification (N_2 method) from stations within Boston Harbor in 1992-1994 (Nowicki *et al.* In press) versus 1995. BH03 is compared to the adjacent BH03A site. Note that only during the amphipod event of 1993 did earlier rates approach those of 1995. In 1995 the Ampelisca complex was prevalent throughout Boston Harbor and at our BH02, BH03A, and BH08A sites where they had only been occasionally encountered previously.

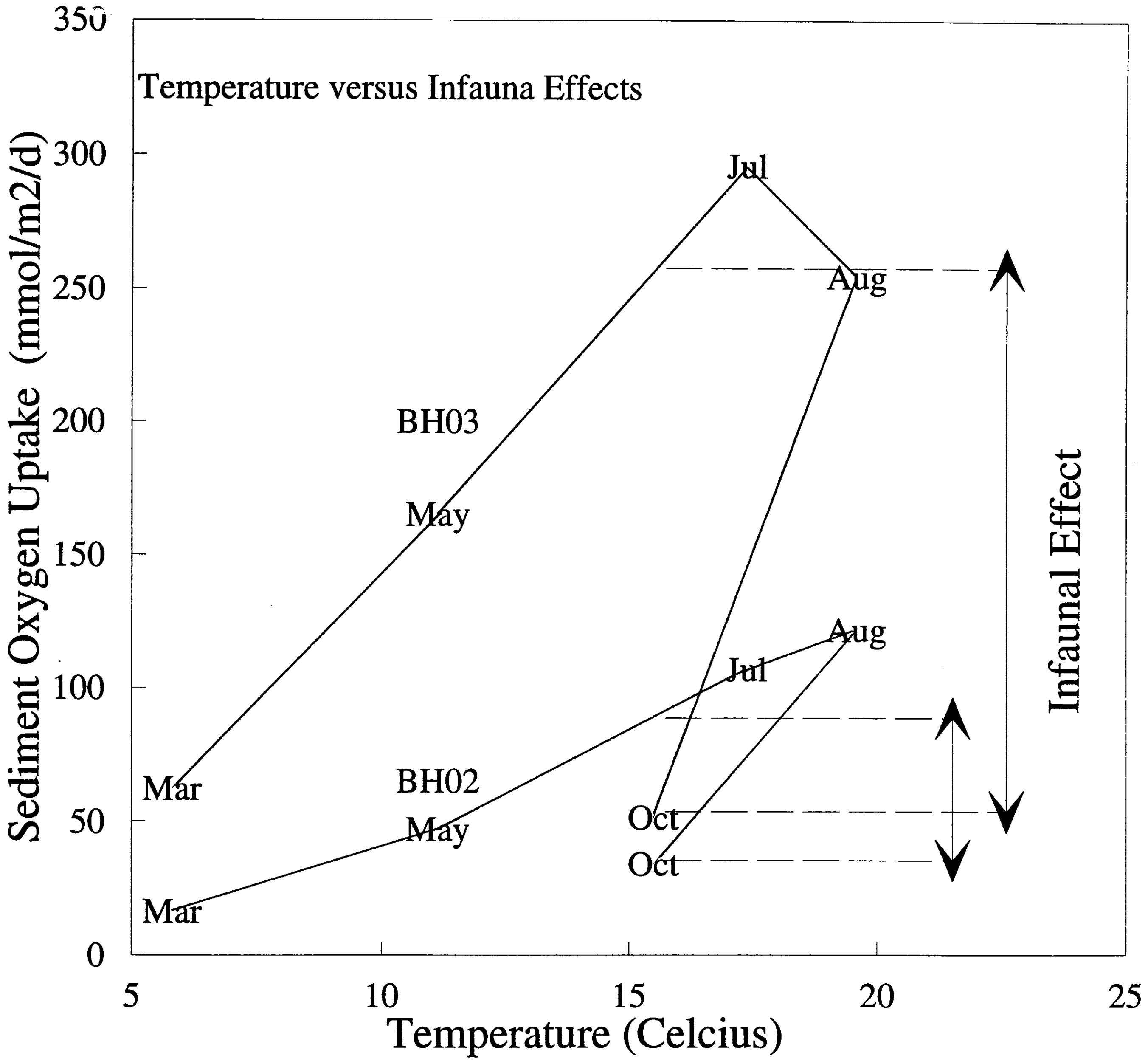


Figure 8. Sediments at BH03A and BH02 were heavily colonized by amphipods (Ampelisca and Leptocheirus) from March through August 1995. The dense amphipod mats began to break-up in August and were virtually gone by the October sampling. The nearly linear increases in community respiration with temperature measured at both stations when the mats were present (Mar-Aug) contrasted strongly with the much lower rates in October when the mats had senesced. The influence of the infaunal community upon organic matter turnover is seen in the 5 fold (BH03A) and 2 fold (BHO2) higher rates of oxygen uptake at similar temperatures in the presence versus absence of the amphipod community.

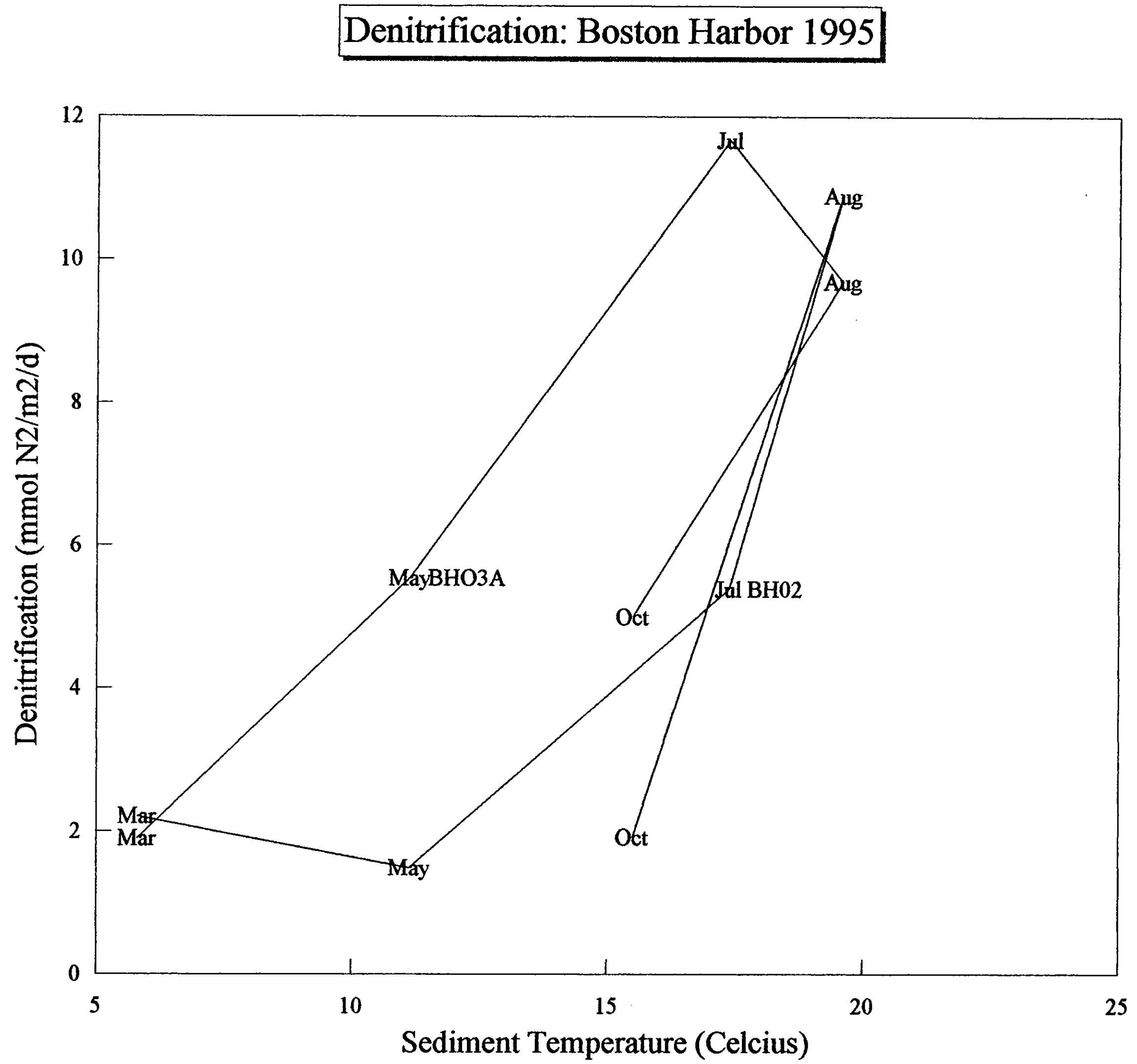


Figure 9. Denitrification rates measured in parallel with sediment oxygen uptake at BH03A and BH02 shown in Figure . The influence of the infaunal community upon rates of denitrification is similar to effects on SOD with 2 fold higher rates of oxygen uptake at similar temperatures in the presence versus absence of the amphipod community.

Similarly, within the coastal zone, organic matter loading to sediments tends to decrease with increasing horizontal distance from shore, creating a parallel trend in sediment respiration. Both vertical and horizontal effects on sediment oxygen uptake reflect linkages between carbon fixation-transport- decay.

Within Massachusetts Bay, watercolumn respiration accounts for more than 2 times the carbon mineralization of the sediments (Figure 10). This results from the higher temperatures and more labile carbon within the watercolumn (Cibik *et al.* 1996). The importance of watercolumn respiration within Massachusetts Bay includes the mixed layer where turbulence maintains particles in suspension, which coupled with summer temperatures helps to degrade organic matter before it can reach the bottom waters and finally the sediments. In contrast, within the shallow mixed waters of Boston Harbor, while watercolumn respiration is higher than Massachusetts Bay (reflecting the higher POC levels), the rapid delivery to the sediments results in proportionally higher rates of sediment respiration (Figure 10). This is also supported by the lack of a temperature gradient from surface waters to sediments. The apportioning of respiration is seen both in areas with amphipod mats (eg. BH03A, BH08A, BH02; Figures 2 & 7), which are likely cycling some of the older sediment accumulation in addition to freshly deposited organic matter, and in areas where infaunal activity is minimal (QB).

Since Boston Harbor has shallower water (ca. 10m) than the stations of Massachusetts Bay (ca. 33m), the rate of watercolumn respiration per unit volume is lower within the Bay. The lower per volume watercolumn rate and sediment rate reflects both the lower temperatures and lower organic matter production within the Bay versus the Harbor. Increasing production within the mixed layer of Massachusetts Bay is likely to produce at least proportional increases in the annual amount of watercolumn and sediment respiration. However, to the extent that increased deposition occurs just prior to stratification or that vertical transport during stratification occurs, there may be an enhanced (non-linear) increase in bottom water oxygen deficit supported by both respiratory pathways within the region of enhanced carbon cycling within the Bay.

Deposition of phytoplankton and rates of sediment metabolism: Sedimentary levels of chlorophyll a and pheophytin a were measured as potential indicators of the availability of "freshly" deposited phytoplankton. Since sediment remineralization rates can be controlled by the availability of labile organic matter (particularly in Massachusetts Bay), pigment concentrations could serve as a useful surrogate measure, since measurement of organic matter lability uncertain.

Within Boston Harbor, surficial sediments had levels of chlorophyll a that were relatively similar among the 4 stations in spite of their 5 fold range in respiration (Figure 11). Chlorophyll a and respiration were similarly related within the 4 Bay stations (Figure 12). However, the sum of chlorophyll a and its initial breakdown product, pheophytin a did show differences between sites which were generally proportional to the differences in observed oxygen uptake (Figures 2 & 11, 3 & 12). When the data are combined a clear relationship was found between the average annual chlorophyll a + pheophytin a (0-10cm) and the

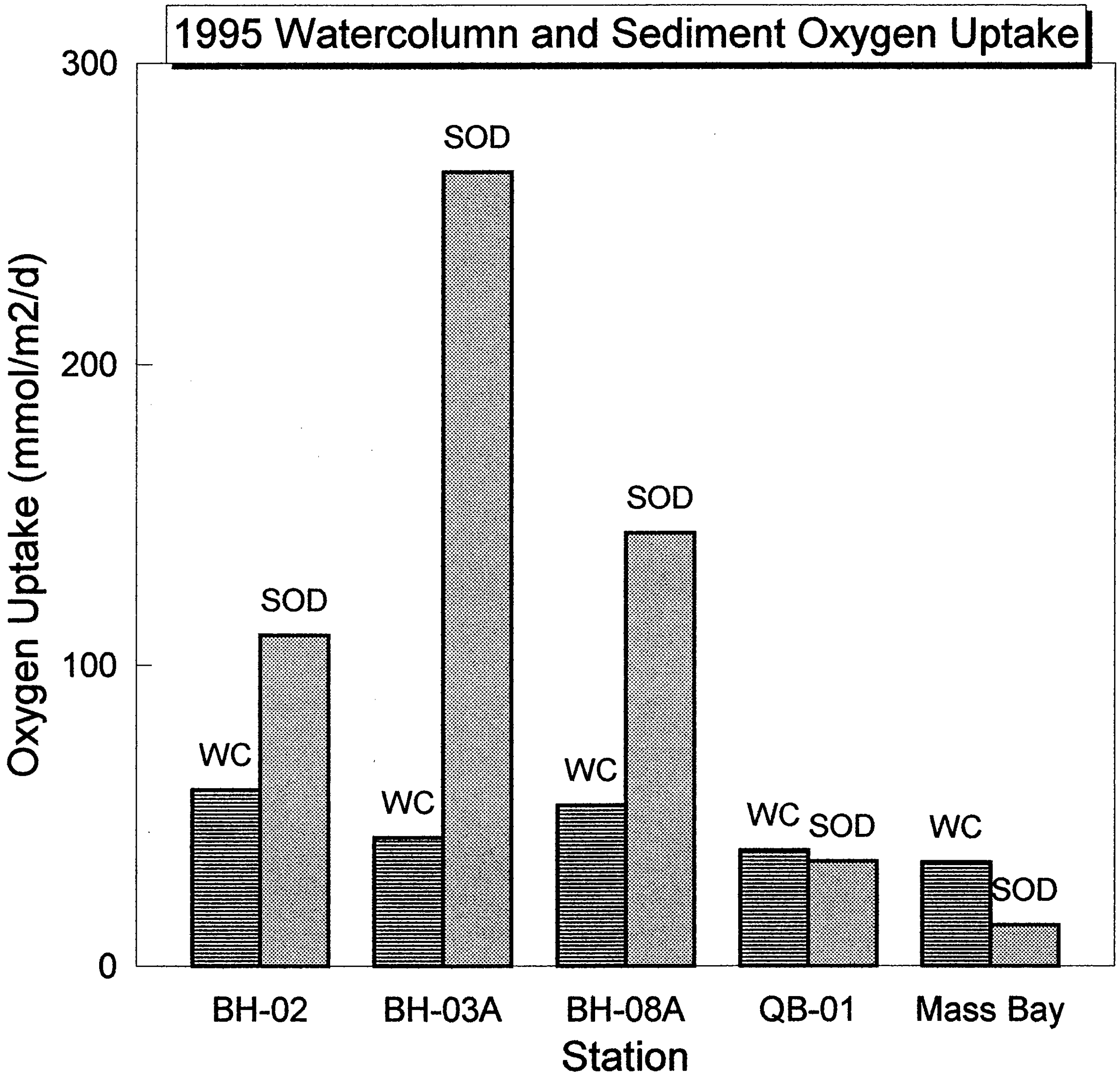
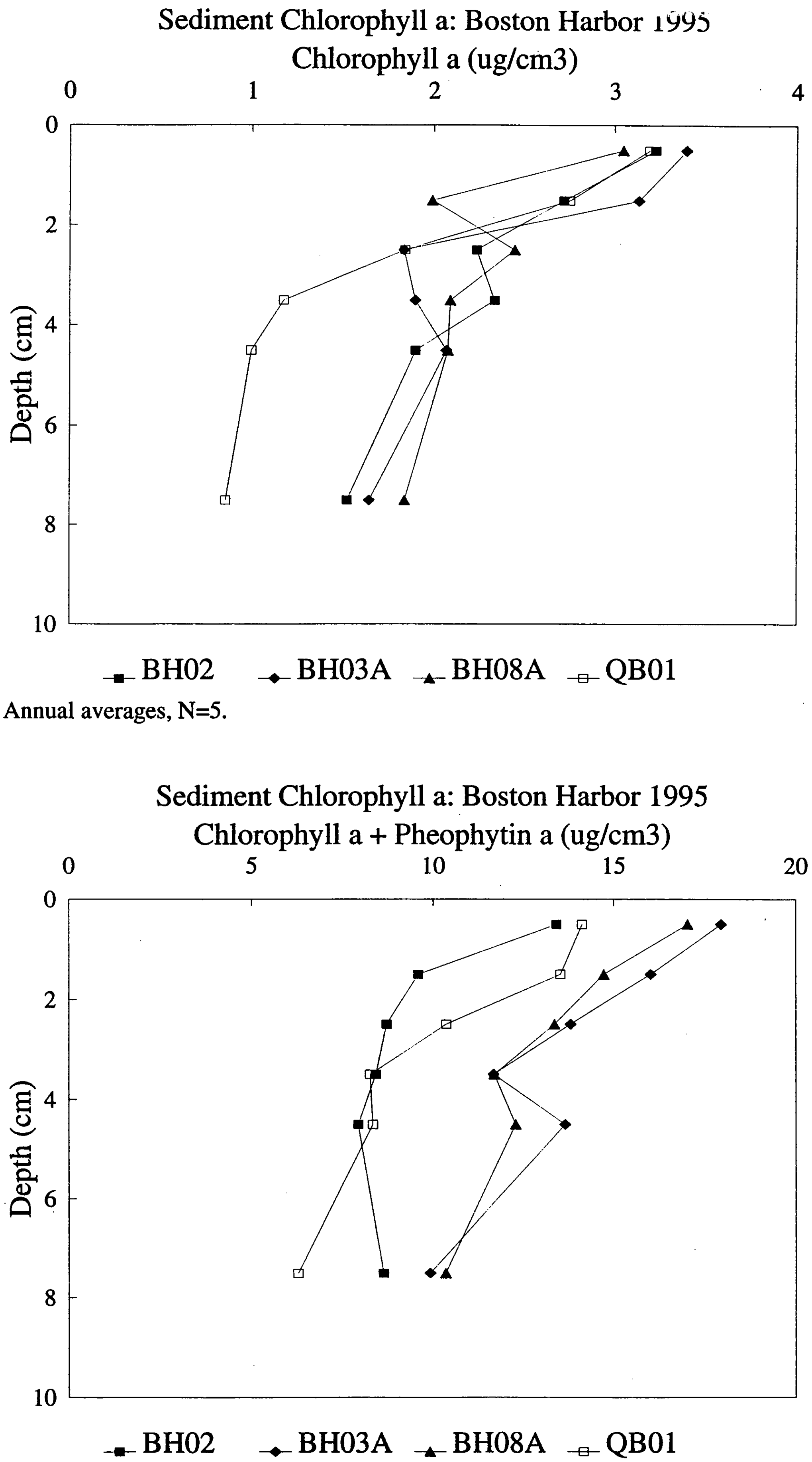
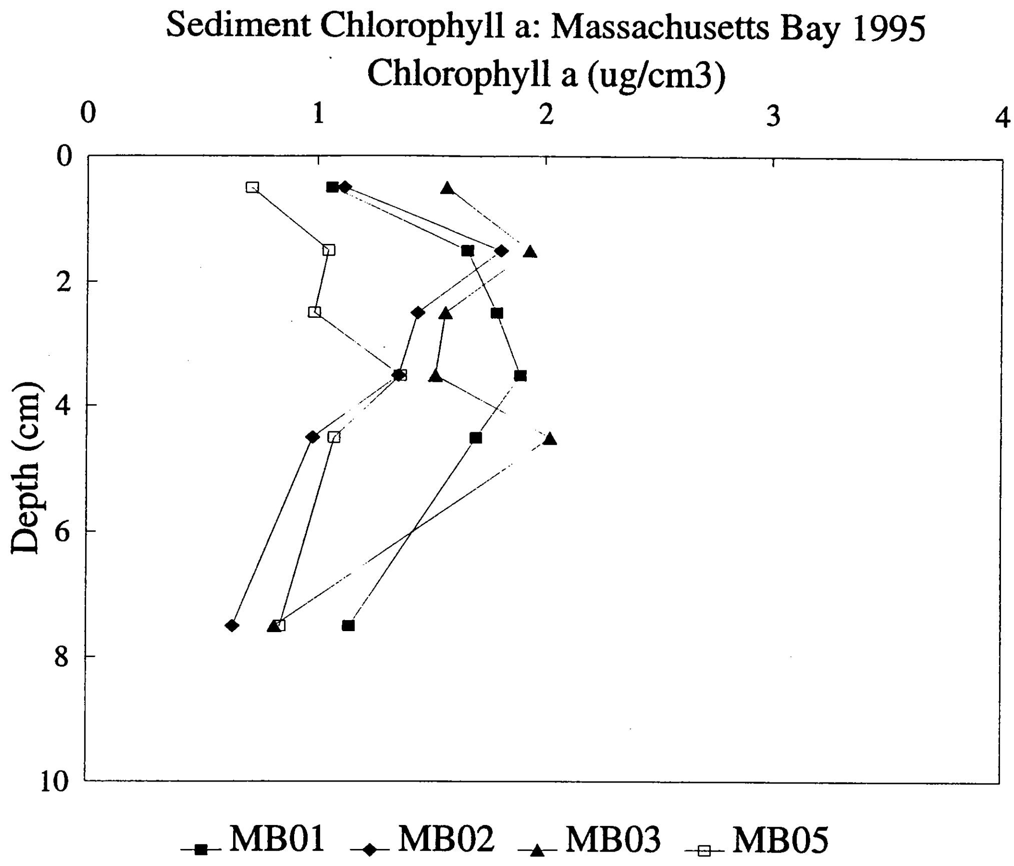


Figure 10. Summer rates (mean of July & August) of sediment and integrated watercolumn respiration within Boston Harbor (BH02, BH03A, BH08A, QB01 and Massachusetts Bay stations. Massachusetts Bay stations are about three times the depth (ca. 33m) of those in the Harbor.



Annual averages, N=5.

Figure 11. Average annual profiles of (A) chlorophyll a and (B) pheophytin a + chlorophyll a in sediments of Boston Harbor flux sites. The lower penetration of chlorophyll a at QB01 is consistent with low bioturbation. The masses of total pigment at each site parallel follow the observed carbon remineralization rates.



Annual averages, N=5.

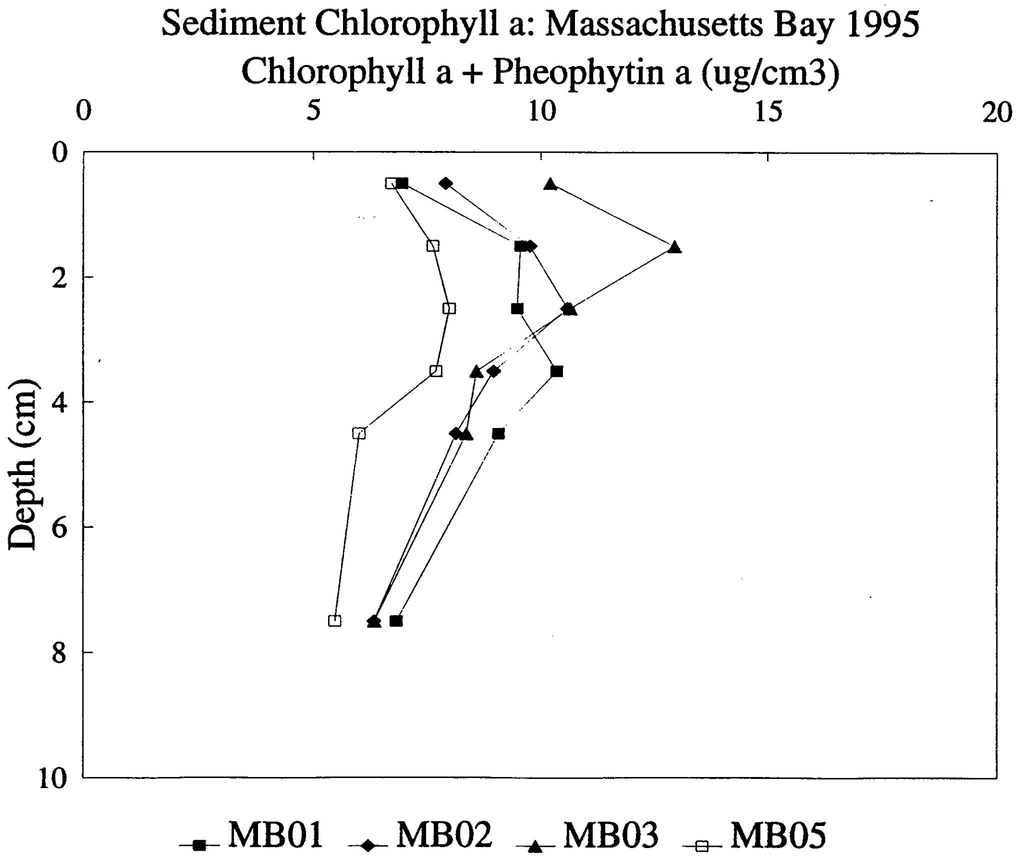


Figure 12. Average annual profiles of (A) chlorophyll a and (B) pheophytin a + chlorophyll a in sediments of Massachusetts Bay flux sites. The lower amounts of pigment at MB05 is consistent with its greater depth and lower rates of carbon remineralization.

average summer rate of oxygen uptake (R^2=0.90, N=8). The difference between Harbor and Bay sediment pigment levels was consistent at all depths and for both chlorophyll a and its sum with pheophytin a (Figure 13). It appears that sediment pigment concentrations may be a useful tool in assessing the delivery of labile organic matter to both the Harbor and Bay sediment systems.

Efflux of regenerated nutrients to the watercolumn: Given the potential underestimation of total sediment metabolism from surface oxygen exchange measurements, dissolved inorganic carbon (DIC) flux is sometimes also used. While DIC flux avoids the potential lags between organic matter mineralization and reduced sulfur formation at depth and the reoxidation of reduced sulfur by surface oxygen exchange, there are still lags associated with DIC transit. In addition, given the high background of DIC in coastal water (ca. 2200 uM) and the intrinsic difficulties in core incubation, it can be difficult to reliably detect the <100 uM changes that may occur during incubations. DIC flux measurements are also subject to overestimation of efflux due to surface disturbance (as are nutrient fluxes and to a much less extent oxygen) and carbonate dissolution. While time-course incubation can help to refine DIC rate estimates, the low signal to background ratio and the need for relatively short incubations generally restricts their use in the present study. Nevertheless, the ratio of DIC to oxygen flux (RQ) can yield important insight into the cycling of organic matter and nutrients in coastal sediment systems.

Rates of DIC and oxygen flux generally showed similar rates of carbon turnover within Boston Harbor sediments (Figure 2 & 14). Highest rates were generally found in the warmer months and in the sites of highest amphipod activity (BH03a). A similar relationship between DIC and oxygen fluxes was found within the sediments of the Massachusetts Bay sites (Figures 3 & 15). However, within the Bay DIC fluxes were typically more than 2 fold higher than parallel measurements of oxygen uptake which is consistent with the findings in previous years. This would indicate a large storage of reduced compounds within these sediments.

Comparing the rate of oxygen uptake at all stations with their measured ratio of DIC to oxygen fluxes reveals that the greatest excesses of DIC were found at the lowest rates of SOD (Figure 16). This pattern suggests that some other factor may influencing the DIC fluxes in 1995 as this pattern was not observed in all previous studies. DIC/oxygen flux ratios of about 2 which have been commonly observed within the Bay sediments over several years are more difficult to interpret than similar ratios in the Harbor as the "excess" DIC results from the storage of reduced end-products of anaerobic metabolism. The difficulty stems from the observations that at lower rates of system metabolism a greater proportion of carbon flow is through aerobic pathways (Jorgensen 1982). At present it appears that further evaluation of DIC efflux is needed.

Dissolved inorganic nitrogen (DIN) fluxes followed the general pattern of organic matter mineralization in both Boston Harbor and Massachusetts Bay (Figures 17 & 18). As with oxygen and DIC fluxes, DIN flux from Harbor sediments were up to 25 times higher than the Bay. This regional difference in DIN release is a direct consequence of the higher organic

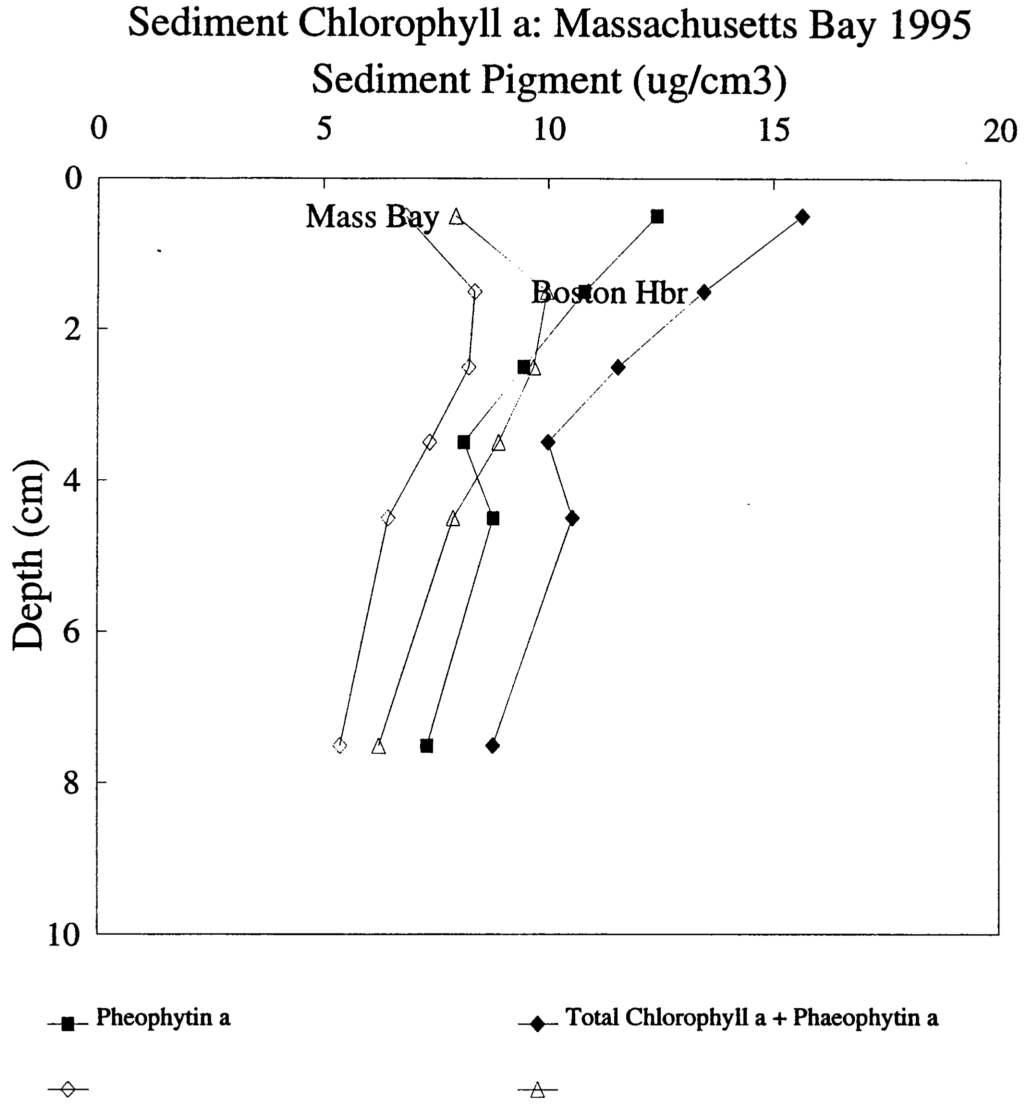


Figure 13. Profiles of chlorophyll a and pheophytin a + chlorophyll a in sediments of Boston Harbor and Massachusetts Bay. The more than 1.5 fold difference in pigment levels in the surface 2 cm are reflected in the higher rates of organic matter turnover in the Harbor versus Bay sediments. Profiles are averages of all stations and surveys.

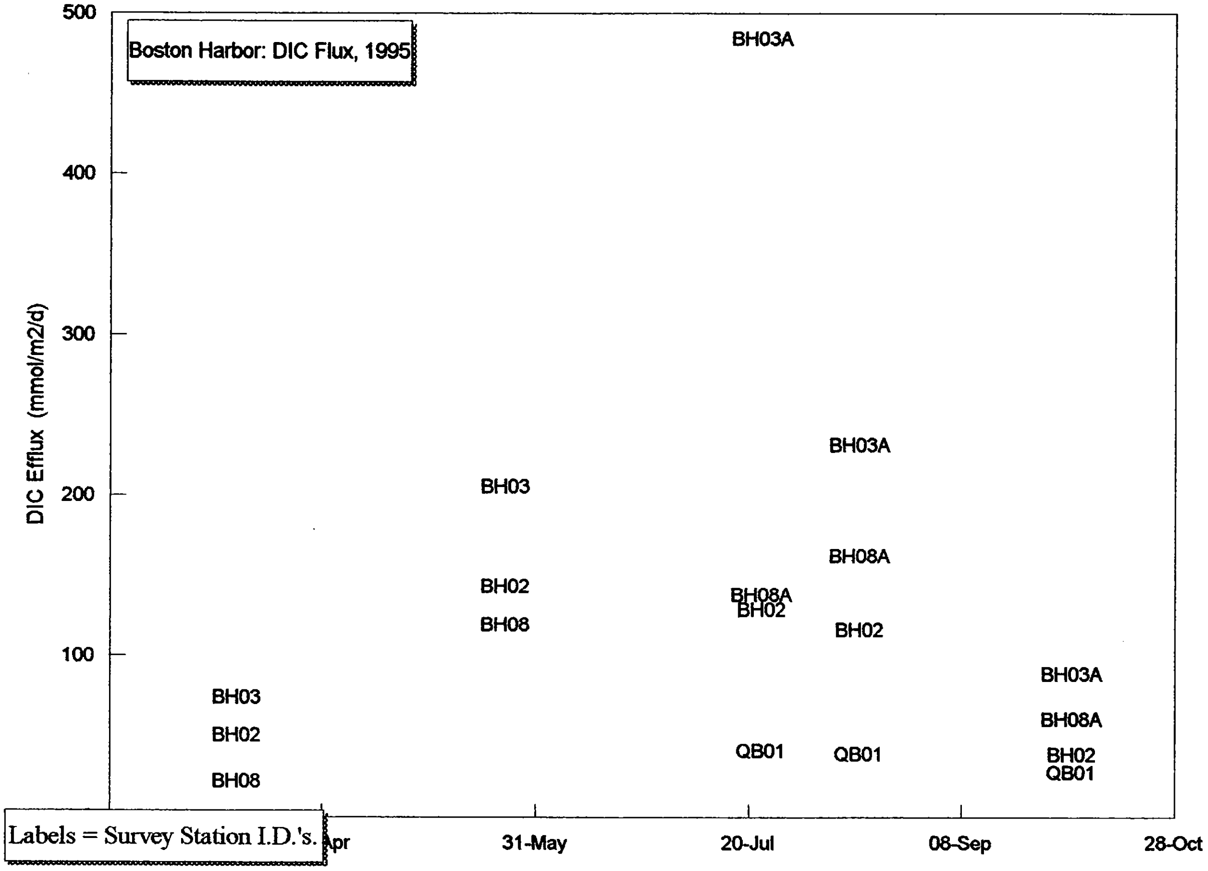


Figure 14. Sediment efflux of dissolved inorganic carbon (DIC) from Boston Harbor sediments during 1995. DIC fluxes were consistent with measured oxygen uptake rates showing highest fluxes during summer and in regions of dense amphipod mats.

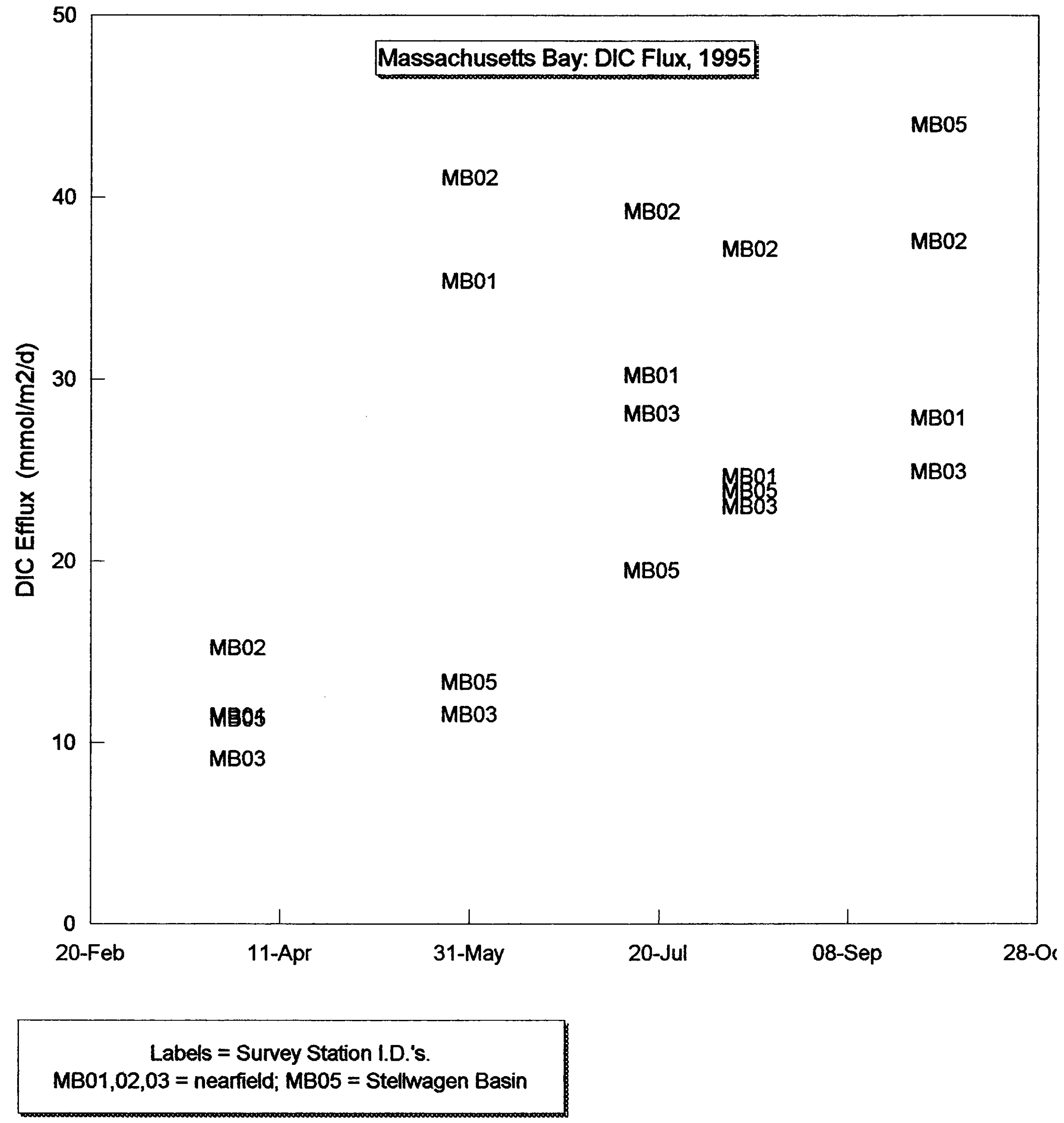


Figure 15. Sediment efflux of dissolved inorganic carbon (DIC) from sediments of the western nearfield region of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin during 1995. DIC fluxes were consistent with measured oxygen uptake rates generally showing highest fluxes at higher temperatures. However, stations with the highest oxygen uptake did not always have the highest DIC fluxes.

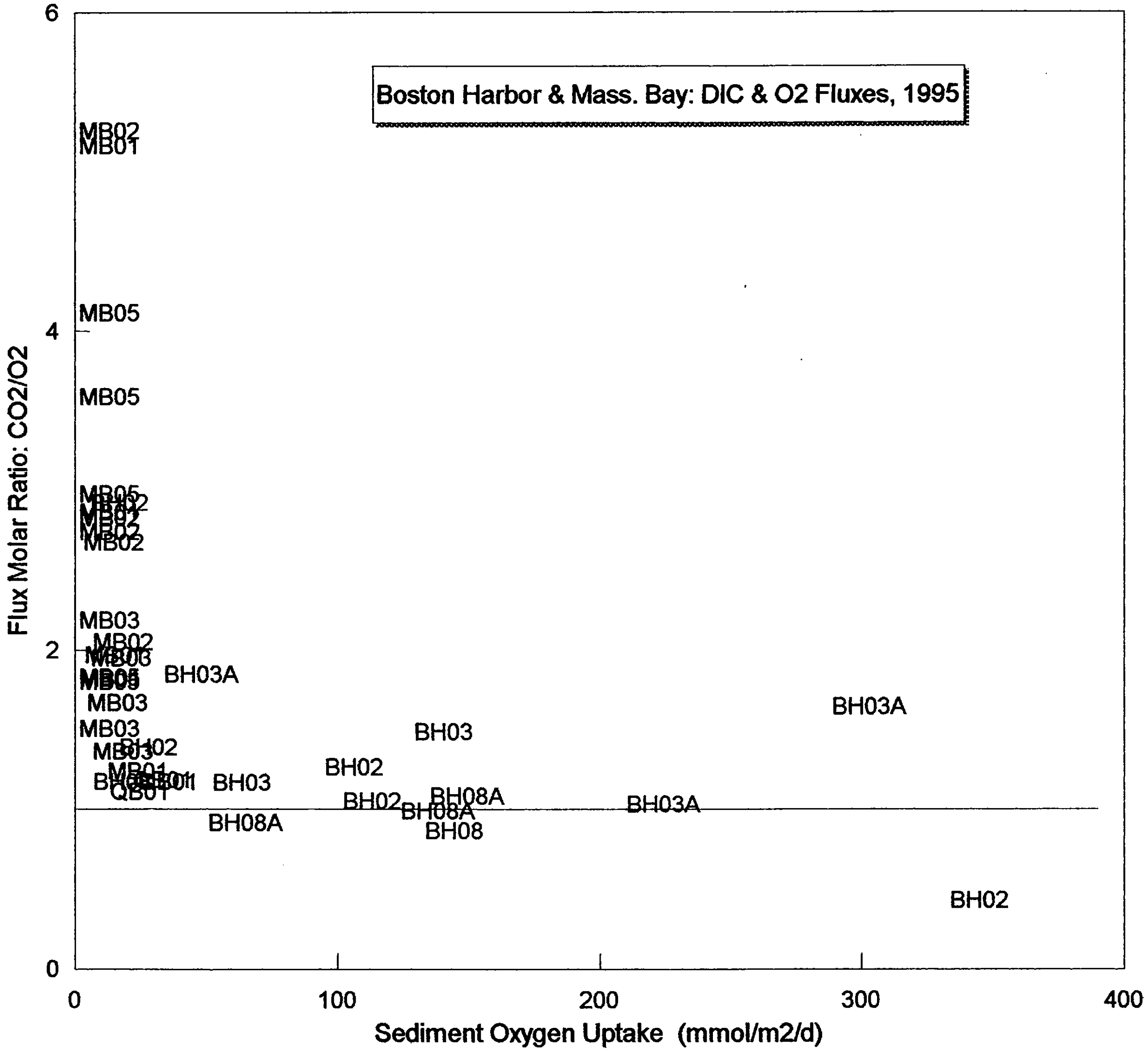


Figure 16. Molar ratio of DIC to Oxygen flux from each station in Boston Harbor and Massachusetts Bay throughout 1995. DIC efflux was generally higher than oxygen uptake. The high DIC/O_2 ratios in sediments with lower oxygen uptake rates may result in part from proportionally higher denitrification rates and from the greater potential contribution of artefactual fluxes of DIC from carbonate dissolution or core disturbance.

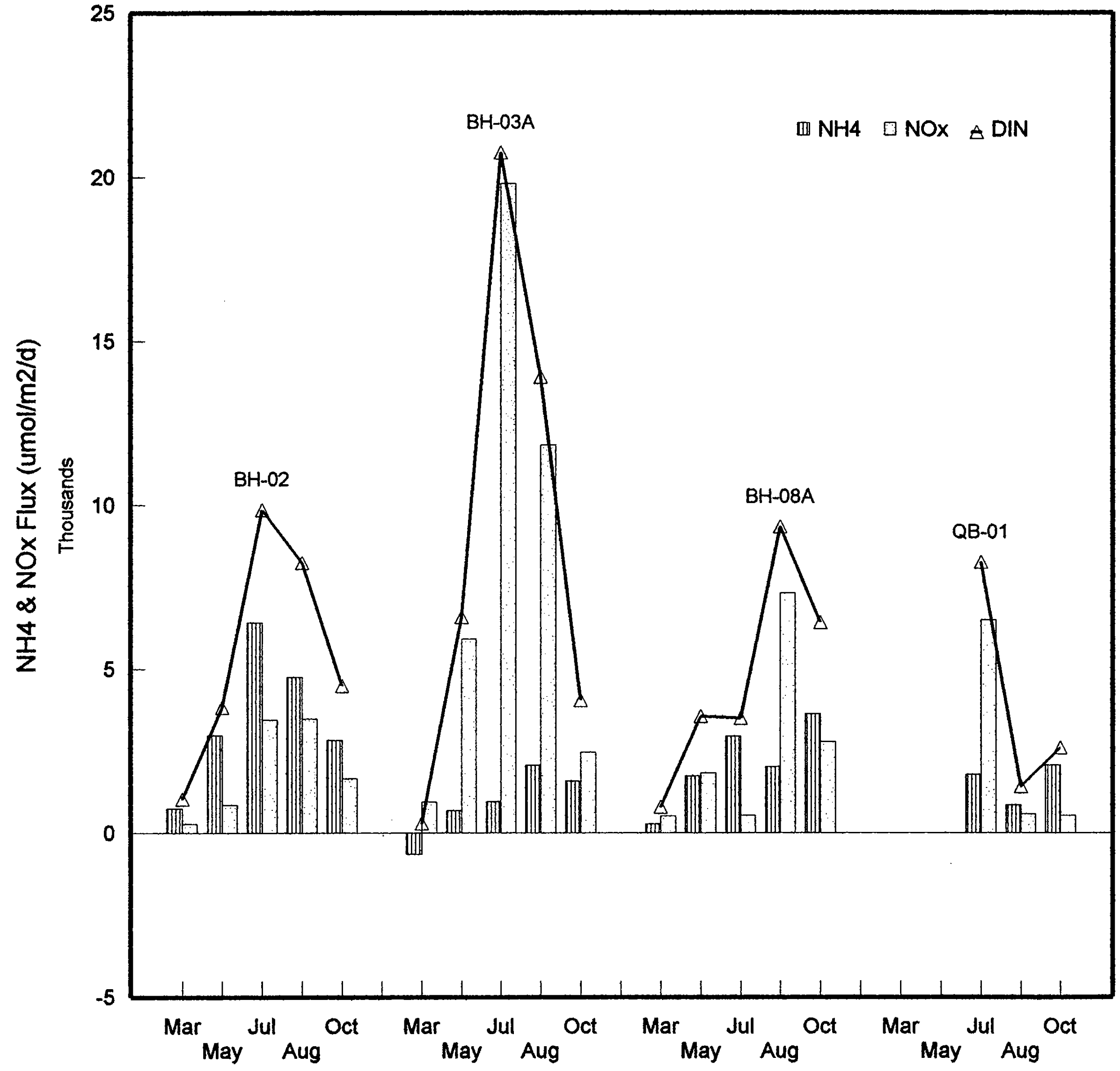


Figure 17. Dissolved inorganic nitrogen (DIN) efflux from the sediments of Boston Harbor during 1995. Nitrate was the primary component of DIN at BH03A with its dense amphipod mat and oxidized sediments. BH03A and BH02 showed less of an effect.

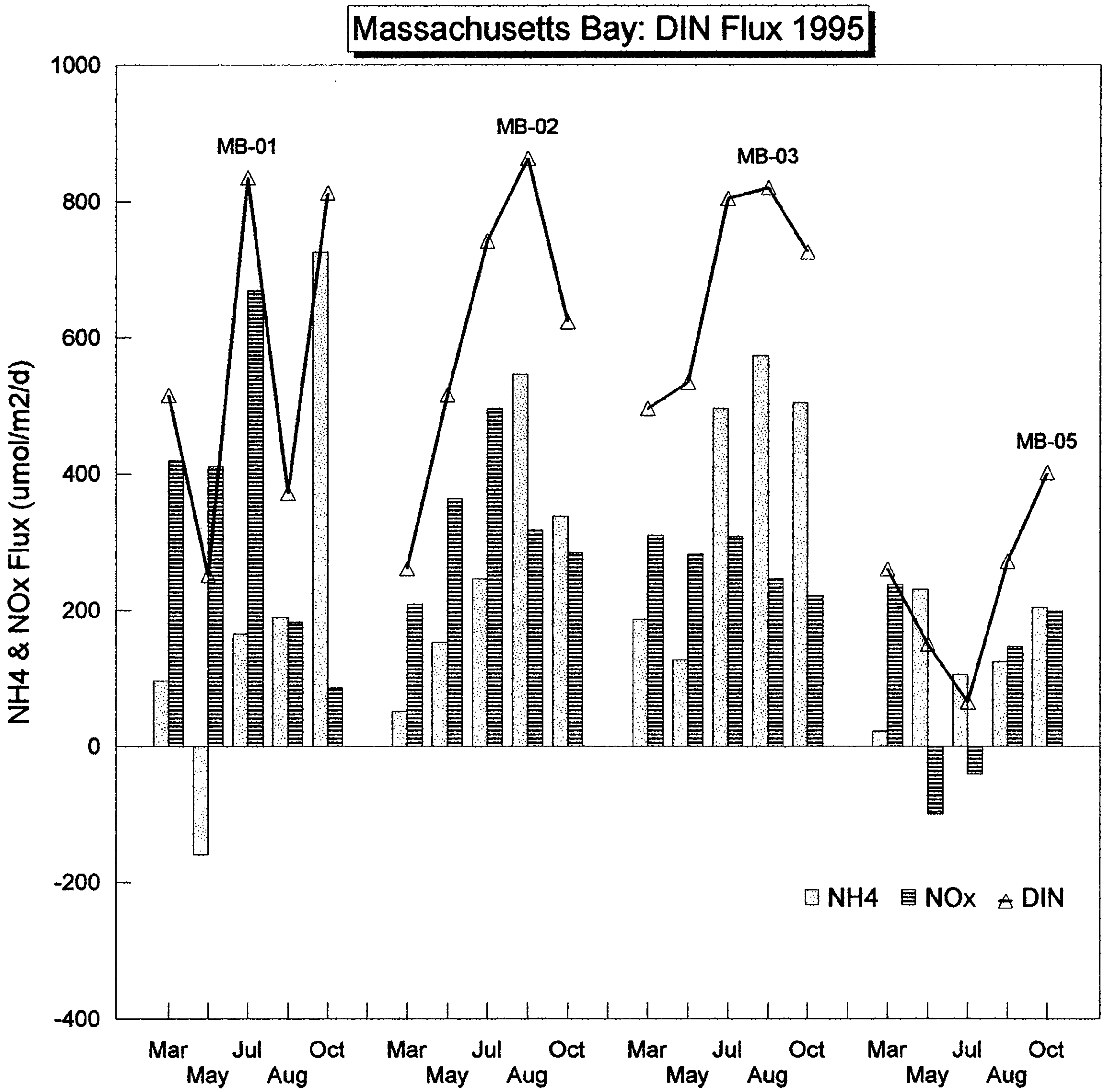


Figure 18. Dissolved inorganic nitrogen (DIN) efflux from the sediments of the western nearfield region of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) during 1995. There was a seasonal shift from a predominance of nitrate in the winter and spring to ammonium in summer and early fall.

matter deposition rates to Harbor sediments due to the greater terrestrial and in situ sources and the more direct delivery to the benthos compared to the Bay. The shallower waters of the Harbor also result in higher summer water temperature supporting a greater capacity to rapidly remineralize deposited organic matter.

The composition of the DIN flux showed similar spatial variations within both the Harbor and Bay, however, temporal patterns of DIN flux compostion differed. DIN efflux from Harbor sediments with with dense amphipod mats tended to have high nitrate fluxes (BH03A), while less intensively colonized sites tended to support higher ammonium than nitrate losses. In contrast, the fraction of DIN fluxes from the Bay sites appear to be seasonally mediated with nitrate dominating during the colder lower oxygen demand portion of the year. As the bottom waters warm, DIN flux shifts to ammonium which formed the majority of the flux at all Bay stations by the end of the summer. Stellwagen Basin had low and variable DIN fluxes but also showed a clear but less intense seasonal shift from nitrate to ammonium during summer. The seasonal shift to ammonium likely reflects the increased ammonification in excess of nitrification as sediment temperatures rose. The shift cannot only be the result of increased rates of sediment metabolism, since at the highest rates of oxygen uptake measured in 1995 >90% of the DIN flux was nitrate (Figure 19). Within the Harbor DIN fractionation appears to be modified by infaunal activities which appear to result in increased nitrification, helping to explain the enhanced denitrification discussed above.

It is noteworthy in the latter period of stratification that the nitrate pool in the hypolimnion is increasing at about twice the rate as ammonium, yet the sediment flux at this time is ammonium (Cibik *et al.* 1996). Certainly some of this effect results from nitrogen regenerated within the watercolumn and nitrification of ammonium from sediment flux. However, a study of hard bottom community DIN flux during this interval might indicate a difference in DIN speciation between hard and soft bottom areas of the Bay.

In general appearance, ortho-phosphate fluxes appear to follow the pattern of sediment respiration as did DIN fluxes. There was a strong seasonality in rates in both Harbor and Bay Stations, with winter fluxes generally several fold lower than during summer. Harbor stations showed more than 5 fold higher rates of PO_4 loss over the Bay (Figures 20 & 21). The Quincy Bay station (QB01) had significantly lower rates of ortho-phosphate release than the rest of the Harbor and approached levels of the Bay. However, the spatial pattern is complex, upon closer inspection it is clear that within each system that the extent of PO_4 flux is inversely related to oxygen uptake. The stations with the highest summer oxygen uptake BH03A and MB03 showed lower P/O ratios than the other stations in each respective region. At present the mechanism for this relationship is unclear.

Silicate fluxes showed increases thoughout the year. As in previous years and with all other constituents, silicate flux was higher within the Harbor that in the Bay (Figures 22 & 23). However, rates of flux of silicate from sediments from all sites were lower in both the Harbor and Bay in 1995 compared to 1994. These lower numbers contrast with the higher respiration and irrigation rates within the Harbor in 1995 and the similarity of oxygen uptake at the Massachusetts Bay locations in all years. Considering the interannual consistency in

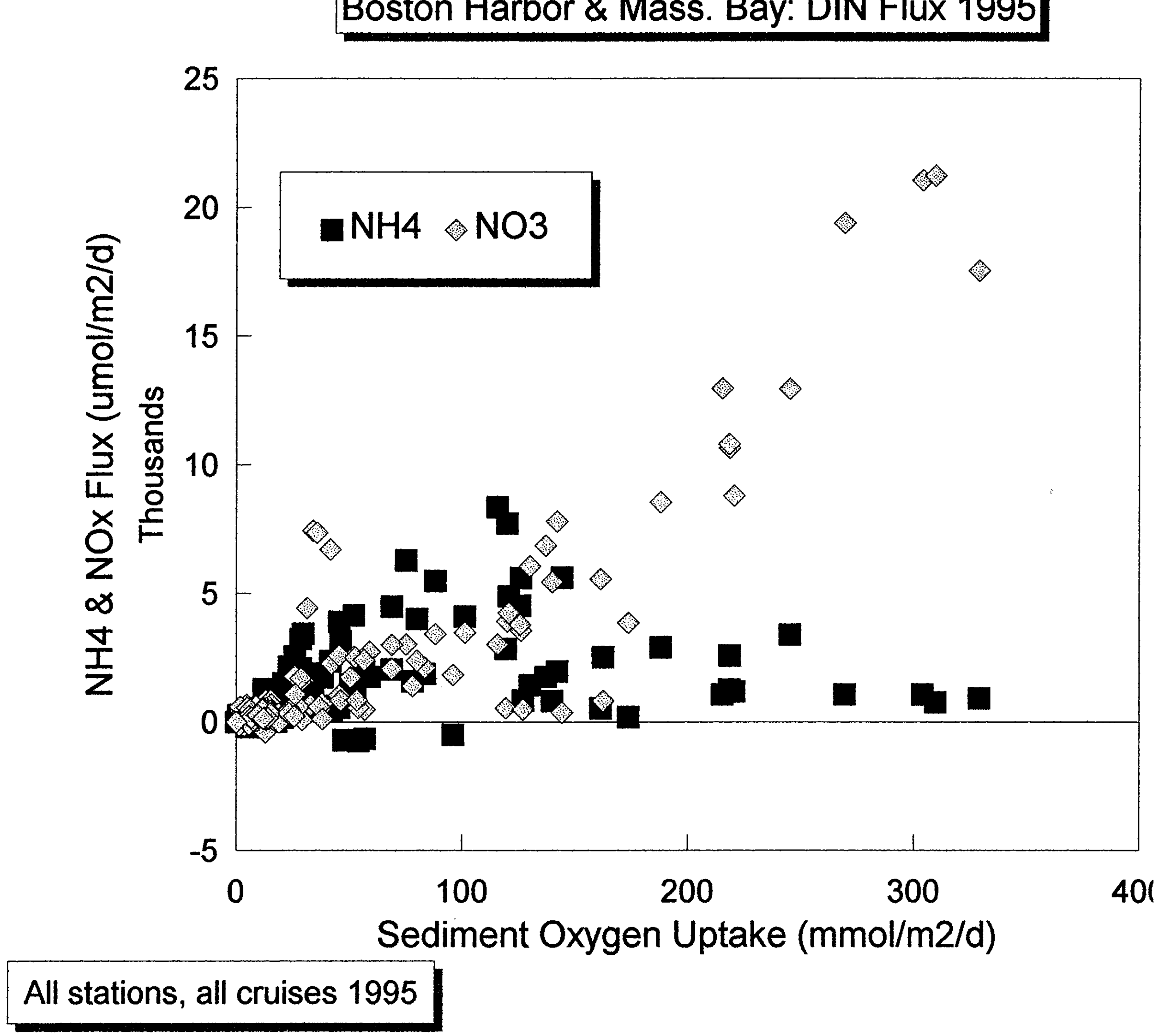


Figure 19. Relationship of ammonium and nitrate fluxes to sediment oxygen uptake within the sediments of Boston Harbor and Massachusetts Bay during 1995. Ammonium was the dominant DIN flux from sediments with low oxygen uptake rates, while nitrate predominated in high SOD sites. The higher SOD sites tended to be associated with amphipod mats where sediment oxidation and sediment bio-irrigation rates were high.

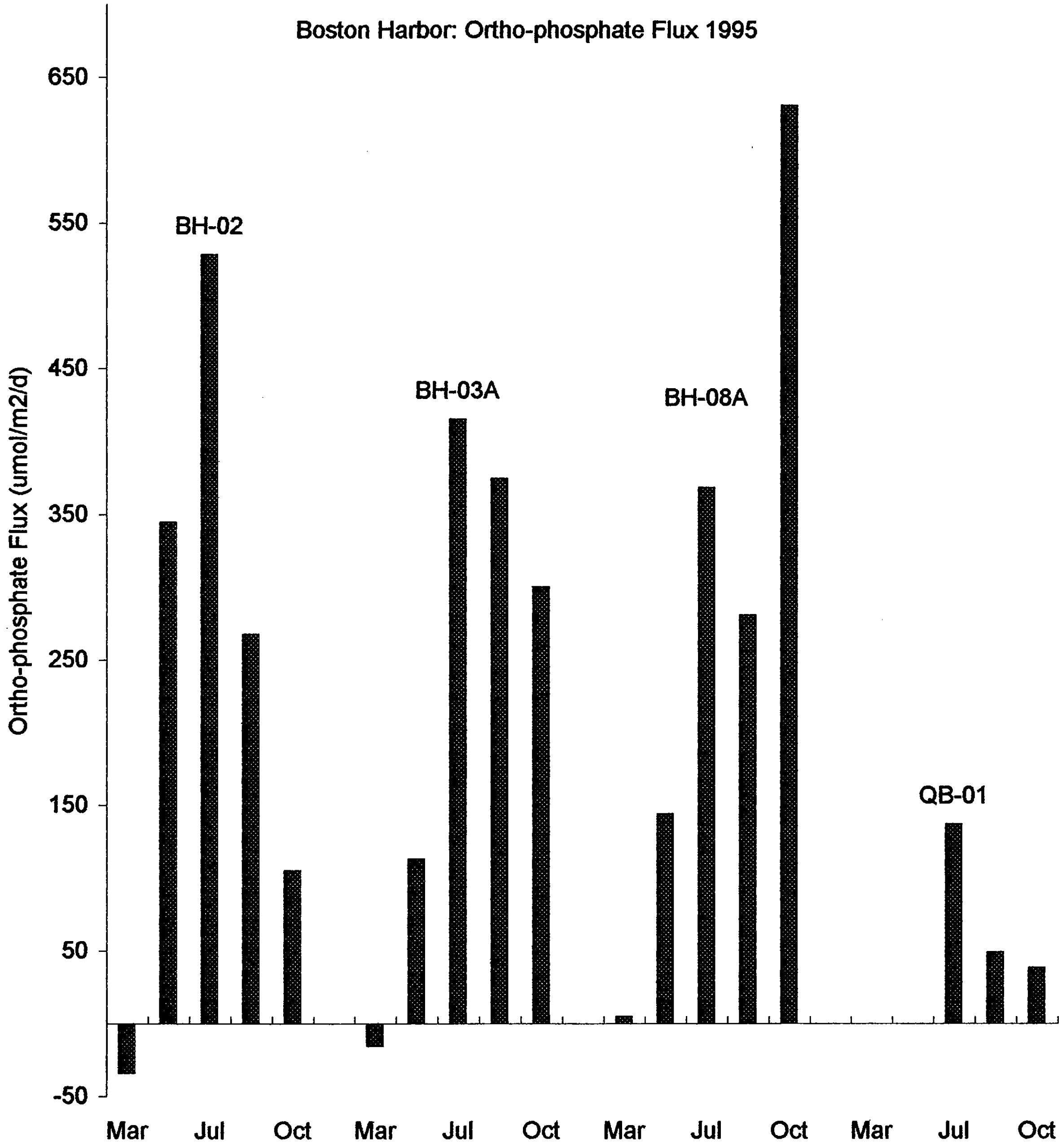


Figure 20. Efflux of ortho-phosphate to the overlying waters from the sediments of Boston Harbor during 1995. Flux rates showed a strong seasonality with low rates (or uptake) during the winter and increasing losses during summer and declining losses in the fall. Rates of ortho-phosphate efflux tended to parallel the seasonality and distribution of oxygen uptake rates.

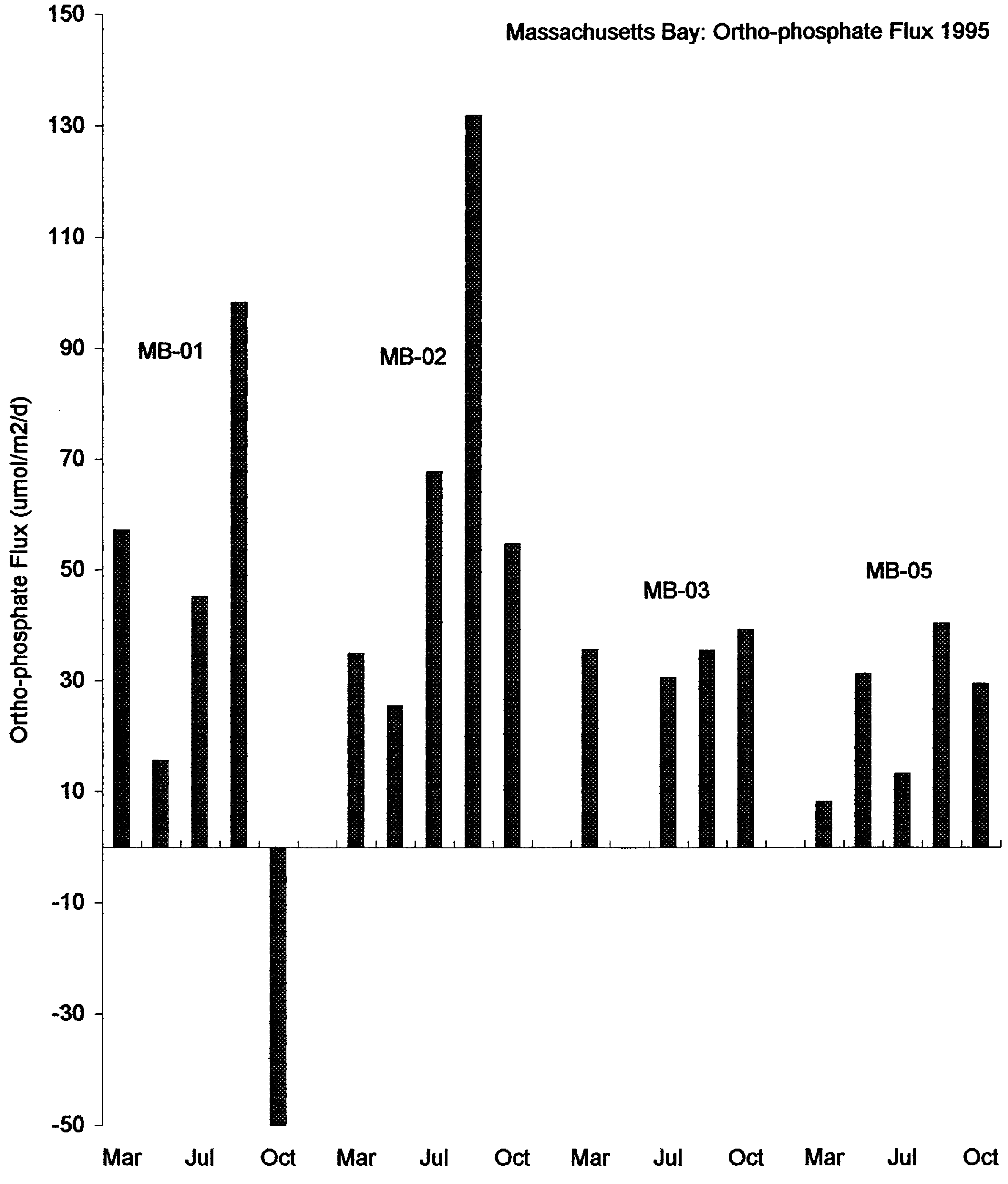


Figure 21. Efflux of ortho-phosphate to the overlying waters from the sediments of the western nearfield (MB01, MB02, MB03) and Stellwagen Basin (MB05) during 1995. Flux rates showed a trend toward higher rates at higher temperatures. Rates of ortho-phosphate efflux were variable but tended to parallel the spatial and temporal pattern of oxygen uptake.

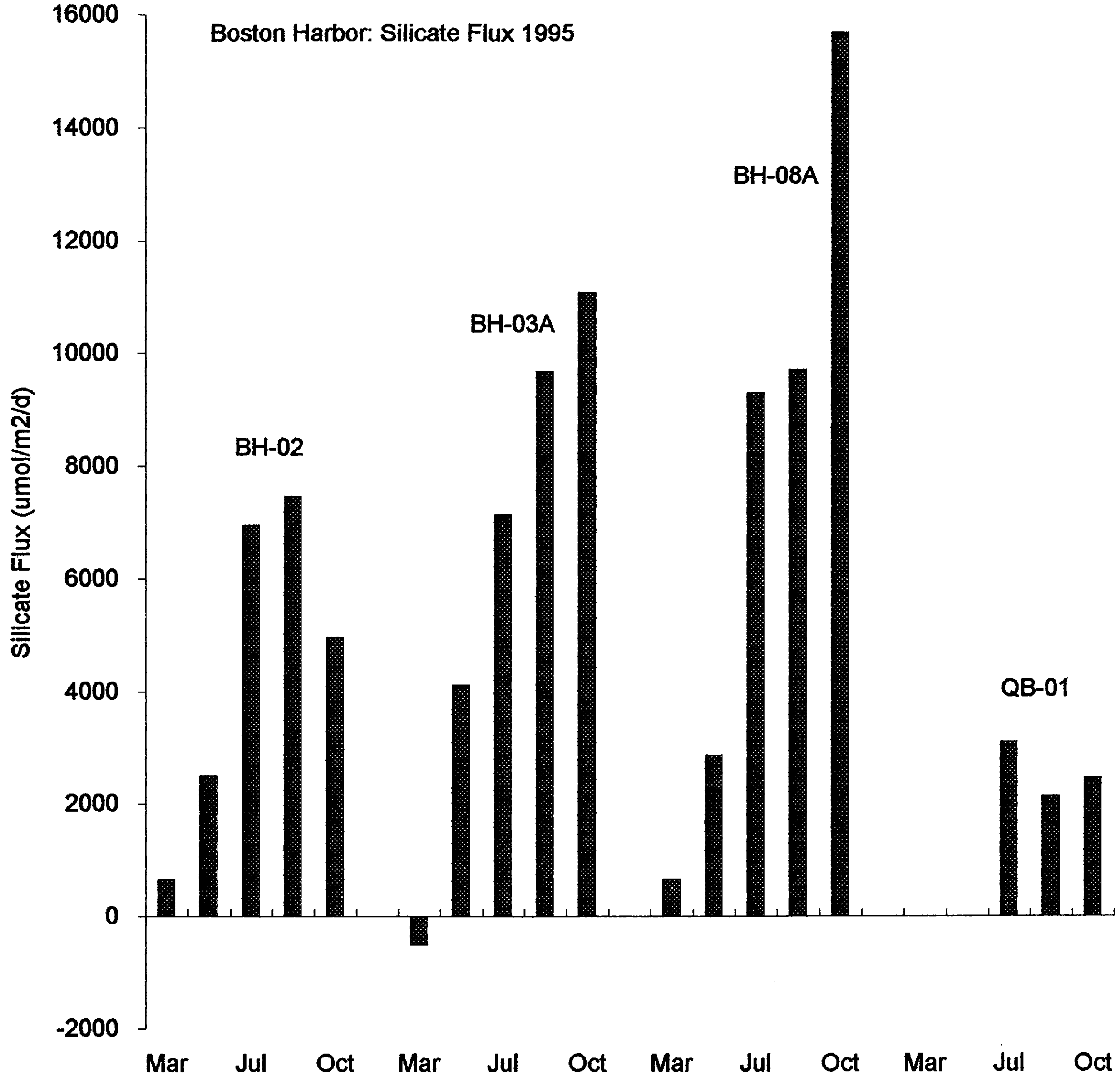


Figure 22. Efflux of silicate from the sediments to the overlying waters of Boston Harbor during 1995. Flux rates showed a strong seasonality with low rates (or uptake) during the winter and increasing losses throughout the summer and fall.

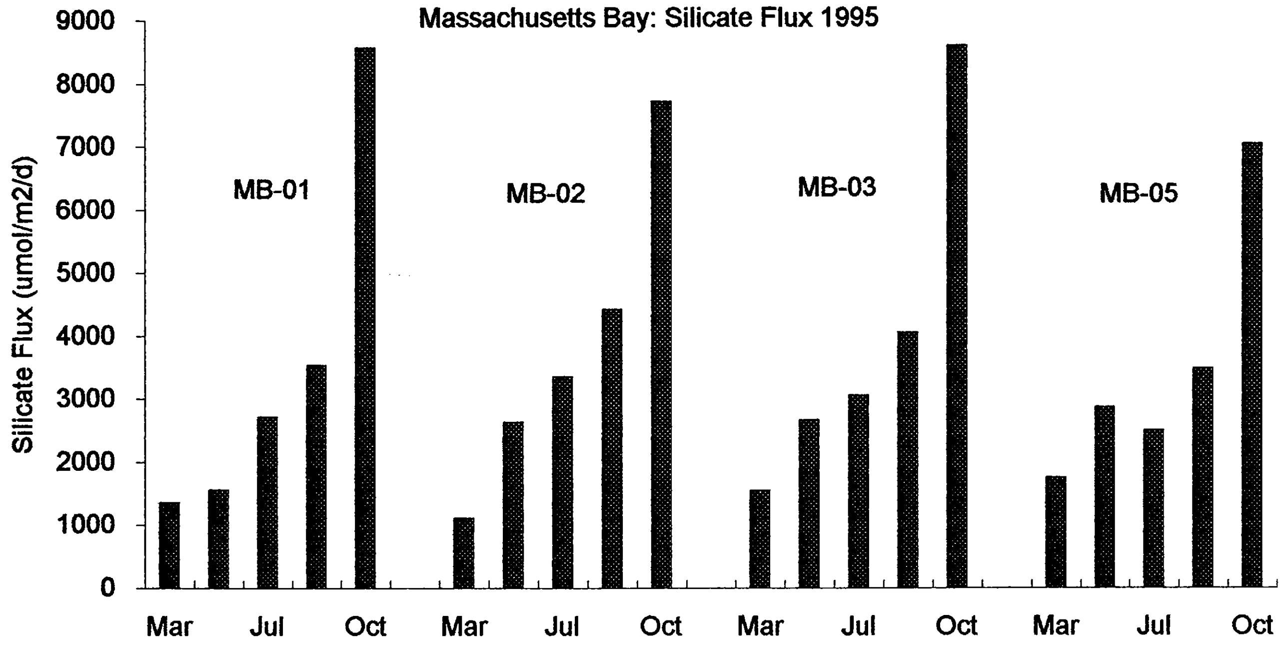


Figure 23. Efflux of silicate to the overlying waters from the sediments of the western nearfield (MB01, MB02, MB03) and Stellwagen Basin (MB05) during 1995. Flux rates showed a strong seasonality with low rates (or uptake) during the winter and increasing losses throughout the summer and fall. Rates for the Harbor and Bay were consistent with the pattern of overall community metabolism.

SOD measurements within the Bay it is unclear why the silicate fluxes and other major inorganic fluxes, DIN and ortho-phosphate, were lower by more than 50% in 1995 versus 1994. It is unclear what would cause interannual changes in the retention of regenerated nutrients. At this point methodological differences relating to core disturbance cannot be ruled out. However, it is important that the mechanism underlying these potential shifts be examined in order to establish pre-discharge conditions and to enhance estimates of bottomwater nutrient balance during stratification. The processes underlying the observed differences in inorganic fluxes will be investigated as the monitoring program continues.

Sediments Fluxes and Watercolumn Nutrients

Watercolumn nutrient levels are the balance of inputs from direct sources (land, rain etc), losses (denitrification, burial), regeneration (watercolumn and benthic) and uptake (eg. photosynthesis). Phytoplankton take up nutrients from the watercolumn in ratios to meet their biochemical requirements (Redfield *et al.* 1963), but the ratios of these nutrients returned to the watercolumn resulting from their degradation within the sediments can be very different. In shallow water systems where nutrient regeneration from sediments plays a major role in organic matter flow, the modifications of the relative composition of nutrients in sediment efflux can have secondary effects of watercolumn processes. It appears that the colonization of Harbor sediments by amphipods may be causing just such a modification in N/P flux ratios.

The ratio of fluxes of DIN to ortho-phosphate (N/P) from Harbor sediments have typically been near 16 or below (Giblin *et al.* In press). Particularly at sites of high oxygen uptake, N/P fluxes show a return of greater amounts of P than N, based on the theoretical ratio of 1P:16N (Redifield *et al.* 1963). In contrast, in 1995 the Harbor surveys showed DIN fluxes frequently greater than 16 times ortho-phosphate fluxes (Figure 24). This apparent shift in 1995 versus previous years does not appear to be methodological as the N/P flux ratio for Bay sites in 1995 (ca. 11, stratification, Table 2) was similar to earlier measurements in the Bay (ca. 8, stratification). The flux ratios in the Bay are supported by the ratio of bottomwater DIN and DIP increases during stratification (N/P=12, Figure 25).

A shift in N/P flux ratios from Harbor sediments can result from a decrease in relative losses through burial and for N, denitrification or be related to "mining" of sediment storage. The mechanism underlying the shift in Boston Harbor in 1995, appears to be related to the increased irrigation of sediments by the colonizing infauna. The irrigation to is to ventilate infaunal burrows, but secondarily results in an increased oxidation of the sediment system in spite of the much higher rates of oxygen uptake. In the BH03A and BH08A, the increased sediment ventilation resulted in high nitrate levels within the porewaters of the surficial sediments during summer (Figure 26). The highest nitrate was found at BH03A where respiration rates were 2 fold higher than the next highest station. The higher sediment oxidation status witin the sediments having the highest oxygen uptake rate is somewhat counter intuitive, in that sediments with high SOD are frequently very reducing. The more oxidizing nature of colonized Harbor areas results from the ability of the infauna to ventilate

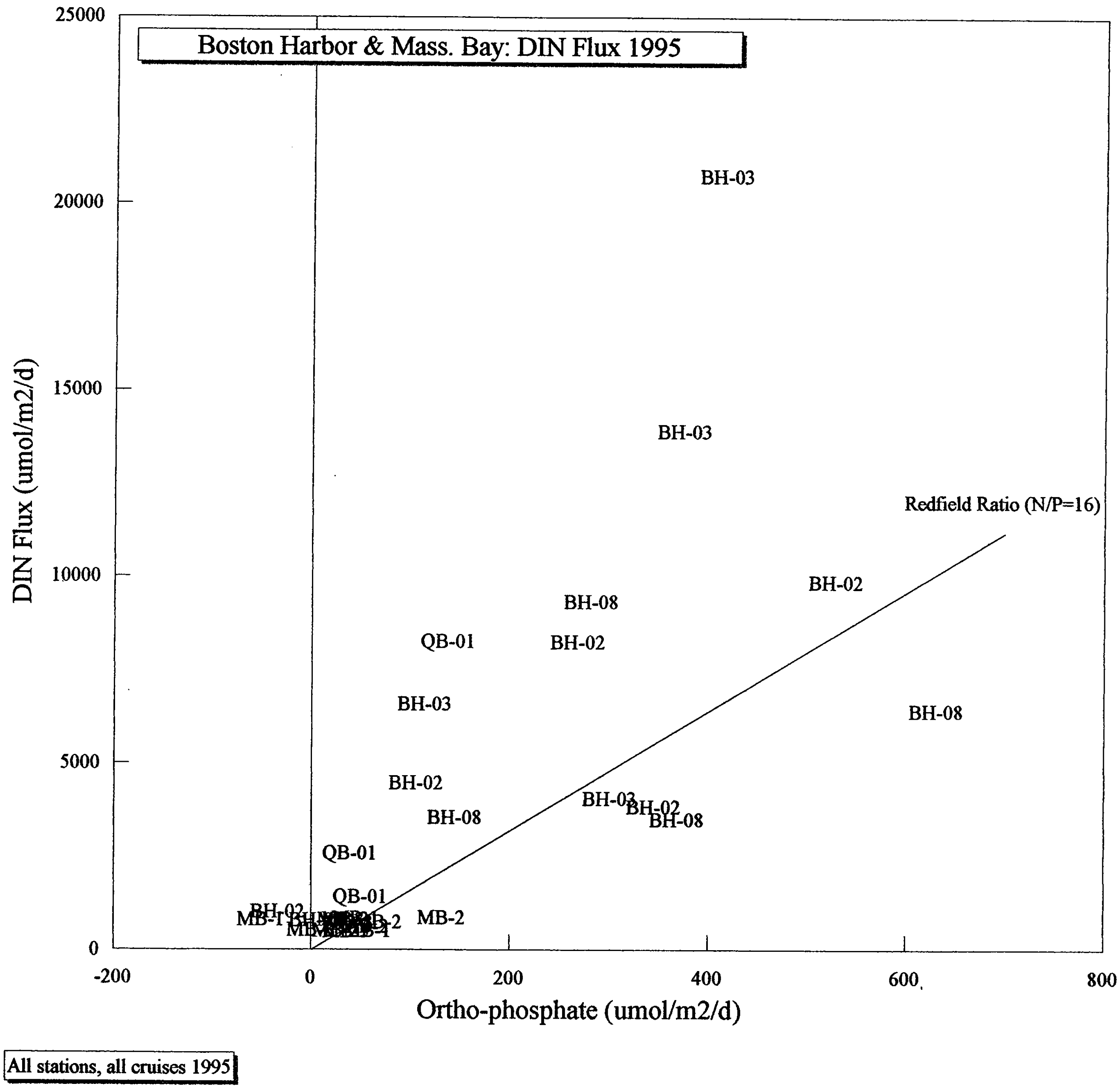


Figure 24. Relationship of DIN to ortho-phosphate fluxes from the sediments of Boston Harbor (BH02, BH03A, BH08A, QB01) and the western nearfield (MB01, MB02, MB03) and Stellwagen Basin (MB05) relative to the ratio predicted by Redfield (1963). During the warmer months, Boston Harbor sediments tended to regenerate DIN significantly in excess of ortho-phosphate. Annual N/P flux ratios were approximately 40 for the Harbor and 13 for the Bay.

Figure 25.

Depth Integrated DIN and PO_4 by Survey in Outer Nearfield

Depth > 12.5m; N04, N07, N16, N20.

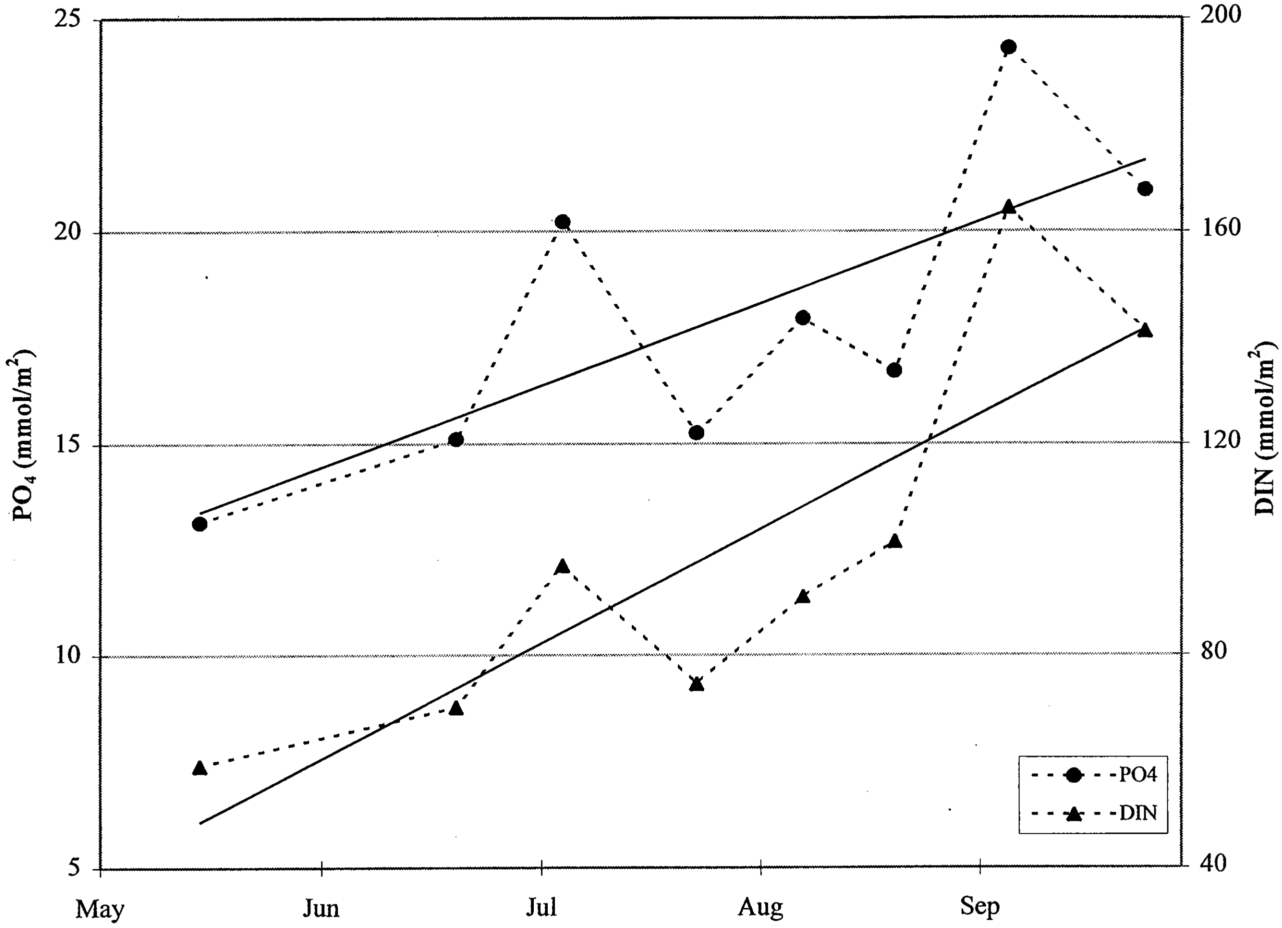


Table 2. Inorganic nitrogen and ortho-phosphate regeneration in the bottomwaters of the Nearfield region of Massachusetts Bay during stratification, 1995.

	Direct Measurement	**Bottomwater Concentration Change**		
Analyte	**Sediment Flux (mmol/m^2/d)**	**Slope* (mmol/m^2/d)**	**Intercept (mmol/m^2/d)**	**R^2**
PO_4	0.068	0.06	12.52	0.54
DIN	0.74	0.70	38.85	0.71

* Predicted on May 1st as: Value=Slope X Date + Intercept
Sediment Flux= mean of Jul, Aug of MB01,02,03.
Bottomwater Increase is during stratified interval.

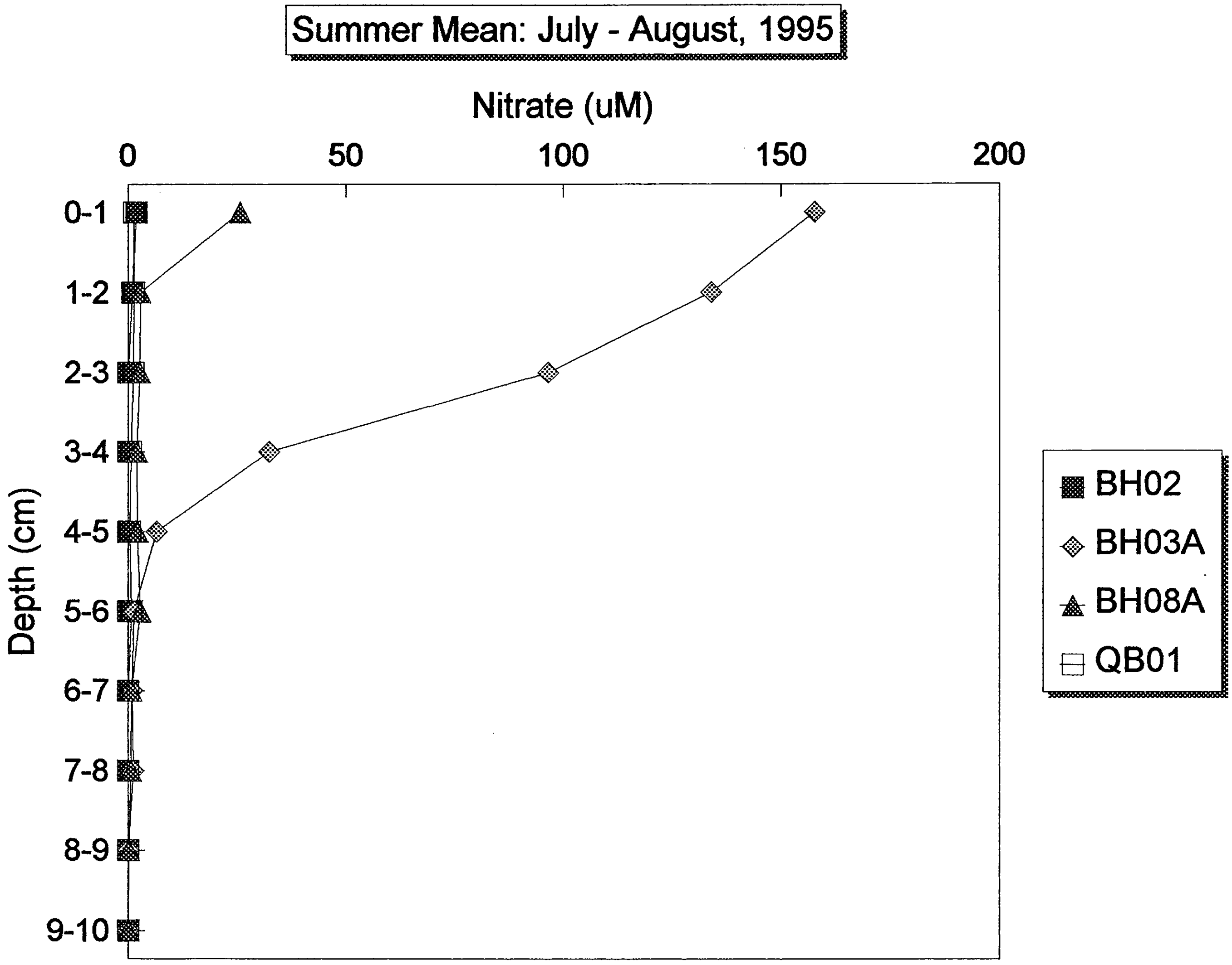


Figure 26. Profiles of nitrate in porewaters of Boston Harbor sediments during summer 1995. Nitrate concentrations at BH03A and BH08A are consistent with their more oxidizing sediments associated with infaunal activity.

in excess of demand. This increased ventilation of the sediment appears also to be stimulating nitrogen fluxes from the sediments.

The nitrate levels in Harbor, BH03A and BH08A, sediments were greater than at the Massachusetts Bay sites (Figure 27). The distribution of nitrate throughout the upper centimeters of the Bay sediments suggests that sulfate reduction rates may be relatively low. The nitrate within both sediment systems results from nitrification and supports the finding of enhanced denitrification within the Harbor sediments associated with amphipod mats. The shift to a DIN flux dominated by nitrate at BH03A is supported by the large fraction of the surface porewater DIN comprised by nitrate (Figure 28). The predominance of ammonium fluxes at BH02 and in the summer in the Bay sediments is consistent with the limited fraction of the porewater DIN contributed by nitrate. The higher fluxes of DIN from Harbor versus Bay sediments is consistent with the the high DIN concentrations (Figures 28, 29, note the scale changes in the figures) and probably bio-irrigation rates in the Harbor compared to the Bay.

If ventilation is enhancing DIN fluxes, it appears to be inhibiting ortho-phosphate release. The proportionally lower DIP fluxes from the colonized harbor sediment (relative to mineralization rates, Figures 2,14,19) is likely also related to the increased ventilation at these sites. Porewater ortho-phosphate levels were similar between Harbor amphipod sites and the Bay (Figures 30 & 31). BH03A had a nearly identical profile to MB01. The cause of the diminished DIP flux after colonization by infauna most likely results from increase retention of remineralized P due to sorption within more oxidized sediments. The differences in sediment oxidation are illustrated by profiles of oxidation-reduction potential (Eh), as dissolved sulfide levels at all sites, except BH02, were typically $\leq$1 uM (Figures 32,33,34,35,36).

It is important when evaluating sediment oxidation status that seasonal shifts are taken into account. In Massachusetts Bay there was a season shifting of the Eh profile, however, the relative shape of the profile remained constant. Failing to account for this seasonal shift might lead to erroneous conclusions as to changes in sediment oxidation status.

In summary the mechanism producing the increased flux of DIN relative to ortho-phosphate (Figure 24) with amphipod colonization appears to result from increased ventilation due to bio- irrigation increasing sediment oxidation (Figure 34). The increased sediment oxidation may enhance DIN fluxes by "mining" sorbed ammonium and exporting oxidized forms, but show much smaller increases in ortho-phosphate fluxes due to sorption of inorganic P to sediment minerals (Krom and Berner 1980). As monitoring continues the duration of this infaunal control on biogeochemical fluxes will be ascertained. Future effects of this shift in the ratio of N/P fluxes on Harbor systems as nutrient inputs are reduced, cannot be gauged (since its sustainablity is not certain). However, at present the effects on watercolumn N/P appear to be small since DIN/DIP ratios within the Harbor remain well below 16 (data from F30, F31, F23 in Cibik *et al.* 1996). This observation is consistent with the large external inputs of N and P and the modest transport of these inputs through the sediment system.

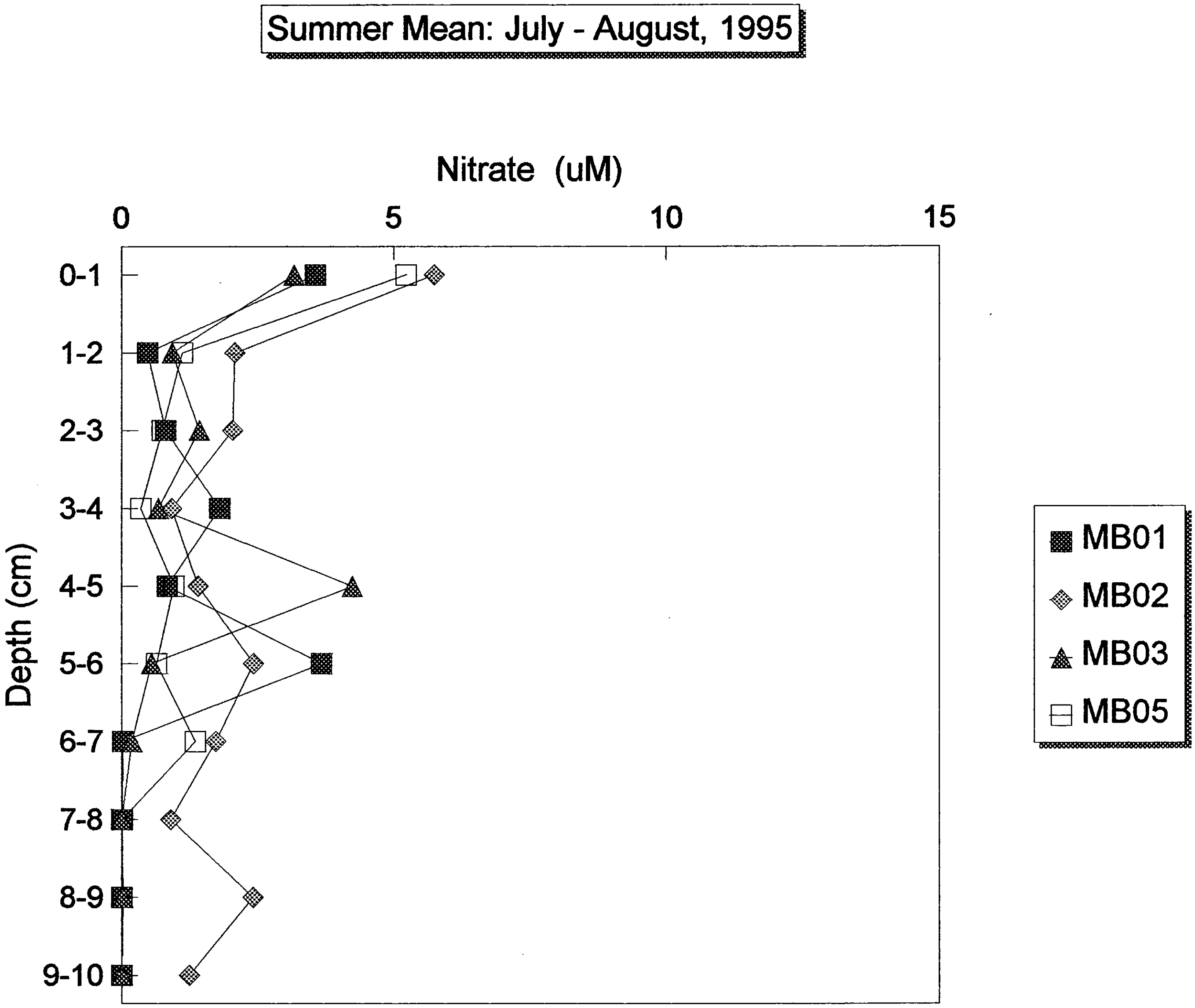


Figure 27. Profiles of nitrate in porewaters of Massachusetts Bay sediments during summer of 1995. Measurable nitrate concentrations throughout the profile were consistent with the deep burrowing infaunal community within the Bay sediments.

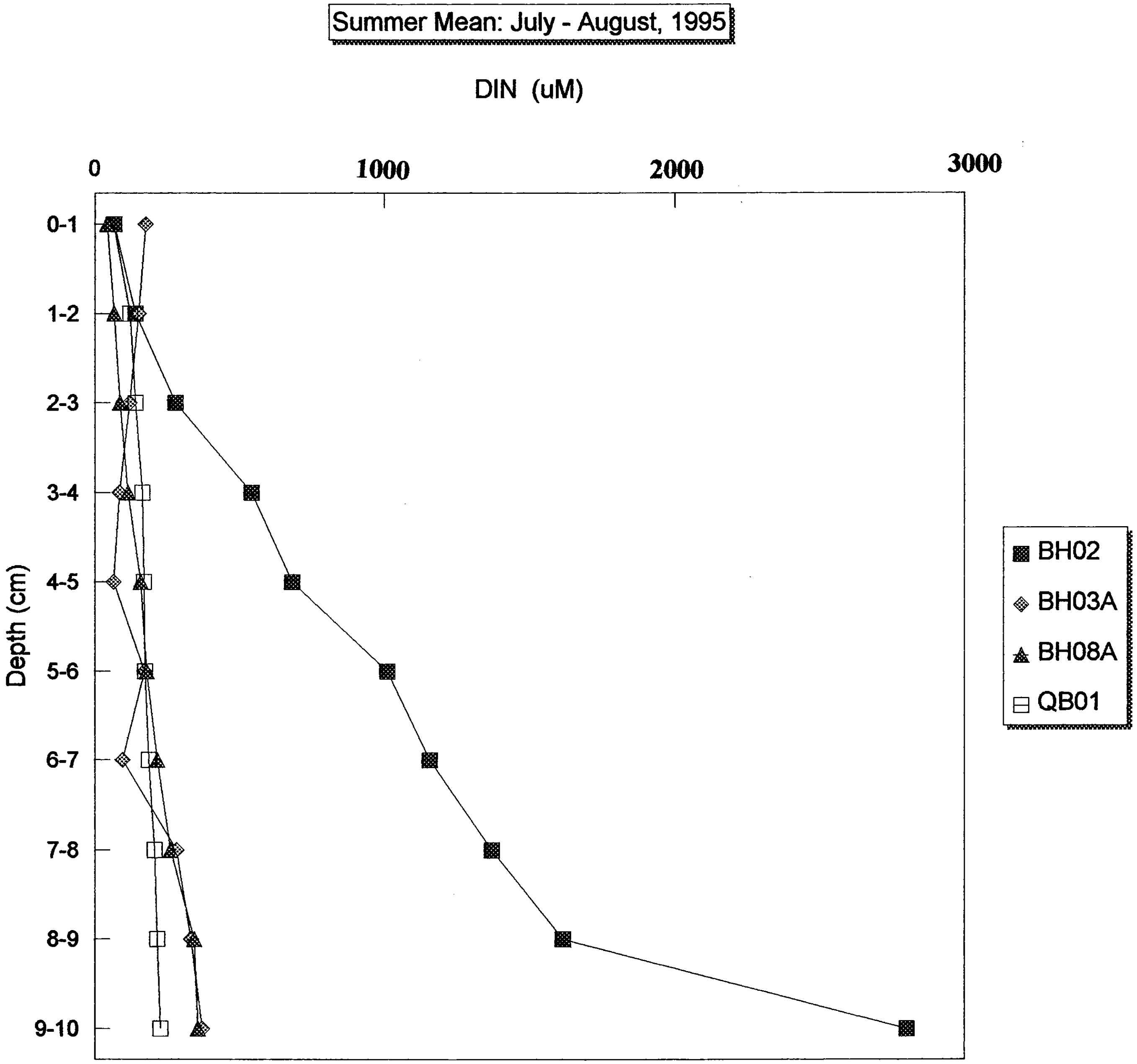


Figure 28. Profiles of dissolved inorganic nitrogen (DIN) concentrations in the porewaters of Boston Harbor sediments. DIN was comprised primarily of ammonium at all sites except the surface depths of BH03A. The high DIN levels at BH02 are typical of highly reducing sulfidic sediments such as found at this site.

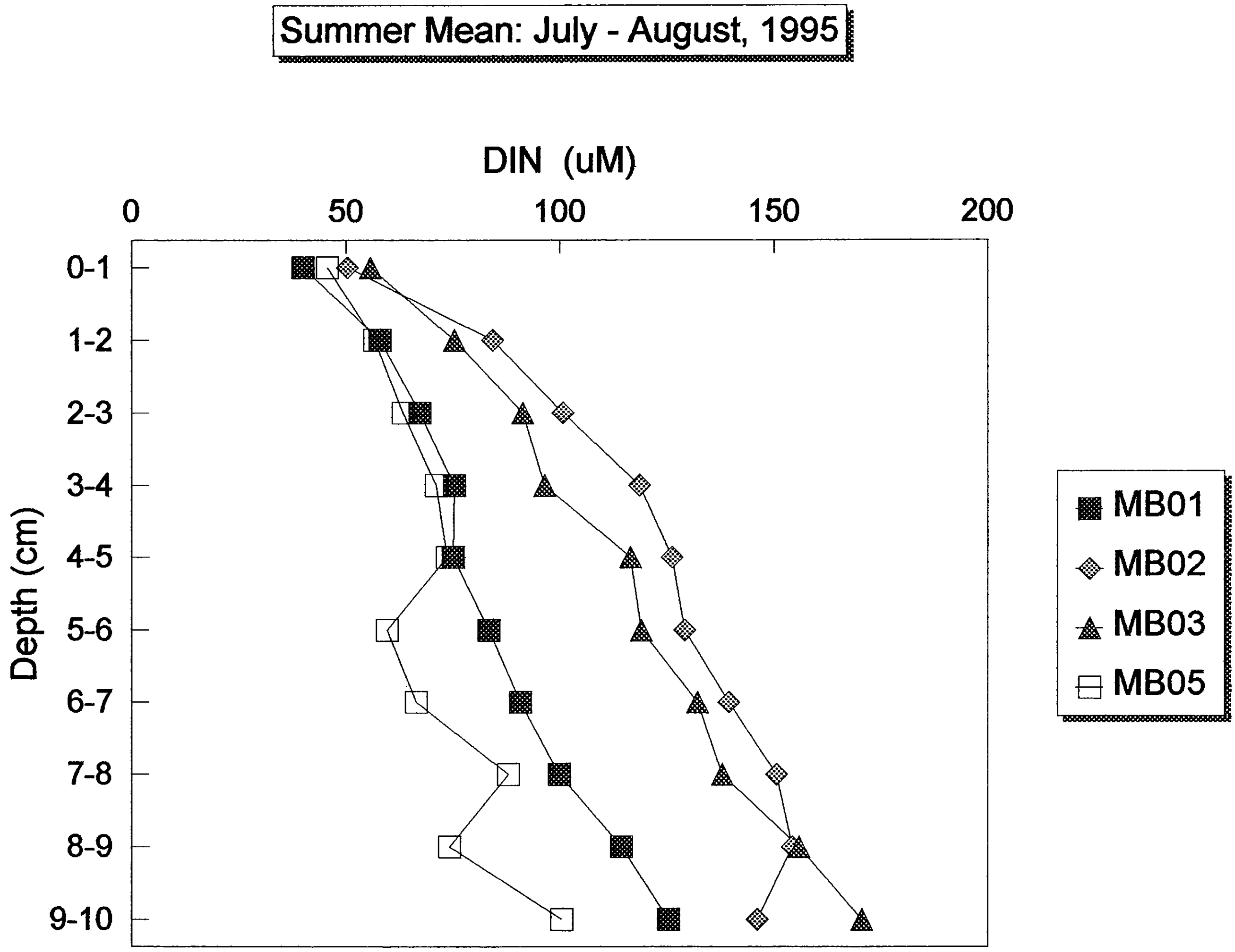


Figure 29. Profiles of dissolved inorganic nitrogen (DIN) concentrations in the porewaters of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) sediments. DIN at all stations was primarily ammonium and increased with depth.

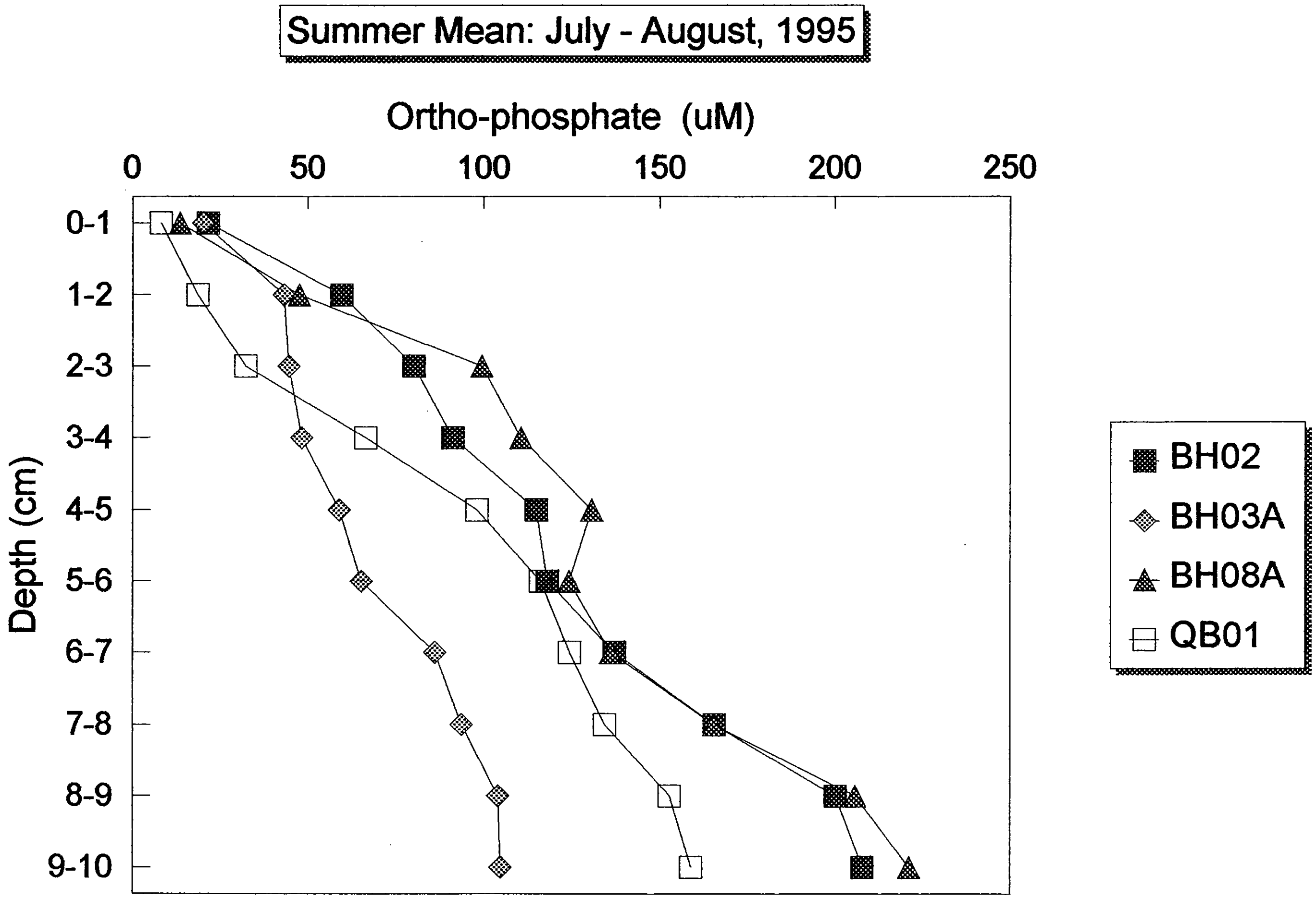


Figure 30. Profiles of ortho-phosphate in porewaters of Boston Harbor sediments during summer 1995. Only concentrations in the upper 2 cm were consistent with the observed surface flux rates. The lower ortho-phosphate concentrations and fluxes at BH03A relative to its measured rate of oxygen uptake suggests a greater sorption of remineralized phosphate in these more oxidized sediments.

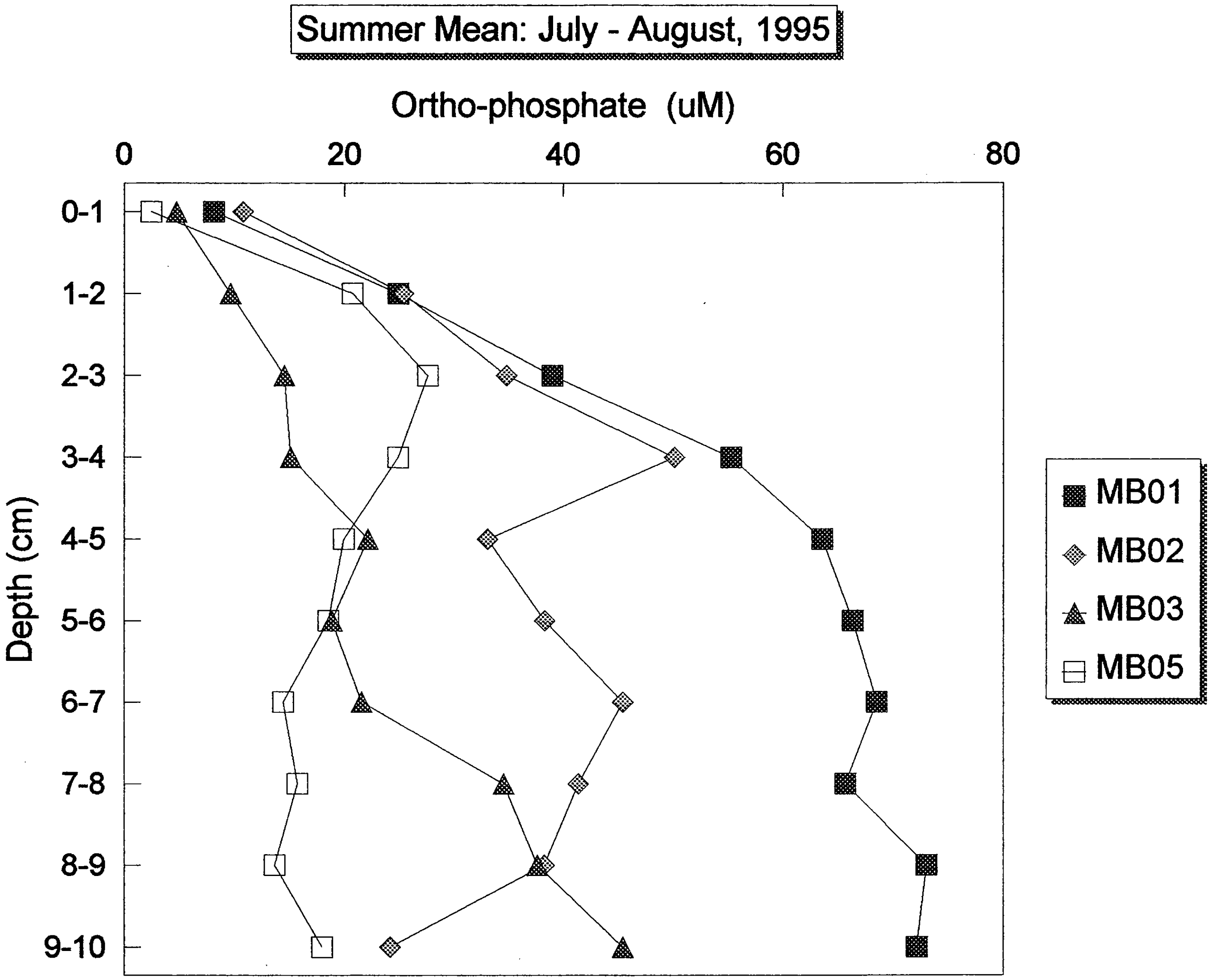


Figure 31. Profiles of ortho-phosphate in porewaters of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) sediments during summer of 1995. Concentrations were ca. half of those in the Harbor. Differences in rates of ortho-phosphate flux were consistent with concentration differences in surficial porewaters.

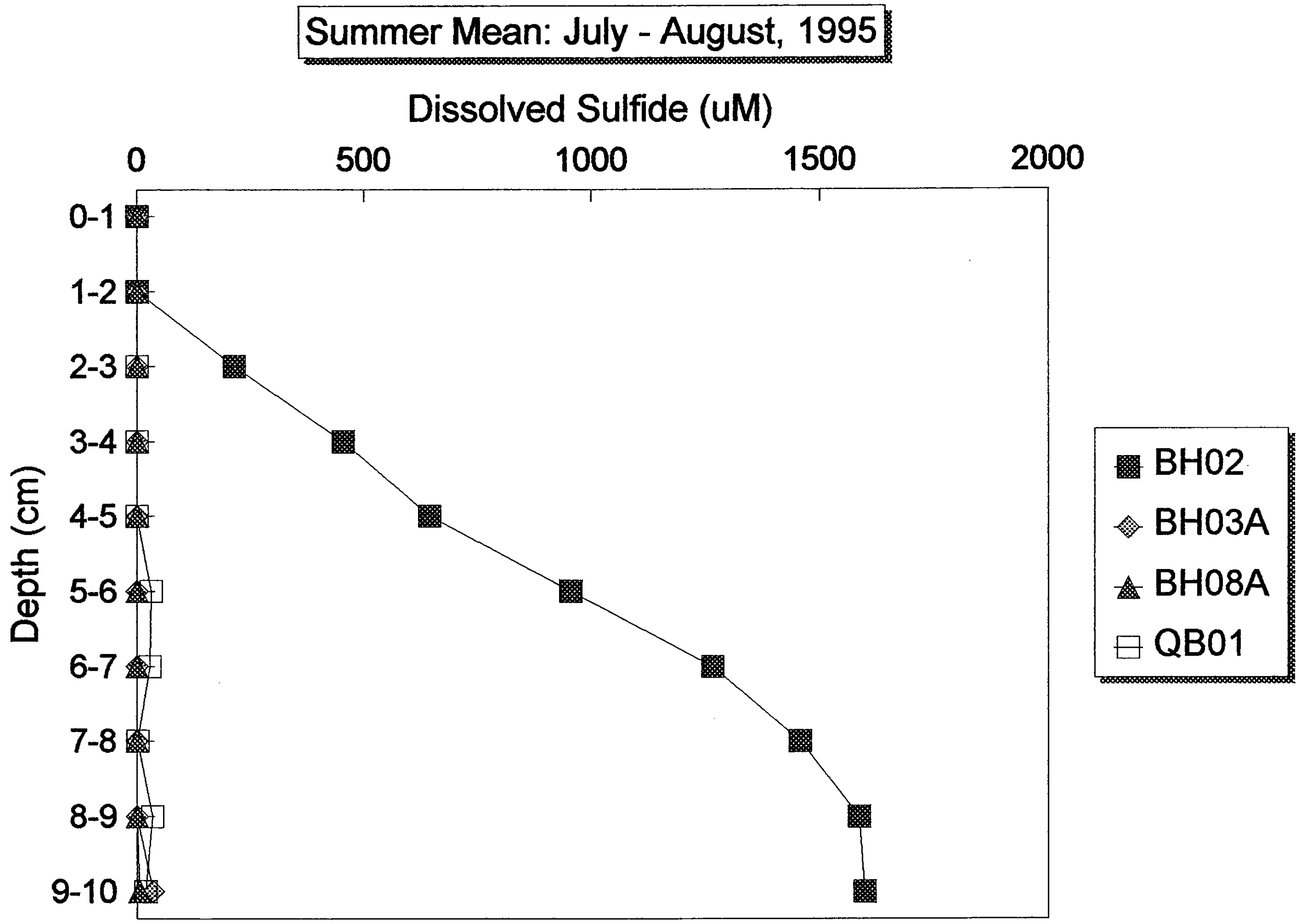


Figure 32. Profiles of dissolved sulfide in the porewaters of Boston Harbor sediments during 1995. Measurable sulfide levels were only consistently observed within the highly reducing sediments at BH02 and in the deeper porewaters at QB01. Re-oxidation and precipitation of sulfides within the surficial sediments are the primary mechanisms for maintaining low dissolved sulfide levels in coastal sediments supporting sulfate reduction.

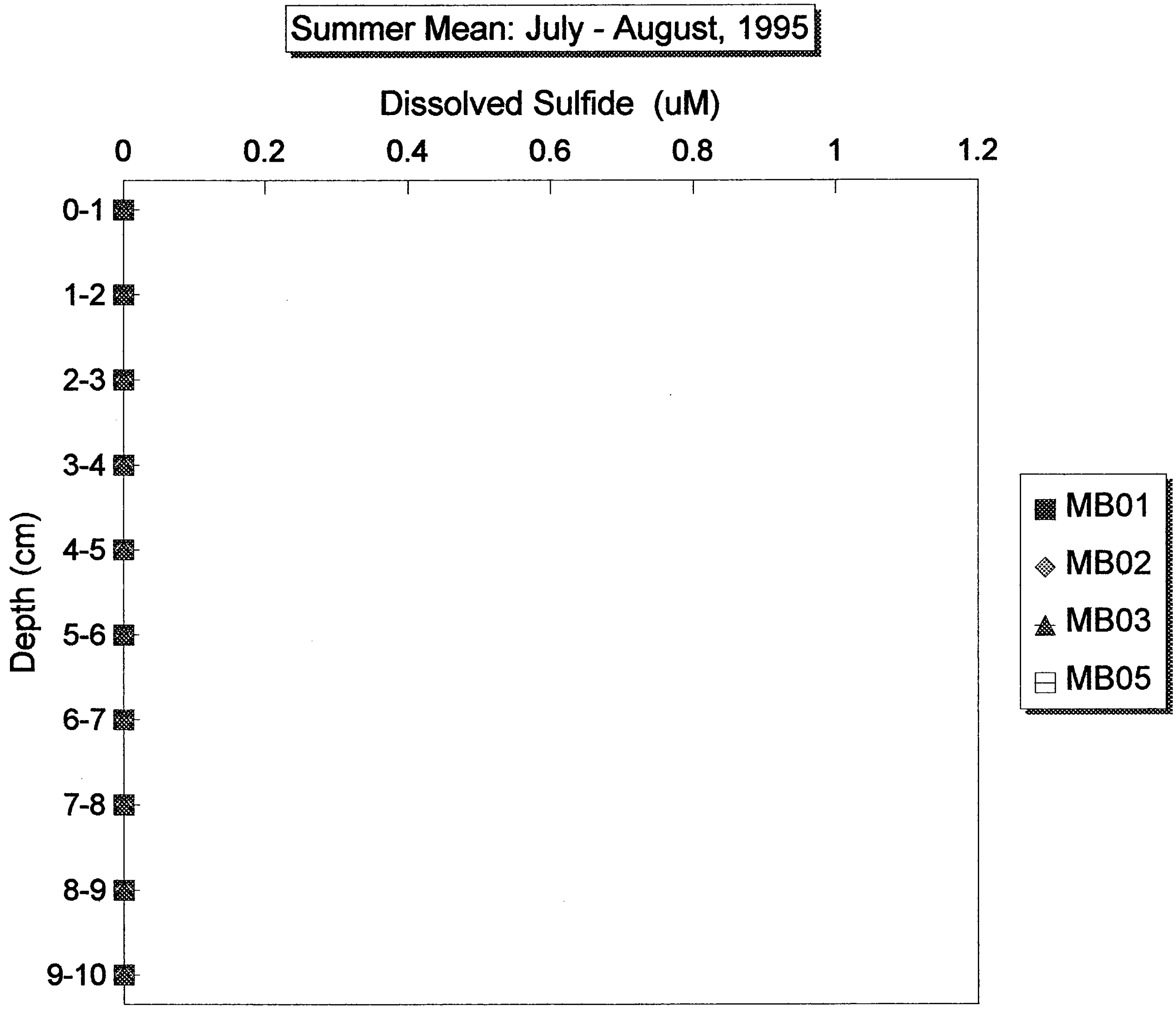
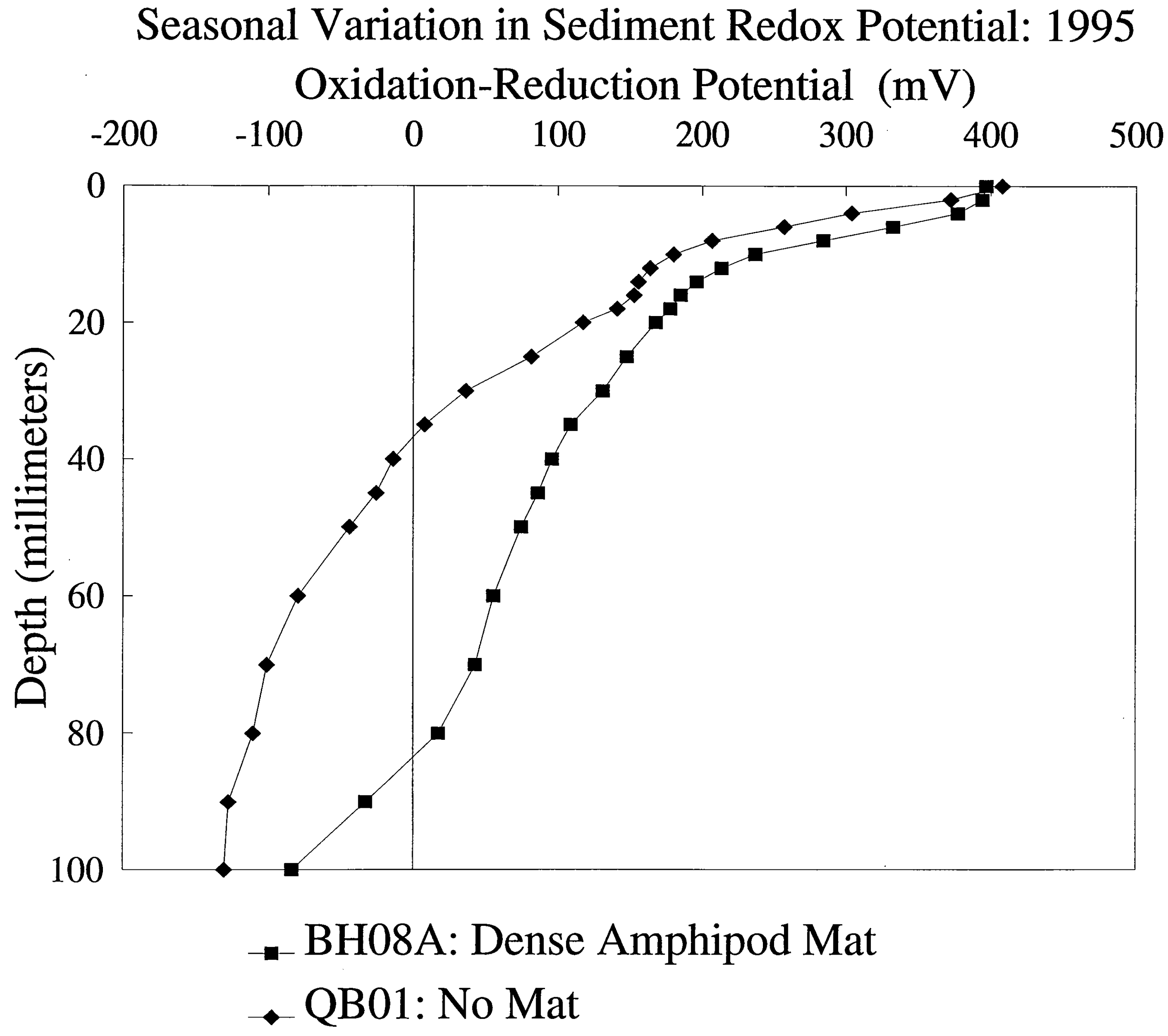


Figure 33. Profiles of dissolved sulfide in porewaters of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) sediments during summer of 1995. Sulfide was below 1 uM in all samples.



Means: July, August, October.

Figure 34. Average summer 1995 profiles of sediment oxidation-reduction potential (Eh) within sediments colonized by amphipods (BH08A) and with a relatively depauperate infaunal community (QB01). Higher values represent more oxidizing conditions. Amphipod mat is ca. 6-8 cm thick.

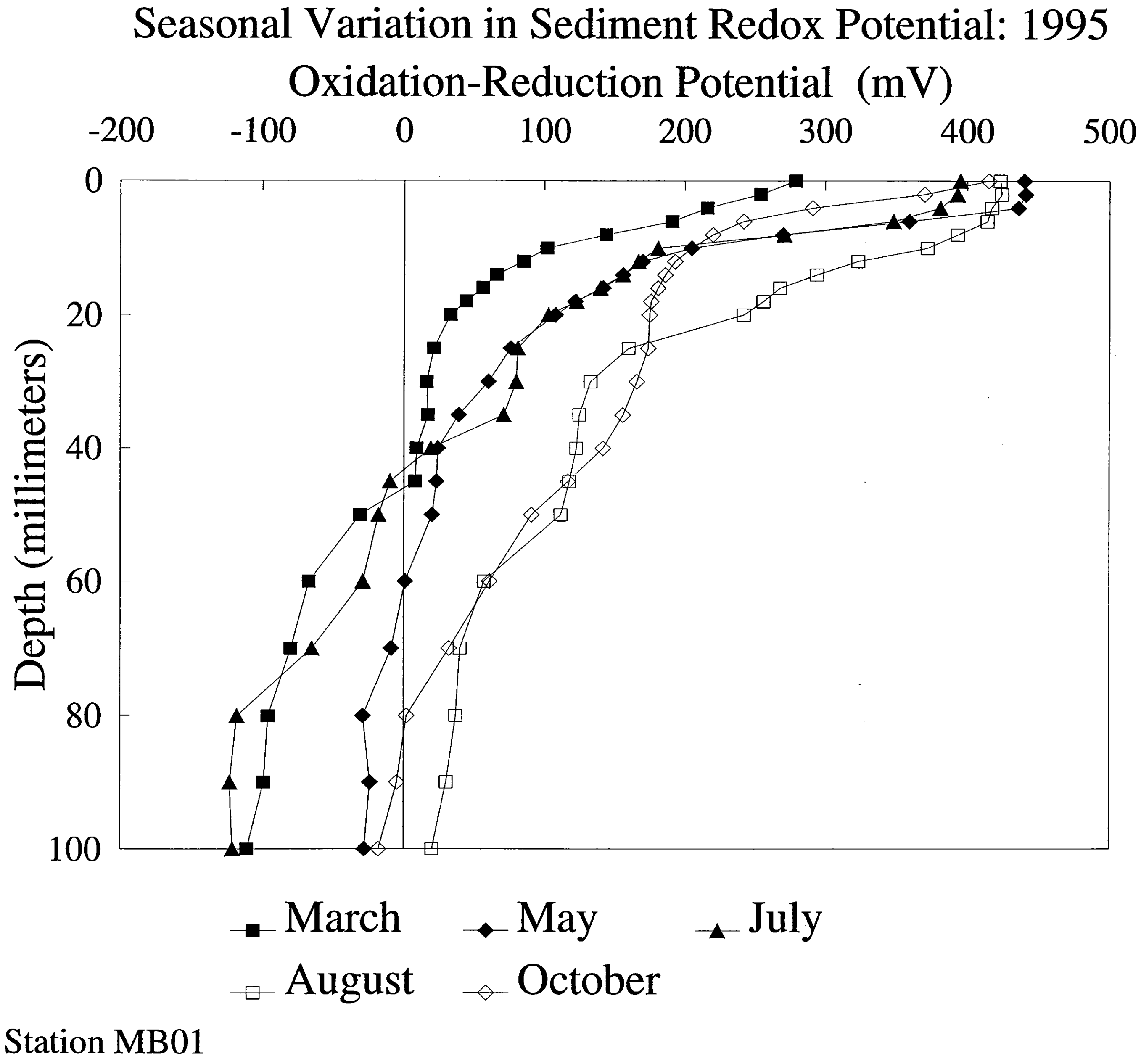
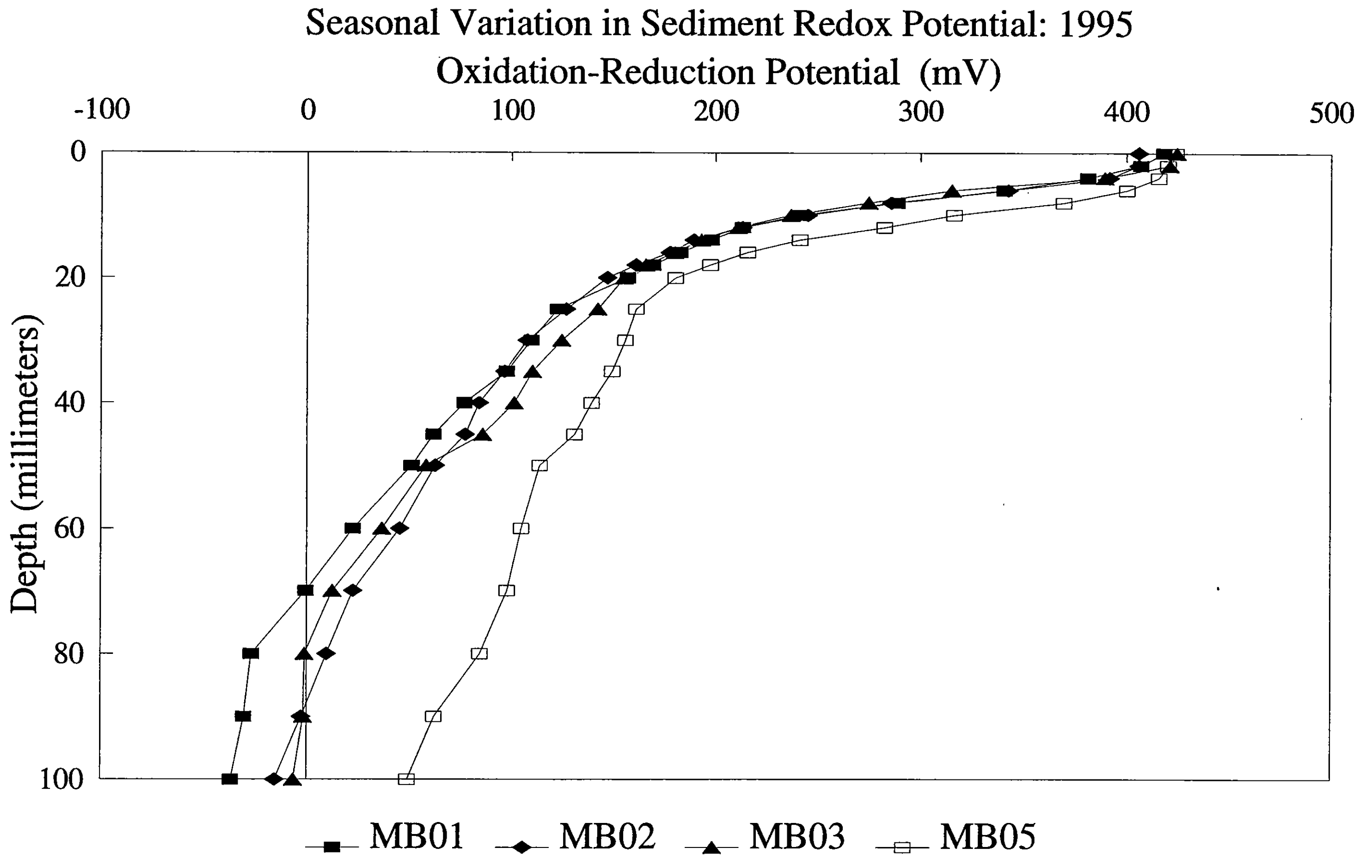


Figure 35. Profiles of sediment Eh within the sediments of western Nearfield Massachusetts Bay (MB01) in 1995. Sediment oxidation showed a seasonal cycle with most reducing conditions in March, increased oxidation in May/July, the highest degree of oxidation in August and an initiation of a return to winter conditions by October.



Means: June, July, August, October.

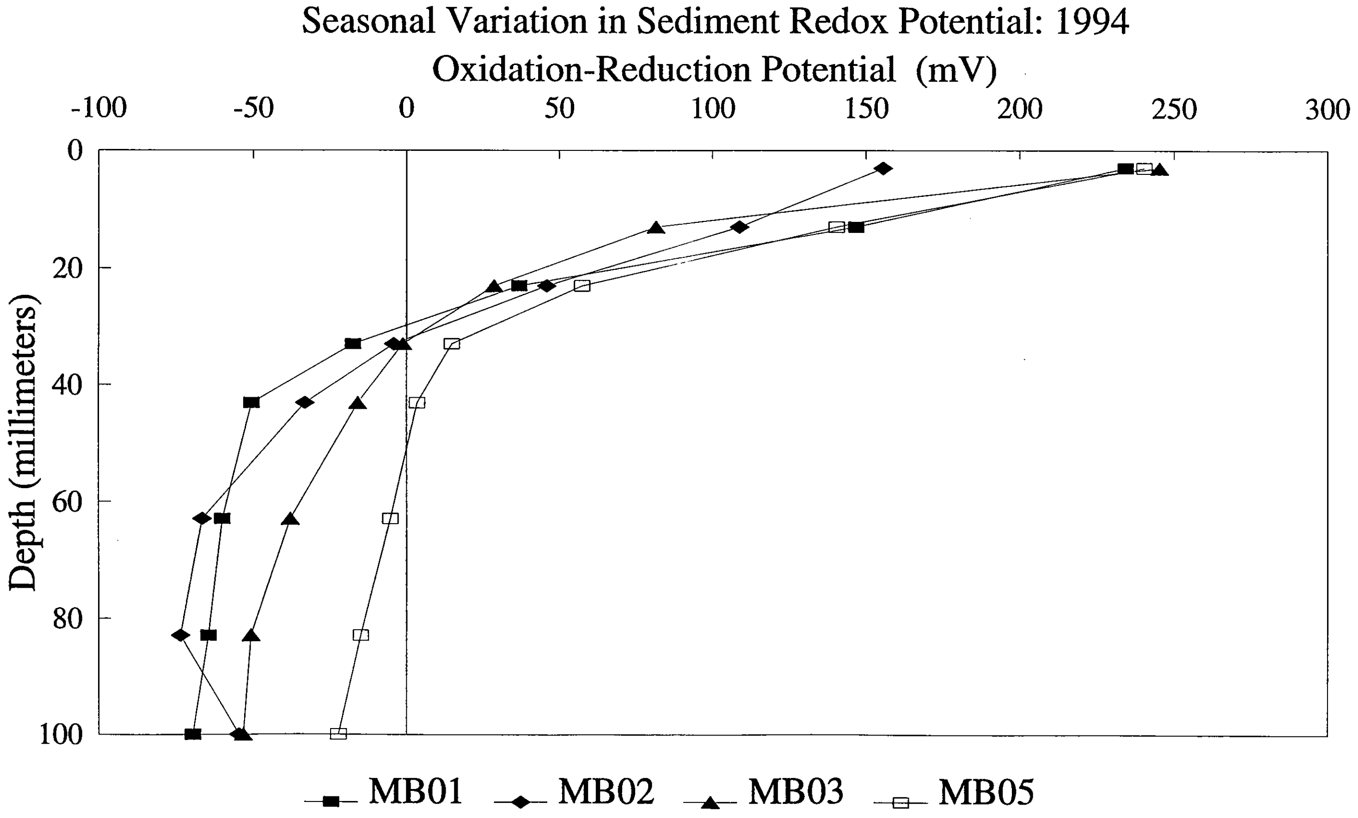


Figure 36. Profiles of sediment Eh within the sediments of western Nearfield Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) in 1995. Sediment oxidation state shows an inverse relation to measured rates of oxygen uptake, where all of the Nearfield stations which are relatively more reducing had higher rates of respiration than the more oxidizing sediments of the Basin. 1994 data are from Giblin et al. 1995.

Benthic regeneration of nutrients can play an important role in determining the nutrient conditions of the overlying water in some systems. This is especially true in the bottom waters of Massachusetts Bay where secondary modification through uptake by phytoplankton is small. Nutrient regeneration is the major source of inorganic nitrogen to Bay bottom waters during stratification. At the onset of stratification inorganic N and P levels are generally at their annual minima due to phytoplankton uptake during winter/spring blooms. During stratification the hypolimnion acts much like a large flux chamber where increases in concentrations through time are a gauge of regeneration rates. Taking this approach, the rates of overall regeneration can be compared to fluxes measured in the soft-bottom areas (Figure 25, Table 2). Using this approach for oxygen suggests that soft-bottom areas likely have only slightly higher rates of organic matter mineralization than hard-bottomed sites. Furthermore, when SOD is combined with watercolumn respiration rates the rates of bottom water oxygen decline predicted are 10%-30% greater then observed in the bottom waters during stratification. The mechanisms for this disparity result from ventilation or photosynthesis effects. Using this same analysis for inorganic N and P, it also appears that the release from hard and soft bottomed areas may be similar. In addition, when these sediment rates are combined with approximations of watercolumn regeneration, the result is a prediction of higher than observed increases in bottomwater inorganic N and P during stratification. The results for the N, P and D.O. appear to be consistent as it is likely that the mechanisms which increase oxygen in the bottom water (ventilation, mixing, photosynthesis) will tend to decrease inorganic N and P levels. However, that there are processes associated with soft versus hard bottom areas which result in different N and P release rates per unit oxygen consumed cannot be ruled out at this time. Resolving these issues is central to understanding the nutrient balance of the Bay bottom waters.

IV. Relationship of Sediment Biogeochemistry to Boston Harbor & Outfall Monitoring Results.

Given the data on sediment oxygen uptake (see above) and watercolumn respiration (Cibik *et al.* 1996) it is possible to construct an oxygen balance for regions within the Bay. This balance provides a framework for data integration which will be refined as work continues. However, at present it suggests some basic principles as to the functioning of Massachusetts Bay and Stellwagen Basin.

The objective of the oxygen balance is to determine the role of in situ respiration in the observed oxygen depletion of bottom waters during the interval of stratification. The balance requires: (1) that the bottomwater remains "in place" during the interval of stratification (ca. 140d) or that horizontal advection is of biogeochemically similar water masses that have moved over seafloor of similar metabolism, (2) the volume of water below the pycnocline, (3) the rate of watercolumn respiration below the pycnocline, (4) the rate of sediment respiration, and (5) the time course of oxygen decline below the pycnocline. It appears that during stratification the bottomwater generally has lower horizontal velocities than during the rest of the year (Geyer *et al.* 1992). The volume of water below the pycnocline can be estimated from CTD hydrocasts on the monitoring surveys. The rates of watercolumn respiration are relatively well constrained for Massachusetts Bay (17 cruises) and Stellwagen Basin (6 cruises and 5 SOD surveys). One major weakness within the bottomwater respiration dataset is the lack of information on the potential vertical distribution of watercolumn respiration within the hypolimnion. Since only near bottom samples are collected, we have to assume that they are representative of rates throughout the hypolimnion. Sediment respiration rates are also limited, primarily in the the assessment of fluxes in hard-bottom areas. In the nearfield where only about 30% of the benthos is represented by depositional sediments (Knebel 1993), it is likely an overestimate to assign the rates from the depositional sediments to the whole region. However, it is likely that the rates in the non-depositional sediments are significantly higher than previously supposed during the stratified period (Kelly and Doering 1995). Given the relatively non-turbulent nature of the bottom waters, it is highly likely that deposition of spring bloom and summer production during stratification is relatively uniform. Since most of the summer's sediment respiration is almost certainly dominated by recent deposition, the rates of oxygen consumption may be relatively uniform (2 fold range) throughout the nearfield. The deposition of marine detritus within the nearfield sediments is apparent from video sampling of the benthos (Hecker 1996). However, direct measurements of oxygen uptake during the stratified interval in non-depositional areas is currently lacking. Finally, measurements of bottom water oxygen concentrations are conducted as part of the hydrocasts. Improvements in the watercolumn program to gain more Winkler measurements of bottom water oxygen levels is currently increasing the accuracy of these measurements. Oxygen declines during the stratified interval as a result of consumption via respiration in sediments and bottom waters and the restriction of ventilation. The rates of potential hypolimnion respiration can be estimated from the rate of decline of the bottom water oxygen pool. Care must be taken in this approach to sample consistently within the same layer of the bottom waters. This is especially true within Stellwagen Basin where there appears to be a relatively steep oxygen gradient between the pycnocline and bottom. The steepness of the oxygen gradient may suggest the importance of sediment oxygen uptake to total oxygen uptake within the hypolimnion.

Table 3.

Contribution of Watercolumn and Sediment Respiration to Bottomwater Oxygen Decline in the Nearfield and Stellwagen Basin, 1995 and 1996.

Source of O_2 Uptake	Year	Rate (mg/L/d)	% Observed Decline
Nearfield: D.O. Depletion	1995	-0.027	100
	1996	-0.025	100
Watercolumn Respiration	1995	-0.016	61
	1996	-0.015	60
Sediment Respiration	1995	-0.021	78
	1996	-0.023	92
Total Respiration	1995	-0.037	139
	1996	-0.038	152
Stellwagen Basin: D.O. Depletion	1995	-0.015	100
	1996	-0.014	100
Watercolumn Respiration	1995	-0.011	73
	1996	-0.013	92
Sediment Respiration	1995	-0.004	29
	1996	-0.005	35
Total Respiration	1995	-0.015	101
	1996	-0.018	128

From the oxygen budget of the nearfield and Stellwagen Basin for the stratified interval of 1995, it is clear that in situ respiration is sufficient to account for the observed rates of oxygen depletion. This suggests that ventilation of bottom waters during stratification is likely small. The general linear decline in bottomwater oxygen levels also suggests that short-term mixing events may not cause major ventilation. However, the mid-July oxygen levels in the nearfield do show an anomaly in the linear oxygen trajectory which could be associated with the apparent July mixing event (Cibik *et al.* 1996).

The approximate oxygen balance suggests that (1) there is little ventilation of bottom waters during stratification and (2) organic matter inputs to the sediments and bottom waters to support in situ respiration are the ultimate cause of bottom water oxygen deficits. These findings when coupled with the indications that respiration is controlled by the quality and quantity of available organic matter and in situ temperature, suggest that additional inputs of labile organic matter may affect the bottom water oxygen deficit.

While in situ respiration appears to be the ultimate cause of bottomwater oxygen depletion, physical factors mediate the extent of the realized depletion. While the respiration rate appears to determine the rate of bottom water oxygen decline the extent is controlled by the oxygen field at the initiation of stratification and the duration of stratification. Due to the physical mediation, the levels of organic matter input and respiration may not be good predictors of bottom water oxygen minimum within any one year. However, if respiration rates are observed to rise then it will only be a matter of time before the proper physical conditions allow an increase in oxygen deficit.

V. Recommendations for Monitoring

1) It appears from the relative constancy of the interannual measurements of sediment oxygen uptake within Massachusetts Bay, that metabolic rate measurements within the sediments should provide a sensitive indicator of increases or decreases in organic matter loading rates. Given the apparently low quality of organic matter generally reaching the bottom a small enhancement (ca. 20%-30%) in the quality or quantity of organic matter should be detectable. Additional sediment indicators (such as Eh, nutrient regeneration, infauna etc) should also be used. However, the oxygen uptake results confirm the need for seasonal sampling, especially within Stellwagen Basin.

2) Denitrification in the sediments of Massachusetts Bay should initially focus on July-Sept interval, if no stimulation is found during the warmest months then potential alterations in rates post-discharge will probably be undetectable throughout the year.

3) Need to investigate the apparent positive feed-back whereby improving habitat quality results in increased persistence and abundance of infaunal populations and increased sediment irrigation leading to accelerated rates of organic matter and nutrient loss and removal from Harbor sediments thereby resulting in improved habitat. This latter feed-back would cause accelerated nutrient related depuration of Harbor sediments and suggests that the use of static analysis in predicting future rates of change in habitat quality may be inappropriate in the Boston Harbor system.

4) The relationship between infaunal communities and sediment metabolism and fluxes needs to be continuously monitored as the Harbor system transitions to a new steady state. It is not yet clear to what degree the enhanced rates represent depuration of stored pools which would result in a gradual decline in the rates even with a stable infaunal community.

5) Since the benthos is the major source of nutrients and sink for oxygen for the bottom waters of Massachusetts Bay, nutrient and oxygen balances require some measurement of inputs from hard- bottom areas during the stratified period. In 1995 oxygen decline and nutrient increases in bottom waters during stratification indicated that during this period fluxes from hard and soft bottom areas may be more similar than previously thought. Direct measurements of benthic flux from hard bottom areas should be conducted to resolve the importance of benthic nutrient flux to the nutrient balance of the bottom waters of Massachusetts Bay. Additional analysis of sediment fluxes with changes in integrated bottomwater nutrient masses will be performed for detailed comparison of 1994-1996 fluxes.

6) Given the variability, complexity and assumptions involved in estimating denitrification from DIC and DIN fluxes, additional methodological evaluation of the method should be performed. Part of this evaluation should be directed at explaining the high DIC to D.O. fluxes under low activity conditions within the sediments of Massachusetts Bay.

VI. Acknowledgments

This work is part of the MWRA monitoring program of Boston Harbor and Massachusetts Bay associated with improvements to wastewater handling within the Boston region. Field and laboratory assistance and data analysis was provided by D. Schlezinger, B.Hilbig, I.Williams, G.Hampson, D.Goehringer, S.Brown-leger, T.Millham, D.White and R.Hamersley. We thank J. Blake, S. Cibik, D.Rhoads, C.Taylor, K.Keay and M.Mickelson for their insights into the conduct and interpretation of this study.

VII. References

Alber, M. and a. Chan. 1994. Sources of contaminants to Boston Harbor: revised loading estimates. MWRA Environmental Quality Department Technical Report Series No. 94-1. Massachusetts Water Resources Authority, Boston, MA. 93 pp.

American Public Health Association. 1985. Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition. (A.E. Greenberg, R.R. Trussell and S. Clesceri, eds.). Published by American Public Health Association. 1268 pp.

Bagander, L.E. and L. Niemisto. 1978. An evaluation of the use of redox measurements for characterizing recent sediments. Estuarine Coastal Marine Science. 6: 127-134.

Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in sea water. Journal Marine Research 11:87-96.

Blake, J.A., D.C. Rhoads and I.P. Williams. 1993. Soft-Bottom benthic biology and sedimentology 1991-1992 monitoring surveys. MWRA Environmental Quality Department Tech. Rept. no. 93-11.

Blake, J.A., B. Hilbig, I.P. Williams and D.C. Rhoads. 1996. Annual Harbor Monitoring Synthesis Report: Soft-Bottom Benthic Monitoring: 1995-1997. MWRA Environmental Quality Department Tech. Rept. 96-Draft.

Cibik, S.J. and B.L. Howes. 1995. Combined work/quality assurance project plan for benthic nutrient flux study: 1995-1997. MWRA Environmental Quality Department Misc. Rept. ms-36.

Cibik, S.J., B.L. Howes, C.D. Taylor, D.M. Anderson, C.S. Davis, T.C. Loder and J. Bowen. 1996.

1995 Annual Watercolumn Monitoring Report. MWRA Environmental Quality Department Technical Report Series, No. 96-X. Massachusetts Water Resources Authority, Boston, MA.

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

Giblin, A.G., J. Tucker, and C. Hopkinson. 1993. Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments. MWRA Environmental Quality Department Technical Report Series, No. 93-2. Massachusetts Water Resources Authority, Boston, MA. 46 pp.

Giblin, A.G., J. Tucker, and C. Hopkinson. In Press. Benthic metabolism and nutrient cycling in Boston Harbor, MA, USA. Estuaries.

Giblin, A.G., C. Hopkinson, J. Tucker, B. Nowicki, and J.R. Kelly. 1994. Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay sediments in 1993. MWRA Environmental Quality Department Technical Report Series, No. 94-5. Massachusetts Water Resources Authority, Boston, MA. 53 pp.

Giblin, A.E. C. Hopkinson, J. Tucker, B. Nowicki, and J.R. Kelly. 1995. Metabolism, nutrient cycling and denitrification in Boston Harbor and Massachusetts Bay Sediments in 1994. MWRA Environmental Quality Department Tech. Rept. no. 95-13.

Hargrave, B. 1973. Coupling carbon flow through some pelagic and benthic communities. Journal Fisheries Research Board of Canada 30:1317-1326.

Henriksen, K., T.H. Blackburn, B.A. Lomstein and C.P. McRoy. 1993. Rates of nitrification, distribution of nitrifying bacteria and inorganic N fluxes in northern Bering-Chukchi shelf sediments. Continental Shelf Research, 13:629-651.

Howes, B.L., J.W. Dacey and J.M. Teal. 1985. Annual carbon mineralization and belowground production of *Spartina alterniflora* in a New England salt marsh. Ecology 66:595-605.

Jorgensen, B.B. 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnology Oceanography, 22:814-832.

Jorgensen, B.B. 1982. Mineralization of organic matter in the sea bed: the role of sulfate reduction. Nature 296:643-645.

Kelly, J.R. In Press. Nitrogen flow and the interaction of Boston Harbor with Massachusetts Bay. Estuaries.

Kelly, J.R. and P.H. Doering. 1995. Nutrient Issues Update 1995: Metabolism in Boston Harbor, Massachusetts Bay, and Cape Cod Bay, MA (USA) during 1992-1994. MWRA Environ. Quality Dept. Tech. Rpt. Series No 95-19. MWRA, Boston MA 38 pp.

Kelly, J.R., A.G. Giblin, J. Tucker, and B.L. Nowicki. 1993. Combined Work/Quality Assurance Project Plan (CW/QAPP) for Benthic Nutrient Flux Studies: 1993-1994. March 26, 1993.

Kelly, J.R. and B.L. Nowicki. 1993. Direct measurements of denitrification in Boston Harbor. MWRA Environmental Quality Department Technical Report Series, No. 93-3. Massachusetts Water Resources Authority, Boston, MA. 39 pp.

Klump, J. & C. Martens. 1983. Benthic nitrogen regeneration. In: Nitrogen in the Marine Environment, (Carpenter & Capone, eds.). Academic Press.

Knebel, H.J. 1993. Sedimentary envrionments within a glaciated estuarine-inner shelf syustem: Boston Harbor and Massachusetts Bay. Marine Geology 110:7-30.

Krom, M.D. and R.A. Berner. 1980. Adsorption of phosphate in anoxic marine sediments. Limnology and Oceanography, 25:797-806.

Kropp, R.K. and R.J. Diaz. 1995. Infaunal community changes in Boston Harbor, 1991-1994. MWRA Environmental Quality Department Tech. Rept. no. 95-21.

Jorgensen, B.B. 1982. Mineralization of organic matter in the sea bed: the role of sulphate reduction. Nature 296:643-645.

Murphy, J., J.P. Reilley. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica chemica Acta 27:31-36.

NOAA. 1993. Comprehensive descriptions of complementary measurements. Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects, 1984 - 1992 (Volume II). NOAA Technical Memorandum NOS/ORCA/CMBAD 71.

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. In Press. Nitrogen losses through sediment denitrification in Boaston Harbor and Massachusetts Bay. Estuaries.

Parsons, T.R., Y. Maita and C. Lalli. 1989. Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, 173 pp.

Pelegri, S.P., L.P. Nielsen and T.H. Blackburn. 1994. Denitrification in estuarine sediment stimulated by the irrigation activity of the amphipod *Corophium volutator*. Marine Ecology Progress Series, 105:285-290.

Revsbech, P.N., J. Sorensen, T.H. Blackburn, and J.P. Lomholt. 1980. Distribution of oxygen in marine sediments measured wiht microelectrodes. Limnol. Oceanogr. 25:403-411.

Redfield, A.C., B.H. Ketchum and F.A. Richards. 1963. The influence of organisms on the composition of seawater, pp. 26-77. In M.N. Hill [ed.], The Sea: Volume 2, The Composition of Sea Water, Interscience Publishers, John Wiley, N.Y.

Rhoads, D.C. and J.D. Germano. Interpreting long-term changes in benthic community structure: A new protocol. Hydrobiology 142:291-308.

Scheiner, D. 1976. Determination of ammonia and Kjeldahl nitrogen by indophenol method. Water Resources 10: 31-36.

Seitzinger, S.S. Nixon, M.E.Q. Pilson and S. Burke. 1980. Denitrification and N_2O production in near-shore marine sediments. Geochim. Cosmochim. Acta 44:1853-1860.

Seitzinger, S.S. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnology and Oceanography, 33:702-724.

Signell, R.P. and B. Butman. 1992. Modeling tidal exchange and dispersion in Bston Harbor. Journal of Geophysical Research, 97:15591-15606.

United States Environmental Protection Agency. 1984. Guidance for preparation of combined work/quality assurance project plans for environmental monitoring. Report OWRS QA-1. Office of Water Regulations and Standards, U.S. Environmental Protection Agency, Washington, DC.

United States Environmental Protection Agency. 1988. Guidance for preparation of quality assurance project plans for the National Estuarine Program. Report prepared by Battelle Ocean Sciences of U.S. Environmental Protection Agency Region 1, Contract No. 68-03-3319, Washington, D.C. EPA 556/2-88-001.

Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.

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