

Sediment metabolism within
Massachusetts Bay and Boston Harbor
relating to rates and controls of
sediment-water column exchanges of
nutrients and oxygen in 1997

Massachusetts Water Resources Authority

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**Sediment Metabolism within Massachusetts Bay and Boston Harbor
Relating to Rates and Controls of Sediment-Water Column Exchanges
of Nutrients and Oxygen in 1997**

for:

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EXECUTIVE SUMMARY

Sediment Metabolism within Massachusetts Bay and Boston Harbor Relating to Rates and Controls of Sediment-Water Column Exchanges of Nutrients and Oxygen in 1997

1997 Overview: Rates of sediment oxygen uptake were measured along the organic matter gradient from Boston's Inner Harbor to Stellwagen Basin. These data were coupled with seasonal measurements of water column-sediment exchanges of nutrients, sediment oxidation, and porewater chemistry. In addition, parallel measurements of denitrification were conducted at two stations within Boston Harbor (high versus low infaunal density). The most notable findings resulting from the 1997 surveys are summarized as follows:

(A) Sediment and water column respiration rates in Massachusetts Bay were higher than in previous years. The increase is likely associated with a series of phytoplankton blooms during spring and early in the stratified interval.

(B) Colonization of sediments of Boston Harbor results in large and significant increases in the rates of carbon and nutrient cycling. Rates of SOD, denitrification and exchanges of dissolved inorganic nutrients all show 2-10 fold increases in spatial comparisons of mat colonized versus uncolonized areas (1995-1997); in intra-annual comparisons during periods when mats are active versus senescent; and in inter-annual comparisons where mats are present one year but absent in subsequent years (BH02, 1995 versus 1996-97).

© Significant areas of Boston Harbor sediments appear to have been mined of stored oxidizable substrates and nutrients over the past 3 years of amphipod colonization.

(D) Infaunal recolonization of Harbor sediments appears to result in shifts in the ratio of key phytoplankton nutrient fluxes from sediments to overlying waters. In contrast to pre-colonization measurement and Massachusetts Bay, colonized areas showed an increase in ratio of N and P fluxes, from ≤ 16 to ≥ 16 . The 1995-1997 fluxes also contrasted with the $[N]/[P] \ll 16$ in Harbor waters.

(E) Bio-irrigation of Harbor sediments results in increased sediment oxidation status. The result is a shift in the form of inorganic nitrogen efflux from ammonium to nitrate and decrease orthophosphate fluxes due to increased retention by sediments. Sediment oxidation also likely supports the higher rates of nitrification-denitrification in highly bio-irrigated sediments.

(F) Bay and Harbor sediments have very different patterns of silicate/DIN flux to the water column. Bay sediments show a consistent and high release of silicate relative to DIN ($Si/N=10$), compared to the more variable and lower ratio of Si/DON in the Harbor, 0.5-2.

(G) Phytoplankton appear to be major contributors of oxidizable organic matter to sediments driving sediment oxygen uptake in both Massachusetts Bay and Boston Harbor. At lower levels of sediment chlorophyll a, sediment respiration rates were directly related to the chlorophyll a pool. At higher SOD levels, other factors appear to be more important than chlorophyll a in determining rates (bio-irrigation, sediment mining).

(H) Sediment metabolism appears to be a good indicator of perturbation. In Massachusetts Bay sites under current conditions, inter-annual variability is generally <20% with departures explainable by observed shifts in carbon availability. In contrast, in Boston Harbor sediment biogeochemical cycling suggests a system undergoing rapid and large changes.

Boston Harbor: Monitoring of sediment carbon and nutrient cycling is currently providing sensitive indicators of changing ecological health of Boston Harbor. Results from studies of the sediment-infauna complex within the Harbor provide an example of a non-linear response to changes in organic matter loading rates and the need for direct measurements.

During 1997, sediment/water column exchanges of nutrients continued to show the effects of the colonization by amphipods. It is clear that the presence or absence of amphipod mats is the predominant feature structuring biogeochemical fluxes and in situ metabolic rates in this system. Dissolved inorganic nitrogen fluxes are predominantly as ammonium in non-amphipod areas and as nitrate in amphipod areas. The Massachusetts Bay sites have lower rates of DIN efflux than the Harbor, but show a fractionation similar to the amphipod sites.

Boston Harbor sediments clearly show higher rates of DIN efflux, SOD and denitrification in amphipod colonized areas. At site BHO3A, rates of DIN efflux and SOD have declined from year 1 to years 2 & 3, while denitrification has increased. This is consistent with the development of a more aerated sediment in which the "mining" of stored organic matter is declining in importance. The flux ratios support the contention that in 1995 significant mining of stored organic matter from previous years was occurring, while 1996-97 data indicate a system more reliant on recent deposition.

Concurrent with the changing rates of diagenesis has been rapid colonization of Harbor sediments by infauna, particularly the establishment of dense amphipod mats (*Ampelisca* and *Leptocheirus*). *Ampelisca* are relatively pollution tolerant amphipods which generally operate as deposit feeders and are capable of building mats, several centimeters thick supporting populations of over 100,000 individuals m⁻². 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 be temporally variable in response to seasonal cycles and episodic events, the amphipod mats appear to be more persistent from year to year (1989-1997). In addition, while the species composition of the mats appears to be shifting, the functional role of the mats on carbon and nutrient cycling appears to be continuing. The expanded distribution and reduction of inter-annual 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 > Hull Bay > North Harbor) compared to areas with lower total infaunal densities (Quincy Bay). 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. The influence of the infaunal community upon organic matter turnover is seen in the two to five fold higher rates of oxygen uptake at similar temperatures during periods when the amphipod mat was active versus senescent (1995: BH03A and BH02) or where mats were present one year but absent the next (BH02, 1995 versus 1996-97). The data clearly support the contention that it is the biogeochemical activity and bio-irrigation associated with the mats which is responsible for the observed increases in sediment metabolism and water column-sediment exchanges within the Harbor.

Similarly, inter-annual comparisons showed large increases in measured rates of sediment oxygen uptake and denitrification in Boston Harbor (1992-1997). In contrast to 1995-1997, the amphipod mat community was not widespread within the Harbor in earlier years and mats were not consistently sampled. In all cases data from 1992-1994 (SOD: Giblin et al. 1995; denitrification: Nowicki et al. 1997) showed significantly lower rates than those of mat areas sampled in 1995-1997, except in the few cases where amphipod mats were noted. Inter-annual comparisons at the more stable Massachusetts Bay stations yielded similar rates of biogeochemical cycling in all years. It appears that with the dense colonization of Harbor sediments, rates of carbon mineralization and denitrification within Boston Harbor are both typically more than two fold higher than rates where amphipod mats have not formed. In earlier years, these non-mat conditions were predominant throughout the Harbor. The extent to which the higher rates were the result of "mining" of sediment deposits versus increased trapping of water column particles requires further study. However, rates of denitrification and community metabolism declined and sediment oxidation began to increase in 1996 and 1997 suggesting that the labile organic matter pool of the sediments may be declining under continued bioturbation.

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 dynamics within the Harbor and transport to Massachusetts Bay may be very dynamic under changing environmental quality. The temporal nature of these biological mediating effects and their potential role in accelerating nutrient removal from the Harbor will be elucidated by the continued monitoring of this system.

Massachusetts Bay: Analysis of sediment properties and exchanges with the water column during the 1997 field season indicated some departures from previous years (1992-1996). Most notably, 1997 rates of sediment oxygen demand (SOD) at stations MB03 and MB05 were significantly higher than the previous years, which all showed variations of less than $\pm 20\%$ of the mean summer values for each station. It is likely that the large spring *Phaeocystis* and *Chaetoceros* blooms are the source of organic matter supporting the higher sediment metabolism in 1997. Evidence from the HOM water column sampling program suggests that *Phaeocystis* derived carbon was reaching the bottom by direct sinking and through grazing, while the *Chaetoceros* bloom occurred at mid-depth facilitating its deposition (Cibik et al. In prep.). The higher sediment chlorophyll levels in the Nearfield measured during stratification are consistent with the deposition of a bloom. Although SOD represents about half of the sub-pycnocline oxygen demand during stratification, the higher rates did not result in a lower D.O. minimum, due to the large physically driven "reaeration" event in mid summer. In contrast, in both 1995 and 1996 the combination of measured oxygen consumption in sediments and water column during the stratified period were only slightly higher than the observed rate of oxygen depletion within the hypolimnion. These data suggest that ventilation of bottom waters during stratification can also be small. It appears that episodic oxygenation of the bottom waters likely explains the lower oxygen depletion compared to that predicted from the integrated of community metabolism. It is likely that at "worst case" baseline oxygen depletion would consist of 1997 respiration rates and 1995 reaeration.

Spatial sampling from 1995-1997 showed a consistent trend with rates of sediment oxygen uptake varying several fold throughout each year at both the nearfield and Stellwagen Basin stations. Rates of metabolism show a gradient from Boston Harbor > nearfield > Stellwagen Basin. The annual variation in organic mineralization rates resulted from the ca. 10°C seasonal temperature cycle and variations in organic matter lability and delivery to the sediments. Measured rates of sediment metabolism appears to track both the seasonal pattern of chlorophyll a concentrations within the surficial sediments and environmental temperature. Chlorophyll a serves as an indicator of the temporal and spatial distribution of deposition of “fresh” phytoplankton. Comparison of the SOD and chlorophyll a data suggests that deposition from the spring bloom fuels sediment carbon turnover during stratification, but that the system may become limited by availability of labile organic matter by late summer.

Analysis of HOM respiration data suggests that the annual oxygen minimum is driven primarily by the spring bloom organic carbon deposition and physical processes controlling stratification and aeration and to a lesser extent organic input from the fall bloom. Sediment respiration rates indicate that only 30-40 g C m⁻² of organic matter deposition is required to support the observed SOD during stratification. Data from the USGS moored sediment traps during the stratified interval, although subject to resuspension artifacts, indicate that organic deposition during stratification is much lower than that required to support SOD during this interval.

Rates of sediment oxygen uptake at the long-term monitoring sites generally show a low level of inter-annual variation (<20%) with divergences from the baseline associated with defined events. The sediments at all stations were relatively oxidized with undetectable dissolved sulfide within the porewaters (0-10cm). This is consistent with the low organic matter delivery rates and the established bioturbating infaunal community at these sites. The inter-annual stability of these integrative, process level measures indicates that they will be a sensitive tool for detecting 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. The carbon budget for the Nearfield, based upon measures of carbon production and decomposition within Bay waters and sediments, suggests that organic matter cycling 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.

Although total system organic matter remineralization is dominated by respiration in the upper water column, bottom water oxygen depletion during stratification is driven by sub-pycnocline water column respiration and sediment oxygen uptake. During stratification both of these processes appear to be organic matter limited indicating that the input of additional labile organic matter without coupled oxygenation may potentially enhance oxygen depletion. An analysis of the effect of CBOD in future effluent discharged below the pycnocline indicates that even at 200 fold dilution, the potential enhancement of oxygen depletion is on the order of 2-5% over current “natural” levels. This indicates that unless there is recycling of bottom water as dilution water (long residence time) or settling of CBOD to sediments, enhanced oxygen depletion due to direct CBOD discharge will be difficult to detect.

Nutrient regeneration and release to overlying waters of Massachusetts Bay was similar to Boston Harbor in that DIN release was less than regeneration suggesting active denitrification. However, the

rates within the Bay were more than an order of magnitude lower than within the Harbor. In contrast, the composition of nutrient release differed between the sub-systems. Bay sediments supported DIN to ortho-phosphate fluxes at or well below the Redfield Ratio (N/P=16), while Harbor sediments were typically at or above a N/P of 16. This possibly results from the different benthic communities between the locations and that Harbor sediment biogeochemical cycling may not yet be at steady state. A more dramatic difference can be seen in the ratio of silicate to DIN (Si/N), with the Bay showing flux ratios of ≥ 10 , while Harbor Si/N exchanges were much lower and more variable.

A complete oxygen and nutrient balance will require evaluation of sediment metabolism from non-depositional areas, since current information is only from depositional areas. However, given the similarity in observed hypolimnion oxygen depletion and predictions based upon system-wide SOD equivalent to that of the depositional areas, it appears that at least during stratification that the non-depositional sites support metabolic rates similar to the depositional sites.

Evaluation of Eh as a monitoring tool indicates a high degree of inter-annual comparability. However, intra-annual analysis indicates that this indicator must be applied with caution, since there is a large seasonal cycle in sediment redox potential which follows the cycle of sediment respiration.

I. Introduction

The overall objective of the Benthic Nutrient Flux Study is to quantify the seasonal exchange of key nutrients and oxygen between the sediments and their overlying waters within Boston Harbor and Massachusetts Bay in the vicinity of the Massachusetts Water Resources Authority (MWRA) future effluent outfall. These fluxes and their associated biogeochemical pools relate directly to total annual carbon, nutrient and oxygen dynamics and the nutrient related ecological health of shallow marine ecosystems. These benthic flux measurements also provide necessary input to integrative carbon and oxygen models (Gerath et al. In preparation) and may provide sensitive indicators of shifts in the rate of organic matter input deposition.

The magnitude of the major sediment-water column biogeochemical exchanges are influenced by many environmental factors including temperature and availability of labile organic carbon. However, the source of available organic matter (effluent, runoff, phytoplankton), although important for resource management, is less important to sediment biogeochemical cycling than the mass amount and timing of deposition. Degradation of organic matter deposited to the Bay and Harbor sediments is partitioned between aerobic and anaerobic pathways. Short-term storage of reduced end-products of anaerobic respiration dampens the range of the seasonal excursion in surface oxygen consumption rates, however, integration of seasonal measures provides an evaluation of annual organic matter deposition. Both positive (eg. denitrification) and negative (eg. sulfide accumulation) effects of this partitioning are also gauged as they influence the role of the sediments within whole ecosystem and their quality as infaunal habitat. The purpose of continued monitoring is to determine changes in sediment organic matter and nutrient cycling and potential secondary effects on the Harbor and Bay environments related to the relocation of effluent discharges.

The organic rich nature and relatively shallow waters of coastal systems like Boston Harbor and Western Massachusetts Bay result in 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 water column heterotrophic processes (Hargrave 1975). In addition, in Boston Harbor external organic matter loading (Alber and Chan 1994) and in situ production are significantly higher than to the Bay (Kelly 1997, 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, Howes 1998a,b). However, given the stratification of Bay waters, sediment metabolism still plays a major role in bottom water oxygen decline, an ecosystem structuring parameter (Cibik *et al.* 1996, Gerath In preparation).

Rates of organic matter remineralization and nutrient regeneration within the Harbor and Bay sediment systems are ultimately controlled by the organic matter input. 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 (Aller 1988, Hylleberg and Henriksen 1980, Kristensen 1985). Infauna influence sediment-water column 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 not fully understood and is likely system specific. However, it is clear that sediments with "high" organic matter deposition rates tend to be more reducing (potentially containing free sulfide), have high inorganic nutrient regeneration and oxygen uptake rates and limited burrow penetration. In contrast, areas with "low" deposition rates have a higher oxidation status (no free sulfide), low inorganic regeneration (with fluxes dominated by oxidized forms) and oxygen uptake rates, and tend to support larger deeper burrowing infaunal forms.

Another major role of sediment metabolism in coastal systems is as a site for microbial denitrification (Seitzinger 1988, Nowicki *et al.* 1997). Due to the delivery 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 (Revsbech *et al.* 1980, Hulth *et al.* 1994). The result is that unlike the water column 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 shallow marine 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 the organic matter and nutrient depuration rates of coastal sediments 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 HOM 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 and the estimation of annual rates. Cores are collected for oxygen and nutrient flux, with separate parallel cores collected for N₂-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 (a) the MWRA's Soft-Bottom Benthic Monitoring Study of Boston Harbor and Massachusetts Bay in order to integrate biogeochemical processes with infaunal community structure and (b) the MWRA's Water Column Monitoring of Massachusetts Bay which allows for evaluation of the role of the sediments in annual oxygen depletion and system carbon and nutrient cycling.

This report details the results of the 1997 benthic flux program. In addition to presenting the 1997

results, comparisons will be made to previous data 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 (Howes 1998a), 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 to assess the sensitivity of benthic processes as indicators of change. Linkages between water column and sediment respiration in Massachusetts Bay relating to (1) carbon balance in the nearfield and (2) controls on Bay bottom water oxygen levels during stratification are presented elsewhere (Cibik *et al.* 1996, In preparation, Gerath *et al.* In preparation).

Objectives: The primary objective of monitoring benthic metabolism in Boston Harbor, Massachusetts Bay and Stellwagen Basin sediments is to detect inter-annual changes in rates of sediment oxygen uptake, nutrient fluxes from sediments, porewater nutrients, and related parameters which are controlled by the rates of organic matter delivery or lability. In addition, factors which affect or are affected by infaunal communities, such as sediment oxidation status, are monitored. Both the removal or introduction of treated effluent discharge interact with natural biogeochemical cycles either through direct organic matter input or indirectly by stimulating organic matter production. The potential role of effluent discharges in CNO cycling in coastal systems can best be evaluated in relation to the magnitude of the natural organic matter cycle. The goal of the HOM Benthic Flux Program is four-fold: (1) to construct (with other monitoring data) an oxygen balance each year which will allow forecasting of oxygen minima and indicate the "cause" of variations in the annual oxygen depletion and rate of oxygen decline; (2) to determine the controls on system metabolism and sediment-water-column oxygen and nutrient exchanges and how they might be influenced by effluent relocation; (3) to detect changes in the sediments relating to organic matter loading (oxygen and nutrient fluxes and sediment oxidation); and (4) to support predictions of future ecological changes under altered rates of primary production, ventilation or direct organic matter inputs.

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 and four surveys, respectively, in 1997. Three sampling events focussed on periods of higher microbial activity: (1) after the deposition of the spring bloom and after onset of stratification, May/June and (2 & 3) during the warmest months of peak activity, July and August. There was a single low temperature sampling in March. There was an additional sampling in Boston Harbor in the fall as the amphipod mats began to senesce in October. In 1995 and 1996 both Bay and Harbor stations were sampled at the 1997 Harbor sampling interval. Locations of the 8 sites sampled during 1995-1997 are shown in Figure 1 with co-ordinates in Table 1.

TABLE 1
Locations for Long-Term Monitoring of Benthic Flux

Station I.D.	Depth (m)	Latitude	Longitude
BH08A	9.5	42°17.46'N	70°55.33'W
BH03A	6.7	42°19.70'N	70°58.05'W
BH08	11.9	42°17.18'N	70°54.68'W
BH03	4.9	42°19.79'N	70°57.69'W
BH02	6.1	42°20.62'N	71°00.13'W
MB05	75.6	42°25.01'N	70°39.26'W
MB01	34.7	42°24.16'N	70°50.20'W
MB02	35.4	42°23.54'N	70°50.02'W
MB03	34.1	42°20.87'N	70°48.90'W
QB01	3.05	42°17.614'N	70°59.274'W
Notes: 1. Stations followed by "A" are near historic stations with the same numerical prefix. BH03 & BH08 were only sampled in March Survey of 1995. 2. Station MB02 was not sampled in 1997. 3. Station QB01 was sampled by HOM in 1995 & 1997 and by CMAST-UMass in 1996.			

Sites, MB01 and MB03 are in depositional areas in western Massachusetts Bay within the Nearfield grid sampled by the high-frequency watercolumn monitoring program. Station MB02, not sampled in 1997, but frequently included in inter-annual comparisons is similarly situated. The relocated outfall

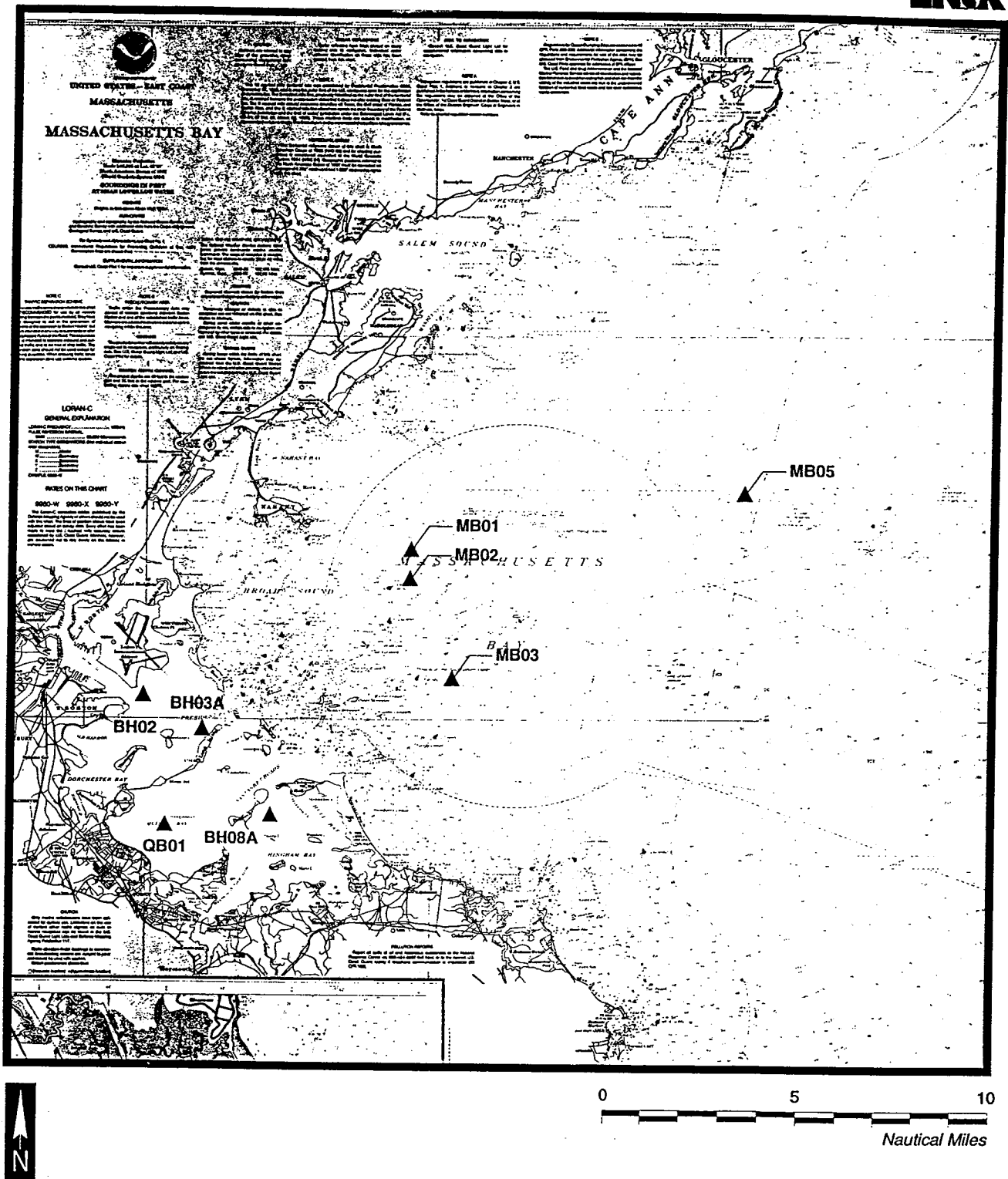


Figure 1. Locations for annual sampling of benthic flux and associated sediment assays 1995-1997. Station MB02 was not sampled in 1997.

is within a few km of these sites. MB05 is in the deeper waters of Stellwagen Basin and is also linked to the watercolumn surveys (Station F19). The historic station BH03, which was sited on a steep slope, was relocated a short distance in 1995 to BH03A which was selected due to its similar infauna and sediment characteristics to BH03. BH08 was similarly relocated to BH08A, which had sediments of a finer grain-size. The original stations, BH03 and BH08, were sampled only during the March 1995 Survey. A separate reference 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 throughout 1995-1997. QB01 was sampled by the HOM program in 1995, and by the Center for Marine Science and Technology at University of Massachusetts as part of a research initiative in 1996 & 1997. Data is included in this report to allow comparisons with amphipod mat areas. Vessel positioning was by Northstar 941XD differential Global Positioning System (GPS) with an accuracy of 10 meters.

Sediment cores were collected by SCUBA divers within the Harbor and by box core sampler (40 x 40 x 50 cm) within the Bay. Cores were maintained from collection through incubation at *in situ* temperatures. On board ship, temperature control was 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 solid phase analysis (two 6.5 cm id) were processed at a field laboratory within 0.1 mile of the ship dockage, 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 N₂-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 and temperature and salinity by electrode. Twenty liters of bottom water were collected and filtered (0.45 µm) to replace the headspace water of the flux cores prior to incubation.

Sediment Incubations:

Sediment-watercolumn exchange and porewater measurements follow the methods of Jorgensen (1977), Klump and Martens (1983), and Giblin *et al.* (1995) for nutrients and metabolism, and the with a modification of the method of Nowicki *et al.* (1997) for denitrification measurements. Cores were maintained in the dark within 2°C of the *in situ* temperature.

Benthic flux: Upon return to the field laboratory the four 15 cm (id) cores per station were transferred to pre-equilibrated temperature baths. The headspace water overlying the sediment 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 the initial 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 (a) 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 and (b) modeling of gas exchange rates in denitrification assays (Hamersley and Howes, In preparation). Argon was measured at the end of each incubation and the ratio of N₂ to argon used to assess the total mass of denitrified nitrogen associated with the core. This calculation uses argon as a tracer for N₂ whose source was the atmosphere versus denitrification. N₂, O₂ and argon were measured by gas chromatography 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: Two 6.5 cm cores were collected from each location, one for analysis of TOC and porosity and the second 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. Sub-samples 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 cm³) of whole sediment from the chlorophyll core were collected from 1-cm sections from the surface to 5-cm depth and from the 5-10 cm section. Sediments 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 was 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. Typically, annual oxygen uptake is slightly less than annual organic matter deposition due to the inclusion of a small fraction of refractory forms which contribute to sediment accretion and due to the storage of reduced end-products from anaerobic processes. However, in systems which are in steady-state, annual oxygen uptake generally approximates total organic matter decomposition and deposition. In contrast, sediment systems which are not in steady state (i.e. perturbed) may show higher or lower rates of oxygen uptake than organic deposition depending upon whether they are experiencing declining or increasing nutrient or organic matter loading, respectively. In addition, shifts in infaunal communities between shallow and deep burrowing forms may also result in short-term increases or decreases in the storage of reduced chemical forms within the deeper sediments.

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, Hulth *et al.* 1994). 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). Generally, imbalances in the rate of sulfide input and loss through oxidation result in a build-up of sulfides during the summer and a net oxidation during the colder winter months. However, during these periods the concentration of dissolved sulfide typically remains low due to binding to sediment iron minerals. Increases or decreases in dissolved sulfide levels within the sediments of the Harbor or Bay are indicative of shifts in the level of organic matter deposition (i.e. sulfate reduction) or the rate of oxygen input (i.e. relating to oxygen concentration in overlying water, direct diffusional effects, changes in bioirrigation rates).

In most systems, since 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). It should be noted that the DIC/SOD ratio is little affected by denitrification of remineralized nitrogen nitrified *in situ*, due to the uptake of oxygen by the coupled nitrification step which results in a net RQ of ca. 2. The small impact on the system RQ is further supported by the dominance of carbon mineralization in the DIC and SOD fluxes and the fact that most of the remineralized N is not

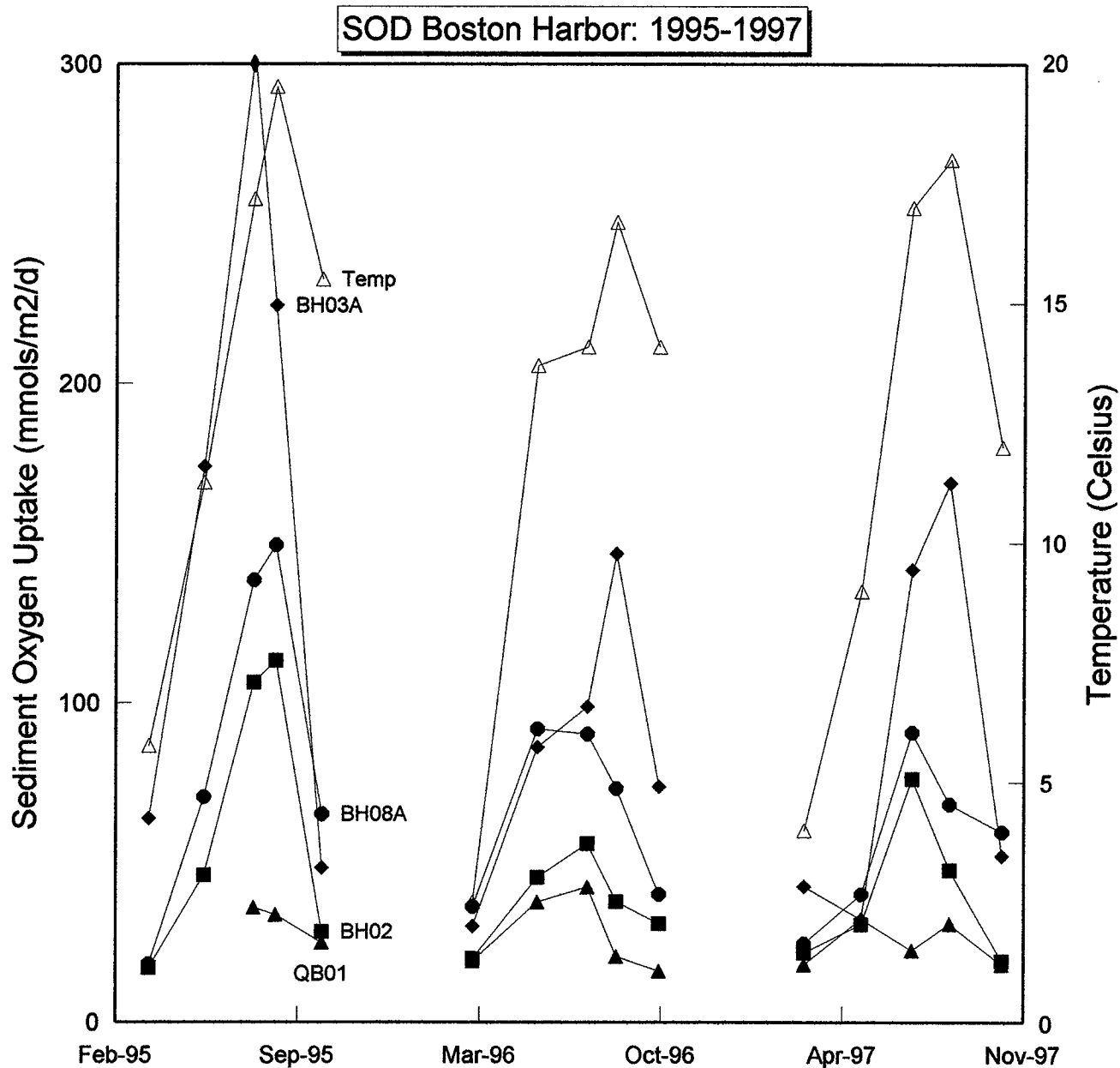
denitrified and much of the remineralized N is not nitrified but remains as ammonium. In systems like present Massachusetts Bay, carbon flow through sulfate reduction is almost certainly small relative to aerobic processes (Jorgensen 1982) and therefore errors due to the oxidation time-lag are likely 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 from an ecological basis in that where low oxygen or high sulfide levels occur, infaunal populations, hence food chain dynamics, may be affected.

Annual Cycle of Benthic Metabolism: Similar to other temperate coastal systems, there was a pronounced seasonality in rates of sediment oxygen uptake, denitrification and dissolved inorganic nitrogen (DIN) flux to the watercolumn at each of the Boston Harbor stations in 1995-1997 (Figures 2, 3, 4). The rates of these key biogeochemical fluxes exhibited increases of 5-10 fold from winter lows to summer maxima at most sites (BH03A, BH02, BH08A; Figure 2). 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. Metabolic rates tended to most closely follow sediment temperature, while DIN fluxes frequently were dominated by summer maxima not associated with the highest temperatures (Figure 4). While the seasonality of metabolic rates within each site appear to relate largely to temperature effects, the large inter-site differences within the Harbor are not likely temperature related. Bottom water within the sub-tidal portion of Boston Harbor does not appear to exhibit major heterogeneity in the temperature field on individual sampling dates. During 1997 (as in 1995 and 1996) the greatest temperature range among the 4 stations was 2.1°C, during mid-summer. This temperature range resulted from the relatively shallow water and inner location of QBO1 compared to the "deeper" stations (BH02, BH03A and BH08A) which showed at most a 0.5 °C range over the year.

Similarly, the intra-site and inter-annual differences also do not appear to be related to differences in environmental temperature or the average bulk organic content of the surficial sediment, although differences in labile organic matter deposition may contribute. In addition, it is not clear if changes in deposition rates related to the lower Charles River discharge during 1997 contributed to the generally higher SOD, denitrification and DIN flux rates in 1997 versus 1996 at station BH02 (located within nearest the mouth of the river).

What does appear clear is that the bulk of the differences in sediment metabolism and associated fluxes within the Harbor are 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 QBO1 in both years, weakly to moderately developed at BH02 in 1995 and absent in 1996 and 1997, but from 1995-97 were moderately developed at BH08A and consistently very dense at BH03A. Survey of the distribution of the amphipod mats during 1996 indicated that most of the central harbor region is now fully colonized with variable inter-annual distributions at the margins since



1995 was the first major "amphipod effect" year.
Station Means: N=4

Figure 2. Annual cycle of oxygen uptake and bottom water temperature within the sediments of the Boston Harbor monitoring sites in 1995-1997. For locations see Figure 1 and Table 1.

Boston Harbor Denitrification: 1995-1997

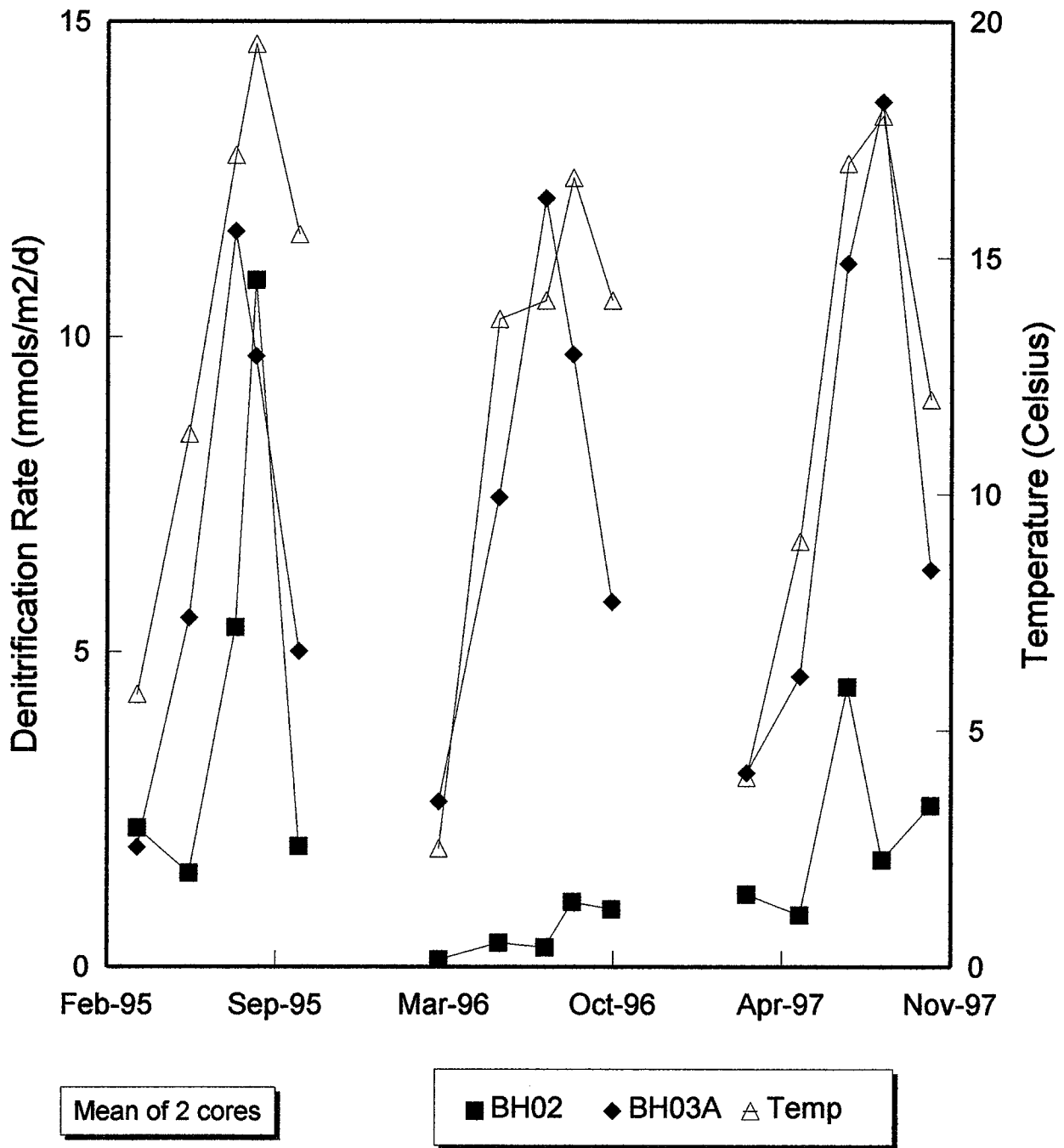


Figure 3. Seasonal temperature and denitrification rates within the sediments of 2 sites within Boston Harbor in 1995-1997. Site BH02 had a low-moderate amphipod mat in 1995 and no mat in 1996 and 1997, while BH03A supported a dense amphipod mat in each year.

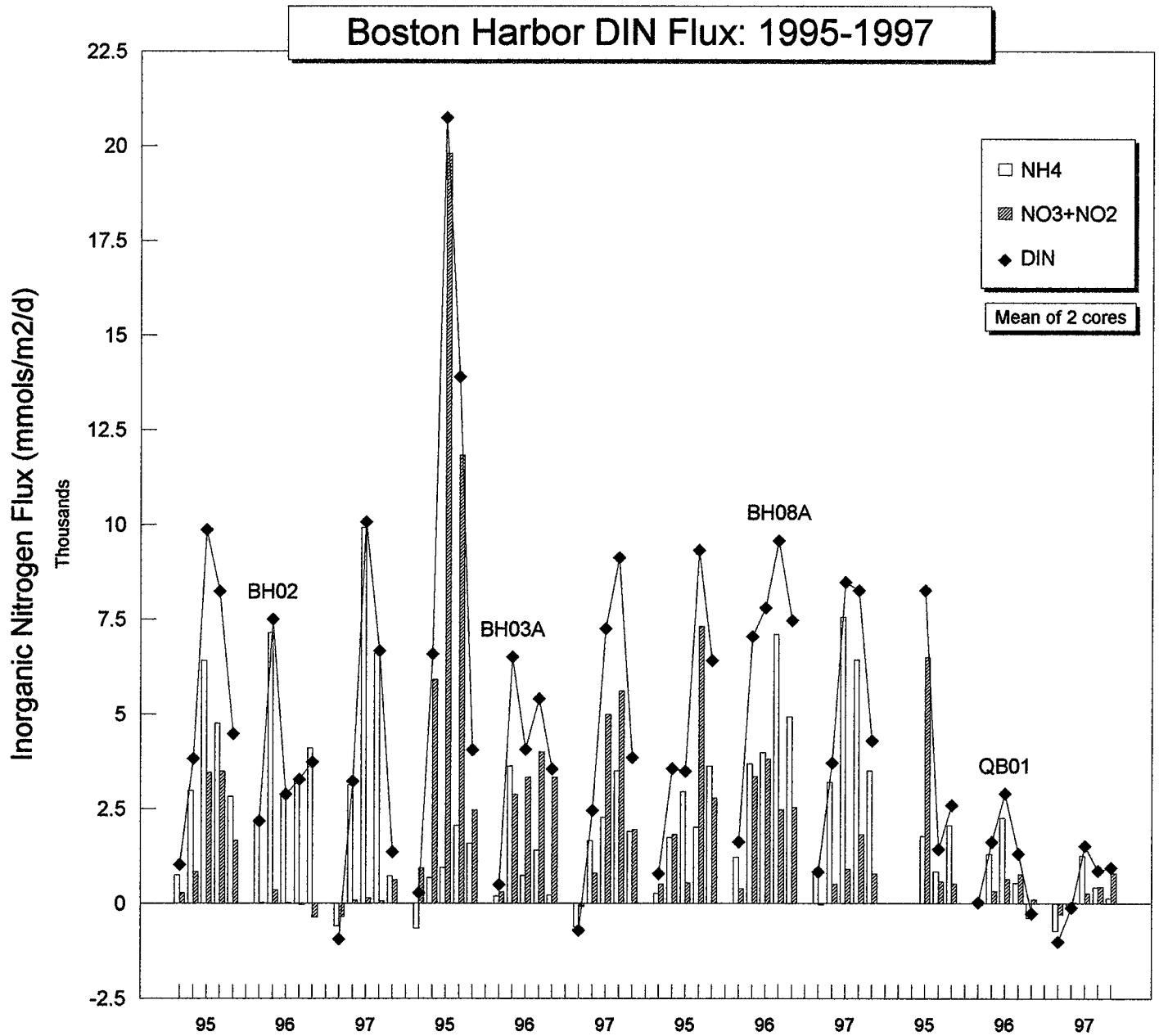


Figure 4. Seasonal rates of inorganic nitrogen exchange between sediments and overlying water at 4 locations (BH02, BH03A, BH08A, QB01) within Boston Harbor from 1995 to 1997. Dissolved inorganic nitrogen (DIN) presented as the sum of ammonium and nitrate+nitrite fluxes, negative fluxes represent uptake by sediments.

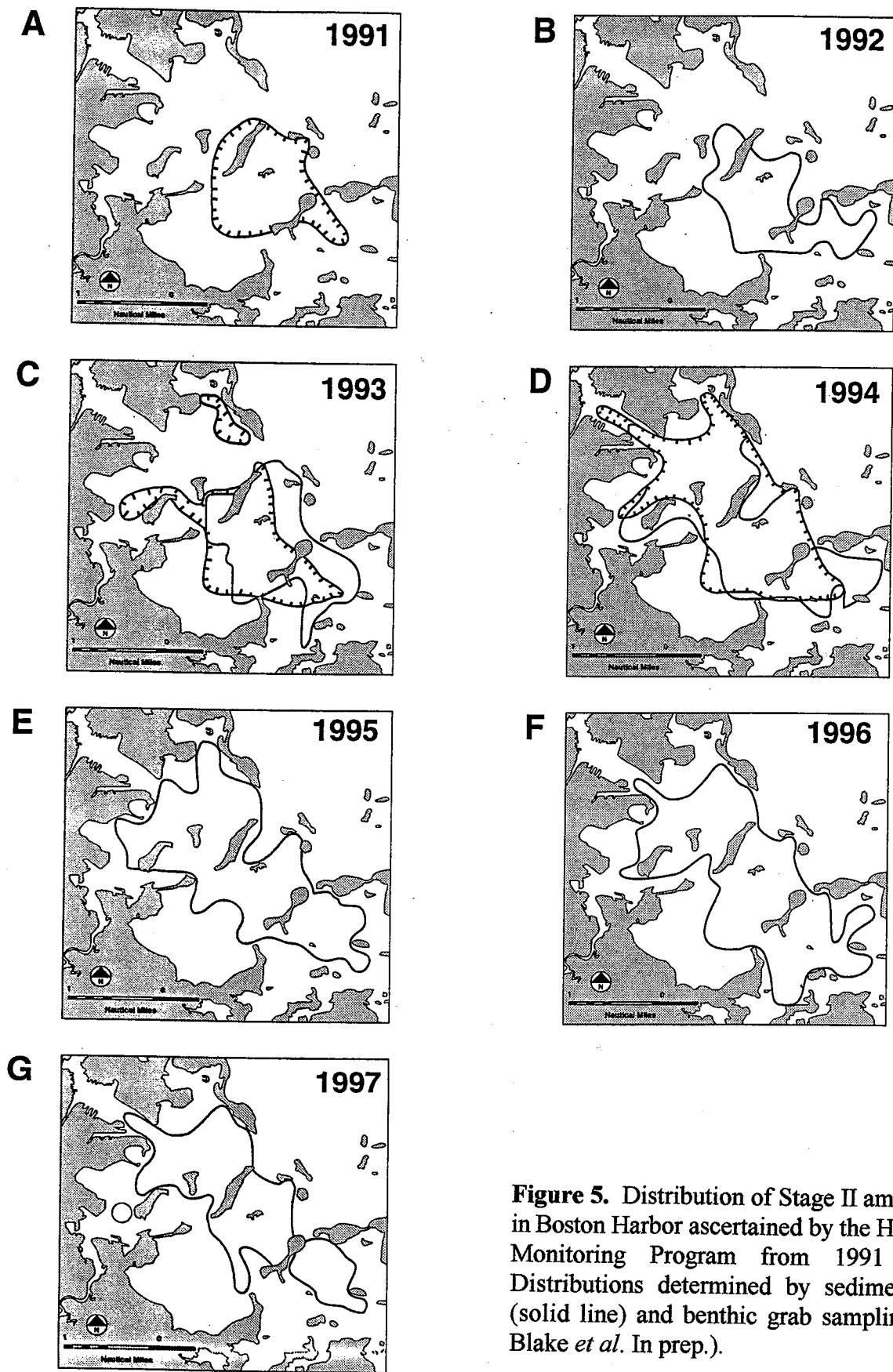


Figure 5. Distribution of Stage II amphipod tube mats in Boston Harbor ascertained by the Harbor and Outfall Monitoring Program from 1991 through 1997. Distributions determined by sediment-profile image (solid line) and benthic grab sampling (hatched line; Blake *et al.* In prep.).

1994-95 (Figure 5).

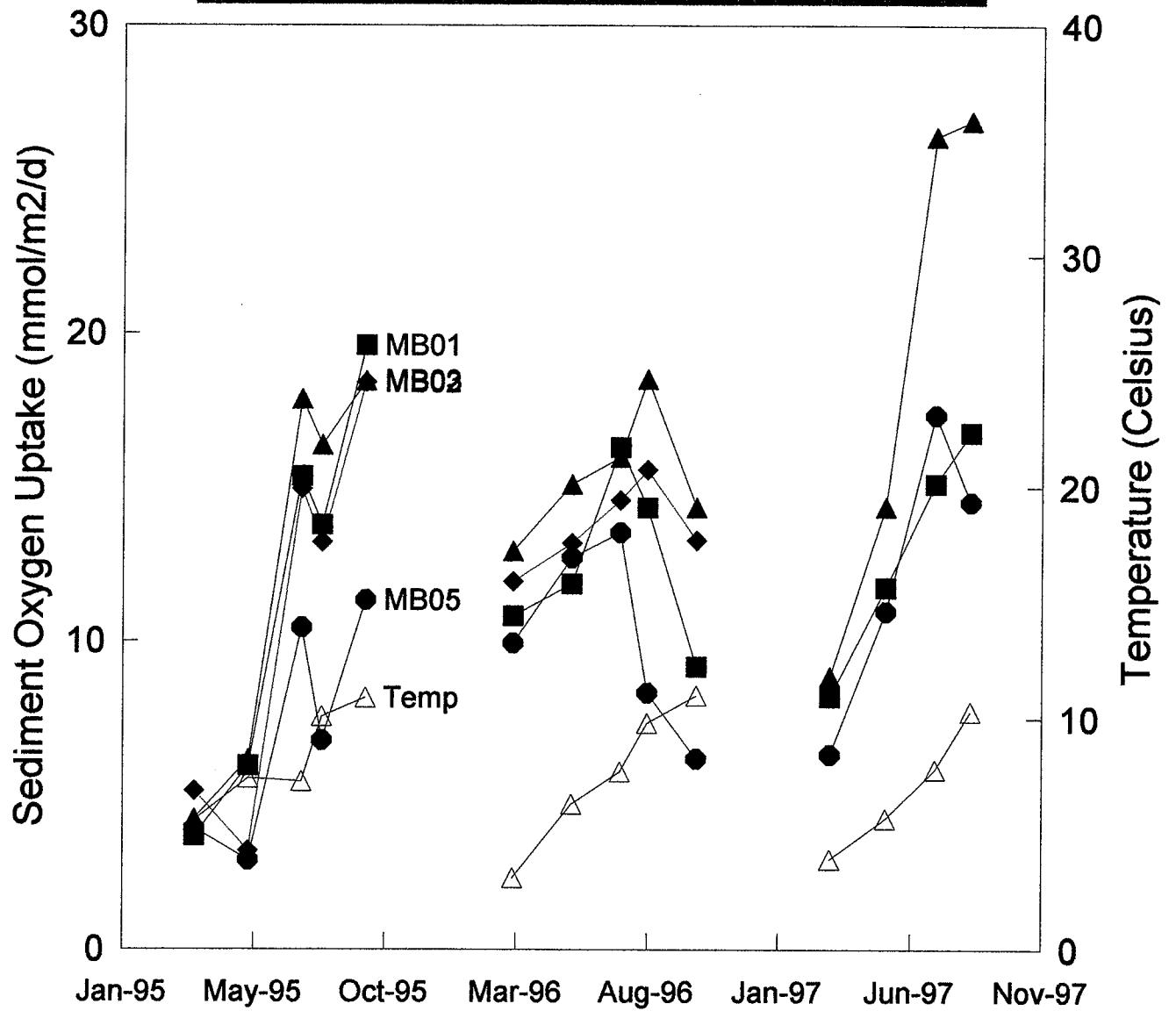
On the larger spatial scale, the Bay sediments were found to support significantly lower rates of respiration than the Harbor sediments. This spatial trend most likely results from differences in rates and quality of organic matter deposition to sediments and environmental temperature (Figure 6; see below).

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 6). However, in 1995-1997 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 the overall seasonal pattern does not track the temperature cycle. The independence of sediment oxygen uptake from environmental temperature was particularly clear in the 1996 sampling, where at the warmest temperature (October) rates were significantly lower than earlier in the season. It is likely that the declining rates of respiration during and just-post stratification represent a depletion of labile organic matter deposited during the winter/spring bloom. In contrast, the 1997 sampling showed higher respiration rates at each station late in the stratified period. It is possible that these higher rates of respiration result from enhanced deposition of labile organic matter during 1997 associated with blooms of *Phaeocystis* and *Chaetoceros*. 1997 water column monitoring, indicated a large widely distributed *Phaeocystis* bloom which likely reached the sediments of the Nearfield through direct deposition and indirectly through zooplankton grazing. The large *Chaetoceros* bloom occurred through the onset of stratification, but was located below the pycnocline. The depth distribution of this diatom bloom would facilitate its deposition to the sediments (Cibik *et al.* In preparation).

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. In addition, the stratified deeper water column results in a more temporally variable cycle of organic matter deposition than found in the well mixed Harbor. Similarly, the seasonal temperature cycle shows a maximum later in the year due to the restriction of heat transfer imposed by stratification in the Bay versus the mixed conditions of the 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. As seen in Figure 6, rates of respiration in 1996 appear to follow the timing of bloom deposition not merely the temperature cycle. However, it appears that the reduction in organic matter deposition imposed by water column stratification may result in lower respiration rates in late summer as the readily decomposable spring bloom material is remineralized. While this latter scenario is "typical", sub-pycnocline blooms, such as the *Chaetoceros* bloom in 1997, may bypass the high rates of remineralization in the mixed layer and result in enhanced respiration rates in bottom waters and sediments during stratification. While the role of the 1997 blooms in the higher observed sub-pycnocline respiration cannot be quantified, an association is consistent with the higher observed sediment chlorophyll a levels in the Nearfield (see below).

In contrast to spring or sub-pycnocline summer blooms, deposition of the fall bloom occurs while the bottom waters are still near the annual temperature maximum which should promote rapid degradation

1995-1997 Massachusetts Bay: SOD



Bars represent stratification.
Station Means: N=4.

Figure 6. Seasonal cycle of sediment oxygen uptake within the western nearfield of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) and mean bottom water temperature, 1995-1997. Station MB02 was not sampled in 1997.

of the bloom material. In addition, the mixed water column should slow deposition resulting in a higher fraction of remineralization of the labile organic matter. 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.

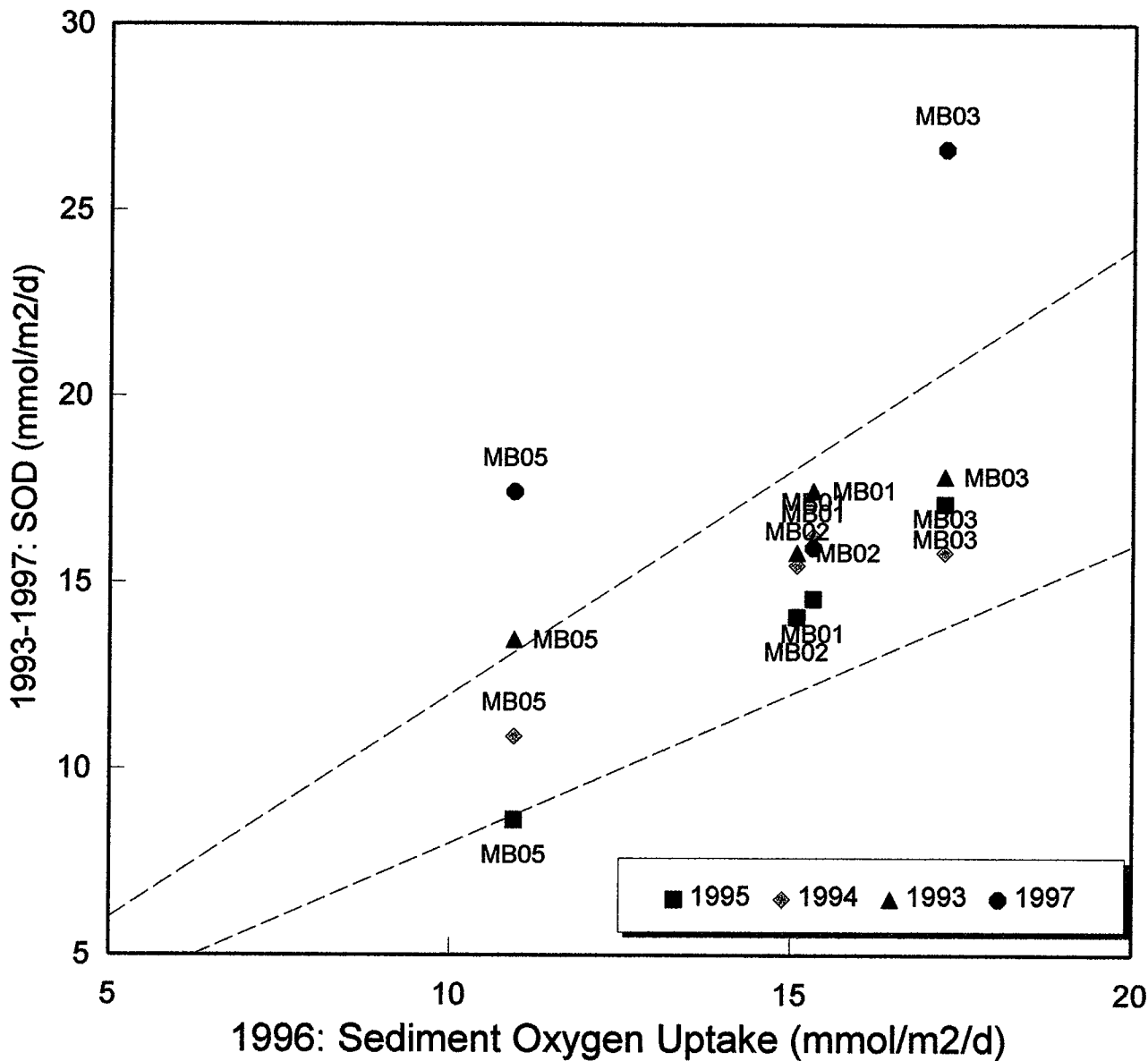
Inter-annual comparisons of metabolism: Given the long-term nature of the Outfall Monitoring Program it is important to evaluate inter-annual variability pre-discharge as a baseline from which to gauge the significance of differences in environmental parameters after relocation of the effluent discharge. 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 1996 and earlier years (Figure 7). From these data it appears that inter-annual differences in SOD measurements are small, generally <20%. Although there is limited data, SOD rates in the deeper less active sediments of Stellwagen Basin (MB05) are more variable than those from the shallower 3 stations. At present it is unclear the extent which this increased variability results from methodological difficulties versus inherent variation within the Basin sediments. However, 1997 yielded higher rates than the baseline at Nearfield station MB03 and in Stellwagen Basin (Figure 7). In addition, MB01 showed a nearly linear response to increasing temperature, not seen in previous years (Figure 6). These results are consistent with the greater availability of labile organic matter within the sediments at these locations in 1997 compared to previous years of observation.

It appears that measurements of sediment oxygen uptake are likely relatively sensitive indicators of potential changes in organic matter deposition resulting from the relocated outfall. This conclusion is supported by the general inter-annual consistency of the SOD data from which to base comparisons. In addition, the observations during 1997 of both higher water column and sediment respiration rates and likely enhancement of sub-pycnocline organic matter loading (from phytoplankton) supports this contention.

In strong contrast to the Bay, sediment oxygen uptake within Boston Harbor in 1997 continued to be several fold higher than typically encountered prior to 1995. As stated above, the spatial variation within the Harbor in 1995-1997 parallels 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 1995-1997 rates were associated with infrequent sampling of amphipod mats (Giblin *et al.* 1994). Additional support for the contention that the observed inter-annual differences result from infaunal activity stems from the similarity of sediment oxygen uptake at the non-mat station (QB01) with uncolonized analogous sites in previous years (Figure 2 and Giblin *et al.* 1997), but the 2-5 fold higher rates at all amphipod mat sites. Even more enlightening is the large reduction in both

Sediment Oxygen Uptake: Interannual 1993-1997



All Data: Mean of July and August
Lines represent 20% difference from 1996.

Figure 7. Inter-annual comparison of oxygen uptake during summer stratification by sediments within the western nearfield and Stellwagen Basin monitored 1993-1997. Solid line represents equivalence, dashed lines are ±20%.

SOD and denitrification rates at site BH02 from 1995 when it supported a modest mat to 1996 and 1997 when the mat did not develop (Figures 2, 3). 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 (Blake *et al.* 1993, Hilbig *et al.* 1996; Kropp & Diaz 1995). *Ampelisca* are deposit feeding amphipods capable of building several centimeter thick mats and reaching densities of over 100,000 individuals m². 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 mats appear to be becoming more persistent from year to year and currently occur throughout much of the central Harbor (Figure 5). 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 associated with the amphipod mats, the rates of denitrification were similarly enhanced (Nowicki *et al.* 1997 and Figure 3). 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 1995-1997. It is significant that while the rates of oxygen uptake appear to have decreased at the dense mat site, BH03A, the rates of denitrification remain high throughout the same interval, 1995-1997. This reduction in carbon mineralization with continued high nitrification-denitrification rates is consistent with a mining of oxidizable organic substrates and continuing sediment oxidation. 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.

Phytoplankton deposition: The primary source of organic matter to sediments within the central Harbor and western Massachusetts Bay results from phytoplankton production (Kelly 1997, Cibik *et al.* 1996). Rates of sediment oxygen uptake reflect the level of organic matter loading. Therefore, the pattern of phytoplankton deposition relates directly to the spatial and temporal pattern of sediment metabolism. 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). 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 photosynthetic carbon fixation, organic matter transport and decay.

Within Massachusetts Bay, watercolumn respiration acts a "filter", reducing the amount of organic

matter deposition to the sediments. Within the Bay more than two thirds of the organic matter input is remineralized before reaching the sediments (Howes 1998a). This results from turbulence within the mixed layer keeping particles in suspension, which coupled with summer temperatures increases the rate of their degradation before transport to the bottom waters and finally the sediments (Cibik *et al.* 1996). 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 (Howes 1998a).

Levels of chlorophyll a and pheophytin a in sediments were measured as potential indicators of the spatial and temporal availability of "freshly" deposited phytoplankton within Harbor and Bay sediments. Since sediment remineralization rates can be controlled by the availability of labile organic matter (particularly in offshore environments like Massachusetts Bay), pigment concentrations could also serve as a useful surrogate measure of organic matter availability. This latter feature is important since direct measurement of the available pool of labile organic matter in sediments is problematic.

Within Boston Harbor, surficial sediments had levels of chlorophyll a that were relatively similar among the 4 stations compared to their 5 fold range in respiration (Figure 8 Top). Only the least metabolically active station, QB01, showed significantly lower chlorophyll a levels than the rest of the Harbor. However, this difference was not seen in comparisons of total chlorophyll a pigments (chlorophyll a + pheophytin a). In addition, there was a suggestion of a trend in sediment chlorophyll a, with slightly higher levels occurring in the spring and early summer. This absence of a clear seasonal cycle suggests phytoplankton input throughout the warmer months, which is consistent with the shallow waters and observed annual patterns in photosynthesis (Station F23, Cibik *et al.* 1996, In prep.).

In the 4 Bay stations, sediment chlorophyll a and total chlorophyll a pigments showed similar concentrations (Figure 9). In contrast to the shallow Harbor stations, sediments within western Massachusetts Bay showed a consistent tendency to higher chlorophyll a levels during spring and early summer than during stratification (9 of 11 station-years showed the highest levels in Survey 1 or 2). This observation is consistent with the deposition of "fresh" phytoplankton from the spring bloom which then degrades, but is not sufficiently replaced during the summer stratified interval to maintain sediment chlorophyll concentrations (Figure 9 Top). Both the intra-annual patterns of SOD during 1995 and 1996 and the increased late stratification SOD in 1997 at stations MB03 and MB05 followed the pattern of chlorophyll a mass in the surficial sediments (Figures 6, 9). This further supports the concept of an enhanced deposition of phytoplankton carbon in the Nearfield in 1997.

Differences in sediment chlorophyll a levels in Harbor and Bay stations can be examined by comparing average depth-integrated masses on an areal basis (Figure 10). Since most of the biogeochemical activity is within the surface 10 cm, comparison to rate measures can be made. It is clear that the higher metabolic rates within the Harbor versus Bay sediments (Figures 2, 6) are directly correlated with the accumulated chlorophyll a mass (Figure 10). Harbor sediments generally contained between 2-5 fold higher chlorophyll a levels than the Bay. Also, as seen in the individual station data, evidence for seasonal deposition of bloom material was only found within the Bay sediments. Again the highest levels of chlorophyll a found within the Bay sediments was early in the stratified interval in 1997, consistent with the observed blooms and SOD rates.

The several fold higher concentrations of chlorophyll a and chlorophyll a + pheophytin a in Boston

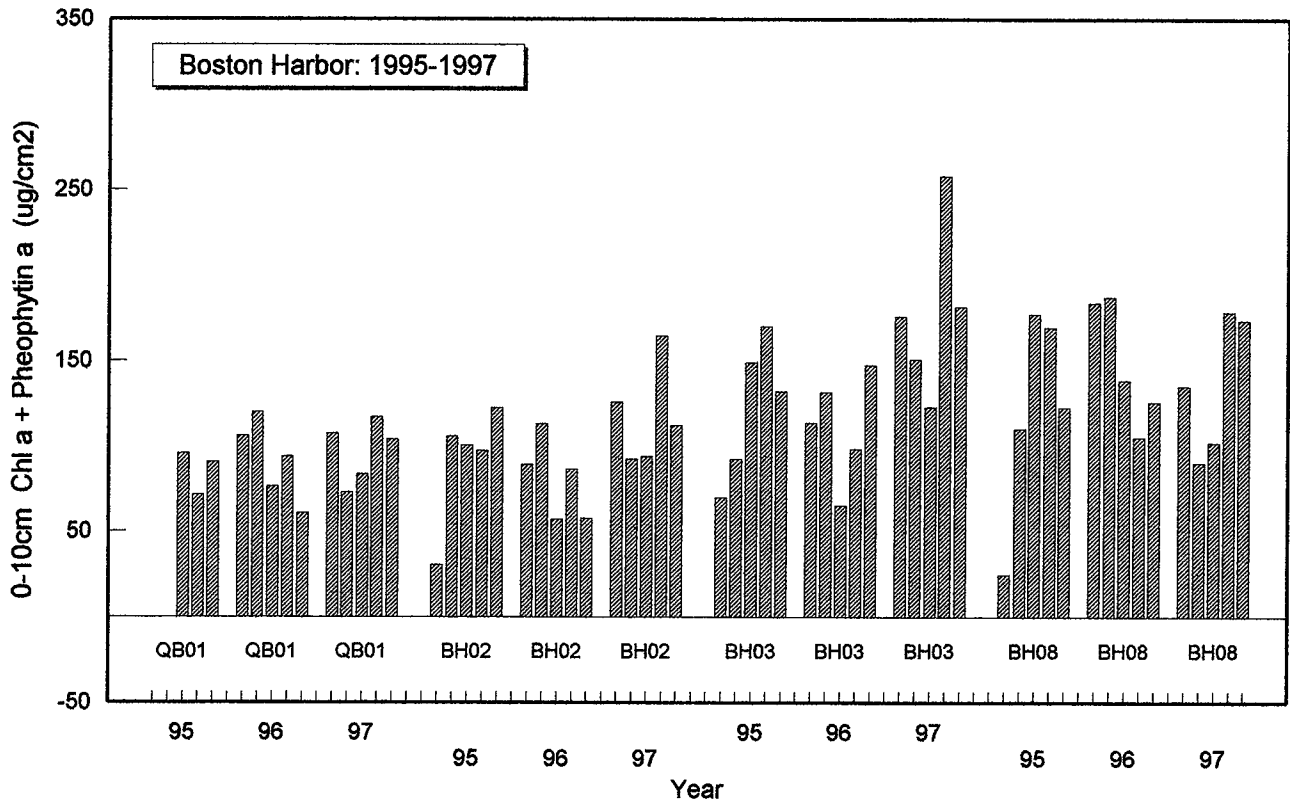
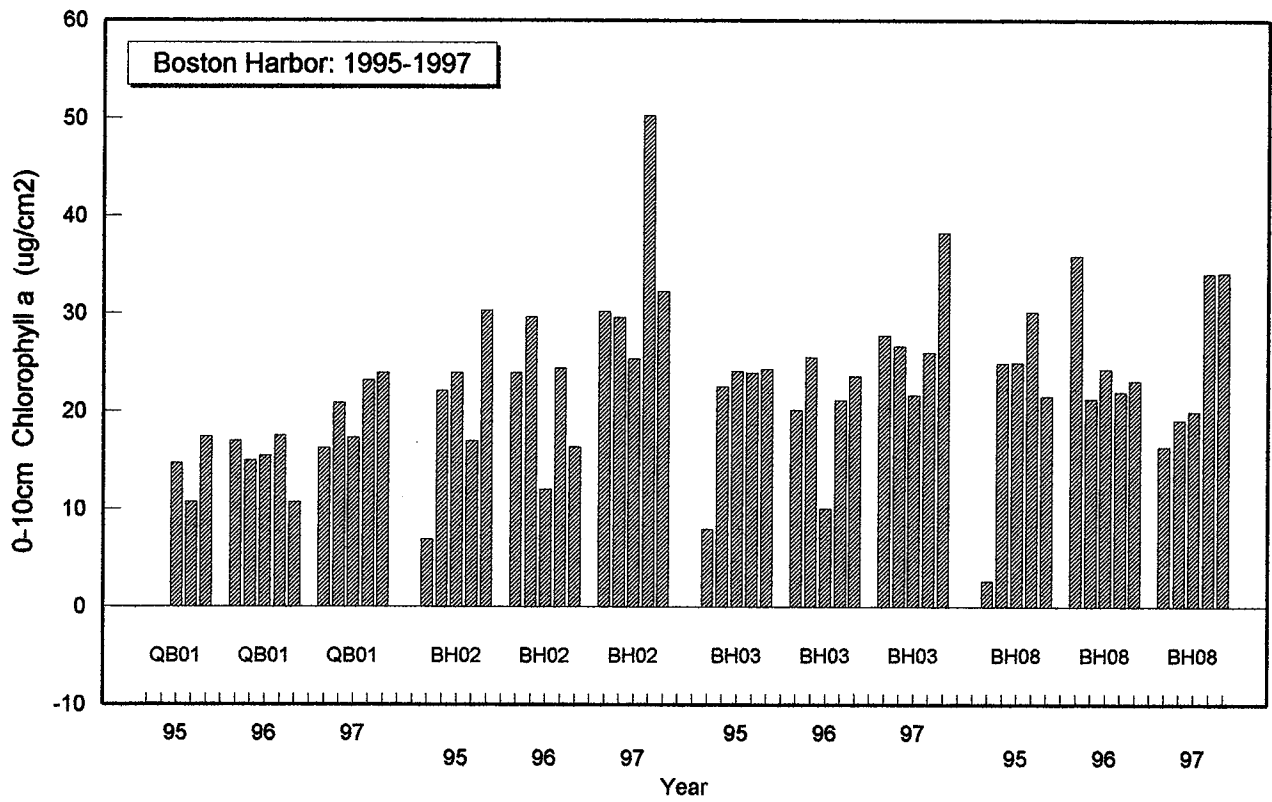


Figure 8. Seasonal variation in the mass of chlorophyll a (top) and chlorophyll a + pheophytin a (btm) within the surface 10 cm of sediment in Boston Harbor, 1995-1997.

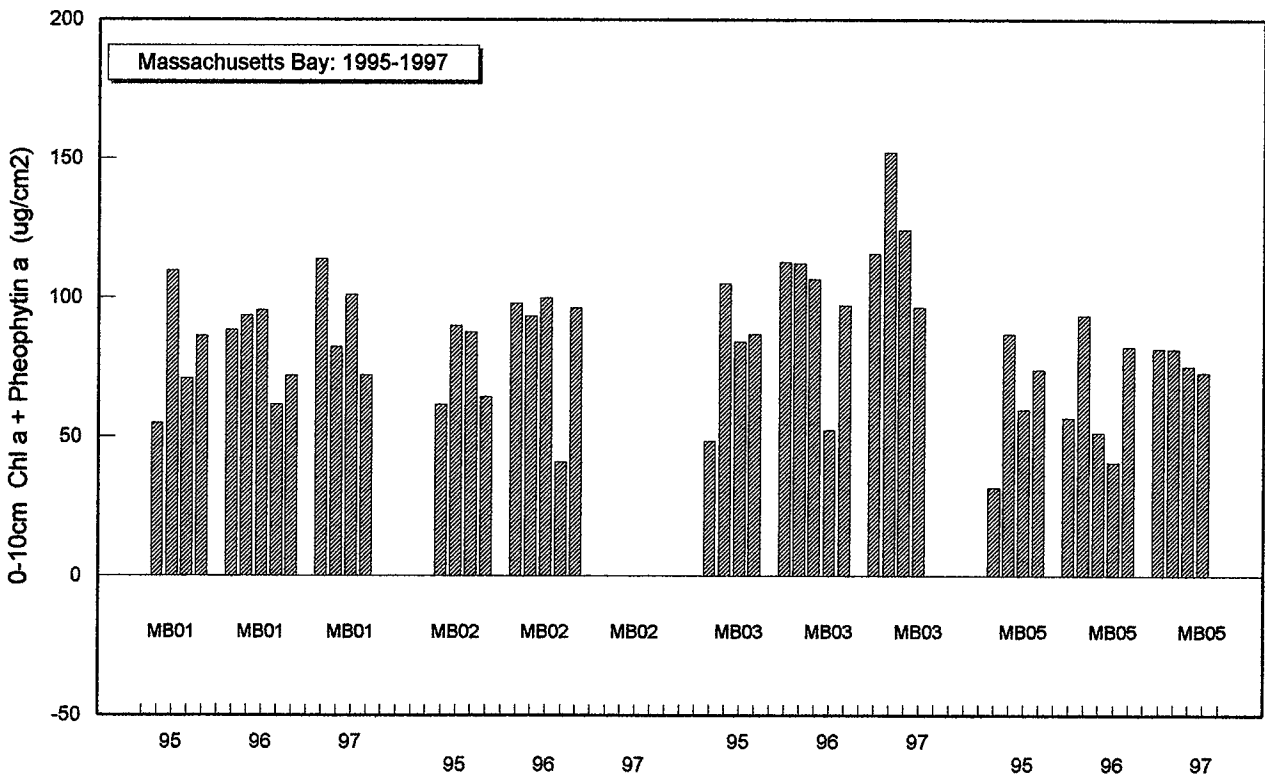
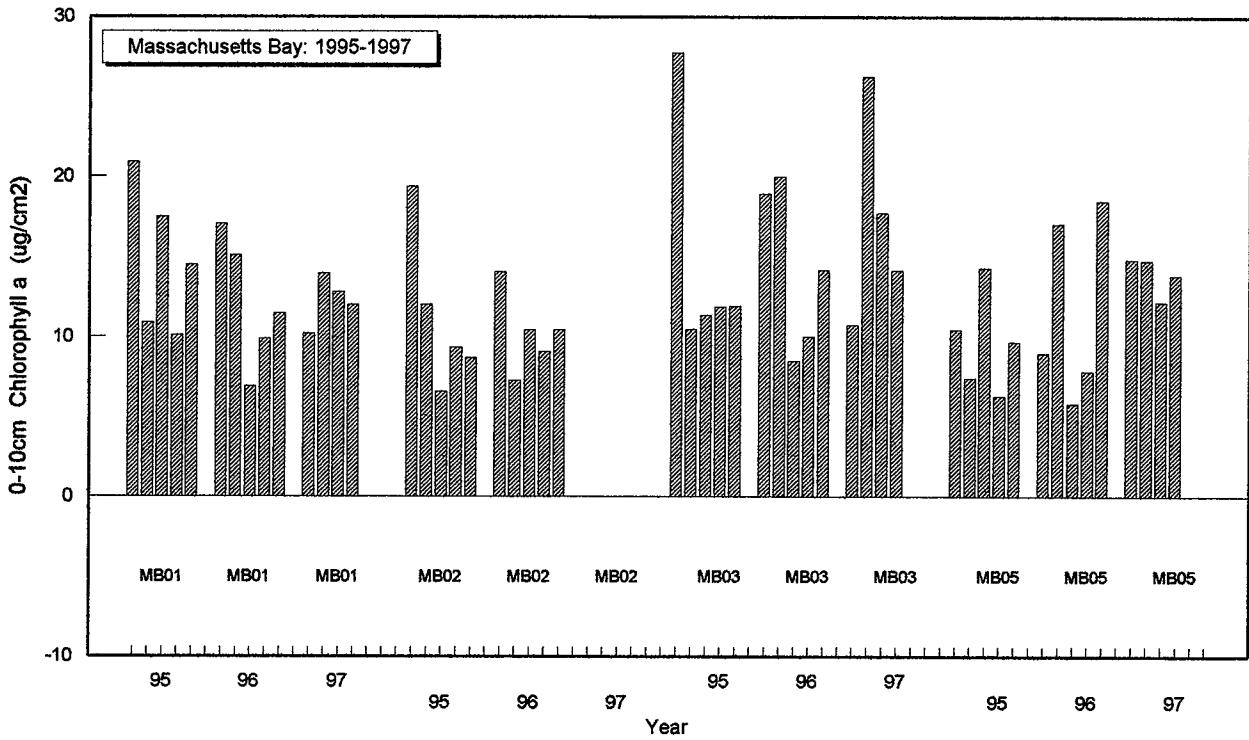


Figure 9. Seasonal variation in the mass of chlorophyll a (top) and chlorophyll a + pheophytin a (btm) within the surface 10 cm of sediment in Massachusetts Bay, 1995-1997. Station MB02 was not sampled in 1997.

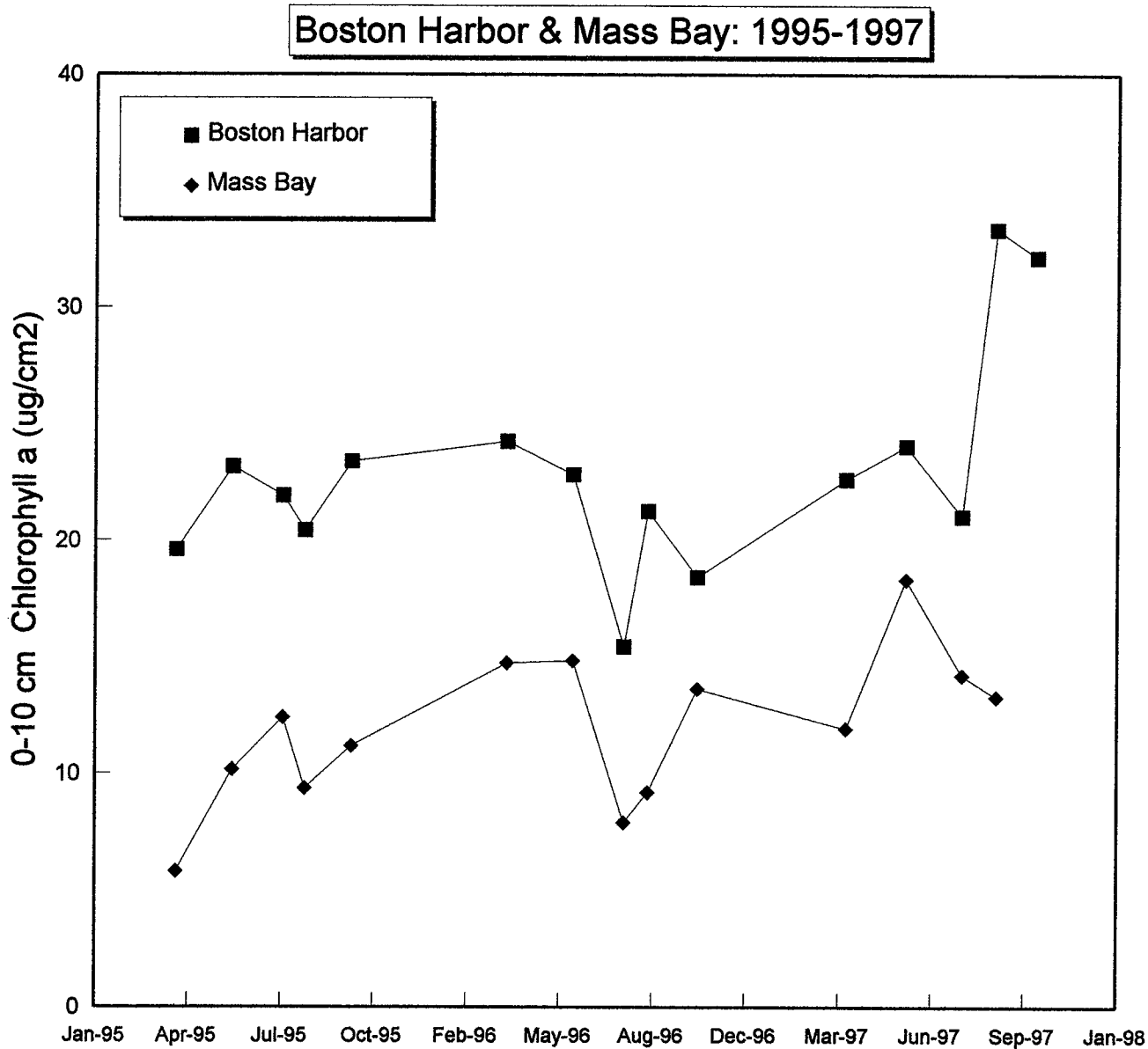


Figure 10. Comparison of the seasonal pattern of chlorophyll a within the surface sediments of Boston Harbor and Massachusetts Bay. Values are the areal mass of sediment chlorophyll a (cm^{-2}), integrated over 0-10 cm and averaged over the stations within each sub-system.

Harbor versus Massachusetts Bay sediments were not only consistent through time but also maintained with depth in the surficial sediments (Figure 11). In addition, the proportion of chlorophyll a to the total chlorophyll a pigment was relatively constant over the sediment profile. The general trend of higher pigment levels near the sediment surface and a decline with depth is consistent with surface deposition and bioturbative downward mixing. The finding of proportionally high chlorophyll a levels at depth (about a 50% decline from 0 to 10 cm) suggests relatively high vertical transport rates of the surficial sediments at these sites.

Comparison of phytoplankton pigment levels within the sediments of each station with the measured summer rates of oxygen uptake indicates a direct but non-linear relationship between SOD pigment levels (Figure 12). It is likely that the non-proportionality of SOD to chlorophyll a mass results from confounding effects of infaunal activities and the input of allochthonous organic matter at some sites. This is supported by the degradation of the relationship at the higher SOD rates which are from the amphipod mats. However, it does appear that sediment pigment concentrations may be a useful tool in assessing the rate and timing of delivery of labile organic matter to both the Harbor and Bay sediment systems. In addition, the relative constancy of concentrations from year to year at a station suggests the potential for assessing changing phytoplankton deposition patterns after relocation of effluent discharge.

Efflux of regenerated nutrients to the water column: Dissolved inorganic nitrogen ($\text{DIN} = \text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$) fluxes followed the general pattern of organic matter mineralization in both Boston Harbor and Massachusetts Bay (Figures 2 vs 4, 6 vs 13). As with oxygen fluxes and sediment pigment levels, 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 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 about 10°C higher summer water temperatures which support a greater capacity to rapidly remineralize deposited organic matter. Consistent with a common organic substrate, the spatial pattern of DIN flux followed SOD rates within each sub-system. Stellwagen Basin showed the lowest DIN efflux and had the lowest SOD. Similarly, QB01 which was not colonized by amphipods, showed concomitantly low DIN regeneration in both 1995-1997 compared to the other Harbor sites. In general, while there was more spatial and temporal variation in DIN flux than SOD rates, the patterns were reproducible from year to year.

The seasonal pattern of DIN flux also was similar between the Harbor and Bay and paralleled the cycle of organic matter mineralization. Within the Bay DIN flux tended to reach a late summer maxima, following water temperature more than SOD. This suggests that the bioturbation plays an important role in the release of DIN as the temporal pattern of infaunal activity appears to be more closely correlated with DIN flux than is the remineralization rate. In contrast, within the Harbor sediments, maximum DIN efflux tended to closely follow sediment respiration reaching a maximum in mid-summer.

Comparison of the annual SOD with DIN efflux rates suggests that both the Harbor and Bay sites support active denitrification (Figure 14). Since annual SOD is a good indicator of total annual carbon mineralization and there is little net annual storage of DIN within the sediments, rates of DIN emission lower than those predicted by the Redfield ratio of C:N of 6.6:1 suggest losses through denitrification.

Sediment Chlorophyll a: 1995-1997

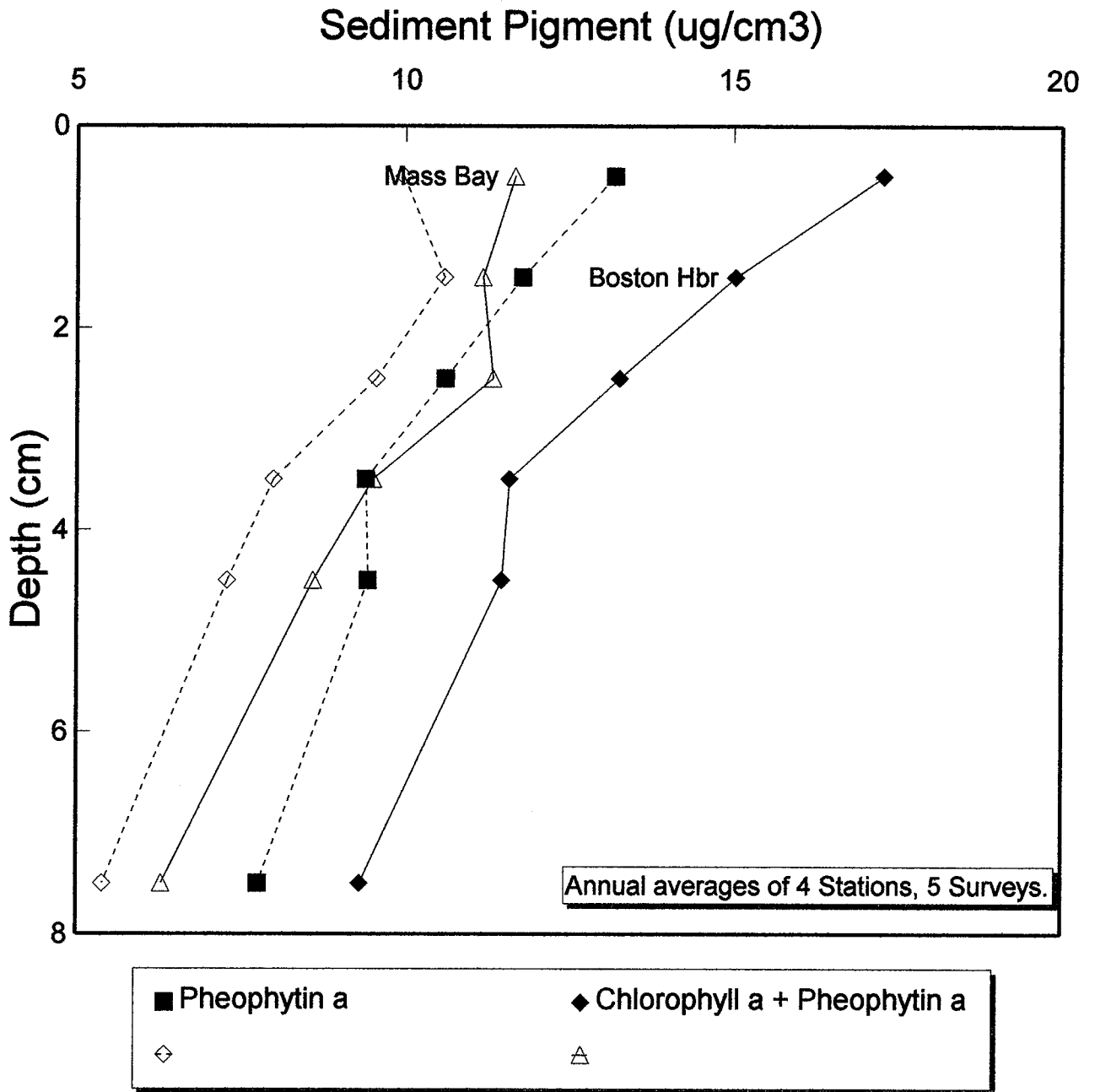


Figure 11. Average profiles of (A) chlorophyll a and (B) pheophytin a + chlorophyll a in sediments of Boston Harbor and Massachusetts Bay sediment flux stations from March 1995 to October 1997.

Sediment Chlorophyll & SOD: Summers 1995-1997

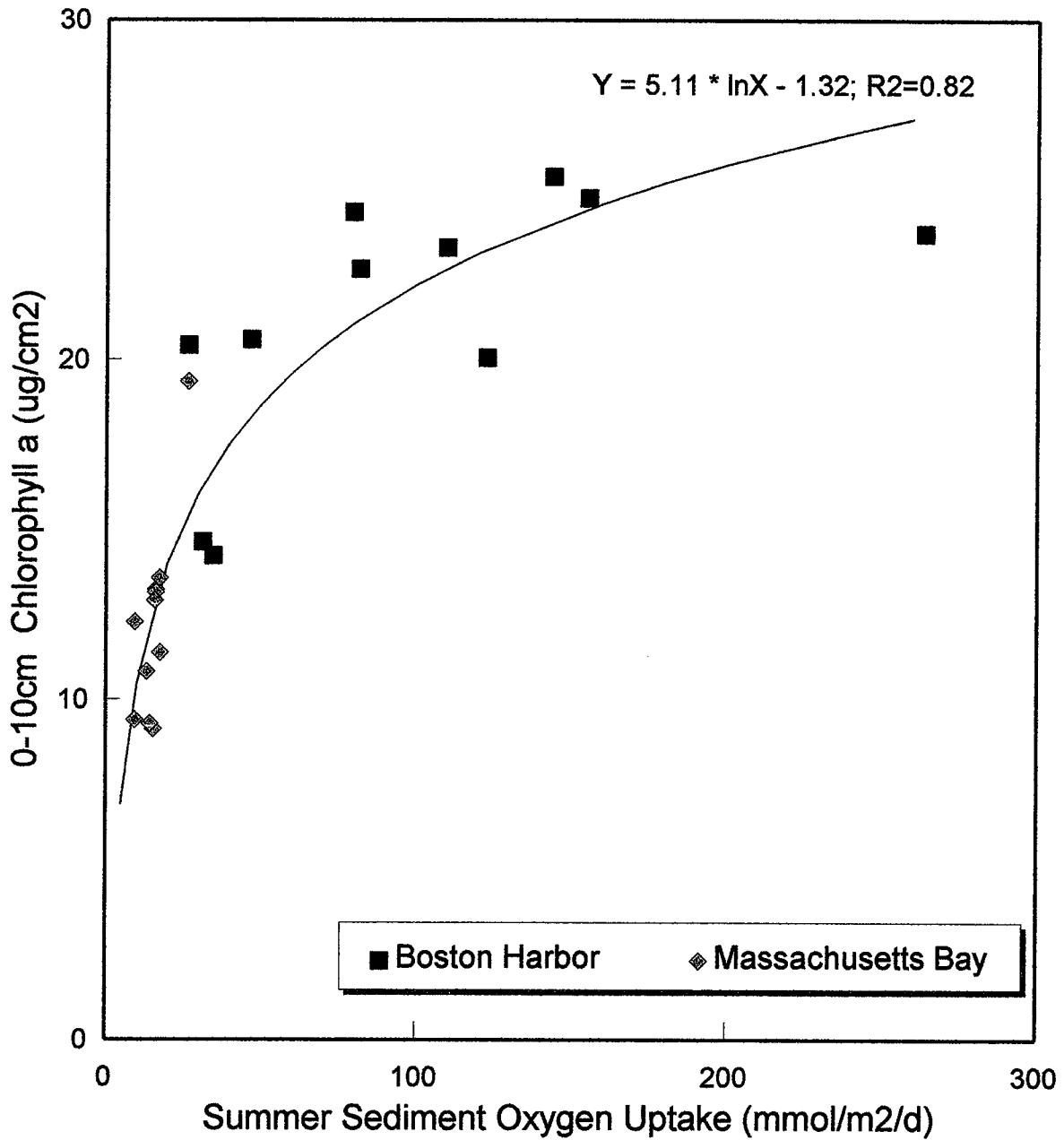


Figure 12. Relationship between summer sediment oxygen uptake and chlorophyll a mass within the surface sediments of Boston Harbor and Massachusetts Bay. Values represent summer averages at each of the stations, 1995-1997. The line derived from the logarithmic equation represents the “best fit” least squares regression of data.

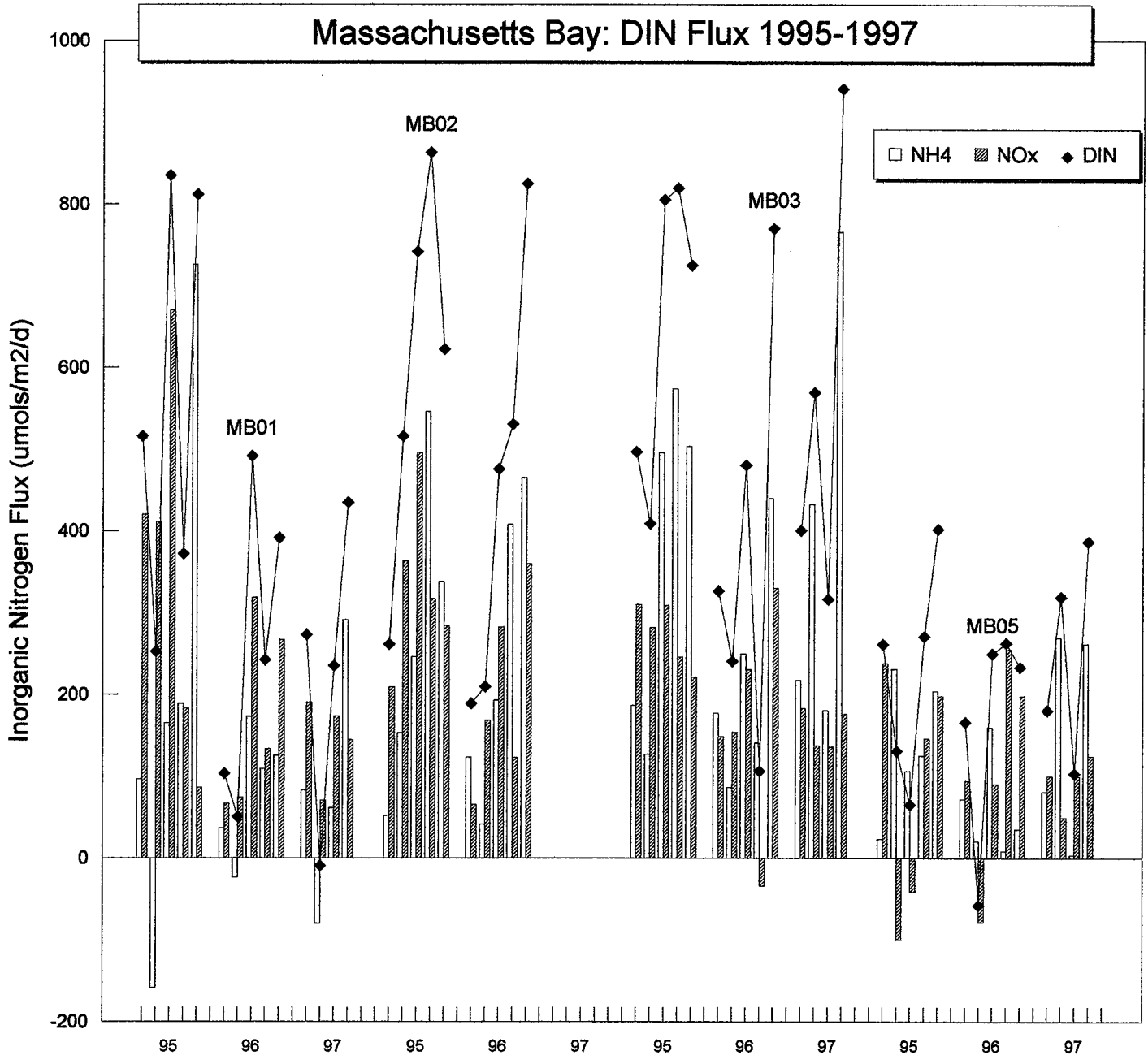
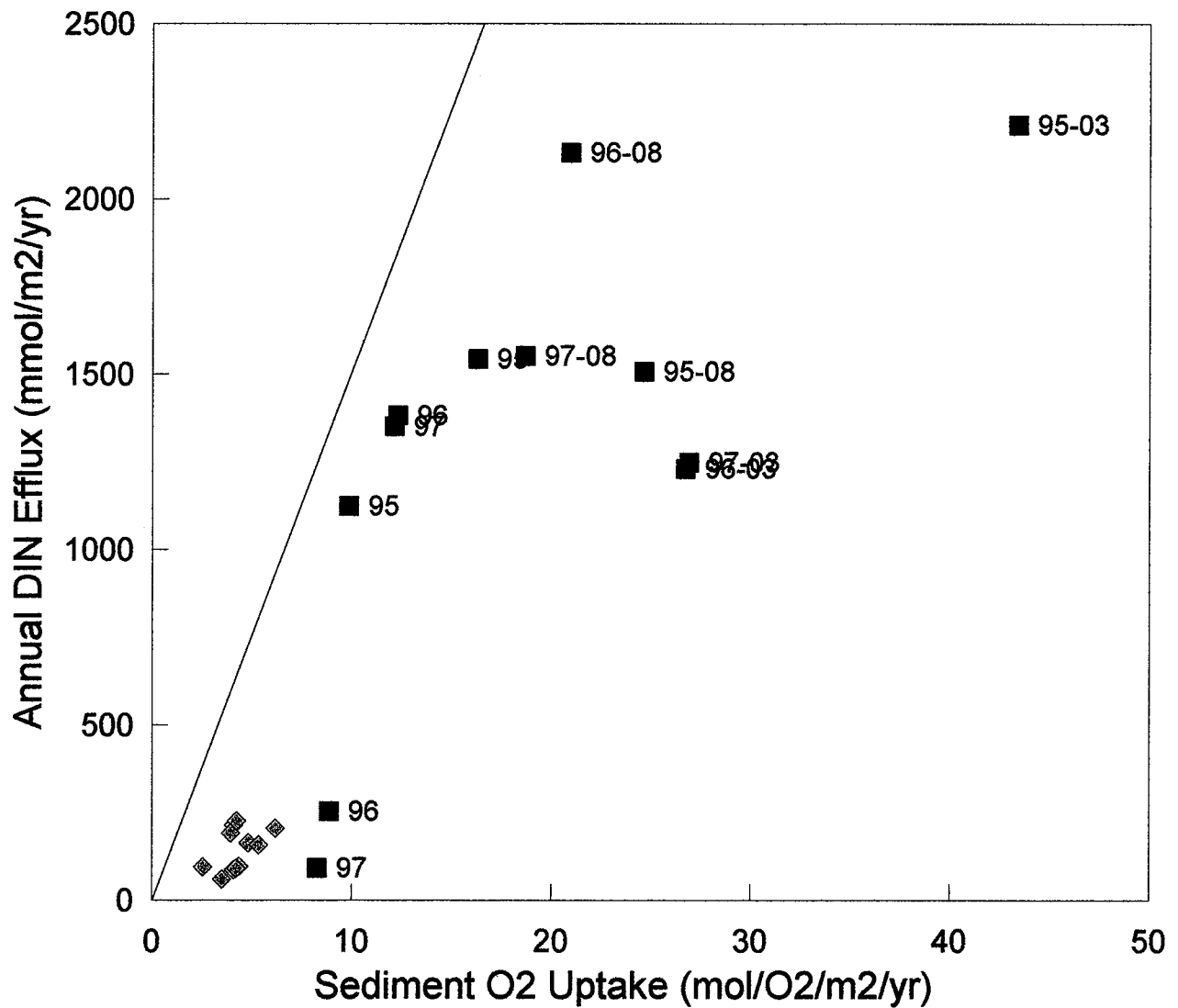


Figure 13. Seasonal pattern of dissolved inorganic nitrogen (DIN) efflux from sediments of western Massachusetts Bay, 1995-1997. DIN was calculated as ammonium + (nitrate + nitrite).

Mass Bay & Boston Hbr Annual Flux: 1995-97



Annual Fluxes; Line indicates DIN Flux to meet C/N of 6.625
 Values below line indicate N burial or denitrification.

Figure 14. Comparison of annual rates of dissolved inorganic nitrogen (DIN) efflux versus sediment oxygen uptake from the sediments of Massachusetts Bay and Boston Harbor, 1995-1997. Values below the line indicate DIN efflux lower than predicted from the Redfield ratio and measured

The annual data from 1995-1997 all indicate annual flux of DIN less than predicted. The largest "missing" masses of DIN within the Harbor are at stations BH03A and BH08A, again suggesting that enhanced bio-irrigation associated with the mats may be providing for increased rates of nitrification-denitrification.

While the overall pattern of DIN flux was similar between the Harbor sites, the composition of the efflux appears to depend upon the infaunal community and/or the overall magnitude of sediment regeneration. At sites with SOD rates $>150 \text{ mmol m}^{-2}\text{d}^{-1}$ more than 50% of the DIN flux was nitrate+nitrite (Figure 15). It is most likely that the effect is due to bio-irrigation rates (sediment oxidation) which are associated with the high sediment oxygen uptake rates, rather than a causal relationship with SOD. At active Harbor sites where the total DIN flux is comparable (BH02, BH03A and BH08A), the presence of amphipods appears to shift the dominant inorganic nitrogen form from ammonium to nitrate. This is best seen in the BH02 measurements with and without an amphipod mat (1995 vs 1996 and 1997) and BH02 versus BH08A and BH03A. These sites typically support DIN efflux rates at least 5 fold higher than QB01 and Massachusetts Bay stations. At these lower activity stations ammonium and nitrate both represent major fractions of the DIN efflux. This shift to more oxidized DIN species with either high bio-irrigation rates or low SOD is related to the availability of oxygen to support in situ nitrification of remineralized nitrogen before loss to overlying water. The higher nitrate fluxes are consistent with measured sediment oxidation-reduction potentials during this period (see below).

The pattern of nitrate (referred to as NO_x or $\text{NO}_2^- + \text{NO}_3^-$) versus ammonium flux at stations BH02 and BH03A to the extent that it indicates nitrate availability, would explain the variations in denitrification rates, 1995-1997, at these stations (Figure 3). Measurements of porewater nitrate levels generally are consistent with the high rates of denitrification, however, it appears that close coupling of nitrification-denitrification is preventing substantial build-up of interstitial nitrate concentrations (Figure 16). In addition, the depth distribution within the mat at BH03A parallels the depth of bio-irrigation expected from the mat thickness and measured Eh profiles (see below). The highest levels of nitrate and denitrification at BH02 were found in 1995, the year that a mat was present. The nitrate concentrations in porewater at these harbor sites were higher than found at the other Bay and Harbor stations. This close coupling is further supported by the relatively much larger porewater levels of ammonium at all sites indicating a ready substrate for nitrification (but limited oxygen). At all sites, ammonium accounted for $>95\%$ of the porewater DIN pool and if the total sediment ammonium pool (dissolved+sorbed) is considered, the fraction of DIN accounted for by nitrate is even smaller. The importance of nitrate to the overall DIN flux indicates an active nitrifying community which is oxidizing regenerated ammonium in excess of reduction to N_2 through denitrification.

Within the relatively comparable stations in Massachusetts Bay, DIN efflux tended to roughly parallel the concentration gradient from porewater to overlying water (Figures 13, 17). In contrast, within the Harbor inter-station differences in bio-irrigation appeared to be the major process controlling sediment-watercolumn exchange of DIN. This is evidenced by the highest rates being supported by the smallest gradients in the amphipod mats (BH03A and BH08A) and similar gradients at stations with and without mats (QB01) supporting several fold higher flux rates in the mat areas (Figure 18). Similarly, the highest concentrations of DIN in 1997 were found at BH02 (no mat) which had a DIN flux equivalent to the mat sites, but an annual remineralization rate only 45%-60% that of the mat sites (Figures 2, 14).

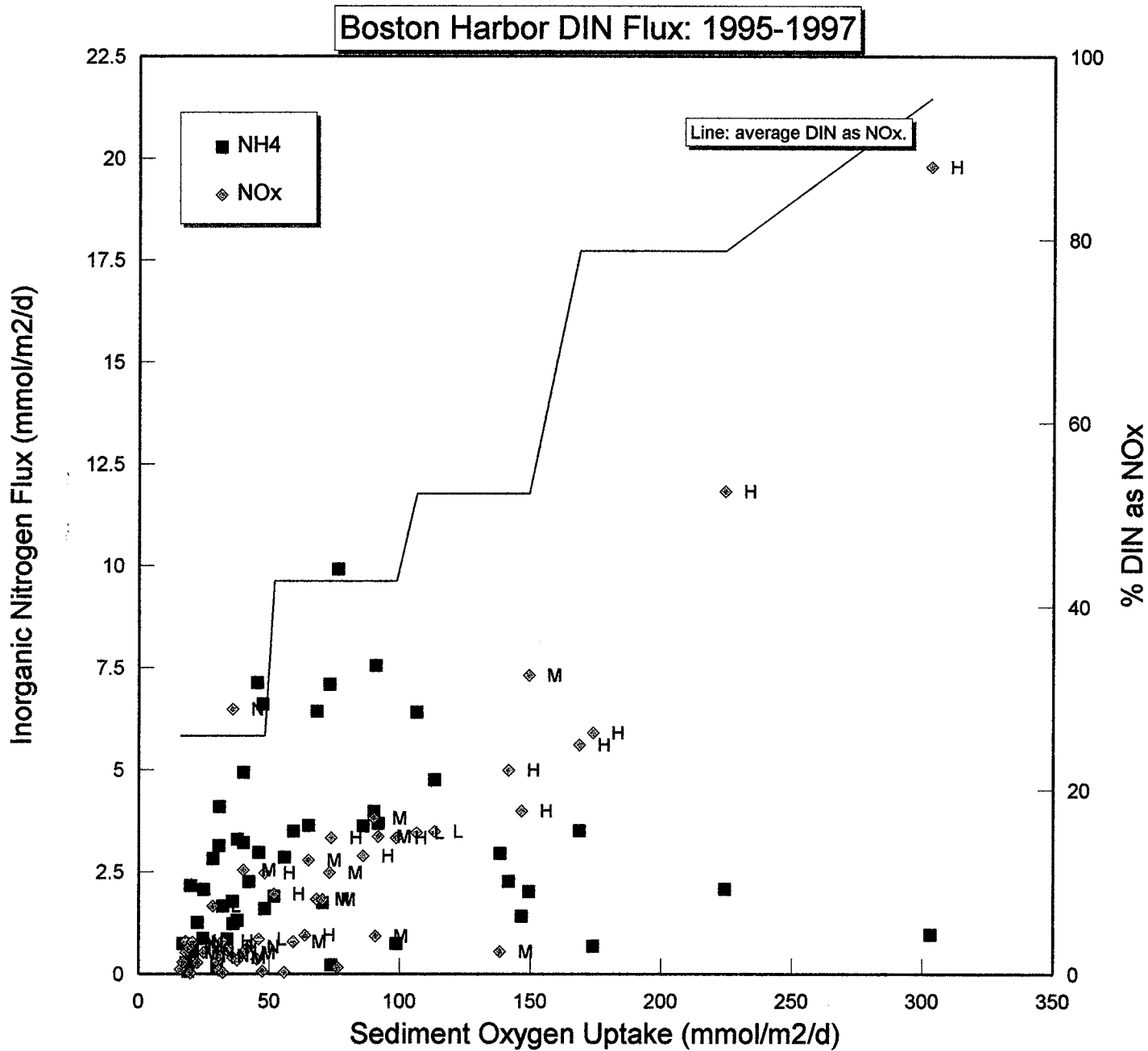


Figure 15. Seasonal pattern of dissolved inorganic nitrogen (DIN) efflux from sediments of Boston Harbor, 1995-1997. Density of coverage of surficial sediments by amphipod mats is noted below each annual series. The fraction of the DIN flux represented by nitrate+nitrite is shown by the lines.

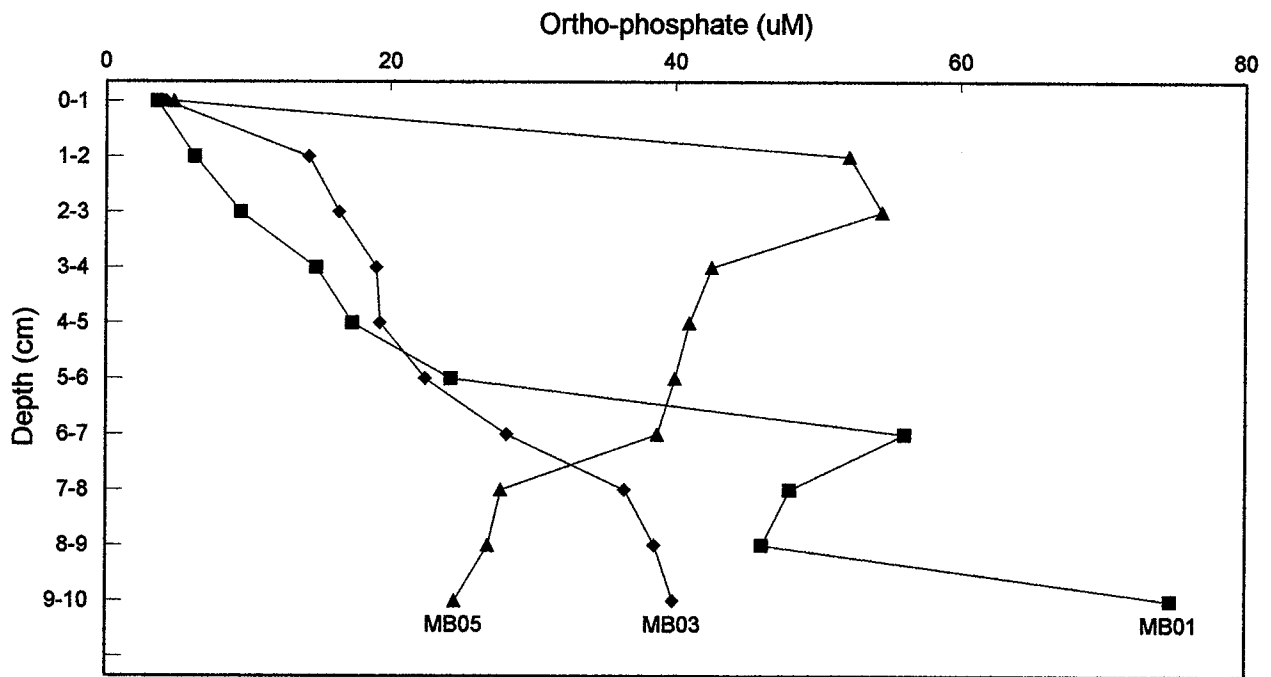
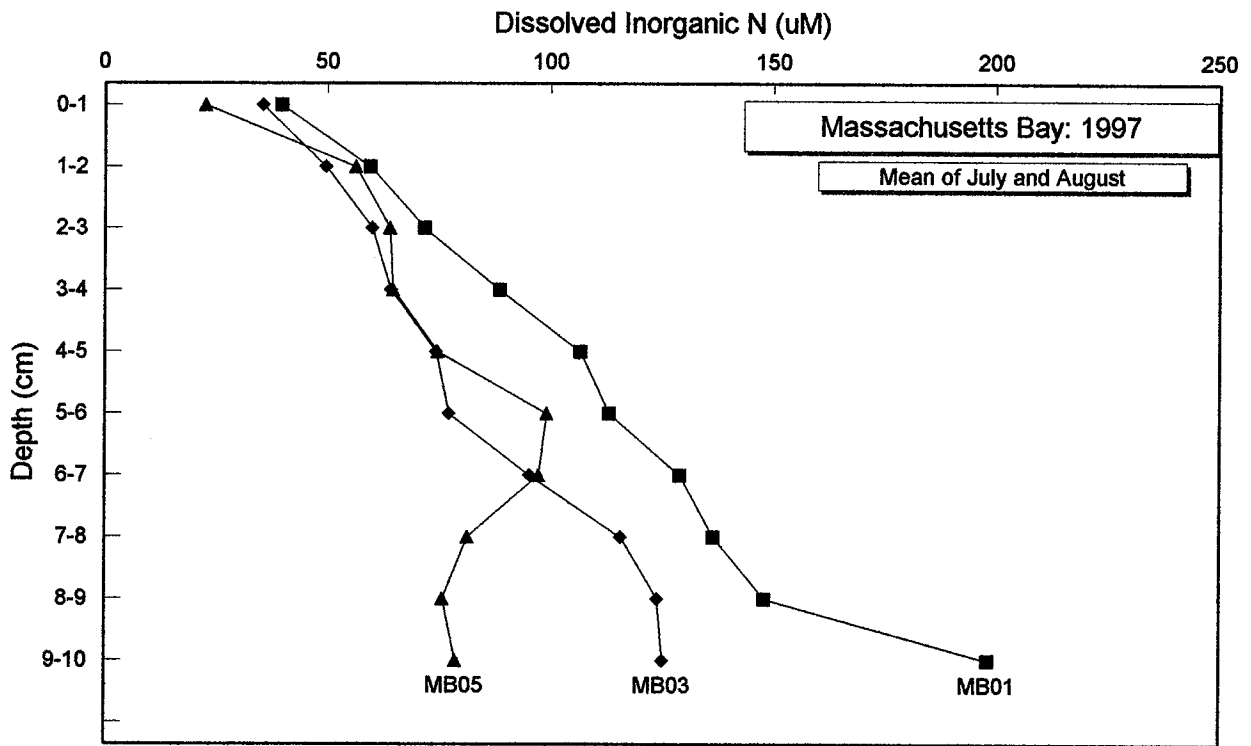


Figure 17. Average summer profiles of dissolved inorganic nitrogen (top) and ortho-phosphate (btm) within the sediments of western Massachusetts Bay in 1997. DIN was calculated as (nitrate + nitrite) + ammonium.

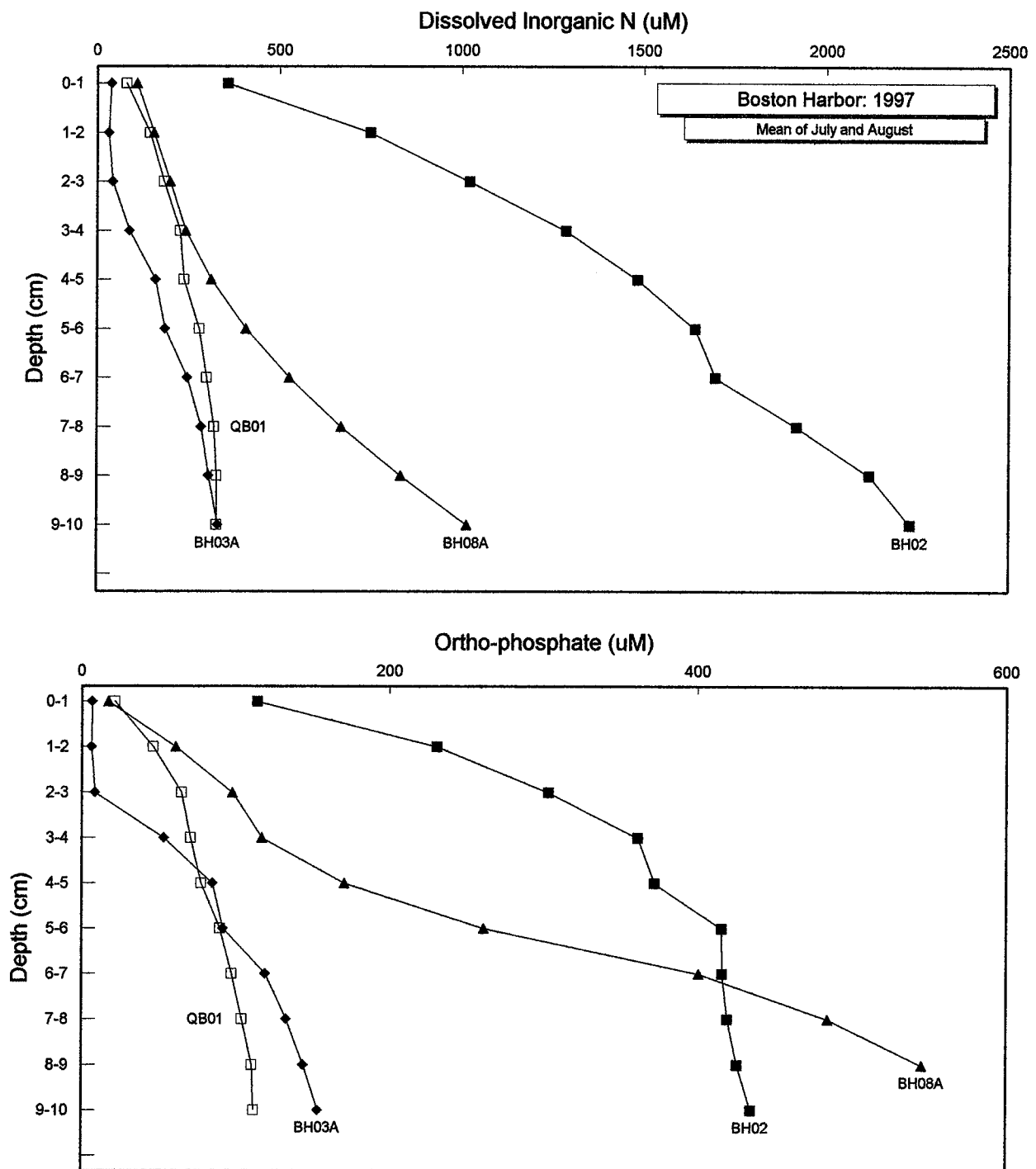


Figure 18. Average summer profiles of dissolved inorganic nitrogen (top) and ortho-phosphate (btm) within the sediments of Boston Harbor in 1997. DIN was calculated as (nitrate + nitrite) + ammonium.

It is noteworthy in the latter period of stratification that the nitrate pool in the sub-pycnocline waters of Massachusetts Bay is increasing at about twice the rate as ammonium, yet the sediment flux at this time tends to be equally partitioned or is dominated by ammonium (Cibik *et al.* 1996, Figure 13). 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. It would not be surprising to find a predominance of nitrate in the DIN flux from hard-bottomed sediments which tend to not accumulate fine organic sediments and therefore may have higher oxygen availability for nitrification than in the depositional sediments of the Bay.

In general appearance, ortho-phosphate fluxes appear to follow a similar spatial pattern as sediment respiration as did DIN fluxes. There was a strong seasonality in rates in both Harbor and Bay Stations, with fluxes at lower temperatures generally several fold lower than during summer. It was common for Harbor stations to show ortho-phosphate uptake from overlying water during winter (7 of 11 winter station-surveys, Figure 19). Harbor stations showed more than 5 fold higher rates of PO_4 loss over the Bay (Figures 19, 20). 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. Phosphate flux appears to be being controlled by similar processes of remineralization, sediment oxidation and bio-irrigation which control DIN loss to the overlying water. It is clear that in the more uniform conditions of sediments within the Bay, ortho-phosphate efflux appears to be principally driven by the concentration gradient between the surficial porewater and the overlying watercolumn (Figure 17 btm). In contrast, within the Harbor factors other than porewater concentration are modifying the rate of flux to the watercolumn. It appears that, like DIN, loss of phosphate is driven by gradient and the presence of infauna. Comparison of BH02 with (1995) and without (1996, 1997) amphipods shows about a one half reduction in rates. Note that the high DIP fluxes during 1996 and 1997 at BH02 resulted from the sediments being extremely reducing even to the surface. This absence of an oxic surface layer resulted in a large DIP loss due to the lack of retention by precipitation with oxidized iron minerals. During the rest of the surveys an oxidized layer was apparent and DIP flux was generally low. It is uptake by this oxidized surface layer which most likely accounts for the negative effluxes recorded during the late winter survey. It is during late winter that sediments are most oxidized and DIP sorption is generally highest. It is most likely bio-irrigation which results in the typically higher DIP efflux from BH03A and BH08A which have low porewater PO_4 pools but significant amphipod mats compared to BH02 and QB01 which have high porewater pools and depauperate infaunal communities (Figure 18, 19).

More than other fluxes, the rate of silicate flux from almost all sites in Boston Harbor and Massachusetts Bay tracked bottom water temperatures. Highest silicate efflux rates were found at all sites during the warmest periods (Figures 21, 22). The direct relationship between temperature and silicate flux, particularly in Massachusetts Bay suggests a only a loose coupling between organic carbon mineralization rate and silicate flux. This is further evidenced by the more similar rates of silicate flux than sediment oxygen uptake or nutrient efflux between the Harbor and Bay. The pattern was reproduced in each year 1995-1997. However, there was some linkage between biogeochemical activity and silicate flux as rates were consistently higher within the Harbor than in the Bay and higher at BH02, BH03A and BH08A versus QB01. Although rates of silicate flux followed the general pattern of SOD rates, like DIN and DIP fluxes they appeared to be mediated by another factor. Bio-irrigation appears to exert some effect as evidenced by the moderately high silicate fluxes observed at BH03A being supported by porewater concentrations only about one-third to two-thirds that of the

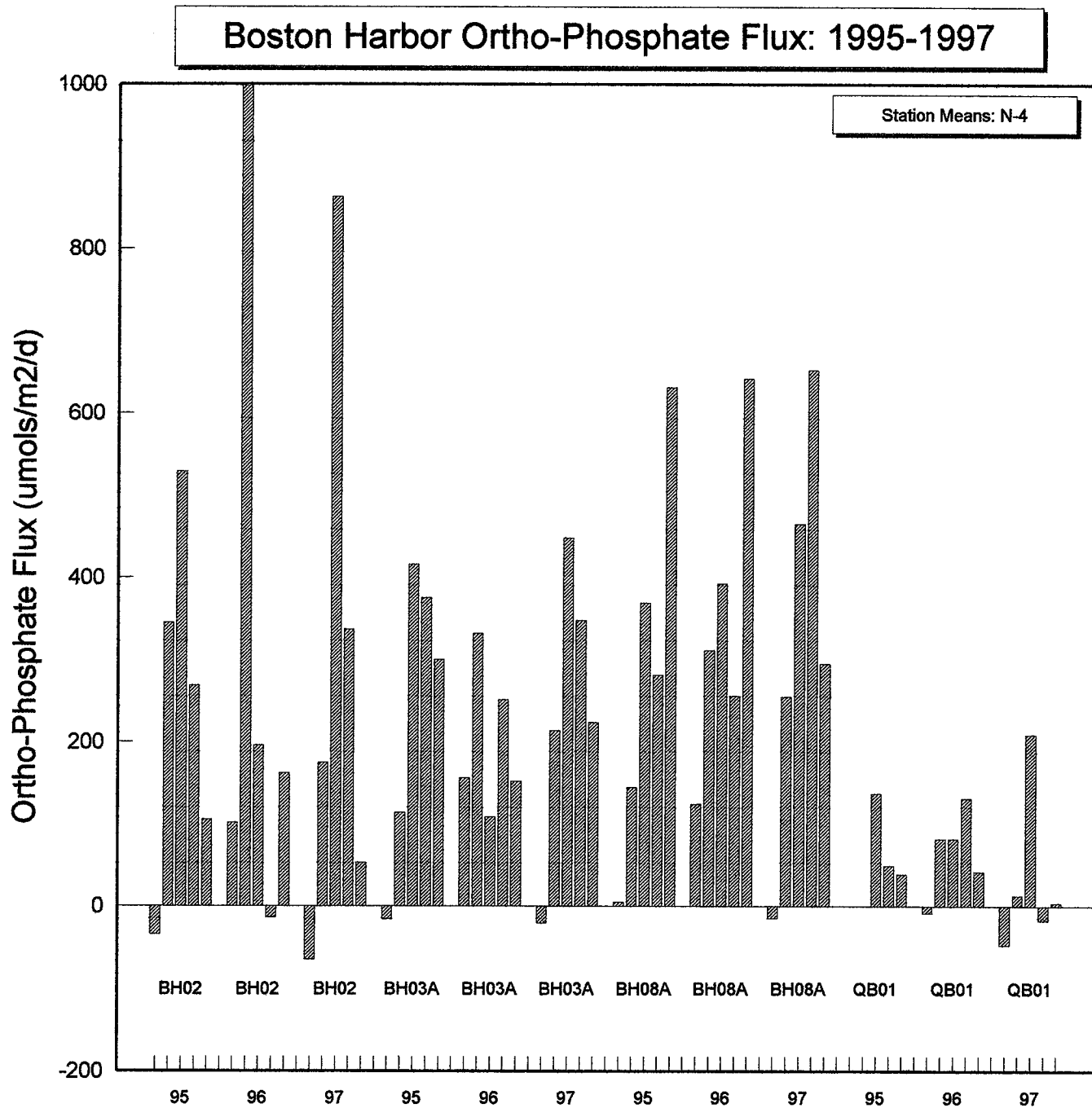


Figure 19. Seasonal distribution of ortho-phosphate efflux from the sediments of Boston Harbor, 1995-1997. Values are means of 4 cores. Negative values represent uptake by sediments.

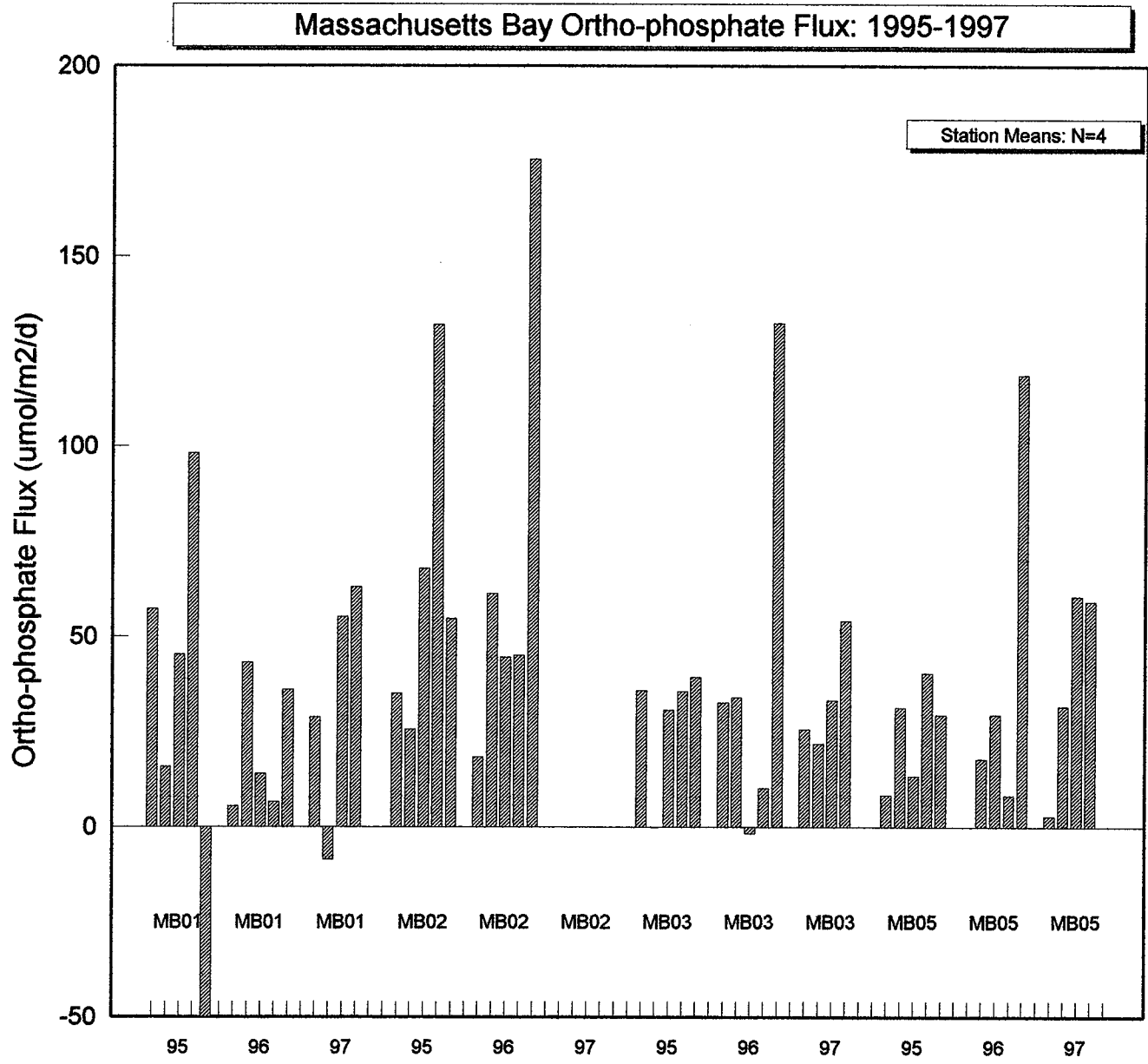


Figure 20. Seasonal distribution of ortho-phosphate efflux from the sediments of western Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) during 1995-1997. MB02 was not sampled in 1997. Negative values represent uptake by sediments.

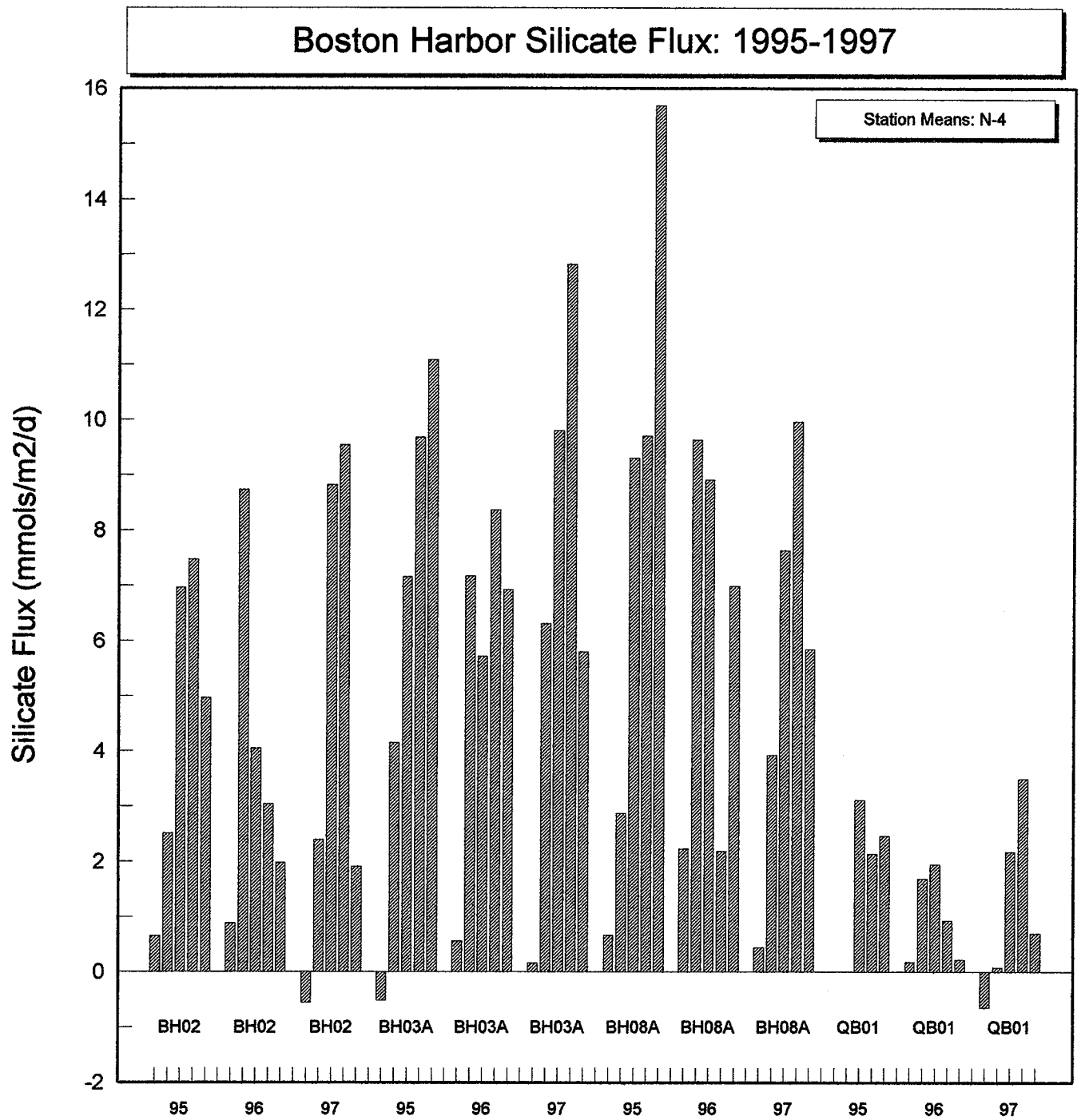


Figure 21. Seasonal distribution of silicate efflux from the sediments of Boston Harbor, 1995-1997. Values are means of 4 cores. Negative values represent uptake by sediments.

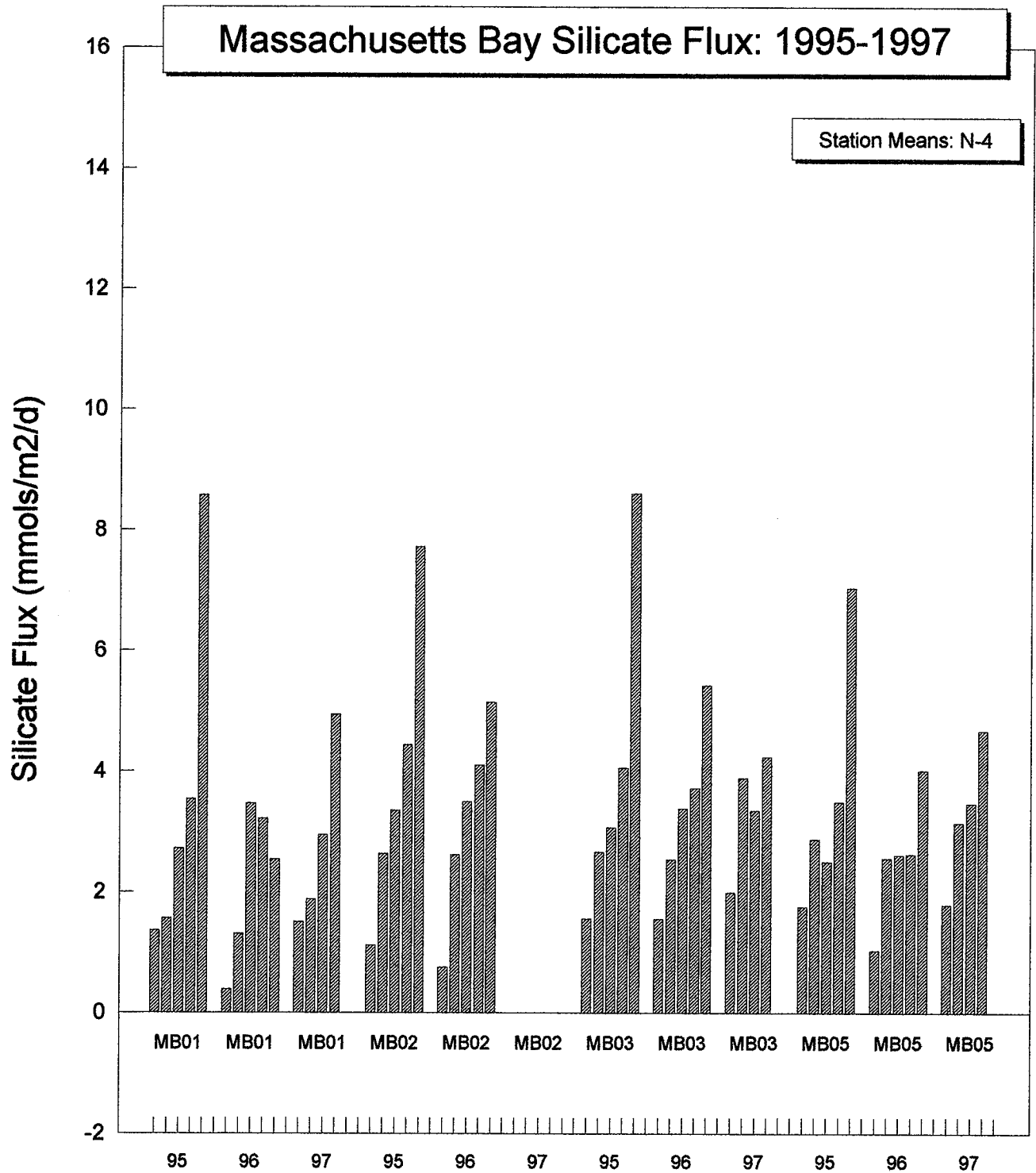


Figure 22. Seasonal distribution of silicate efflux from the sediments of western nearfield region of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05), 1995-1997. MB02 was not sampled in 1997. Values are means of 4 cores.

other Harbor sites (Figure 23). Most striking is that the least bioturbated site, BH02, has only moderate silicate flux rates, but porewater silicate levels more than 2 times all other sites.

Rates of flux of silicate from sediments from all sites were lower in both the Harbor and Bay in 1995-1997 compared to 1994. These lower numbers contrast with the higher respiration and irrigation rates within the Harbor in 1995 and 1996 and the similarity of oxygen uptake at the Massachusetts Bay locations in all years. Considering the interannual consistency in 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 1995-1997 versus 1994. It is unclear what would cause interannual changes in the retention of regenerated nutrients. At this point methodological differences 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. One possible mechanism for the higher silicate flux could be associated with the rapid settling of a large *Asterionellopsis glacialis* bloom in the fall of 1993 (Libby *et al.* 1994). It is possible that remineralization of this bloom with the advent of warmer waters in 1994 may have helped to support the higher fluxes. However, it is not clear at this time why this would affect the nutrient fluxes more than the rate of oxygen uptake. In addition, deposition of the *Chaetoceros* bloom in 1997 resulted in no increase in the silicate flux from the Bay sediments in 1997 versus 1995 and 1996. The observed rates of silicate flux are consistent with the observed increases in Massachusetts Bay bottom waters during stratification.

Comparison of silicate and DIN flux rates indicates that there are differences in either the source material or a facilitated transport of silicate versus DIN from the sediments of Massachusetts Bay versus Boston Harbor (Figure 24). Silicate flux to overlying waters from the Bay sediments is more than 10 fold higher than its associated DIN flux compared to the Harbor locations. Since diatoms incorporate silicate at 1 to 2 moles per mole of nitrogen, the flux from the Bay sediments helps to explain the seasonal cycle of nutrient concentrations within the Bay. Under current conditions nitrogen becomes depleted within the euphotic zone of the Bay before silicate (excess silicate). The "excess" silicate flux from the Bay sediments most likely results from a solubilization of non-biogenic silicate. Regeneration of silicate and DIN from Harbor sediments suggests a system where nitrogen regeneration is supported by a mixture of diatoms and non-diatom related organic matter or a enhanced efflux of DIN over silicate compared to the Bay. The effect of input of effluent enriched in DIN over silicate needs to be evaluated relative to nutrient regeneration from sediments.

Infauna, sediment oxidation and biogeochemical cycles: The evidence is mounting that sediments within Boston Harbor colonized by amphipods support significantly higher rates of oxygen uptake and denitrification than those depauperate in infauna which were typical of most of the Harbor in the early 1990's. There are several data sets which support this conclusion. First, comparison of rates of SOD and denitrification in sediments colonized by amphipods in 1997-1995 and 1993 compared to uncolonized sites in 1992-1997 (Giblin *et al.* 1997, Nowicki *et al.* 1997, Howes 1998a,b) all indicate several fold higher rates of metabolism where amphipods are present. Second, in the Harbor sediments where the *Ampelisca* complex was found (BH03A, BH02, BH08B) in 1995 the rate of oxygen uptake was 2-5 fold higher than where *Ampelisca* were absent (QB01). Third, seasonal sampling of low (BH02) and high (BH03A) density mats in 1995 indicated that these areas were colonized by amphipods (*Ampelisca* and *Leptocheirus*) from March through August, but began to break-up in August and were virtually gone by the October sampling. Nearly linear increases in community

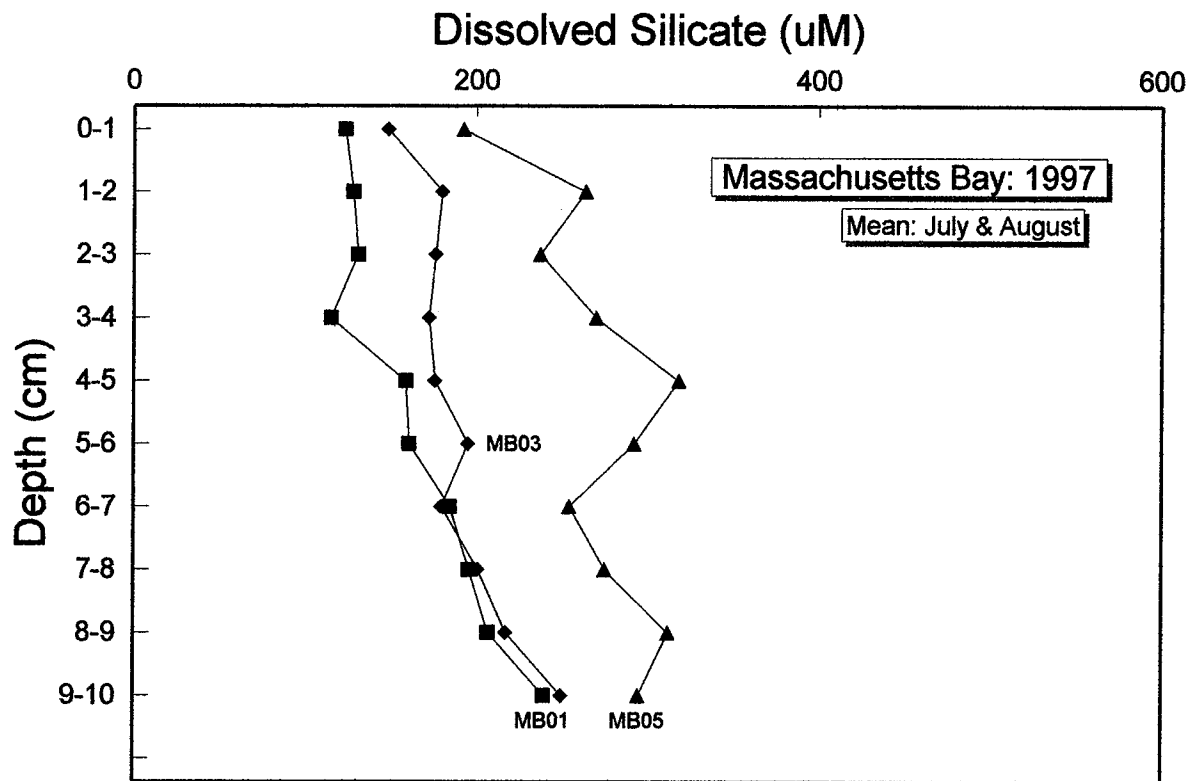
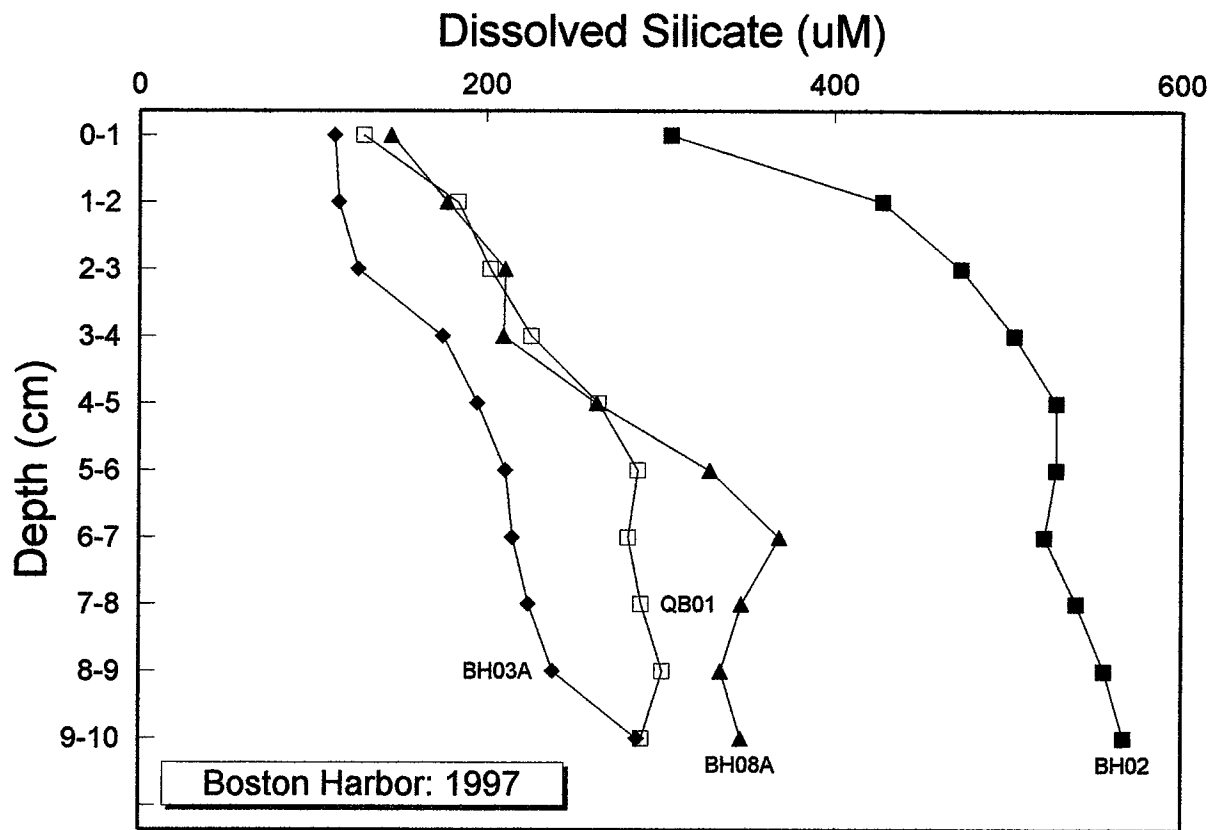


Figure 23. Average summer profiles of dissolved silicate within the sediments of (top) Boston Harbor and (btm) the western nearfield region of Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) in 1997.

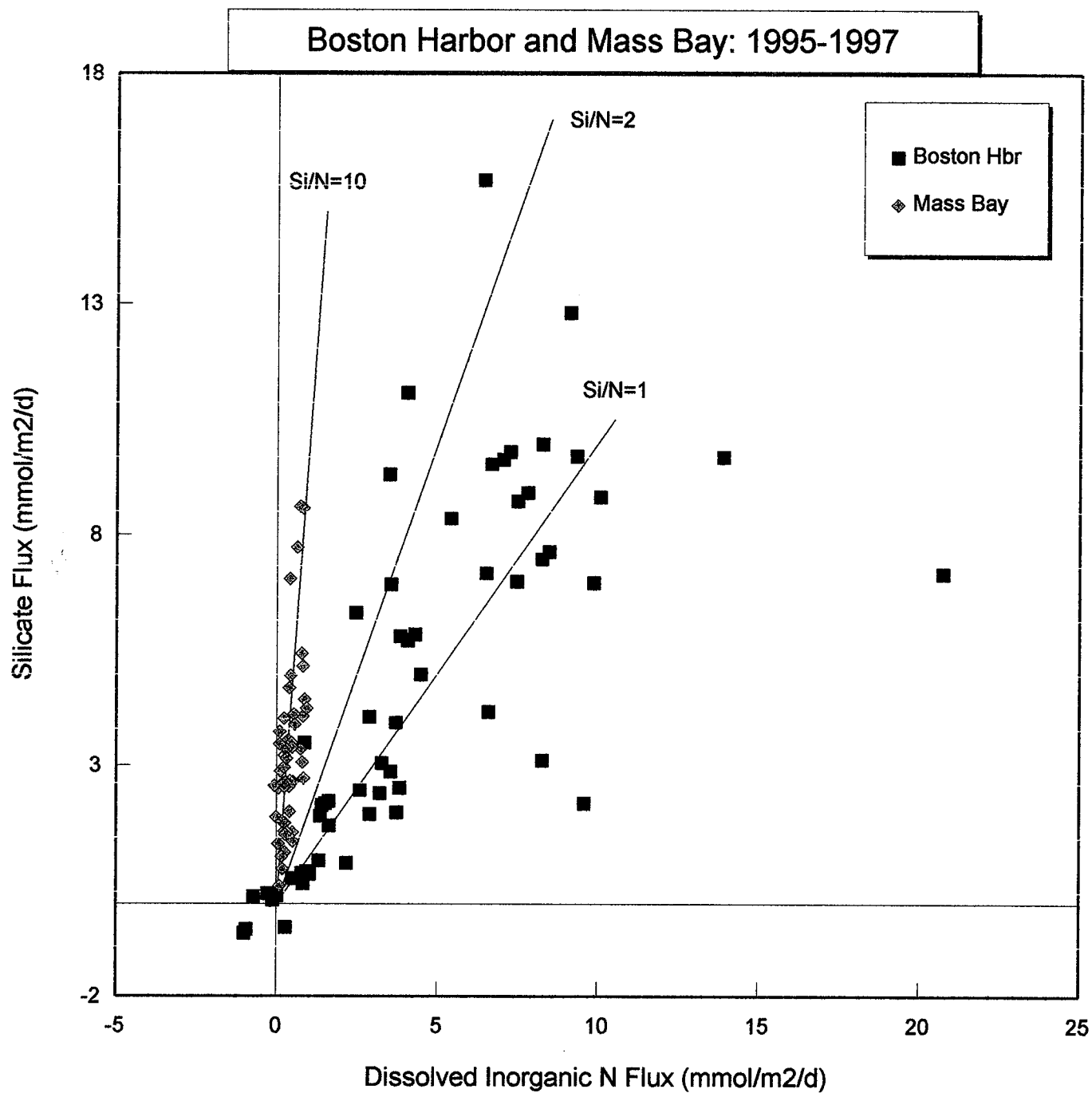


Figure 24. Relationship of silicate to dissolved inorganic nitrogen (DIN) fluxes from the sediments of Massachusetts Bay and Boston Harbor, 1995-1997. Lines represent Si:N ratios of 1,2 and 10.

respiration with temperature were found at both stations when the mats were present (Mar-Aug) which 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 (BH02) higher rates of oxygen uptake at similar temperatures in the presence versus absence of the amphipod community. 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 (Howes 1998a). Fourth, the several fold higher rates of oxygen uptake and denitrification at BH02 found in 1995 when a modest mat was present compared to the significantly lower rates at the same station in 1996 and 1997 when a mat failed to form.

While the enhancement of sediment metabolism within sediments is now becoming clear, the duration of the effect and its impact on biogeochemical cycling within the Boston Harbor system is less certain. However, it appears that following the rapid colonization of the central Harbor region (Hilbig *et al.* 1996, Figure 5), there have been several major changes in the relative role of the sediments within the Harbor nutrient and organic matter cycles. First, after colonization there has been a shift from an equal distribution of oxygen uptake between the sediments and overlying watercolumn to a predominance of the sediments as the focus of system carbon remineralization (Howes 1998a,b). Second, with mat formation there appears to be a shift in the molar ratio of regenerated DIN and DIP relating to increased bio-irrigation and oxidation of the sediments. 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). The relative amounts of inorganic nitrogen and phosphorus available to support phytoplankton production frequently result in N or P becoming depleted, causing nutrient limitation. 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 on 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.* 1997). Massachusetts Bay sediments show a similar pattern to Harbor regions without mats (Figure 25). N/P fluxes show a return of greater amounts of P than N, based on the theoretical ratio of 1P:16N (Redfield *et al.* 1963). In contrast after colonization by amphipods, DIN fluxes frequently were equal to or greater than 16 times ortho-phosphate fluxes (Figure 26). The annually integrated ratio of DIN:DIP fluxes is 20.1 (SE=2.3, N=7) in mat areas, 15.4 (SE=2.0, N=4) in non-amphipod mat regions of the Harbor and 12.0 (SE=2.1, N=11) within Massachusetts Bay, 1995-1997. This apparent increase in DIN flux relative to DIP flux in mat areas does not appear to be methodological as the N/P flux ratio for Bay sites (ca. 11, 1995-97 stratified periods) remains similar to earlier measurements in the Bay (ca. 8, 1992-94 stratified periods). The flux ratios in the Bay are consistent with the observed bottom water DIN and DIP ratio during stratification (N/P=12).

The shift to higher N/P flux ratios from Harbor sediments colonized by amphipods 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 within the recolonizing central Harbor sediments, appears to be related to the increased irrigation of sediments by the colonizing infauna. The irrigation is to ventilate infaunal burrows, but secondarily results in an increased oxidation of the

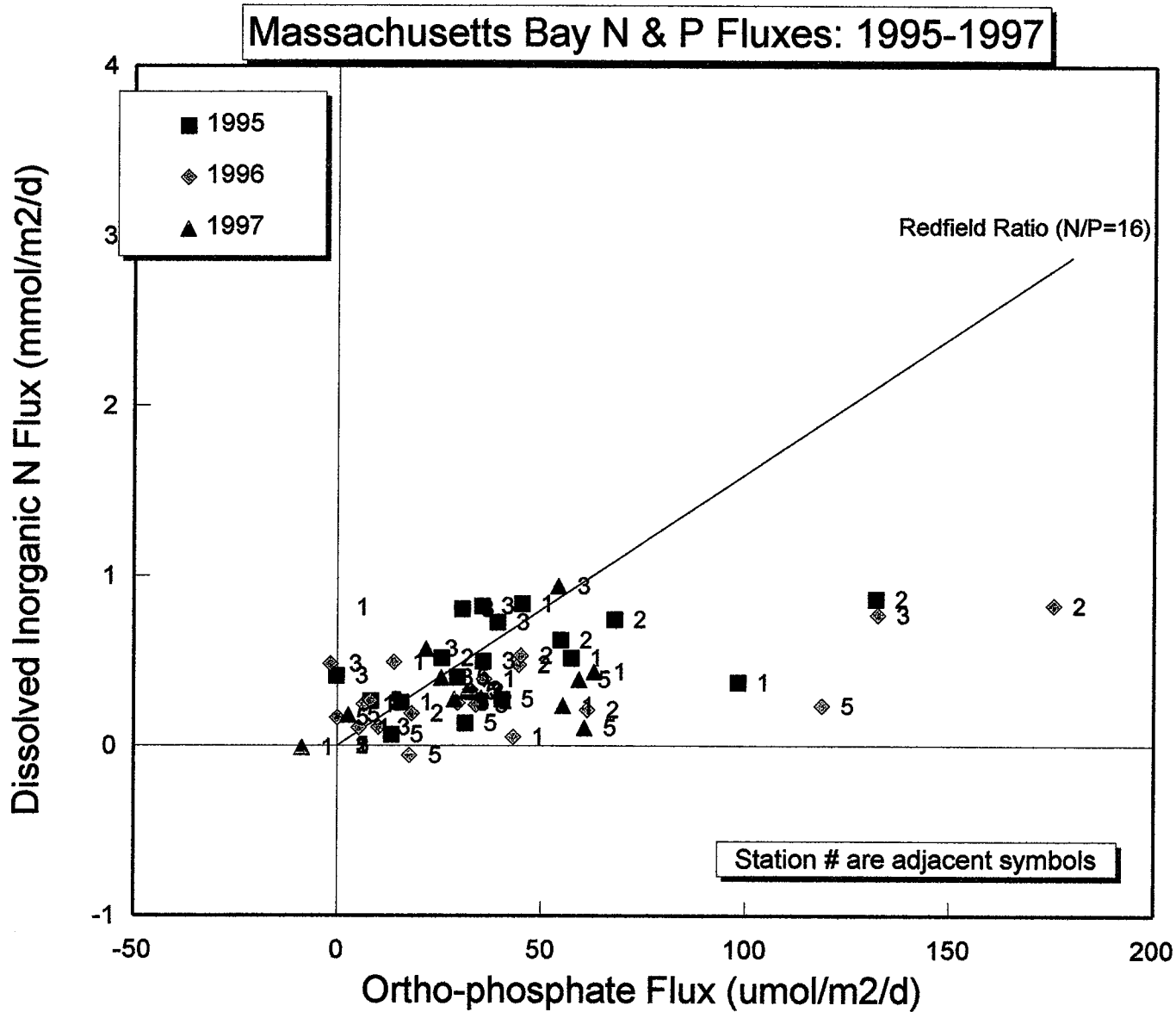


Figure 25. Relationship of dissolved inorganic nitrogen (DIN) to ortho-phosphate fluxes from the sediments of the western nearfield of Massachusetts Bay and Stellwagen Basin relative to the theoretical molar ratio (16) predicted by Redfield (1963), 1995-97.

Boston Harbor Inorganic N & P Fluxes: 1995-1997

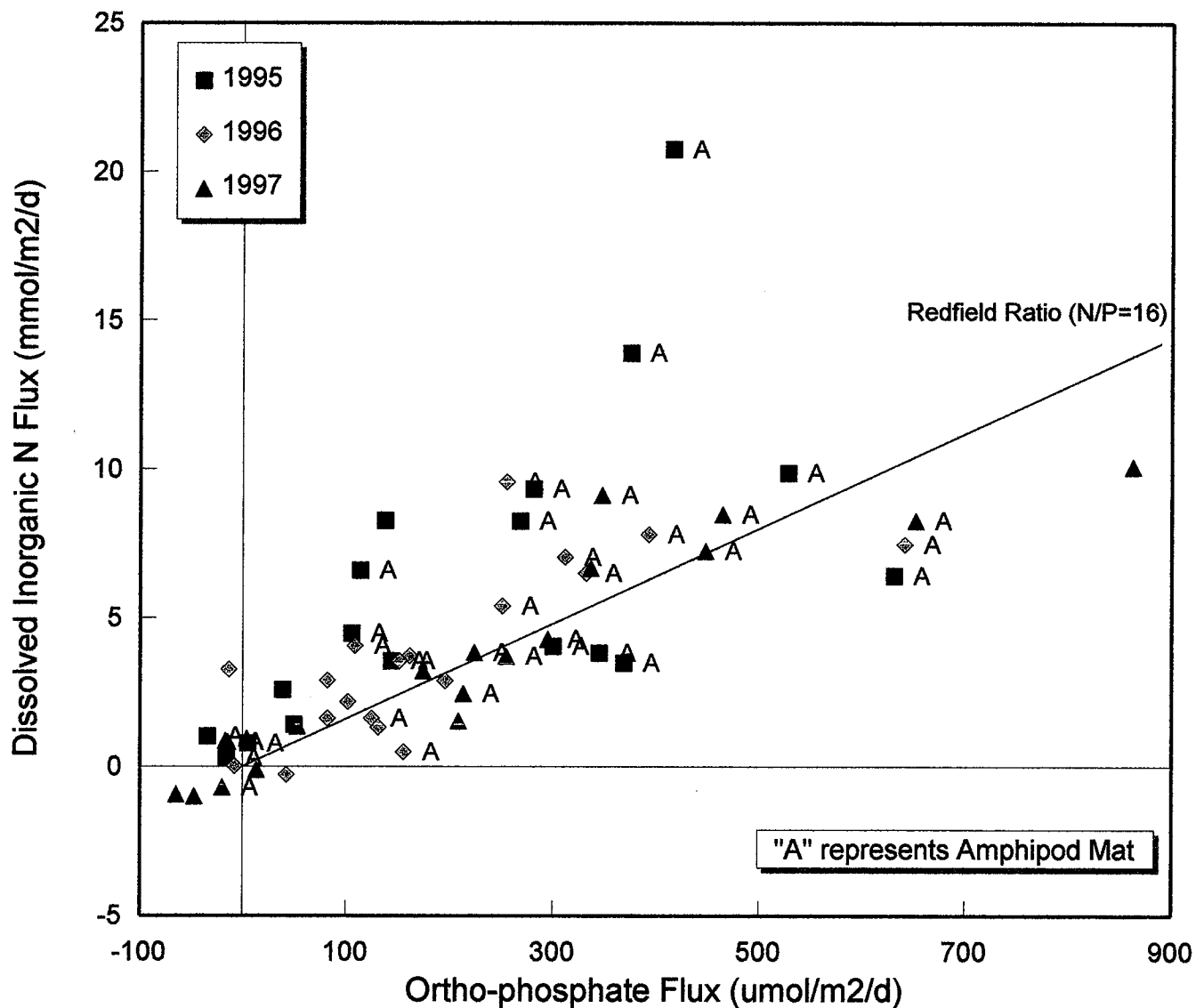


Figure 26. Relationship of dissolved inorganic nitrogen (DIN) to ortho-phosphate fluxes from the sediments of Boston Harbor relative to the theoretical molar ratio (16) required to support phytoplankton production predicted by Redfield (1963), 1995-1997.

sediment system in spite of the much higher rates of oxygen uptake. The increased sediment ventilation appears to support higher rates of nitrification, hence denitrification. Similarly, the DIN flux shifts from one dominated by ammonium to one where nitrate is also a major fraction (Figure 14). This increased ventilation of the sediment appears also to be stimulating nitrogen fluxes from the sediments. In contrast, the effect of amphipod mats on DIP flux is much more variable. At the highest density sites ventilation may be inhibiting ortho-phosphate release. DIP fluxes from BH03A sediments are low relative to mineralization rates (Figures 27). However, this effect is only seen at the highest mat densities. Other factors such as periodic high fluxes of DIP in response to the periodic formation of an anoxic surficial sediment (eg. BH02) or the development of very steep gradients from porewater to overlying water support high fluxes in non-mat areas. However, at QB01 which has a relatively low SOD, DIP flux is also low relative to the observed rate of mineralization. The more oxidized Bay sediments showed an intermediate level of DIP flux relative to mineralization rates (SOD/DIP flux = 294), similar to the moderately bioturbated sites within the Harbor (mean SOD/DIP flux = 233).

The cause of the diminished DIP flux relative to remineralization rates after colonization by infauna most likely results from increased retention of remineralized P due to sorption within more oxidized sediments. However, it appears that the major cause of shift in the ratio of DIN:DIP flux in sediments supporting amphipod mats is the result of increased DIN efflux more than increased DIP retention. The potential effect of this shift, in the relative regeneration rates of the major phytoplankton nutrients, on the Harbor nutrient field after terrestrial inputs are reduced (by the relocation of the outfall) needs to be analyzed as monitoring continues.

A third major effect of the recolonization of the Harbor sediments on biogeochemical cycling is that the enhanced rates of sediment carbon mineralization and nitrogen cycling appears to be supported, in part, by "mining" of materials stored within the surficial sediments. At sites where oxygen uptake, denitrification and nitrogen efflux are measured it is possible to calculate the carbon to nitrogen ratio which approximates the annual average of the sediment source of the C and N (Figure 28). For example in the region of the medium/weak mat, the annual carbon mineralization calculated from the annually integrated oxygen uptake was 6.1 times the total inorganic nitrogen flux calculated from the efflux of DIN and rate of denitrification. Using a conversion of 1 carbon remineralized for each O₂ reduced indicates that the C/N ratio of the remineralized substrate was 6.1. This suggests that the organic matter substrate supporting these fluxes is likely phytoplankton, as the average C/N ratio in the watercolumn of the Harbor ranges from 6.0-6.5. A similar ratio C/N flux ratio was found in the region of no mat (7.4-5.8). In contrast, in the area of dense amphipod mat the C/N ratio of the substrate calculated from the fluxes was significantly higher, >11 in the first year after colonization. As this was at a site where the mat was likely a recent phenomenon, it is very likely that the higher oxygen uptake relative to N release results from the oxidation of stored reduced end-products of anaerobic metabolism formed in previous years. With continued amphipod activities in 1996 and 1997, the rates of sediment oxygen uptake and DIN efflux declined while denitrification remained high. As a result the calculated C/N ratio of the substrate decreased to values indicative of a phytoplankton source. A likely explanation is that the oxidizable substrates stored within the sediments during the interval of diminished infaunal activity are oxidized within the initial years after colonization. The "mining" of reduced sediment substrates is consistent with the much higher dissolved sulfide levels in Harbor sediments from "non-mat" sites (Howes 1998a,b). It appears from this C/N analysis that the "mining" effect may be short in duration, possibly only 1 to 2 years.

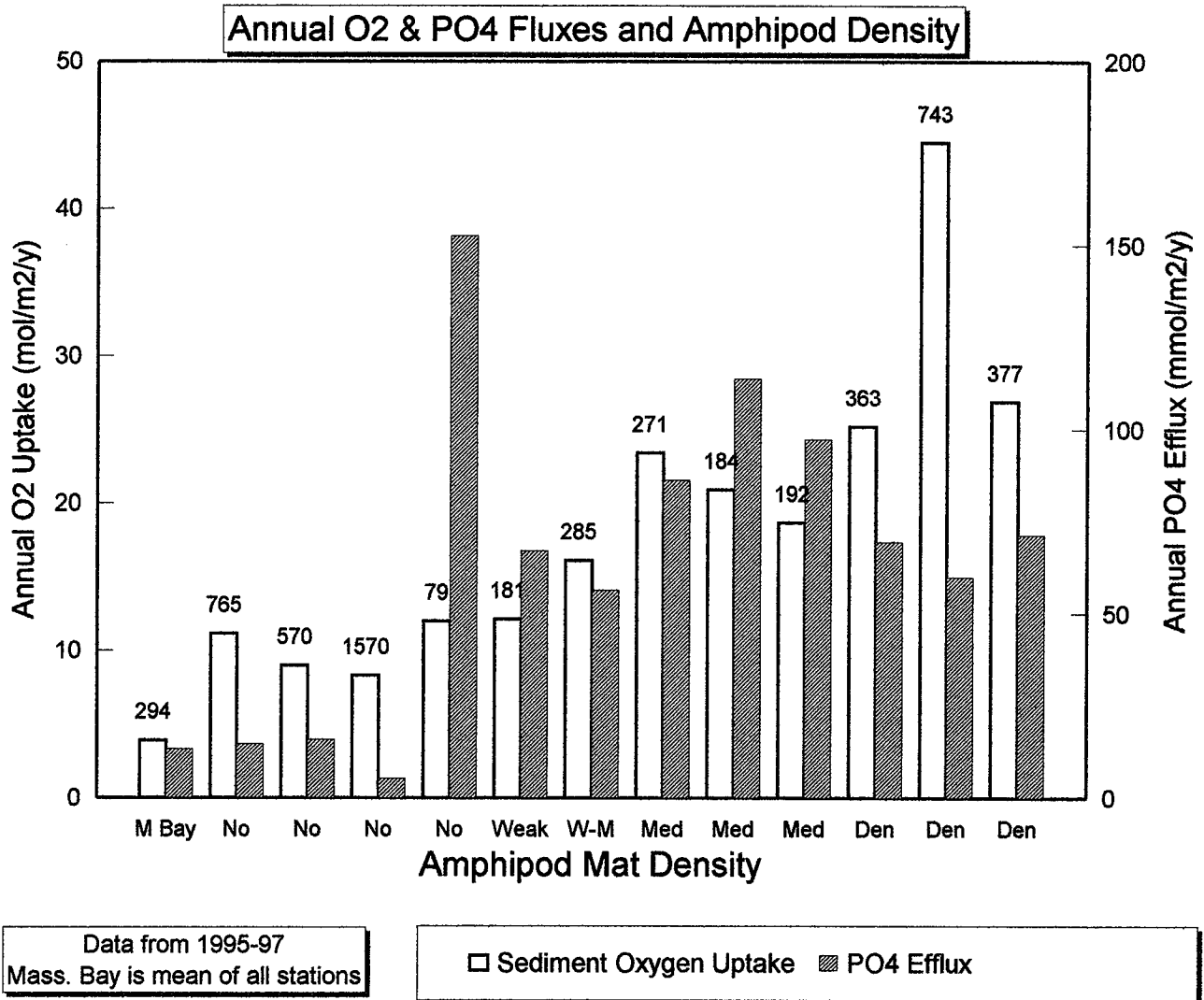
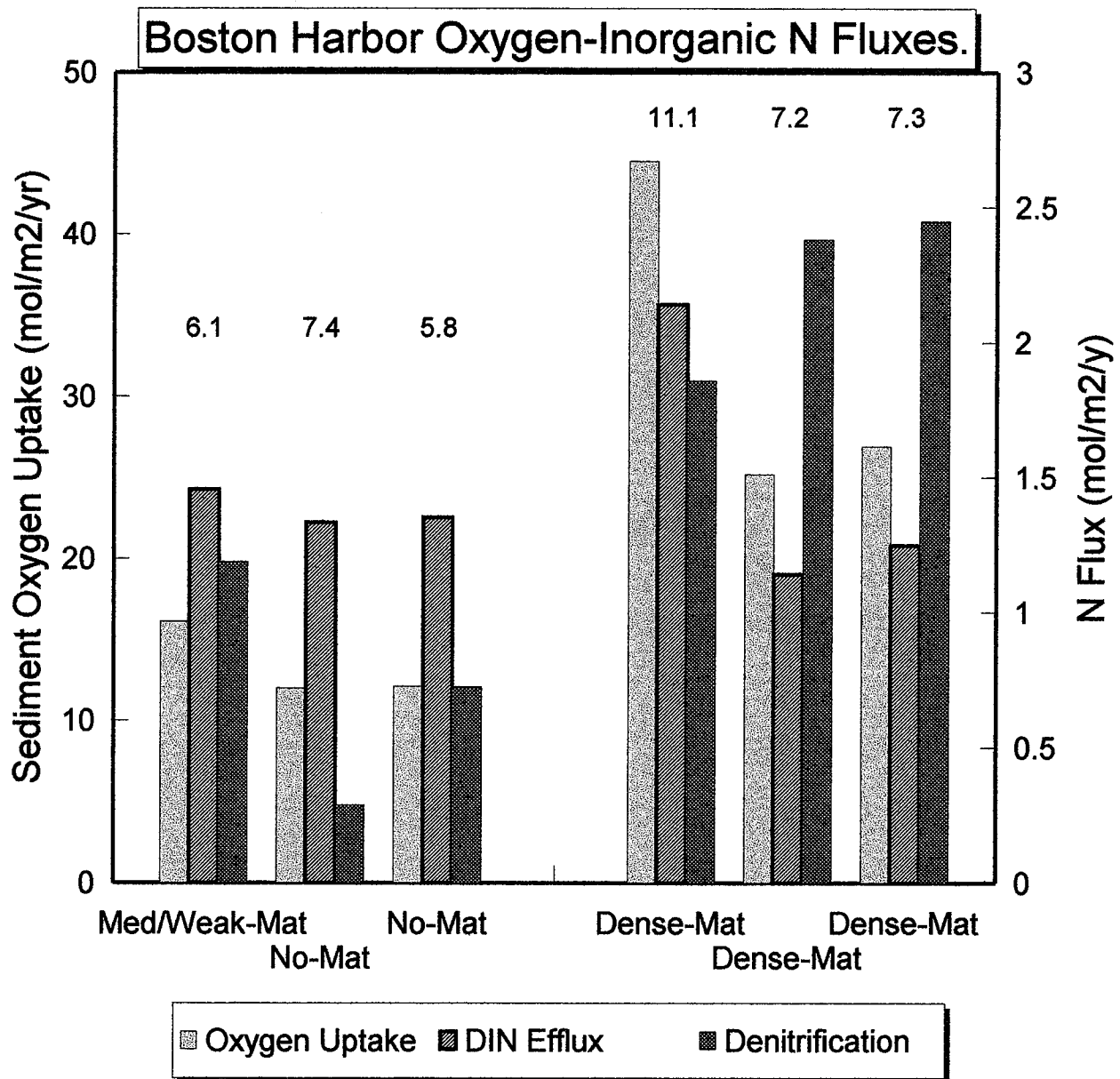


Figure 27. Relationship of sediment oxygen uptake and ortho-phosphate efflux from sediments of Boston Harbor supporting varying densities of amphipod mats, 1995-1997. Note that the high ortho-phosphate flux in the one station with no mat resulted from the absence of an oxic surface layer at that site during one of the samplings (BH02 in 1996).



Values above bars are calculated "C/N" ratios.
 Data: 1995, 1996, 1997

Figure 28. Relationship of integrated annual oxygen uptake, denitrification and DIN efflux from sediments within Boston Harbor (BH02, BH03A) in 1995-1997. Values above the bars represent the calculated C/N ratio of the organic substrate supporting the measured fluxes.

That the oxidation of dissolved sulfide can occur on annual time scales is supported by the seasonal changes found within the porewater at BH02, the Harbor site with the highest sulfide levels. As a result of seasonal variations in the rate of sulfide production and oxidation, dissolved sulfide levels at BH02 increase more than 4 fold from March to August. Then the levels rapidly fall, close to March levels over the next 2 months (Figure 29).

One of the more sensitive measures of changes in organic matter loading and infaunal ventilation of coastal sediments is the oxidation-reduction profile of surficial sediments. This is especially informative where there are low levels of dissolved sulfide as found at most of the flux monitoring stations. Sediment oxidation status is the balance between the input of reduced metabolites from the decomposition of deposited organic matter and their reoxidation primarily via oxygen either diffusing or being advected into surficial sediments during burrow ventilation. There is a seasonal cycle in sediment Eh (similar to that seen in sulfide at BH02, Figure 29), with more oxidizing conditions occurring in winter as oxidation exceeds input of reduced compounds and more reducing conditions in summer as respiration increases (Howes 1998a).

Measured Eh profiles during 1997 indicated that within Massachusetts Bay and Boston Harbor sediments the level of oxidation roughly corresponds to the level of organic matter turnover (Figures 2, 6, 30). The relationship of sediment oxidation between the sampling sites within the Bay and Harbor observed in 1997, was equivalent to the pattern in 1995 and 1996 (Figures 31, 32).

Massachusetts Bay sediments were significantly more oxidized than those of the Harbor. In addition, within the Bay system sediments were significantly more oxidized (more positive mV) in the deeper Stellwagen Basin than in the western nearfield sites (Figure 30). This pattern is fully consistent with the relatively lower metabolic rates, nutrient fluxes and pigment levels at the station MB05. In contrast, in the Harbor sediment oxidation was positively related to metabolic and organic deposition parameters, the sites with the highest rates exhibiting the most oxidized sediments. This is contrary to the expectation that higher rates of organic matter loading result in more reducing sediments. However, it is possible if an additional mediating process is occurring. Within the Harbor this process is enhanced bio-irrigation rates associated with the significantly different infaunal communities at the more reduced (QB01, BH02) versus oxidized stations (BH03A, BH08A). The measured Eh profiles within the Harbor are consistent with parallel measurements of dissolved sulfide (Howes 1998a,b). The more oxidizing nature of colonized Harbor areas results from the ability of the infauna to ventilate in excess of demand. The effect of ventilation by the mat communities can be seen in the depths over which the sediments are significantly more oxidizing within the mat versus non-mat areas (BH03A and BH08A versus BH02 and QB01). During summer the mats were observed to reach to 5-8 cm depth, consistent with the measured redox discontinuity depth (0 mV depth). Note that at depth in the sediment all sites approach similar reducing conditions (Figure 30).

The relationship between sediment oxidation status and oxygen uptake and the impact of infaunal ventilation can be evaluated by comparing the measured rates with the calculated depth of the redox discontinuity ($RDP = 0$ mV). From this analysis two relationships between RDP and SOD emerge depending upon the presence of dense amphipod assemblages (Figure 33). Where mats are not present in the Harbor and within the Bay, the relationship follows a power function of rapidly increasing RDP with decreasing SOD. This fits the basic biogeochemical observation that under higher organic matter loading rates sediments tend to become more reducing (all other factors remaining unchanged).

Boston Harbor: Summer 1995-97

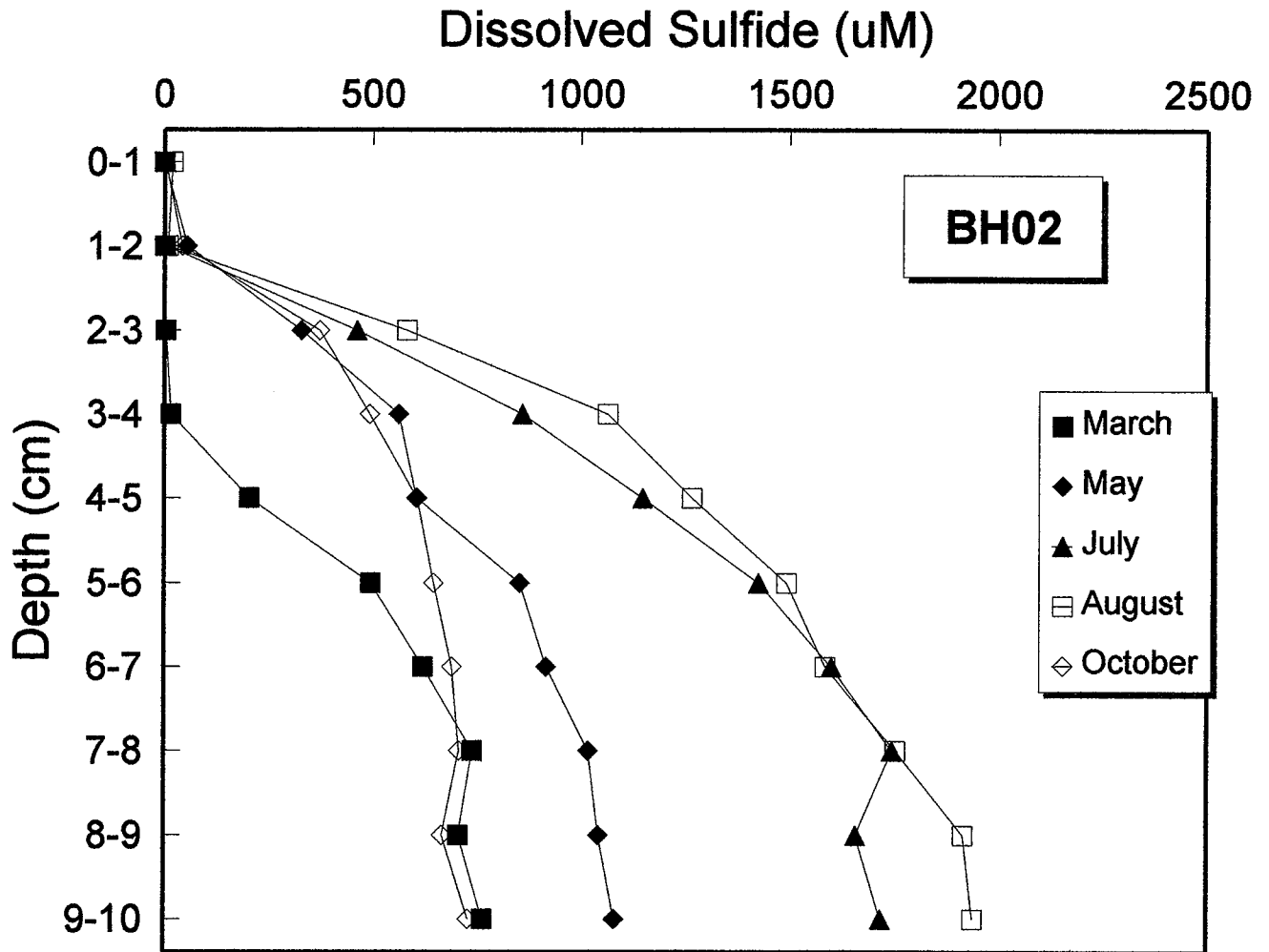


Figure 29. Profiles of dissolved sulfide in porewaters of Boston Harbor station BH02 throughout 1997.

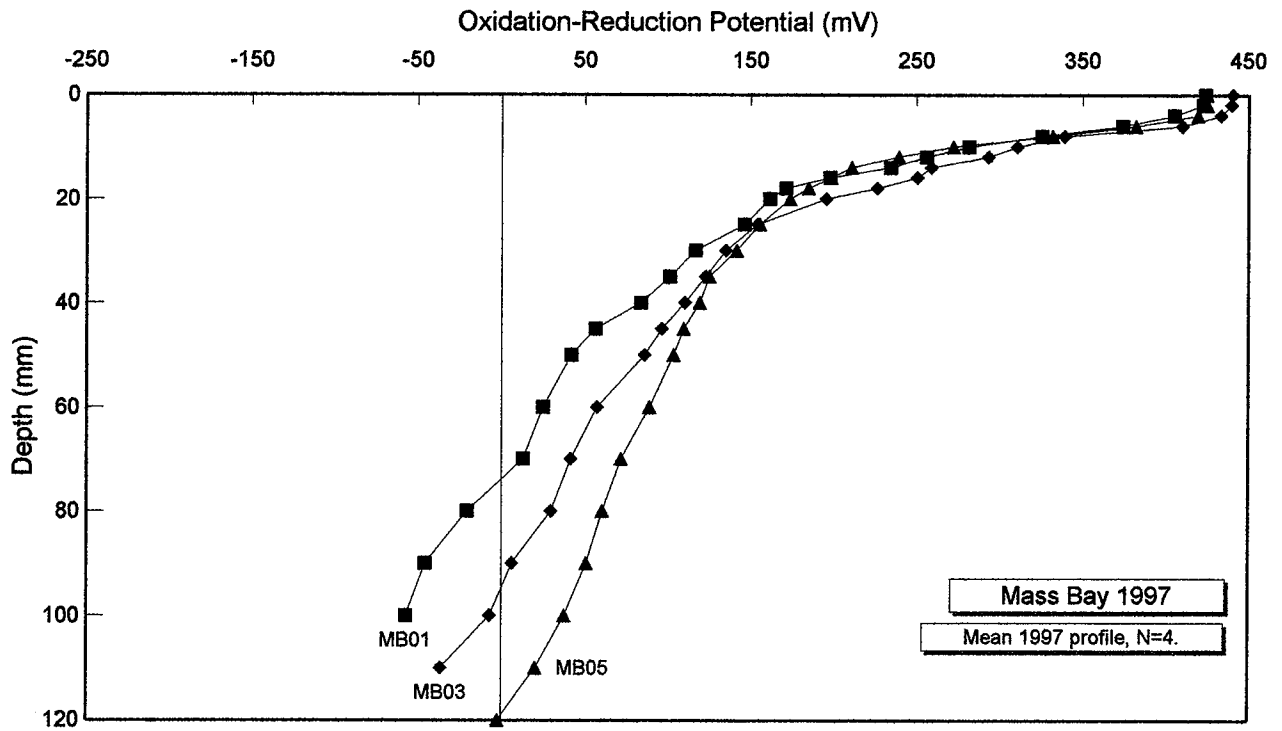
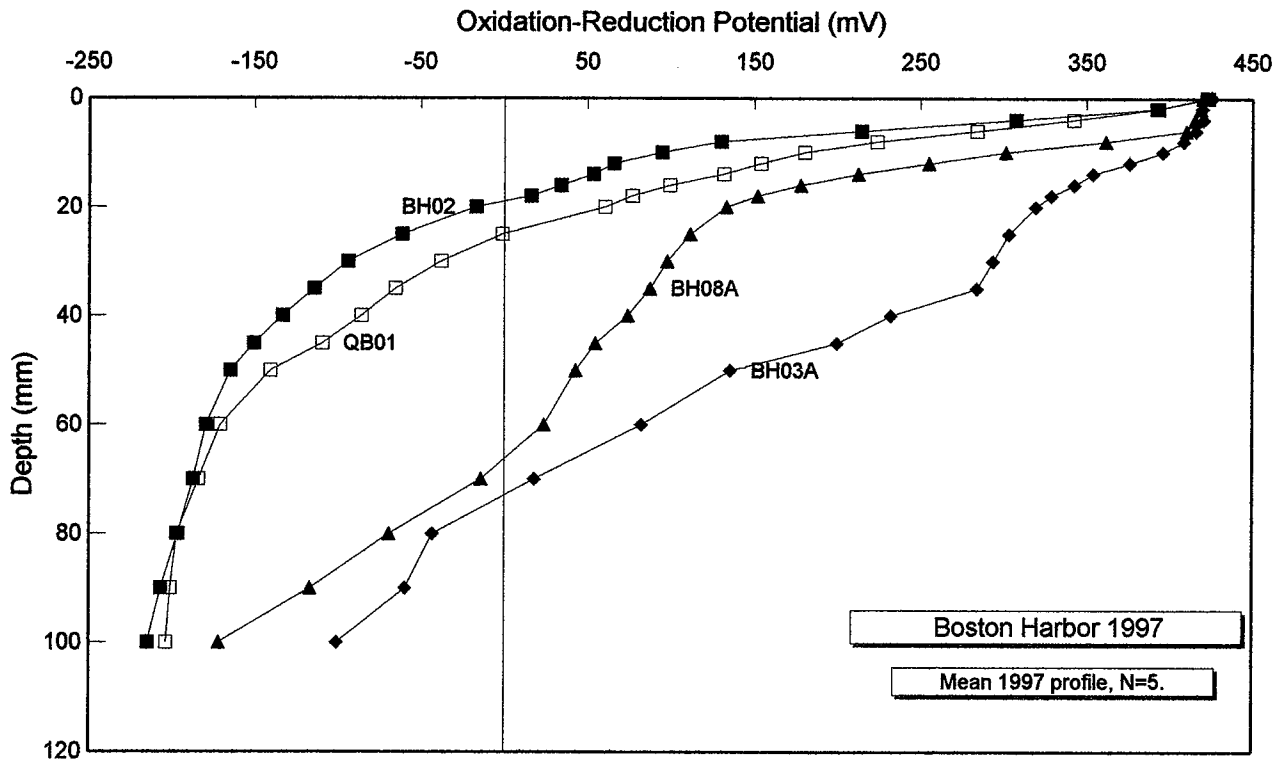


Figure 30. Average depth distribution of oxidation-reduction potential (Eh) within the sediments of (top) Boston Harbor and (btm) the nearfield region of western Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05) during 1997.

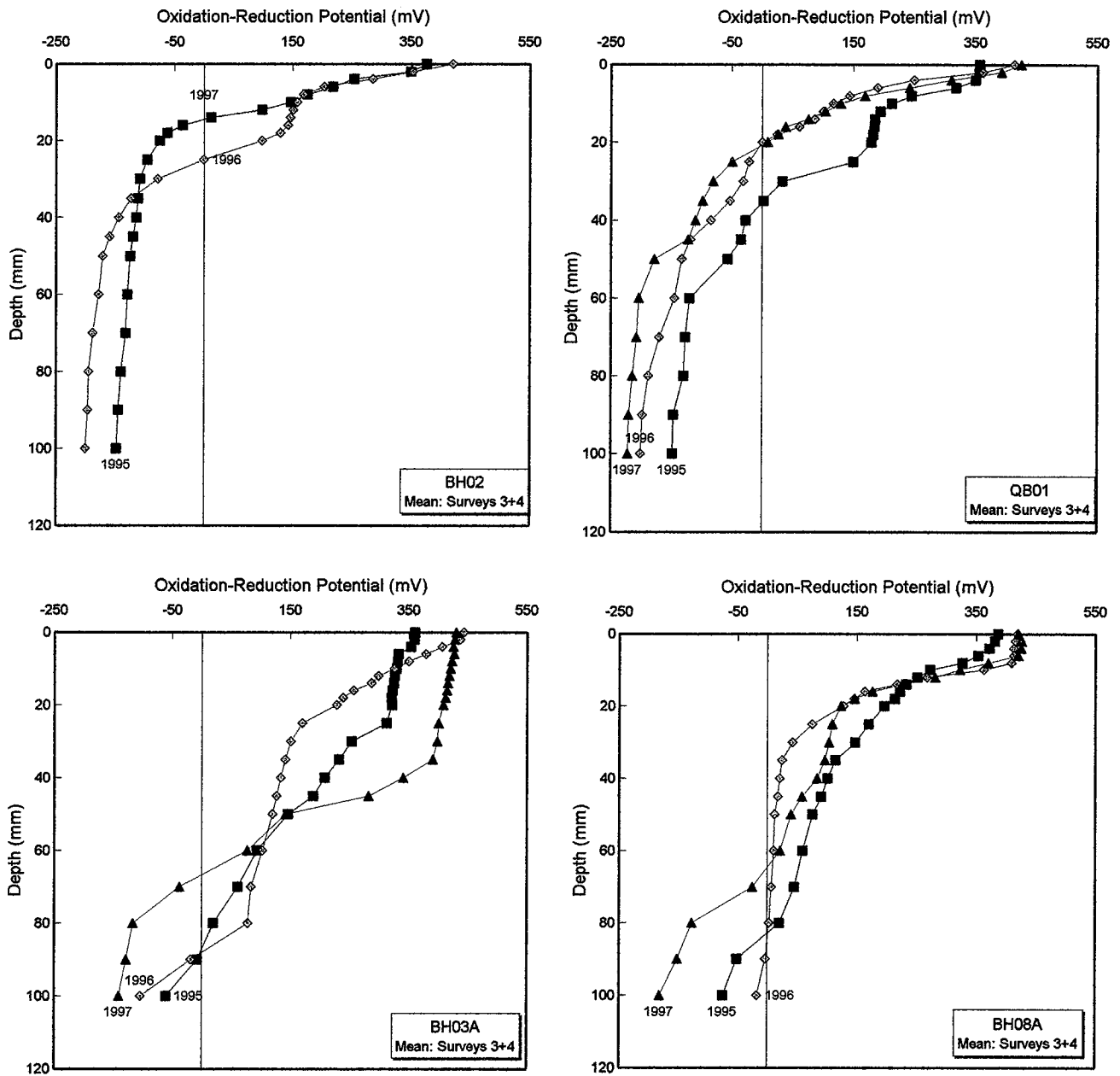


Figure 31. Average summer depth distributions of oxidation-reduction potential (Eh) within the sediments of Boston Harbor, 1995-1997.

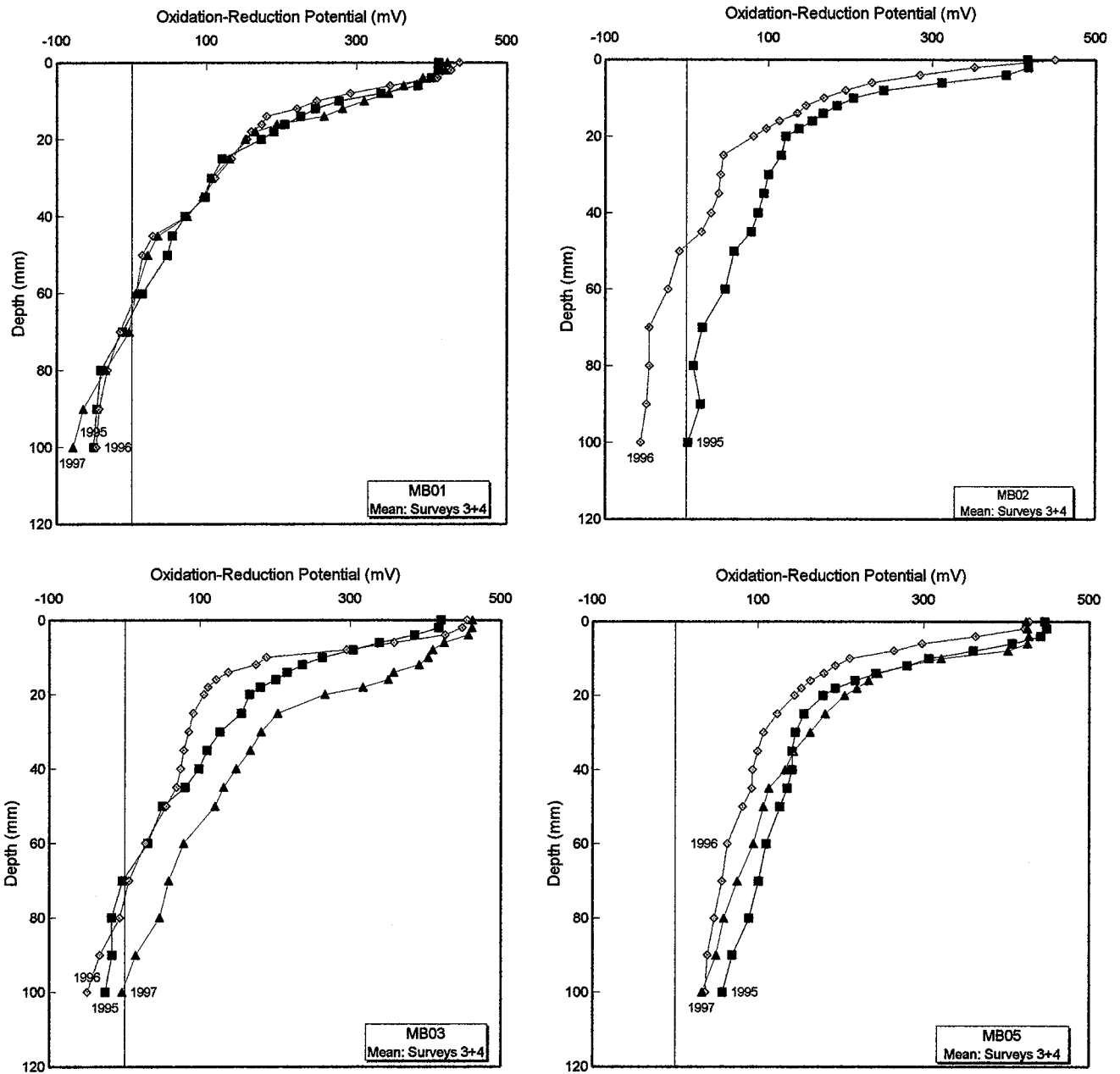


Figure 32. Average summer depth distributions of oxidation-reduction potential (Eh) within the sediments of the nearfield region of western Massachusetts Bay (MB01, MB02, MB03) and Stellwagen Basin (MB05), 1995-1997.

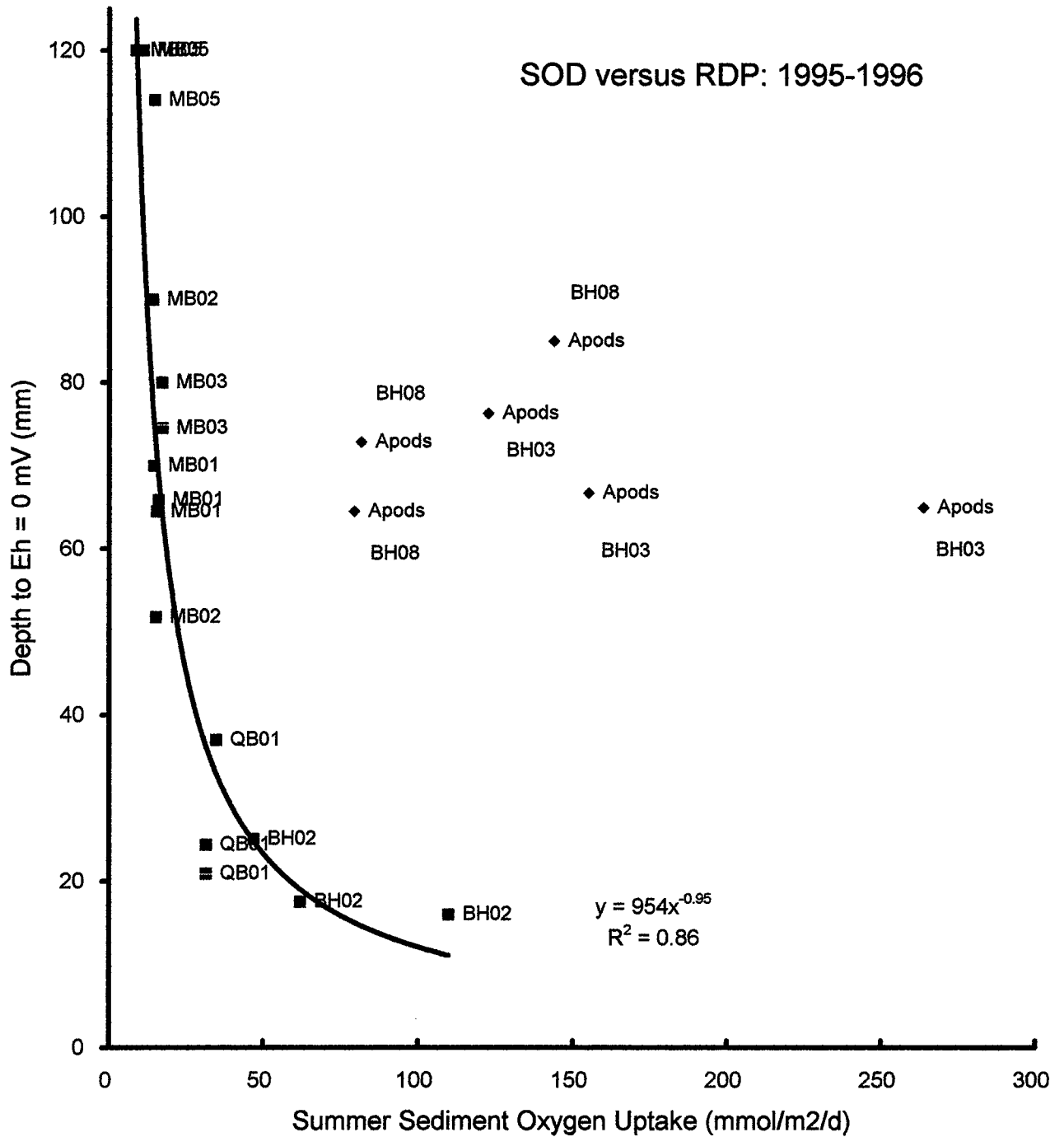


Figure 33. Relationship between redox discontinuity depth (RDP) and summer oxygen uptake in Massachusetts Bay and Boston Harbor, 1995-1997. Line represents the power model of the non-amphipod dominated stations.

However, where amphipods are present their ventilation of the sediments maintains relatively oxidized surficial sediments even at high levels of SOD. This data further supports the contention that bioturbation within the Harbor is having a significant effect on sediment biogeochemistry. In addition, it indicates that the use of RPD as an indicator of changing organic matter loading requires parallel measures of infaunal communities.

From the above data and the reproducibility of sediment Eh within a site from year-to-year (Figures 31, 32), RDP appears to be a potentially useful indicator of changing organic matter cycling in sediments. Comparisons of summer profiles from 1995, 1996 and 1997 at each of the monitoring sites suggest little inter-annual variation (Figure 34). However, since there is a seasonal cycle in sediment oxidation similar to that in dissolved sulfide (Figure 29, Howes 1998a), it is essential that several samples be collected within the season of interest and that only similar time periods be compared. In addition, use of RDP depth as an indicator requires information on sediment metabolic parameters and infaunal populations for interpretation of changes should they be encountered.

It appears from the flux and Eh measurements that the mechanism producing the increased flux of DIN relative to ortho-phosphate with amphipod colonization likely results from increased ventilation due to bio-irrigation increasing sediment oxidation. 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). Initial results suggest that nitrogen and carbon depuration may be relatively rapid (1-2 years) after colonization by amphipods. While the data on the continuity of amphipod mat colonization at this site is imperfect, data from Kropp and Diaz (1995) indicate that the mat was not in place at BH03A in 1993 (cf. Howes 1998a). In addition, even if mats were continuously present, the depuration of the sediment (as evidenced by the flux measurements), since the cessation of sludge disposal and reduction of other terrestrial inputs, has still occurred in about half a decade. 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 sustainability 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. It appears 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.

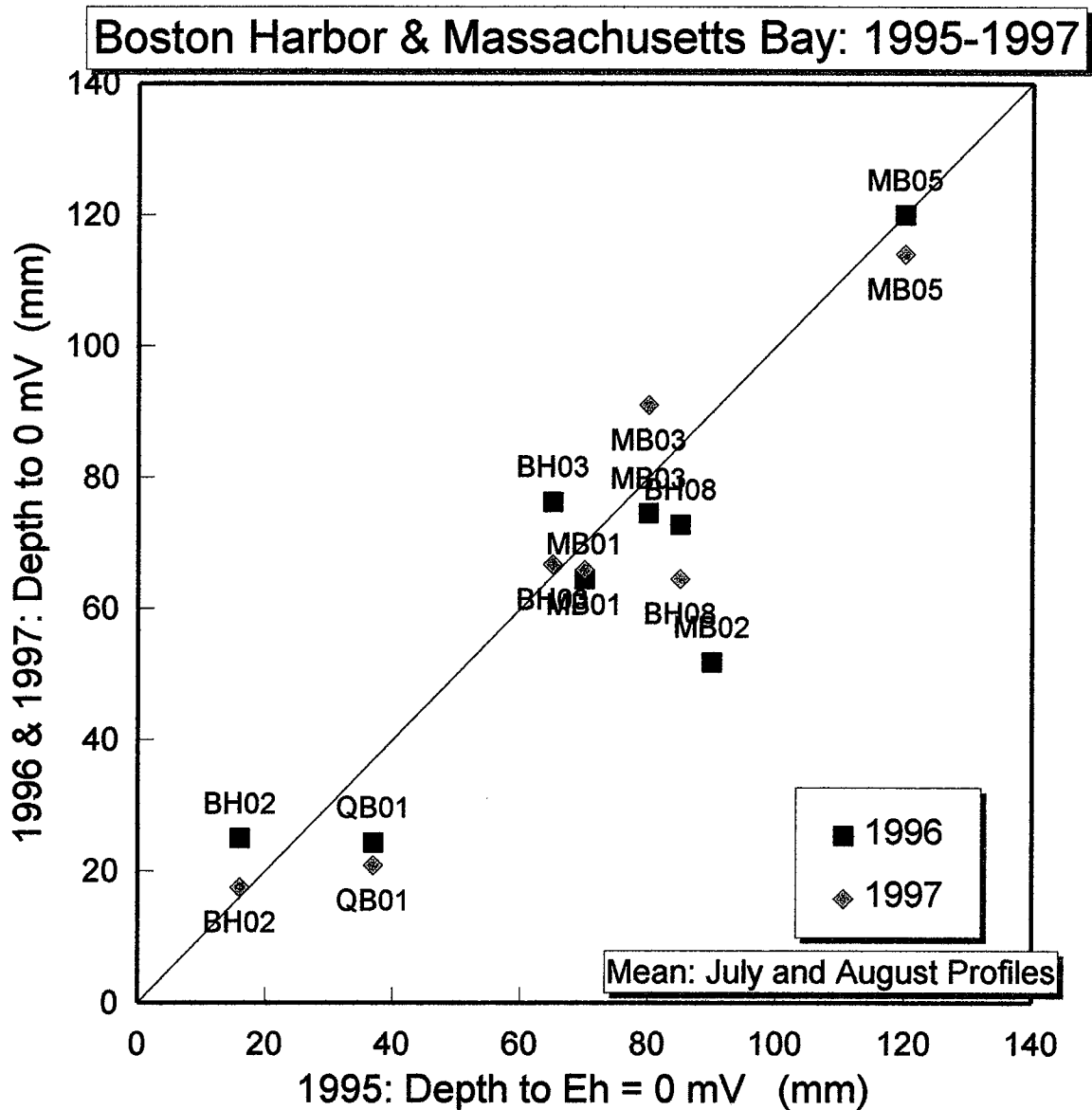


Figure 34. Inter-annual comparison of summer redox discontinuity depth (RDP) in western Massachusetts Bay and Boston Harbor sediments, 1995-1997. Values were calculated from profiles of sediment oxidation-reduction potential measured by platinum electrode.

IV. Oxygen and Carbon Balance of Massachusetts Bay and Stellwagen Basin Bottom Waters

Oxygen Balances: Given the data on sediment oxygen uptake (see above) and watercolumn respiration (Cibik *et al.* 1996, 1997) it is possible to construct an oxygen balance for regions within the Bay. This balance provides a framework for data integration and will form the basis for a more quantitative modeling effort to construct an annual carbon and oxygen mass balance (with daily time steps) for the nearfield region of Massachusetts Bay (Gerath In preparation). However, even in its simplest form 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 bottom water 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 bottom water 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). Unfortunately, sediment respiration rates are spatially limited, primarily in the lack of data on 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 nearly certain 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 (as seen from the chlorophyll a and seasonal SOD data), 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 (Hilbig *et al.* 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. 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 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.

Table 2.

Contribution of Watercolumn and Sediment Respiration to Bottom water Oxygen Decline in the Nearfield and Stellwagen Basin, 1995, 1996 and 1997.

Source of O ₂ Uptake	Year	Rate (mg/L/d)	% Observed Decline
Nearfield: D.O. Depletion	1995	-0.027	100
	1996	-0.025	100
	1997*	-0.020	100
Watercolumn Respiration	1995	-0.016	61
	1996	-0.015	60
	1997	-0.023	115
Sediment Respiration	1995	-0.021	78
	1996	-0.023	92
		-0.026	130
Total Respiration	1995	-0.037	139
	1996	-0.038	152
	1997	-0.049	244
Stellwagen Basin: D.O. Depletion	1995	-0.015	100
	1996	-0.014	100
	1997	-0.012	100
Watercolumn Respiration	1995	-0.011	73
	1996	-0.013	92
	1997	-0.019	158
Sediment Respiration	1995	-0.004	29
	1996	-0.005	35
	1997	-0.007	58
Total Respiration	1995	-0.015	101
	1996	-0.018	128
	1997	-0.026	217
Mean Pycnocline = 18m			
* D.O. Intrusion year			

From the oxygen budget of the nearfield and Stellwagen Basin for the stratified interval of 1995-1997, 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 can be relatively small (cf. Gerath

et al. In prep.). However, the mid-July oxygen levels in the nearfield frequently show an anomaly in the linear oxygen trajectory which could be associated with physical processes (Cibik *et al.* 1996, In prep.). The much higher rates of sub-pycnocline respiration measured in 1997 were likely associated with an enhanced organic matter deposition in spring and early summer associated with phytoplankton blooms. These high rates of oxygen uptake likely would have resulted in a baseline maximum oxygen depletion had it not been for a large re-aeration event in mid-summer. These events can be seen in each years record, 1992-1997 (Cibik *et al.* In preparation)

The approximate oxygen balance suggests that (1) there is significant inter-annual variation in ventilation of bottom waters during stratification (from small-1995, to large-1997) 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 bottom water 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 physical conditions occur which allow an increase in oxygen deficit.

Carbon Balance within the Nearfield during stratification: In order to determine the potential importance of production and deposition of organic matter to the sediments of the nearfield during the non-stratified period (spring and fall blooms), a simple mass balance can be used. Based upon the measured rates of organic matter production by phytoplankton and rates of organic loss through water column and sediment respiration (Cibik *et al.* 1996, In preparation), we can construct a carbon balance for the nearfield during the stratified interval. The stratified interval is particularly ecologically significant as it is the period of oxygen depletion of bottom waters within the Bay system.

During the 1995 and 1996 stratified interval, sufficient carbon was fixed within the euphotic zone of the nearfield to support the observed rates of water column carbon mineralization (Figure 35). Based upon the measured rates of production and mineralization and the water column particulate organic carbon (POC) pool during this interval, it appears that the average residence time (turnover) of the POC pool is about 7 days. This is consistent with observations of blooms within the nearfield.

Given the variability inherent in the water column carbon cycling measurement, there appears to be sufficient residual organic matter production to fuel the observed benthic mineralization rate. However, organic matter deposition rates during the stratified period within intervals of low resuspension (M.Bothner, USGS data), indicate that summer-time deposition¹³ is very low. The deposition of organic matter during the stratified interval appears to be almost an order of magnitude lower than that required to fuel benthic respiration. It appears that most of the carbon to support sediment metabolism during the stratified interval was deposited prior to stratification (or in other years potentially through sub-pycnocline production).

**Mass Bay Nearfield
Carbon Balance:
Stratified Period**

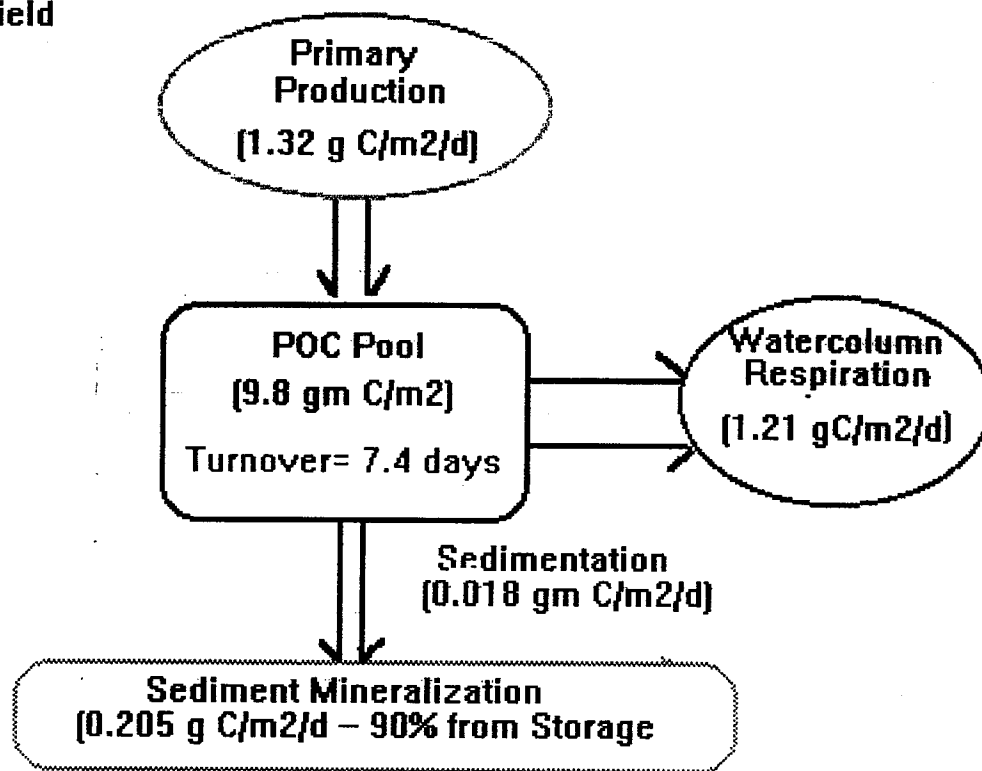
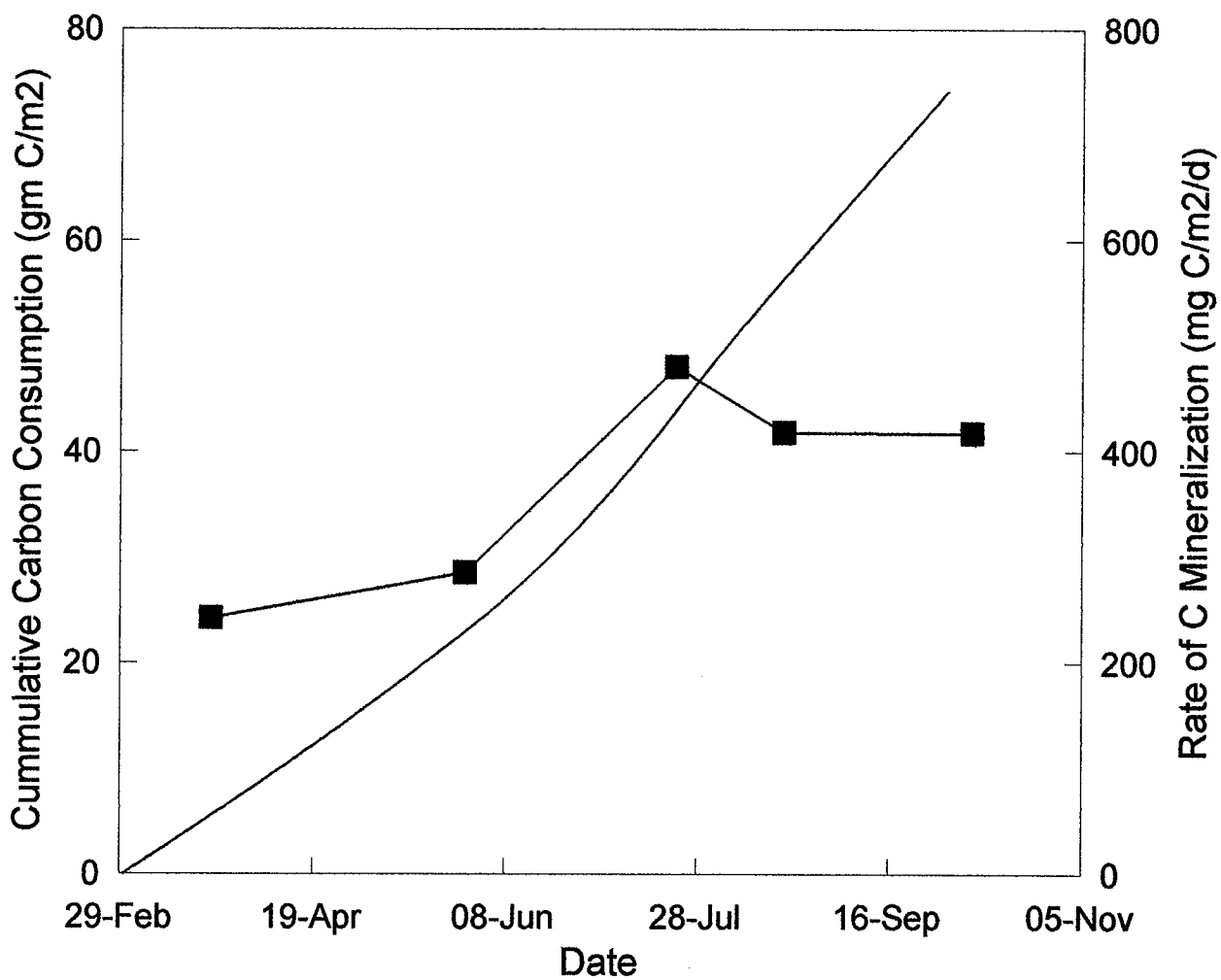


Figure 35. Simplified carbon balance for the nearfield region of western Massachusetts Bay during the stratified interval, 1995 and 1996. Water column production and respiration data are from Cibik et al. (1998, In preparation), deposition rates are from sediment traps during low resuspension periods (Bothner-USGS unpublished data).

It is possible to determine the magnitude of organic matter deposition during the mixed interval, necessary to support the observed rates of sediment respiration (Figure 36). The cumulative mass of carbon remineralized from March 1 through October 1 is about 75 g C m^{-2} with about 60 g C m^{-2} being oxidized during the stratified interval. During the spring bloom, 1995-1997, primary production exceeded system respiration by more than 60 g C m^{-2} . Given the respiration rates during deposition of the fall versus spring blooms, it is likely that much of the organic matter fueling benthic metabolism during stratification results from the spring bloom (see section III. above).

The potential effect of effluent CBOD injected below the pycnocline during stratification can also be evaluated using based upon the carbon cycle measurements (Figure 37). Based upon an effluent dilution of 200 fold, the increase in oxygen consumption is only 2%-5% of the current combined bottom water and sediment oxygen consumption. Unless there is a very long residence time of water within the nearfield which causes multiple loadings of CBOD to the same volume, the effect on oxygen depletion should be difficult to detect. However, if the CBOD is as particles which settle to the bottom, then this effectively increases the "residence time" and enhanced depletion should occur.

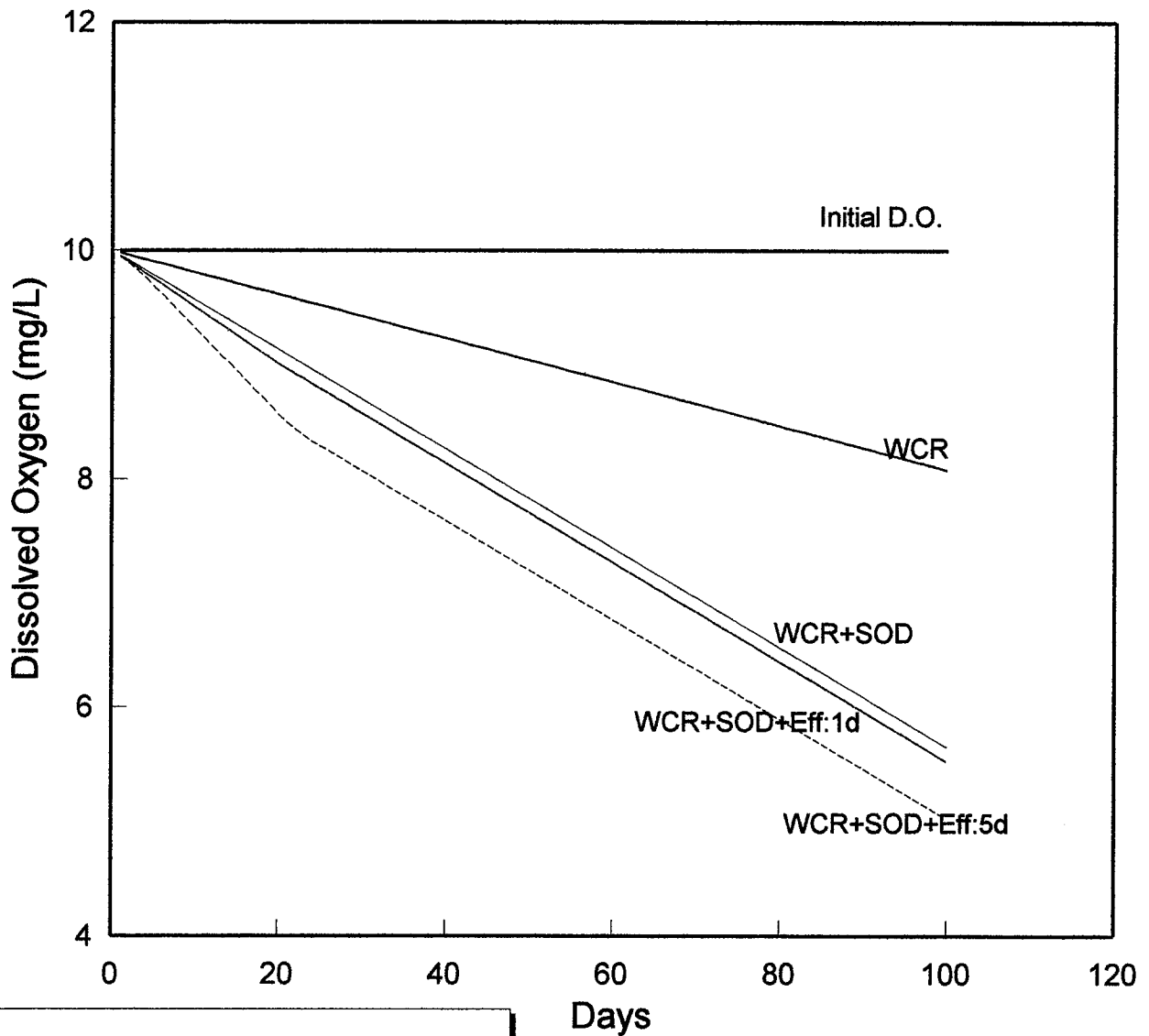
Mass Bay Sediment Carbon Mineralization: Stratified Period



Means of 1995, 1996. Higher rates were found in 1997.
 ca. 100 gm C of Unstratified Production is "Available for deposition."

Figure 36. Carbon mineralization rates and resulting cumulative carbon consumption by the sediments of the nearfield region of western Massachusetts Bay, average 1995 and 1996.

Relative Roles of WCR, SOD and Effluent Carbon on Bottom Water D.



Effluent dilution is only 200 fold
Based on ZERO ventilation, 1 & 5 d loading

Figure 37. Oxygen depletion within a liter of bottom water resulting from the combined consumption by water column respiration, sediment respiration and effluent CBOD at 200 fold dilution (1 and 5 day cumulative input).

V. Recommendations for Monitoring and Further Research

- 1) It appears from the relative constancy of the inter-annual 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%) 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) Sediment pools of phytoplankton pigments varied seasonally and appeared to follow temporal patterns associated with deposition of the spring bloom and degradation during the stratified interval. The relative constancy of sediment chlorophyll a pools may serve as an additional indicator of long-term changes in the annual mass or temporal distribution of phytoplankton deposition.
- 3) 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.
- 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. However, it does appear that mining of stored pools of organic matter and nutrients is occurring.
- 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 both 1995 and 1996 the oxygen decline in bottom waters during stratification indicated that during this period uptake by 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. However, these measurements require a targeted scientific study and appear to be outside of the mission of the HOM program.
- 6) Given the increased regeneration of DIN versus DIP from amphipod mats compared to non-mat areas and the recent recolonization of the central Harbor by amphipods, nutrient ratios in Harbor waters need to be evaluated for historical changes. In addition, the effect of this shift from DIP to DIN in regenerated nutrients needs to be evaluated as to its effects on Harbor nutrient cycling when effluent discharge is shifted to the new outfall site.
- 7) Monitoring of concentrations of biogeochemical species in interstitial waters from the summer period (2 surveys) appears to yield sufficient information on these parameters from which to ascertain shifts related to environmental changes.

VI. Acknowledgments

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