Technical Report #482

# SEDIMENTS AS AN INTERNAL SOURCE OF NUTIRIENTS TO UPPER NEWPORT BAY, CALIFORNIA

**Martha Sutula**
**Krista Kamer**
**Jaye Cable**
**Hilary Collis**
**William Berelson**
**Jeff Mendez**

*Southern California Coastal Water Research Project*

# SEDIMENTS AS AN INTERNAL SOURCE OF NUTRIENTS TO UPPER NEWPORT BAY, CALIFORNIA

*FINAL REPORT TO:*

Santa Ana Regional Water Quality Control Board

*Submitted by:*

Martha Sutula
***Southern California Coastal Water Research Project***
***Westminster, California***

Krista Kamer
***Moss Landing Marine Laboratories***
***San Jose State University***

Jaye Cable and Hilary Collis
***Louisiana State University***

William Berelson
***University of Southern California***

Jeff Mendez
***California Institute of Technology***

**March 15, 2006**

Technical Report #482

# TABLE OF CONTENTS

# LIST OF TABLES

# LIST OF FIGURES

# Executive Summary

Newport Bay (the Bay) is the second largest estuarine embayment in southern California and provides critical natural habitat for terrestrial and aquatic species. The upper portion of Newport Bay (UNB) is a State ecological reserve and serves as refuge, foraging areas, and breeding grounds for a number of threatened and endangered species. The Bay also provides significant spawning and nursery habitats for commercial and non-commercial fish species. Land use changes in the San Diego Creek watershed, the major source of freshwater to UNB, have led to increased freshwater and nutrient loads. These nutrient loads are known to fuel the productivity of macroalgal blooms in UNB, leading to water column hypoxia or anoxia, which can be extremely stressful to resident organisms. As a result of these excessive nutrient loads, the Santa Ana Regional Water Quality Control Board (SARWQCB) placed UNB on the federal 303(d) list of impaired water bodies. This 303(d) listing precipitated the development and adoption of a Total Maximum Daily Load (TMDL) for nitrogen (N) and phosphorus (P) for the Bay in 1998. The implementation phase of the nutrient TMDL has several elements, one of which calls for the evaluation of N and P water quality objectives (WQOs) to determine whether or not they are appropriate. Current WQOs are based on surface water inputs from the rest of the watershed and do not account for internal sources of nutrients, such as sediments, to surface waters. Sediment-derived nutrients are biologically available to primary producers and may cause algal blooms to persist even when nutrient loading from the watershed is reduced to levels calculated for the purpose of limiting macroalgal biomass. The contribution of nutrients from sediments should be incorporated into the overall nutrient budget for the Bay in order to refine WQOs established by the SARWQCB. This study addressed four major questions that are relevant to evaluating and refining UNB WQOs:

1) What is the load of N and P associated with wet-season input of sediments into the UNB?
2) What is the exchange of N and P between the surface waters and the sediment?
3) What are the major processes controlling this exchange?
4) What is the importance of sediment-derived nutrients to surface waters relative to other nonpoint inputs to UNB?

To address these questions, this study consisted of four major components:

1. Intensive sampling of sediments, surface waters, and macroalgae in order to:

1.1. Describe major temporal and spatial patterns in the major nutrient pools found in these three components

1.2. Estimate seasonal and annual sedimentation rates and associated particulate-nutrient loads with radioisotope tracers

1.3. Estimate the flux of nutrients from sediments based on concentration gradients between sediment pore waters and surface waters (i.e. diffusive flux);

2. Direct measurement of nutrient fluxes *in situ* with the use of benthic flux chambers in order to compare with predicted diffusive fluxes and investigate factors controlling flux;

3. Investigation of the interactions of macroalgae presence/absence, surface water nutrient concentrations, and dissolved oxygen on sediment nutrient fluxes in intact sediment cores under controlled laboratory conditions;

4. Integration of the results of the first three study components in order to estimate the annual flux of nutrients from sediments and to compare the relative importance of this estimate to other non-point sources of nutrients to UNB.

This study found that particulate N and P associated with sediment were deposited in UNB during the wet season and that these particulate nutrients were remobilized as dissolved inorganic nutrients to the surface waters during dry season. The direction of sediment-surface water exchange of nutrients was driven by the concentration gradient between pore waters and surface waters; the magnitude of the exchange was driven to a greater extent by advective transport processes, particularly bioirrigation by benthic infauna. When water column nutrient concentrations decrease, often occurring during the summer dry-season when nutrient inputs are low and primary productivity is high, flux from sediments may be promoted by macroalgae. Sediment release of nutrients during the dry season provides a major source of nutrients for primary producer uptake in UNB – an uptake value equal in magnitude to dry season watershed runoff of N. Estimates of benthic nutrient flux to UNB surface waters represent approximately 20% of the 2002 TMDL load allocation for N and P to UNB during the dry season. N and P uptake by macroalgae can enhance benthic flux; macroalgal uptake provides a mechanism for N retention in the estuary and decreases the importance of denitrification as a pathway of permanent N removal from the estuary. This is a possible explanation for eutrophic conditions persisting in an estuary even after anthropogenic nutrients loads have been curtailed. The major findings of this study that support this summary are described in detail below.

*Wet-season sediment deposition from the San Diego Creek watershed resulted an estimated 122,000 lbs of N and 44,000 lbs of P.*

Through the use of radioisotope tracer techniques, this study determined that a mean rate of 11.2 g wet wt sediment $cm^{-2}$ $d^{-1}$ was deposited during the 2003-2004 wet season. This translates to an annual sediment deposition rate of 27,000 tons of sediments to the Bay, with an associated particulate load of total nitrogen (TN) and total phosphorus (TP), 122,000 lbs and 44,000 respectively. The isotope-derived annual estimate of sediment and particulate TP deposition to the Bay is within the range reported for the load measured in San Diego Creek at Campus Drive (30,400 tons sediment and 65,400 lbs TP), a point just upstream of where San Diego Creek discharges into the Bay (OC RCMD 2004). The rate of annual sedimentation derived from beryllium-7 ($^{7}Be$; 0.91 $\pm$ 2.00 cm $yr^{-1}$) for the November 2003-September 2004 study year would be expected to be greater than the long-term annual sedimentation rate calculated with lead-210 ($^{210}Pb$; 0.166 $\pm$ 0.019 cm $y^{r-1}$). This rate averages 50 years of sedimentation and also reflects the compaction that occurs in sediments over time. $^{7}Be$ data suggest that intertidal mudflat areas within UNB are accreting faster than in the subtidal areas, in part because subtidal areas are more subject to erosion during storm flows or peak tidal velocities.

*Newly deposited particulate N and P in UNB sediments was mineralized and provided a source of nutrients to surface waters.*

In this study, "mineralization" refers to the process by N and P bound up in organic matter are broken down and released in dissolved, more biologically available forms. Through processes of sediment diagenesis, such as organic-matter decomposition and oxidation-reduction reactions, this newly-deposited particulate N and P was mineralized, resulting in pore water ammonia ($NH_4^+$), soluble reactive phosphate (SRP), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) concentrations that are elevated relative to surface water levels. Through processes such as diffusion, as well as sediment resuspension and advective flow of water through sediments from tidal currents and bioirrigation by benthic infauna, these pore waters were exchanged with the surface waters. Estimates of predicted diffusive flux showed a net release of $NH_4^+$, SRP, DON and DOP from the sediments to the surface waters throughout the year. The exception was nitrate ($NO_3^-$), which fluxed into the sediments and presumably denitrified. $NH_4^+$ and DON flux from the sediments were equal in magnitude during the wet season, while $NH_4^+$ flux dominated TN flux during the dry season. $NO_3^-$ flux into the sediments was highest in the wet season when surface water $NO_3^-$ was highest, and negligible

during the dry season. SRP flux dominated TP flux, with higher rates in the wet season than during the dry season. This release of nutrients provides a source of bioavailable nutrients for growth of primary producers such as macroalgae in UNB. This type of release can also sustain eutrophic conditions in wetlands, even when external loads are curtailed.

*Sediment nutrient concentrations, the magnitude of benthic nutrient, $O_2$, and total inorganic carbon fluxes indicate that UNB is an anthropogenically-impacted, eutrophic estuary.*

UNB sediment N and P concentrations relative to reported values in other estuaries were considered to be in the mesotrophic to eutrophic range. This study observed a slight enrichment of sediment N, but no enrichment of sediment P, during the wet season. Sediment N and P decreased downstream from the principal source of loading (San Diego Creek). Macroalgal biomass was highly spatial and temporally variable throughout the period sampled, with peak biomass (240 g dry wt $m^{-2}$) found in February 2004 at Site 3.

Based on flux data, UNB has been classified as an eutrophic estuary. Fluxes of total inorganic carbon (TCO2; 107 ± 81 mmol $m^{-2}$ $d^{-1}$), $O_2$ (-43 ± 20 mmol $m^{-2}$ $d^{-1}$), nutrients (5.7 ± 2.7 mmol $NH_4$ and 0.36 ± 0.52 mmol SRP $m^{-2}$ $d^{-1}$), and trace metals were among the highest values reported for *in situ* benthic-flux measurements and comparable to the most anthropogenically-impacted estuaries. $SO_4^{-2}$ reduction, common in eutrophic estuaries, was a dominant process occurring in sediments; this process was particularly dominant for the site at the mouth of the San Diego Creek. The high rate of TCO2, nutrient efflux, and sediment $O_2$ demand in UNB indicate the occurance of a high rate of sediment and organic-matter loading from the watershed and rapid degradation of this organic matter into this system. The efficiency of organic matter degradation in this system can be attributed to several factors, including: 1) abundant supply of terminal electron acceptors (e.g. $NO_3^-$, Fe(III), Mn(IV), and $SO_4^{-2}$ that fuel oxidation-reduction reactions, such as denitrification and $SO_4^{-2}$ reduction) and the degradation of organic matter in sediments; and 2) significant reworking of sediments by physical or hydrodynamic mixing, including bioturbation and bioirrigation. The combination of these factors causes reincorporation of fresh organic matter and terminal electron acceptors into the sediments, where repetitive oxidation-reduction reactions (redox) result in the efficient decomposition of organic carbon.

*Measurements of in situ benthic nutrient fluxes agree with the direction (into or out of sediments) of predicted diffusive fluxes, but show that diffusive fluxes underpredict measured fluxes by 1-2 orders of magnitude.*

This difference is due to the importance of advective transport (bioirrigation, tidal pumping) in controlling the magnitude of flux. Diffusive fluxes (estimated from Ficke's law of diffusion) underpredicted fluxes measured *in situ* with benthic chambers or by incubation of sediment cores by 1-2 orders of magnitude. Thus advective transport was identified as one of the major factors controlling benthic flux of nutrients in UNB. Loss of bromide ($Br^-$), a conservative tracer, in benthic chambers indicated very high rates of exchange with pore waters, particularly at sites downstream of the salt dike in UNB. Two additional lines of evidence corroborate the importance of advective transport in UNB. First, pore water advection estimated with multisamplers at the site near Shellmaker Island showed a high rate of advective exchange of water, with rates ranging from 8-65 cm $d^{-1}$. Second, Worsnopp et al. (2004) used to determined rates and major processes responsible for advective transport in UNB synoptically with the chamber work in this study. Although their work is preliminary and not presented in this report, it suggests that advective transport enhances solute fluxes by a factor of 3-5 times that of diffusion. Although the primary process responsible for this advective transport has not been definitively identified, evidence points to certain dominant mechanisms such as bioirrigation and/or tidal pumping, rather than groundwater input, as integral to such transport.

SRP, iron (Fe), and manganese (Mn) fluxes were higher at the site closest to the mouth of San Diego versus lower in the estuary: a finding consistent with the concept of San Diego Creek as the primary source of particulate trace metals and P loading into UNB. Low $O_2$ in bottom waters at this site enhance $SO_4^{-2}$ reduction and SRP fluxes from sediments. In contrast, site differences in *in situ* measurements of oxygen-uptake, TCO2, and $NH_4^+$ fluxes were somewhat unexpected based on spatial gradients in particulate matter deposition, bulk-sediment characteristics, and pore water nutrient concentrations, which were highest at the site nearest the San Diego Creek mouth. This may have been due to higher density of benthic infauna (tube worms and bivalves) at sites downstream of the salt dike versus sites nearer to the mouth of the creek. Increased bioirrigation at the downstream sites would result in larger nutrient fluxes.

*Other factors such as $O_2$ availability in surface waters and sediment and presence of algae can modify benthic nutrient fluxes and have a major impact on nutrient cycling in UNB.*

$O_2$ availability in surface waters can affect flux of dissolved inorganic nutrients in several ways. First, hypoxia can promote $NO_3^-$ flux into sediments and SRP flux out of sediments due to enhanced denitrification, $NO_3^-$ conversion to $N_2$ gas, in pore waters. Second, oxic conditions can promote $NH_4^+$ flux into sediments and transformation of $NH_4^+$ to $NO_3^-$ by nitrifying bacteria,

thus reducing the concentration of $NH_4^+$ in pore waters of surficial sediments. Third, in sediments that have low available $N0_3^-$ in surface waters, but maintain an oxic surface layer, couple nitrification-denitrification is enhanced, thereby providing a pathway for permanent loss of ammonia-N from the estuary. Fourth, under hypoxic conditions, increased SRP flux is due to desorption of P from Fe(III)- hydroxyoxide precipitates as Fe reduction occurs in hypoxic sediments. The release of SRP is further enhanced by $SO_4^{-2}$ reduction as sediments become completely anoxic.

The study also found that green macroalgae, such as *Enteromorpha intestinalis* (*E. intestinalis*), known for its capacity to quickly and dramatically deplete the water column of inorganic nutrients, can potentially affect benthic nutrient flux and nutrient cycling in several ways. First, macroalgal uptake of dissolved inorganic nitrogen can reduce the importance of denitrification as a permanent mechanism for N removal from the estuary. Macroalgae efficiently uptake $NO_3$ and $NH_4^+$ available in the water column, thus decreasing $NO_3$ or $NH_4^+$ flux into the sediments. As it is stored in macroalgal biomass, N is retained in the estuary, with the possibility of being further recycled back to inorganic N rather than being permanently lost through the coupled nitrification-denitrification to nitrogen gas. Second, the flux of nutrient species such as SRP or $NH_4^+$, which typically have high pore water concentrations relative to surface waters, becomes enhanced by the presence of macroalgae. In the laboratory experiment, nutrient uptake by *E.intestinalis* prevented accumulation of inorganic nutrients in the water column, thus enhancing the concentration gradient and diffusive transport from pore waters to surface waters.

The findings of this study also have significant relevance to nutrient cycling in natural estuarine systems, particularly those already suffering from eutrophication. Particulate N and P deposition occurring through increased nutrient loads to an estuary are temporarily stored in sediments. As the particulate N and P are mineralized, water-column nutrient concentrations decrease, a combination that often occurs during the summer dry season when nutrient inputs are low and primary productivity is high, flux from sediments may be promoted by macroalgae—which also provide a mechanisms for N retention in the estuary. This regeneration of overlying water-column nutrients could significantly enhance primary production and extend the duration of algal blooms. It also explains the persistence of eutrophic conditions in an estuary, even after anthropogenic nutrient loads have been curtailed.

*Benthic nutrient loads represent a significant proportion of total annual and dry season loading to UNB.*

This study found that internal loading of nutrients from sediments to surface waters represents a significant proportion of total annual and dry season loading to UNB. Total annual load of TN from the sediments (102,685 lbs), estimated for the period of October 2003–September 2004 using corrected fluxes, represented approximately 10% of the estimated average-annual load from the San Diego Creek watershed during years 1990-1997. This study estimated that approximately 48,000 lbs of particulate P were deposited in UNB during the 2003-2004 wet season. This number is within the range of the wet-season TP load measured in San Diego Creek at Campus Drive (65,400 lbs TP). Annual benthic release of TP to surface waters (18,302 lbs) represents approximately 40% of the total wet-season TP deposition to UNB. Benthic release of nutrients will have the most significant biological impact during the dry season, when other factors such as light availability and increased temperature enhance the growth of macroalgal blooms. During this time period, benthic release of TN (40,300 lbs) and TP (18,000 lbs) represents a significant portion of summertime watershed nutrient loads. In particular, dry season estimates of benthic nutrient flux of nutrients were equivalent to N loads from San Diego Creek and approximately 20% of the allocated summertime TMDL of N and P to UNB for 2002.

Seasonal and annual nutrient loads from benthic exchange were estimated from corrected fluxes. This correction was based on a linear regression between benthic exchange rates, measured *in situ* in April and October 2004, and diffusive fluxes predicted from pore water profiles during this time period. These loading estimates were considered reasonable in terms of predicting the order of magnitude and direction of benthic nutrient exchange and functional for interpreting the importance of benthic exchange of nutrients relative to other nutrient sources in UNB. We have less confidence in the precise accuracy of these estimates, for reasons which can to a large extent be best addressed through the development of a benthic nutrient exchange component in the UNB water-quality model and additional empirical calibration of corrected fluxes using synoptic measurements of pore water concentrations with *in situ* flux measurements, the precision of these estimates was less supportable.

## Acknowledgements

This study was funded by the State Water Resources Control Board through the Santa Ana Regional Water Quality Control Board. We would like to thank the John Scholl and Brian Shelton of the California Department of Fish and Game Upper Newport Bay Reserve for their logistical support. We also thank Emily Briscoe, Will Beamont, Ryan Prevost, Richard Newell, Andy Aguilar, Dan Kiefer, Josh Koepke, Ericka Jarvis, Rie Prevost, and several graduate students from the University of Southern California and the California Institute of Technology for their assistance in field work and laboratory processing of samples.

# 1 INTRODUCTION

## 1.1 Introduction and Purpose of Study

The Bay is the second largest estuarine embayment in southern California and provides critical natural habitat for terrestrial and aquatic species. UNB is a state ecological reserve and serves as refuge, foraging areas, and breeding grounds for a number of threatened and endangered species. The Bay also provides significant spawning and nursery habitats for commercial and non-commercial fish species. Land use changes in the San Diego Creek watershed, the major source of freshwater to UNB, have lead to increased freshwater and nutrient loads. These nutrient loads are known to fuel the productivity of macroalgal communities in UNB. While these primary producers are important in estuarine nutrient cycling and food web dynamics (Mayer 1967, Pregnall and Rudy 1985, Kwak and Zedler 1997, Boyer 2002), their excessive abundance can reduce the habitat quality of a system. Increased primary production can lead to depletion of $O_2$ from the water column causing hypoxia (low $O_2$) or anoxia (no $O_2$; Valiela et al., 1992), which can be extremely stressful to resident organisms.

As a result of these excessive nutrient loads, the Santa Ana Regional Water Quality Control Board (SARWQCB) placed UNB on the federal 303(d) list of impaired water bodies. This 303(d) listing precipitated the development and adoption of a Total Maximum Daily Load (TMDL) for N and P for the Bay in 1998. The implementation phase of the nutrient TMDL has several elements, one of which calls for the evaluation of N and P water quality objectives (WQOs) to determine whether or not they are appropriate. Current WQOs are based on surface water inputs from the rest of the watershed and do not account for internal sources of nutrients to surface waters, such as sediments.

Sediments are a potentially significant internal source of N and P to surface waters in estuarine systems such as the Bay. Watershed-derived sediments deposited in estuaries during the wet season carry an associated particulate N and P load (Sutula et al. 2002). When deposited in the estuary, the particulate N and P can be mineralized to biologically-available forms and may build up in high concentrations in sediment pore waters. These pore waters can diffuse into the overlying water column or be released through advective processes such as bioturbation by benthic infauna, forced flow of water through sediments by bioirrigation or tidal pumping, or physical resuspension of sediments through scouring or resuspension during strong tidal currents or storm flows (Boynton et al. 1980, Grenz et al. 2000, Hamersley and Howes 2003).

Once released to the water column, particulates are available for uptake by primary producers, including macroalgae.

Primary producer abundance is often limited by availability of nutrients (Harlin and Thorne-Miller 1981, Delgado and Lapointe 1994, Kamer et al. 2004). Macroalgae generally obtain nutrients directly from the water column, though evidence exists that algae may intercept nutrients fluxing out of sediments (Lavery and McComb 1991, Larned and Stimson 1996, McGlathery et al. 1997). Thus, sediments may be a critical nutrient source for macroalgae. In Malibu Lagoon (Los Angeles County, California), Sutula et al. (2004) found that wet-season particulate-nutrient loads deposited in the lagoon were mineralized and provided a significant source of nutrients that fueled excessive growth of submerged aquatic vegetation during the dry season. Previous studies of UNB have shown that sediment N peaks in spring following nutrient inputs during the winter wet season and decreases throughout the summer dry season, suggesting remobilization to the surface waters (Boyle et al. 2004). Sediment-derived nutrients are biologically available to primary producers and may cause algal blooms to persist even when nutrient loading from the watershed is reduced to levels calculated to limit macroalgal biomass (Sutula et al. 2004). The contribution of nutrients from sediments should be incorporated into the overall nutrient budget for the Bay in order to refine WQOs established by the SARWQCB.

This study attempted to address four major questions relevant to refining UNB WQOs:

1. What is the load of N and P associated with the wet-season input of sediments into the UNB?
2. What is the exchange of N and P between the surface waters and the sediment?
3. What are the major processes controlling this exchange?
4. What is the importance of sediment-derived nutrients to surface waters relative to other nonpoint inputs to UNB?

To address these questions, the objectives of this study were to:

1. Investigate the seasonal and spatial patterns of bulk and pore water sediment N and P concentrations and macroalgal biomass in UNB;
2. Estimate wet-season and long-term average-annual sediment deposition rates and associated particulate N and P load to UNB;

3. Estimate ambient benthic nutrient exchange under a variety of environmental conditions observed in UNB over an annual cycle and integrate these rates to evaluate annual net nutrient exchange;
4. Investigate the major factors controlling sediment – surface water exchange of nutrients; and
5. Compare the magnitude and relative importance of sediment remobilization and exchange of nutrients with surface waters relative to other nutrient nonpoint sources to UNB.

A dynamic water quality model, a tool to refine the San Diego Creek/Newport Bay nutrient TMDL, has been developed for the SARWQCB. Currently, this model does not account for sediment sources of nutrients to surface waters. Data from this project can be used to develop and calibrate this component of the water quality model, thus enabling better prediction of the response of macroalgae to various nutrient management scenarios.

## 1.2 Study Components and Report Organization

The study consisted of four major components designed to address the five study objectives listed in Section 1.1:

1. Intensive sampling of sediments, surface waters, and macroalgae in order to:
   4.1. Describe significant temporal and spatial patterns of major nutrient pools attributable to sediments, surface waters, and macroalgae
   4.2. Estimate seasonal and annual sedimentation rates and associated particulate-nutrient loads
   4.3. Estimate flux of nutrients from sediments based on concentration gradients between sediment pore waters and surface waters (i.e.diffusive flux);
2. Direct measurement of nutrient fluxes *in situ* with the use of benthic flux chambers for comparison with predicted diffusive fluxes and investigate factors controlling flux;
3. Investigation of the interactions of macroalgae presence/absence, surface water nutrient concentrations and dissolved $O_2$ with sediment nutrient fluxes in controlled laboratory conditions; and

4. Integration of the results of the first three study components in order to estimate the annual flux of nutrients from sediments and compare the relative importance of this estimate to other non-point sources of nutrient to UNB.

Each of these study components has been presented as a chapter in this final project report; each chapter contains sections describing methodologies, results, and discussion of the study component described.

## 1.3 Site Description and location of study sampling activities

The Bay is located in Central Orange County in the southwest corner of the Santa Ana River Basin, approximately 35 miles southeast of Los Angeles and 70 miles north of San Diego. The Bay is a combination of two distinct water bodies – Lower and Upper Newport Bay, divided by the Pacific Coast Highway bridge. The Lower Bay, where the majority of commerce and recreational boating exists, is highly developed. The Upper Bay contains both a diverse mix of development in its lower reach and an undeveloped ecological reserve in the upper reach. The total area of the reserve is 288 ha (721 acres), of which 100 ha (250 acres) are salt and freshwater marsh (Figure 1-1). The Bay is long, narrow, and banked on both sides by bluffs 9-18 m high. In addition to San Diego Creek, the main freshwater source to UNB, two creeks and many small seeps along the bluffs provide year-round fresh-water influence. The area consists of extensive mud-flats with an unmuted tidal influence and an abundant low marsh with tall dense *Spartina foliosa* as the dominant plant. As a result of the Mediterranean climate of southern California, the region has distinct wet and dry seasons, which occur in November–April and May–October, respectively. Because of increased precipitation and stream flow during the wet season, most of the freshwater input to UNB occurs during this period. However, because of irrigation in the watershed, nuisance flows from non-point sources enter the Bay during the dry season as well.

San Diego Creek, the major freshwater source to UNB, drains a highly urbanized watershed encompassing 118 square miles. The watershed, once dominated by agriculture, is now a mixture of residential, transportation, agricultural, commercial, and recreational land uses. This intensive agriculture and urban development has resulted in the enlargement, creation, and re-direction of channels to transport flows that once drained into the Santa Ana River via the Tustin Plain to UNB (ACOE 2000). The result of this has been a significant increase in nutrients and sediments, as well as contaminants, to UNB.

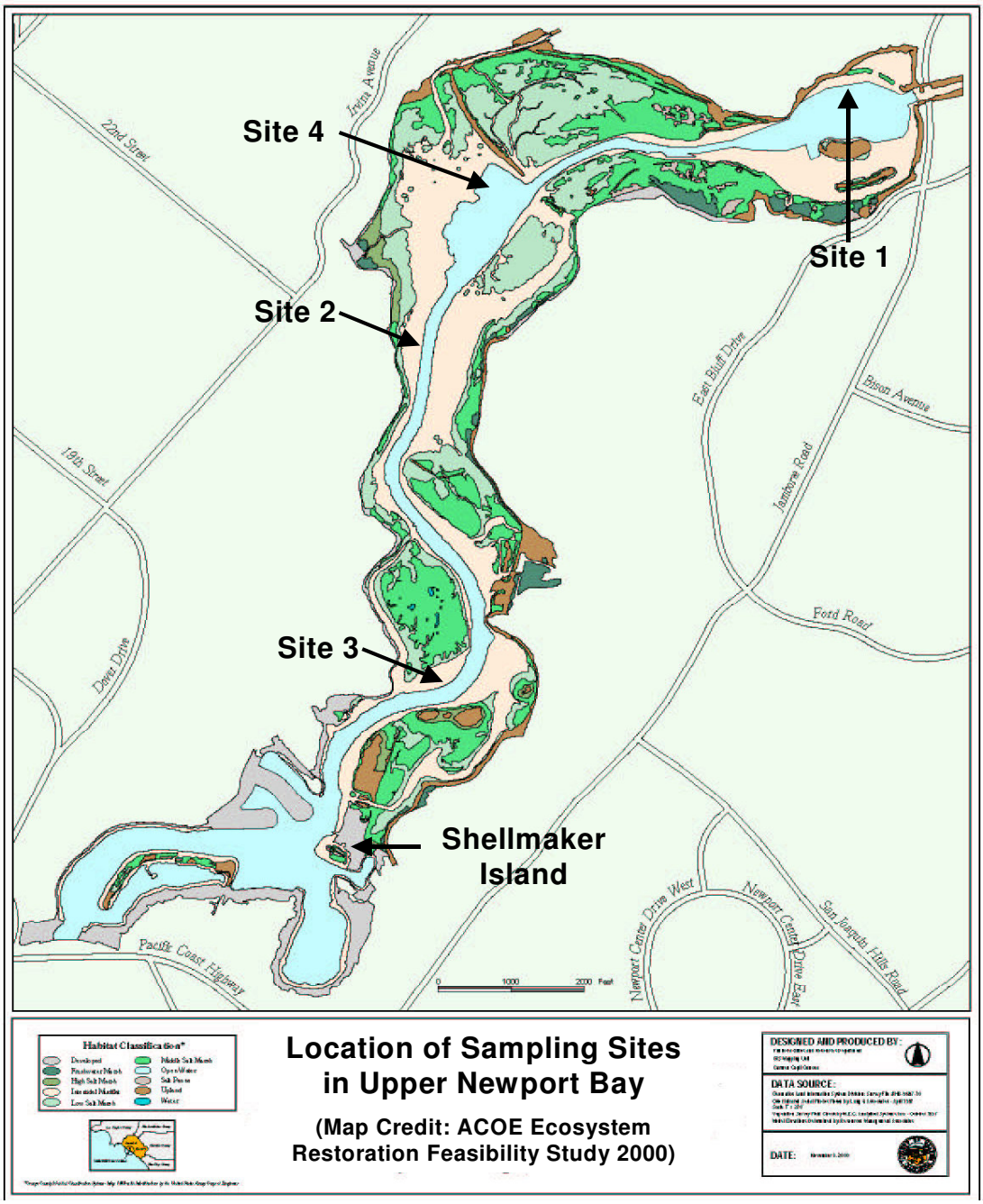


**Figure 1-1. Map of project sampling sites in Upper Newport Bay (UNB).**

Previous studies found temporal and spatial differences in sediment nutrients in the UNB ecological reserve (Boyle et al. 2004, Kamer et al. 2004). To capture this variability and evaluate ways in which it may affect internal loading of nutrients from sediments to surface waters, three permanent sampling sites, ranging from just below the mouth of the creek (Site 1)

to just above Shellmaker Island (Site 3), were established in UNB (Figure 1-1; Table 1-1). Most sampling activities for the project occurred at these three sites and along transects between them. The exception to this was sampling of sediments that occurred just downstream of the salt dike in order to document long-term sediment deposition (Site 4). This site was selected because it is one of the few places in UNB that has not been subject to sediment dredging (T. Ross-Miller, personal communication).

**Table 1-1. Location of project sampling activities.**

| Study Site | Latitude / Longitude |
|---|---|
| Site 1 | 33.651607 / -117.87000 |
| Site 2 | 33.641583 / -117.88902 |
| Site 3 | 33.627516 /-117.88745 |
| Site 4 | 33.651161 /-117.88107 |

## 1.4 REFERENCES

ACOE 2000. Upper Newport Bay Ecosystem Feasibility Restoration Study Final Report. U.S. Army Corps of Engineers, Los Angeles District. September 2000.

Boyle, K. A., K. Kamer, and P.Fong. 2004. Spatial and temporal patterns in sediment and water column nutrients in a eutrophic southern California estuary. Estuaries 27(3): 378-388.

Boynton, W. R., W. M. Kemp, and C. G. Osborne. 1980. Nutrient fluxes across the sediment-water interface in the turbid zone of a coastal plain estuary, p. 533. In V. S. Kennedy [ed.], Estuarine Perspectives. Academic Press.

Delgado, O., and B. E. Lapointe. 1994. Nutrient-limited productivity of calcareous versus fleshy macroalgae in a eutrophic, carbonate-rich tropical marine environment. Coral Reefs 13(3): 151-159.

Grenz, C., J. E. Cloern, S. W. Hager, and B. E. Cole. 2000. Dynamics of nutrient cycling and related benthic nutrient and oxygen fluxes during a spring phytoplankton bloom in South San Francisco Bay (USA). *Marine Ecology Progress Series* 197**:** 67-80.

Hamersley, M. R., and B. L. Howes. 2003. Contribution of denitrification to nitrogen, carbon, and oxygen cycling in tidal creek sediments of a New England salt marsh. *Marine Ecology Progress Series* 262**:** 55-69.

Harlin, M. M., and B. Thorne-Miller. 1981. Nutrient enrichment of seagrass beds in a Rhode Island coastal lagoon. *Marine Biology* 65**:** 221-229.

Kamer, K., P. Fong, R. L. Kennison, and K. Schiff. 2004a. Nutrient limitation of the macroalga *Enteromorpha intestinalis* collected along a resource gradient in a highly eutrophic estuary. *Estuaries* 27(2)**:** 201-208.

Kwak, T. J., and J. B. Zedler. 1997. Food web analysis of southern California coastal wetlands using multiple stable isotopes. *Oecologia (Berlin)* 110(2)**:** 262-277.

Larned, S. T., and J. Stimson. 1996. Nitrogen-limited growth in the coral reef chlorophyte *Dictyosphaeria cavernosa*, and the effect of exposure to sediment-derived nitrogen on growth. *Marine Ecology Progress Series* 145**:** 95-108.

Lavery, P. S., and A. J. McComb. 1991. Macroalgal-sediment nutrient interactions and their importance to macroalgal nutrition in a eutrophic estuary. *Estuarine Coastal and Shelf Science* 32**:** 281-295.

Mayer, F. L. J. 1967. The effect of salinity on growth and reproduction of *Ruppia maritima* L. MS. Department of Wildlife Resources, Utah State University. 56 pages.

McGlathery, K. J., D. Krause-Jensen, S. Rysgaard, and P. B. Christensen. 1997. Patterns of ammonium uptake within dense mats of the filamentous macroalga *Chaetomorpha linum*. *Aquatic Botany* 59: 99-115.

Pregnall, A. M., and P. P. Rudy. 1985. Contribution of green macroalgal mats (*Enteromorpha* spp.) to seasonal production in an estuary. *Marine Ecology Progress Series* 24(1-2)**:** 167-176.

Sutula, Martha, K.Kamer and J.Cable. 2004. Sediments as a non-point source of nutrients to Malibu Lagoon, California (USA). Southern California Coastal Water Research Project, Westminster, CA. Technical Report #441.

Valiela, I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-Andreson, C. D'Avanzo, M. Babione, C. H. Sham, J. Brawley, and K. Lajtha. 1992. Couplings of watersheds and coastal waters sources and consequences of nutrient enrichment in Waquoit Bay Massachusetts. *Estuaries* 15(4)**:** 443-457.

# 2 SPATIOTEMPORAL PATTERNS IN NUTRIENT POOLS, SEDIMENT AND PARTICULATE-NUTRIENT DEPOSITION AND DIFFUSIVE NUTRIENT FLUX

Martha Sutula, Krista Kamer, Jaye Cable, Hillary Collis, and Emily Briscoe

## 2.1 Abstract

This component of the study estimated wet-season and long-term average-annual sediment deposition rates and associated particulate N and P load to UNB, investigated the temporal and spatial patterns of bulk and pore water sediment N and P concentrations and macroalgal biomass in UNB, and predicted diffusive flux of nutrients between surface waters and sediments under a variety of environmental conditions observed in UNB over an annual cycle.

Through the use of radioisotope tracer techniques, it was determined that a mean rate of 11.2 g wet wt sediment $cm^{-2}$ $d^{-1}$ was deposited during the 2003-2004 wet season. This translates to a sediment load of 27,000 tons of sediments, with an associated particulate load of 122,000 lbs TN and 44,000 TP. The annual sedimentation rate derived using beryllium-7 ($^{7}Be$; 0.91 ± 2.00 cm $yr^{-1}$) for the November 2003-September 2004 study year would be expected to be greater than the long-term annual sedimentation rate calculated using lead-210 ($^{210}Pb$; 0.166 ± 0.019 cm $y^{r-1}$) This rate is averaged over 50 years and reflects the compaction that occurs in sediments over time. $^{7}Be$ data suggest that intertidal mudflat areas within UNB are accreting faster than the subtidal areas, in part because subtidal areas are more subject to erosion during storm flows or peak tidal velocities.

Sediment N and P concentrations relative to reported values in other estuaries were considered to be in the mesotrophic to eutrophic range. We observed a slight enrichment of sediment N during the wet season, but no enrichment of sediment P. Sediment N and P decreased downstream from the principal source of loading (San Diego Creek). Macroalgal biomass was highly spatial and temporally variable throughout the period sampled, with peak biomass found in February 2004 at Site 3 (240 g dry wt $m^{-2}$).

In this study, “mineralization” refers to the process by which N and P bound up in organic matter are broken down and released in dissolved, more biologically available forms. Through processes of sediment diagenesis (organic matter decomposition, oxidation-reduction reactions, etc.), newly-deposited particulate N and P was mineralized, resulting in pore water ammonia

($NH_4^+$), (SRP, and DON, and DOP concentrations that were elevated relative to surface water levels. Through processes such as diffusion, as well as sediment resuspension and advective flow of water through sediments from tidal currents and bioirrigation, these pore waters were exchanged with the surface waters. Estimates of predicted diffusive flux show a net release of $NH_4^+$, SRP, DON and DOP from the sediments to the surface waters throughout the year. The exception was $NO_3$, which fluxed into the sediments and was presumably denitrified. $NH_4^+$ and DON flux from the sediments were equal in magnitude during the wet season, while $NH_4^+$ flux dominated TN flux during the dry season. $NO_3^-$ flux into the sediments was highest in the wet season when surface water $NO_3^-$ was highest, and negligible during the dry season. SRP flux dominated TP flux, with rates higher in the wet season than during the dry season. This release of nutrients provided a source of bioavailable nutrients for growth of primary producers such as macroalgae in UNB. It can also sustain eutrophic conditions in estuaries, even when external loads are curtailed.

## 2.2 Introduction

Availability of nutrients in the surface waters of UNB can vary both temporally and spatially in relation to climate, watershed loading, and hydrodynamics. Rainfall in winter months increases stream flow as well as the volume and velocity of freshwater inputs. These seasonal storm flows from the watershed can contribute a large portion of the overall annual nutrient load to southern California estuaries and coastal lagoons (Boyle et al. 2004). During the dry season, creek baseflows are typically lower; consequently, urban runoff and groundwater seepage are the main sources of freshwater inputs and nutrient loads to southern California estuaries (Sutula et al. 2004). Also, spatial variation of nutrient availability in estuaries and lagoons can also be significant during this season. Further, water-column and sediment N and P concentrations are highest near the head of an estuary, the primary source of freshwater-nutrient input, and decrease with proximity to the mouth of the estuary (Rizzo and Christian 1996, Nedwell et al. 2002)-- a pattern that has been observed repeatedly in UNB (Kennison et al. 2003, Boyle et al. 2004, Kamer et al. 2004).

A common problem in estimating nutrient sources to estuaries, coastal lagoons, and lakes is the lack of consideration of particulate load from freshwater sources. This load can be underestimated if loading from freshwater sources is calculated from surface water nutrient concentrations and flow alone. Radioisotope tracers $^{7}Be$, $^{210}Pb$, and cesium-137 ($^{137}Cs$) have been successfully used in combination to study short-term and long-term sedimentation

processes such as deposition, resuspension, and accumulation of sediments within shallow water environments (Giffen and Corbett 2000, Sutula et al. 2004, and others). Natural radionuclides $^{7}$Be (53-day half-life) and $^{210}$Pb (22-yr half-life) are produced in the atmosphere and have a constant rate of supply, via wet (rainfall) or dry deposition, to the earth where they adhere to suspended particles in surface waters. $^{137}$Cs is an artificial radionuclide produced during nuclear fission reactions; its introduction into the environment largely occurred during the 1963 to 1964 bomb-testing period. These radioisotope tracers are deposited with sediments and can be used to track sedimentation and resuspension in aquatic environments such as lakes, lagoons and estuaries (McKee et al. 1983, DeMaster et al. 1985, and Nittrouer et al. 1979).

When sediments are deposited in a lake or estuary from a watershed, over time a series of biological and chemical processes cause the build up of high concentrations of nutrients (and other compounds) in the pore waters of the sediments (Berner 1980). A net exchange of nutrients occurs with the surface waters due to a variety of *diffusive* and *advective* transport processes. *Diffusive transport* refers to the process by which solutes (in this case nutrients) move from an area of higher concentration to lower concentration (Berner 1980). When a difference in concentration between sediment pore waters and the overlying water column exists, diffusion transport will occur to decrease the concentration gradient. For the purpose of this study, *advective transport* refers to a collection of processes by which water is moved through the sediments and surface waters (Koike and Mukai 1983; Huettel et al. 1996), resulting in a physical mixing and net transfer of nutrients between pore waters and surface waters. Factors affecting the build-up of nutrients in sediment pore water and the rate of nutrient exchange with surface waters include:

1. Rate of deposition of new sediments entering the Bay from the watershed and residence time of these sediments in the Bay,
2. sediment quality (organic matter and grain size) and the nutrient concentration of new sediments deposited; and
3. *in situ* physical and biological factors controlling flux, such as advective versus diffusive transport processes, salinity, $O_2$ content, surface-water nutrient concentrations, and temperature, as well as many other surface water and sediment biological activities or processes;

These factors can vary spatially as well as temporally within estuaries, with time scales ranging from hours to months.

One means of determining the rate of exchange of nutrients between sediments and surface waters is to calculate the flux that would occur if diffusion alone were controlling the rate of exchange. While it is clear that non-diffusive processes, such as groundwater flow, bioturbation and tidal pumping also contribute to exchange across the sediment-water interface (Burnett et al. 2002, Giffin and Corbett 2002, Martin et al. 2004), calculation of diffusive fluxes is often used to provide estimates of the magnitude and direction of flux (Berner 1980). Because predicted diffusive-flux estimates are indirect measures of sediment nutrient flux, they are considered less reliable than direct, *in situ* measures of sediment nutrient flux (Callendar and Hammond 1982). However, indirect measures of sediment nutrient flux are much less labor-intensive than *in situ* estimates, thus providing a more accessible means of exploring the way nutrient flux magnitude and direction can change over temporal and spatial time scales.

The objectives of this study component were to:

1. Investigate the seasonal and spatial patterns of bulk and pore water sediment N and P concentrations and macroalgal biomass in UNB,
2. Estimate wet-season and long-term average-annual sediment deposition rates and associated particulate N and P load to UNB, and
3. Predict diffusive flux of nutrients between surface waters and sediments under a variety of environmental conditions observed in UNB over an annual cycle.

Specifically we hypothesized that sediments deposited to UNB during the wet season serve as a temporary storage for nutrients; these nutrients are later remobilized to surface waters, providing fuel for primary producer growth during dry weather periods.

## 2.3 Methods

### *2.3.1 Study Design*

The study design for this component of the project had three elements: 1) characterize the temporal and spatial trends in surface water and sediment nutrient concentrations, macroalgae biomass, and macroalgal tissue concentrations, 2) measure seasonal and average-annual sedimentation rates, as well as the rate of wet-season particulate N and P deposition to the

sediments using radioisotopes $^{7}$Be, $^{210}$Pb, and $^{137}$Cs, and 3) quantify the diffusive flux of dissolved organic and inorganic nutrients between surface waters and sediments, then compare these rates with *in situ* flux estimates determined synoptically using benthic chambers (Chapter 3).

Sampling was conducted in order to capture variability in surface water, sediment nutrients, and macroalgae on seasonal and spatial scales. Table 2-1 presents the targeted seasonal conditions and specific sampling dates. Note that it was not feasible to obtain a pre-wetseason baseline in the fall of 2003 due to delays in contracting. Instead, an early wetseason baseline was sampled in January 2004, and a final sampling was added after the first storm of the 2004-2005 wet season began in order to characterize the difference in sediment deposition and nutrients between these two periods.

**Table 2-1. Sampling period and targeted seasonal condition.**

| Target Seasonal Condition | Sampling Period |
|---|---|
| Pre-wet season baseline | Not sampled |
| Early wet season | January 2004 ($^{7}$Be and bulk nutrients only) |
| Mid wet season – post storm | February 2004 |
| Mid wet season - post storm | March 2004 |
| Dry season – early algal bloom | April 2004 |
| Dry season – mid algal bloom | June 2004 |
| Dry season late algal bloom/pre-wet season baseline | September 2004 |
| Early wet season baseline | November 2004 |

At three sites within UNB, sediment solid phase, pore waters, surface waters, and macroalgae were sampled in the mid-intertidal and upper-subtidal zones. Specific sampling methods for each of these components are detailed in the sections below.

### *2.3.2 Field Methods*

*Surface Water Sampling*

At each of the 3 sites, water column temperature, salinity, and dissolved oxygen (DO) were measured at surface (15 cm) and bottom (15-20 cm from bottom) of the water column using

hand held probes. Duplicate surface and bottom water samples were taken at each site in 1-L pre-cleaned high-density polyethylene (HDPE) bottles that were triple-rinsed in the field with sample water; a Niskin bottle was used to obtain bottom water samples. Samples were placed on ice in a cooler for 1-4 h until filtered (either in the field or in the laboratory). Samples were filtered with a pre-combusted Whatman GF/F glass fiber filter (0.7 μm particle retention size), which were frozen for analysis of total suspended sediment (TSS), chlorophyll *a*, particulate organic carbon (POC), particulate N (PN), and particulate P (PP). Filtered samples were frozen immediately for subsequent analysis of $NH_4^+$, SRP and total dissolved P (TDP), $NO_3$ and ($NO_2^-$), and total dissolved Kjeldahl N (TDKN), which consist of $NH_4^+$ and DON.

*Sediment Sampling for Bulk Characteristics, Nutrients, and Radioisotopes*

At each site, one 30-cm sediment core was taken from each of the mid-intertidal and upper-subtidal zones with 4''-ID polycarbonate tubing. The cores were capped securely (bottom and top) and transported back to the field station for processing. Each core was sectioned vertically in 1-2 cm intervals down to 18 cm. Sections were wet weighed, dried at 50°C to a constant weight, and re-weighed to determine percent solids and wet bulk density. Each section was homogenized and sub-sampled for grain size. The remainder was then ground to a particle size of <125 μm and analyzed for $^7$Be, sediment organic carbon (SOC), sediment total organic nitrogen, and sediment total organic phosphorus.

In April 2005, a single core was taken for analysis of radioisotopes $^{210}$Pb and $^{137}$Cs for the purpose of estimating the long-term annual sedimentation rate. The core was obtained at Site 4 (Figure 1-1) – a location not affected by previous dredging activities in UNB (T. Ross-Miller, personal communication).

*Macroalgal Biomass and Tissue Nutrient Sampling*

To estimate macroalgal biomass and tissue nutrients at each site, a transect line was established parallel to the water line ~1 m from the site's edge. At five randomly chosen points along the transect line, macroalgae (if present) were collected from a 81-cm$^2$ area circumscribed by a plastic cylinder placed on the benthos. Each sample was placed in an individual plastic bag and placed in a cooler for transport back to the laboratory. Samples were refrigerated until they could be cleaned of macroscopic debris, mud, and animals in low nutrient seawater, then sorted by species or functional group. For each sample, individual species were placed in a nylon mesh bag, spun in a salad spinner for 1 minute, wet weighed, rinsed briefly in deionized

water (DIW) to remove salts, dried at 60°C to a constant weight, and re-weighed. Wet and dry macroalgal biomass were normalized to area. The tissues were then ground for TN and TP analysis.

*Pore Water Sampling*

Pore water equilibrators (peepers; Hesslein, 1976) were used to sample pore water from the intertidal and subtidal locations at each site, for a total of six peepers per sampling period (Figure 2-1). When peepers were placed in sediments, solutes from pore water in contact with the filter diffused into the cells such that, after equilibrium was reached, concentrations inside each cell equalled those at corresponding depths in the pore water. Each peeper consisted of a 50x18 cm solid, plexiglass frame into which cells (0.5x 3.0x13 cm) were milled at a spacing of either 1.0 or 2.0 cm. The cells were filled with deionized, autoclaved water that was bubbled with $N_2$ gas to remove $O_2$. A 0.45-mm polycarbonate filter was laid over the surface of the frame. The filter was held in place by an outer plexiglass frame secured with teflon screws. Peepers were pushed by hand into the sediment and inspected visually to ensure the proper vertical orientation, as well coverage of the top well by the surface of the sediment. Each peeper was secured by means of a 30-m cable attached to a stake driven into the upper intertidal zone in order to facilitate peeper recovery. The location of the peeper was noted with GPS coordinates. A two-week period was allowed for equilibration (Hesslein, 1976; Brandl and Hanselmann1991). Peeper recovery occurred during sampling of surface waters, sediments, and macroalgae. Sediment cores for bulk characteristics and nutrients were taken within 20 cm of the peeper location.

Immediately following retrieval, peepers were placed inside plastic glove bags that were purged with $N_2$ gas to minimize artifacts from oxidation of pore water fluids. The pore water samples were extracted, with a syringe, from each well, dispensed into vials, and immediately frozen for analysis of $S^{-2}$, $NH_4^+$, $NO_3^-$, $NO_2^-$, TDKN, SRP, and TDP. Before freezing, $S^{-2}$ samples were preserved with zinc acetate and SRP samples were acidified with 2 N HCl. Salinity of each sample was measured with a hand-held refractometer. Peepers were recovered one at a time so that pore water fluids were completely processed within 15 minutes of recovery. One field blank per core was processed using a procedure identical to the procedure used for pore water samples.

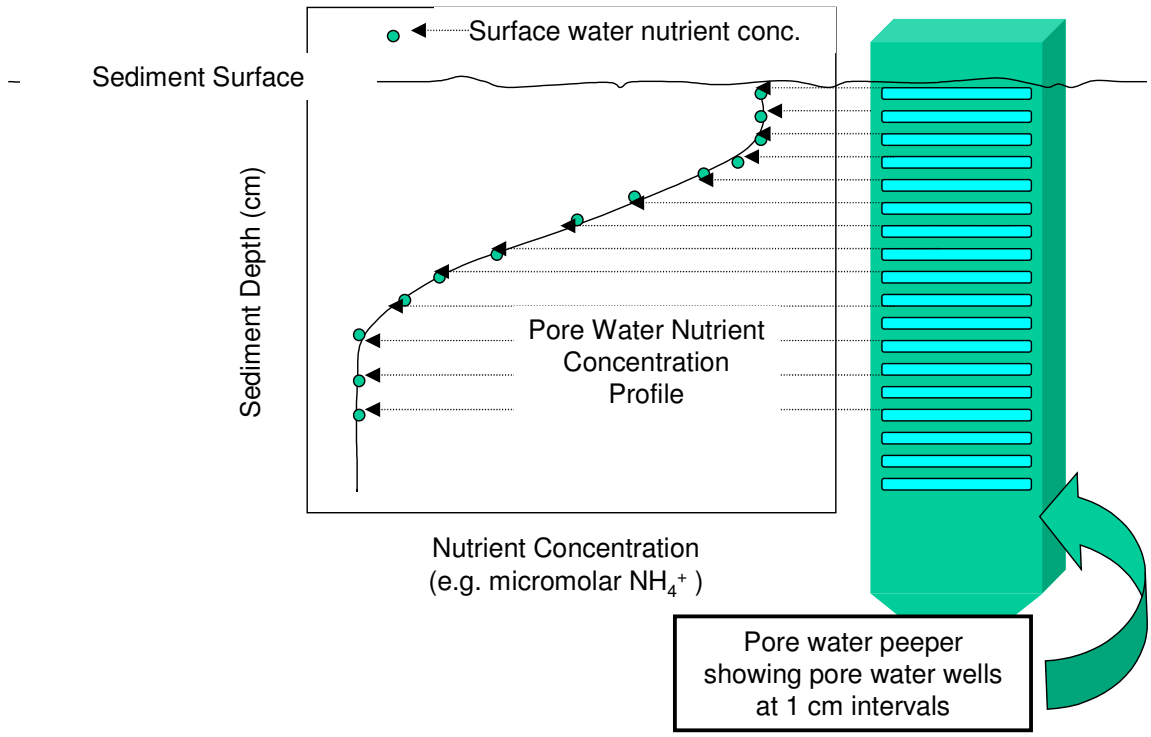


**Figure 2-1. Graphic depicting how pore water profiles are generated from pore water peepers.**

### *2.3.2 Analytical Methods*

Surface and pore water samples were assayed for dissolved inorganic nutrients using an Alpkem Autoanalyzer for the analysis of $NH_4^+$, SRP and $NO_3^-$, and $NO_2^-$ (APHA 1981). TDP was digested by combustion and hydrolysis as in Solorzano and Sharp (1980), then analyzed as SRP by autoanalyzer (APHA 1992). TDKN was analyzed using the micro-kjeldahl method (APHA 1992). DON and DOP were calculated by subtracting the $NH_4^+$ or SRP concentration from TDKN or TDP respectively. Pore water salinity was recorded using a refractometer. TSS was analyzed using the gravimetric technique described by Banse et al. (1963); chlorophyll a was measured with a spectrophotometer after extraction with acetone (APHA 1992).

Suspended matter particulate and sediment samples were acidified to remove carbonates and analyzed for SOC and SN using a CHNS-O Elemental Analyzer. Sediment TP was digested with microwave acid digestion and analyzed using inductively coupled atomic emission spectroscopy (ICP-AES; Sah and Miller 1992, Meyer and Keliher 1992). Sediment dry-grain density was determined by taking pre-weighed sample of sediment and measuring the volume

displaced by that sample in a graduated cylinder filled with water. Sand, silt, and clay grain-size fractions were determined by wet sieving each sample through a 62-mm sieve to separate coarse and fine fractions, then analyzing the fine fraction using the pipette method (Milner 1962).

Seasonal and average-annual sedimentation rates were determined using radioactive isotopes of $^{7}$Be, $^{210}$Pb, and $^{137}$Cs. Average annual sedimentation rate for Site 4 was determined by alpha particle spectrometric analysis of $^{210}$Pb and $^{137}$Cs activities (22-yr half-life). Activity of $^{7}$Be (53-day half-life), used to document wet-season sedimentation rate, was determined by gamma spectrometry using a low-energy Germanium (LeGe) planar detector coupled with low background cryostat and shielding. Samples were counted for 24 hours on an intrinsic germanium detector, and radioisotopes were measured at the following photon peaks: 477.1 keV for $^{7}$Be, 46.5 keV for $^{210}$Pb, and 661.7 keV for $^{137}$Cs. Long-term average-annual sedimentation rates were determined from downcore distribution of excess $^{210}$Pb activities using a non-steady state initial concentration model (CIC) as described in Appleby and Oldfield (1992).

### *2.3.4 Data Analysis*

Data analysis consisted of: 1) statistical comparison of surface-water and sediment-bulk nutrients, as well as macroalgal biomass and tissue concentrations, according to site and season, 2) estimation of seasonal and annual sediment deposition rates, 3) evaluation of net changes in sediment nutrient inventories, and 4) calculation of diffusive fluxes. Statistical analysis was conducted with ANOVA using Tukey's post-hoc comparisons (SAS 8.3, SAS Institute 2004). Details of other calculations are given in detail below.

*Calculation of Porosity and Wet Bulk Density*

Sediment porosity was used to calculate diffusive flux rates. Wet bulk density was used to estimate seasonal and annual sediment deposition rates and to evaluate changes in sediment nutrient and radioisotope inventories. The means of calculating these values from parameters measured in the laboratory is given as follows.

Porosity is essentially a measure of the amount of "empty space" in a material, defined by the ratio of the volume of voids to the total volume of a rock or unconsolidated material. For the purpose of this study, porosity ($\phi$), a dimensionless unit, is given by Eq. 2-1:

$$\phi = \frac{(1-X_{SED})\,(1/\sigma_{H20})}{((1-X_{SED})\,(1/\sigma_{H20}) + X_{SED}\,(1/\sigma_{SED}))} \qquad \text{Eq. 2-1}$$

where $X_{SED}$ is the fraction of solids in the sediment, $\sigma_{H20}$ is the density of water, and $\sigma_{SED}$ is the dry grain density of the sample.

Wet bulk density ($\rho$ in g $cm^{-3}$) is given by the Eq. 2-2:

$$\rho = \frac{\text{Sediment Wet Weight}_{\text{Core Section}}}{\text{Volume}_{\text{Core Section}}} \qquad \text{Eq. 2-2}$$

*Use of $^{7}$Be and $^{210}$Pb to Calculate Seasonal and Annual Sediment Deposition Rates*

To calculate seasonal and annual sediment deposition rates, inventories of $^{7}$Be and excess $^{210}$Pb were calculated, from raw activities at each sampling depth, using Eq. 2-3 from Canuel et al. (1990) :

$$I = \Sigma\, \Xi_i\, (1 / \phi) * \rho * A_i \qquad \text{Eq. 2-3}$$

where: I is the total inventory of the sediment core (disintegrations per minute (dmp) $cm^{-2}$), $X_i$ is the sediment-section interval (*i*) thickness (cm), $\phi$ is the porosity (dimensionless), $\rho$ is the wet sediment density (g $cm^{-3}$), and $A_i$ is the $^{7}$Be or excess $^{210}$Pb activity within a given section interval.

Temporal variability in short-term (seasonal) sediment deposition and remobilization was evaluated using the general conceptual model in which the first sampling event sets a baseline of low $^{7}$Be activity because of a four-month dry season. Subsequent sampling trips (during wet season and throughout dry season) revealed possible changes occurring at the site in the intervening time period, including: (1) an inventory reflecting recent deposition and/or residual inventory reflecting older deposition events; (2) a small residual inventory associated with decay or partial sediment removal when no recent deposition events had occurred; and (3) no inventory, indicating complete removal of the uppermost sediment layer or complete decay when the sampling interval was sufficiently long (i.e.during the dry season; see Giffin and

Corbett (2002) for in depth discussion on interpretation of $^{7}$Be profiles). These time-series inventory comparisons can be used to evaluate the short-term sediment deposition rate, discern whether or not a site is a focal point for sediment deposition or a net-loss site over time, and observe reworking of sediments that may have been caused by bioturbation (birds, burrowing organisms, etc.).

Long-term average annual sedimentation rates were estimated using the vertical profile of excess (or unsupported) $^{210}$Pb in subtidal sediments at Site 4. Supported $^{210}$Pb is derived from the *in situ* decay of radium-226 ($^{226}$Ra), which has been washed into the system as a part of eroded material. Unsupported or excess $^{210}$Pb is derived from radon-222 ($^{222}$Rn), which diffuses as gas through the soil interstitial pore space into the atmosphere, where it decays to $^{210}$Pb. The excess $^{210}$Pb then attaches to aerosol particles and settles out of the atmosphere as dry fallout or washes out in rainfall events. Once deposited and incorporated in the sediment, the activity of excess $^{210}$Pb will be a function of the amount present initially and its 22.6-yr half-life. Thus, long-term average annual sedimentation rates can be determined for a sediment core by measuring the down-core activities of excess $^{210}$Pb and comparing these with excess $^{210}$Pb measured for the recent sediments at the top of the core. Excess $^{210}$Pb is calculated by subtracting the supported $^{210}$Pb (derived from the *in situ* decay of $^{226}$Ra that has been directly washed into the system as part of eroded material) from total $^{210}$Pb activity.

*Calculation of Deposition of SN and SP During the Wet Season*

Ideally, the use of $^{7}$Be radioisotope tracers to calculate N and P associated with new sediment deposition during the wet season requires the establishment of a pre-wet season baseline of $^{7}$Be inventory in the sediments. Because of delays in initiating field sampling for this study, N and P loading associated with new sediment deposition was only calculated for the time period in which data were collected (January – April 2004). An explanation of these calculations is given below.

Intensive temporal sampling of $^{7}$Be inventories in sediment from January – November 2004 yielded the estimated weight of new sediment deposited over the interval between sampling periods "t" and "t+1" ($M_{SED}$ in g wet wt cm$^{-2}$; see table 2-5). This deposition rate, when divided by the average wet-bulk density of the first 0-6 cm of the sediment in the core, yielded the approximate depth of mass accumulation (D) during that time period (Eq. 2-4).

$$D_{MA} = \frac{M_{SED}}{\rho} \qquad \text{Eq. 2-4}$$

The mean SN and SP concentration ($SN_{0-D}$ and $SP_{0-D}$, expressed in % of dry wt sediment) and average fraction of solids in the sediment interval ($X_{SED}$) was calculated the over the depth of mass accumulation (D) for the "t+1" sampling period for each core. Calculation of the mass of SN or SP deposition ($M_{SN}$ or $M_{SP}$) during this sampling interval is given by Eq. 2-5:

$$M_{SN} = M_{SED} * X_{SED} * SN_{0-D} * 100 \qquad \text{Eq. 2-5}$$

$M_{SN}$ or $M_{SP}$ was then divided by the total number of days in the interval to yield a daily SN or SP deposition rate.

*Calculation of Diffusive-flux Rates Between Sediments and Surface Waters*

One means of determining the rate of exchange of nutrients between sediments and surface waters is to calculate the flux that would occur if diffusion alone were controlling the rate of exchange. While it is clear that non-diffusive processes, such as groundwater flow, bioturbation and tidal pumping, also contribute to exchange across the sediment-water interface; calculation of diffusive fluxes can provide estimates in terms of magnitude and direction of flux. In this study, instantaneous diffusive-flux rates were calculated for each species of nutrient using Ficke's law given in Eq. 2-6.

$$J = -\phi D_{AQ} \theta^{-2} (dC / dz) \qquad \text{Eq. 2-6}$$

where J is the rate of flux of species (mol $m^{-2}$ $s^{-1}$), $\phi$ is the porosity (dimensionless), $D_{aq}$ is the aqueous diffusion coefficient, $\theta$ is the tortuosity, and dC/dz is the change in pore water concentration (dC) over the distance from the overlying water to the sediments (dz). $\theta^{-2}$ was estimated from Boudreau's law (Boudreau 1997) given in Eq. 2-7:

$$\theta^{-2} = 1 / (1 - \ln(\phi^2)) \qquad \text{Eq. 2-7}$$

$D_{aq}$ for each nutrient species were obtained from Boudreau (1997) and are given in Table 2-2 below. The constant selected was that closest to the ambient water temperature at time of field sampling:

**Table 2-2. Aqueous diffusion coefficients ($D_{aq}$) for each nutrient species by temperature.**

| Species | 10°C | 15°C | 20°C | 25°C |
|---|---|---|---|---|
| $NO_3^-$ | 1.26E-09 | 1.44E-09 | 1.62E-09 | 1.79E-09 |
| $NH_4^+$ | 1.45E-09 | 1.68E-09 | 1.90E-09 | 2.12E-09 |
| $HPO_4^{-2}$ | 4.75E-10 | 5.56E-10 | 6.37E-10 | 7.16E-10 |
| Lactate (as Proxy for DON and DOP) | 6.44E-10 | 7.54E-10 | 8.64E-10 | 9.72E-10 |

Diffusive flux rates were predicted using the following assumptions:

- Exchange between the sediments and surface waters occurr at steady state;
- Advective transport processes in UNB (groundwater, pumping from tidal currents, and bioturbation) are minor relative to diffusive transport; and
- Chemical or biological processes that can modify chemical fluxes at the sediment water interface ($O_2$ content, benthic diatoms, sediment redox chemistry, etc.) have a negligible impact relative to diffusion on exchange rates.

## 2.4 Results

### *2.4.1 Surface Water Quality*

Figure 2-2 shows the timing of sampling events relative to seasonal patterns of rainfall and flow in San Diego Creek. The 2003-2004 wet season precipitation for the region in 2004 was 11.2 cm, approximately one-half the average precipitation calculated from 1971–2000 (24 cm). Despite the variable input of freshwater throughout the wet season and dry season, surface water salinities during the sampling periods remaining fairly constant (Figure 2-3). Values ranged from 24 to 35 ppt during the wet season, and 26 to 35 ppt during the dry season, with no significant difference between these two periods (p-value$_{\alpha=0.05}$ = 0.41, n=73). Salinity differences among sites were minor, but statistically significant (Mean = 27, 29, 33 for Sites 1-3 respectively; p-value$_{\alpha=0.05}$ = 0.001, n=73).

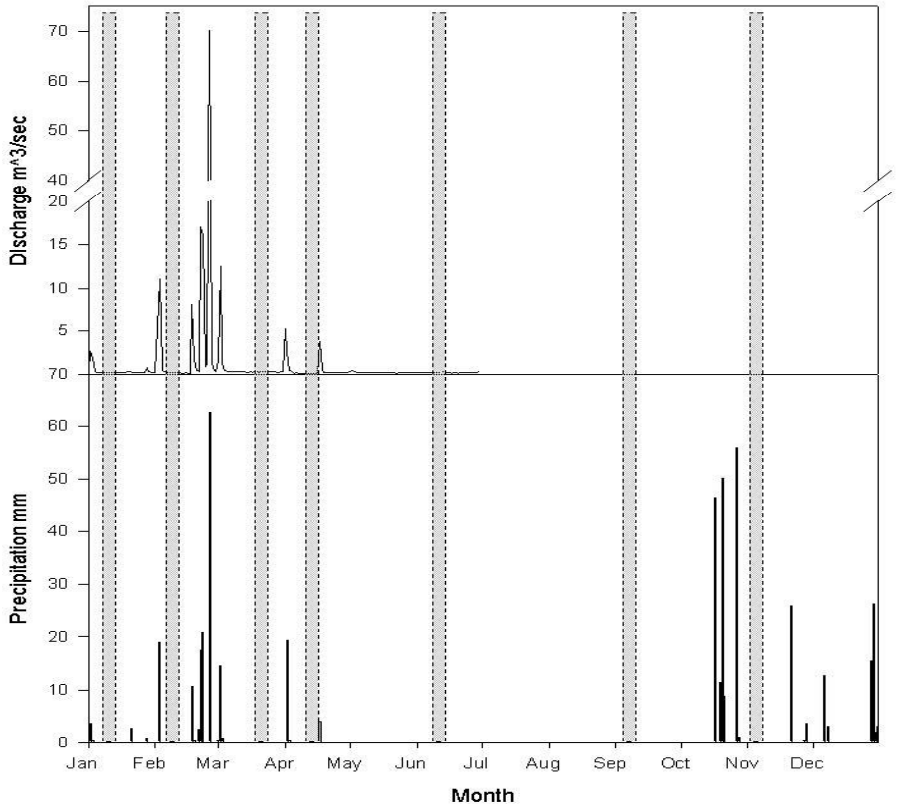


**Figure 2-2: San Diego Creek discharge and regional precipitation. Grey bars represent sampling events.**

**Table 2-3. Mean concentrations and 95% confidence interval (in parentheses) for each constituent by season, mean concentration, and standard deviations (in parentheses) for all sampling periods. Different letters (A,B) after confidence intervals indicate significant difference between seasons at (p-value$_{\alpha=0.05}$ < 0.05, n=73). All values are in μM except for TSS and CHLA, which are in mg l$^{-1}$ and μg l$^{-1}$ respectively.**

| Analyte | Wet Season (Nov-April) | Dry Season (May-October) | Mean (SD) for All Sampling Periods |
|---|---|---|---|
| $NH_4^+$ | 12.2 (10.8-13.9)$^A$ | 6.8 (5.8- 7.9)$^B$ | 10.7 (4.9) |
| N03+N02 | 25.7 (16.6 – 39.9)$^A$ | 3.6 (2.1- 6.2)$^B$ | 29.9 (40.9) |
| DON | 24.3 (17.9-31.8)$^A$ | 18.3 (13.8-23.8)$^A$ | 23.6 (15.5) |
| PN | 7.67 (6.7 – 8.8)$^A$ | 8.3 (7.2 – 9.5)$^A$ | 8.5 (3.5) |
| SRP | 2.6 (2.3 - 2.8)$^A$ | 2.0 (1.7 – 2.3)$^B$ | 2.4 (0.8) |
| DOP | 0.45 (0.33 – 0.57)$^A$ | 0.75 (0.57- 0.94)$^B$ | 0.62 (0.38) |
| PP | 0.49 (0.41 – 0.59)$^A$ | 0.79 (0.66 –0.94)$^B$ | 0.72 (0.41) |
| TSM | 76.5 (65.5-89.4)$^A$ | 97.4 (83.4-113.8)$^B$ | 92.8 (36.2) |
| CHLA | 2.2 (1.7 – 2.7)$^A$ | 2.9 (2.2- 3.6)$^A$ | 2.8 (1.9) |

*Surface Water Nutrients*

Particulate, dissolved inorganic and dissolved organic nutrients show distinct patterns with respect to season, dominant form, and spatial differences (Figure 2-3, Table 2-3). In general, total dissolved nitrogen (including organic and inorganic forms) exceeded particulate nitrogen by a factor of 3.6 during the dry season and 8 during wet seasons. Of the dissolved nitrogen, the combined forms of dissolved inorganic nitrogen (DIN = $NH_4^+$+$NO_3$+$N0_2$) were roughly 1.5 that of DON during the wet season, with $N0_3^-$+$N0_2^-$ the dominant form of DIN (Table 2-3). During the dry season, DON was on average twice the concentration of DIN species. SRP was on average a factor of 6 and 2 higher than DOP during the wet season and dry season respectively (Table 2-3). PP was roughly equal to the amount of DOP found during either season.

All dissolved inorganic nutrients were significantly higher during the wet season than during the dry season (Table 2-3 and Figure 2-3; p-value$_{\alpha=0.05}$ < 0.05, n=73 for all comparisons). This concentration difference was greatest with N03+N02, where wet season concentration was 5 times that of the dry season. Mean wet season $NH_4^+$ was 200% higher and SRP was 25% higher than dry season concentrations.

Seasonal trends were mixed with respect to dissolved organic nutrients and particulate nutrients. No significant differences were found in DON or PN concentrations with respect to season (p-value$_{\alpha=0.05}$ > 0.05, n=73 for both). Mean DOP and PP concentrations were both higher in the dry season sampling periods than for wet season sampling periods (p-value$_{\alpha=0.05}$ < 0.01, n=73 for both).

Spatial trends were evident for dissolved inorganic nutrient concentrations and particulate nutrients, but not for dissolved organic concentrations (Figure 2-3). All dissolved inorganic nutrient concentrations were significantly different among sites, regardless of season (p-value$_{\alpha=0.05}$ < 0.05, n=73 for all comparisons). During the wet season months of January, February, and March 2004, $N0_3$+$N0_2$, $NH_4^+$, and SRP were highest at Site 1 (nearest the mouth of San Diego Creek) and decreased downstream. These trends continued throughout the dry season for these constituents, though the differences among sites were not as extreme as those observed during the wet season. PN and PP were significantly different among sites, regardless of season. Concentrations were highest at Site 1, with a mean of 0.86 µM PP and 10.1 µM PN, and decreased downstream to a mean of 0.45 µM PP and 6.1 µM PN at Site 3. No significant difference existed among sites for DON or DOP, regardless of season

(p-value$_{\alpha=0.05}$ = 0.15 and 0.13, n=73 for DON and DOP respectively). This lack of trend is due to the high variability in these parameters within replicate water samples at each site.

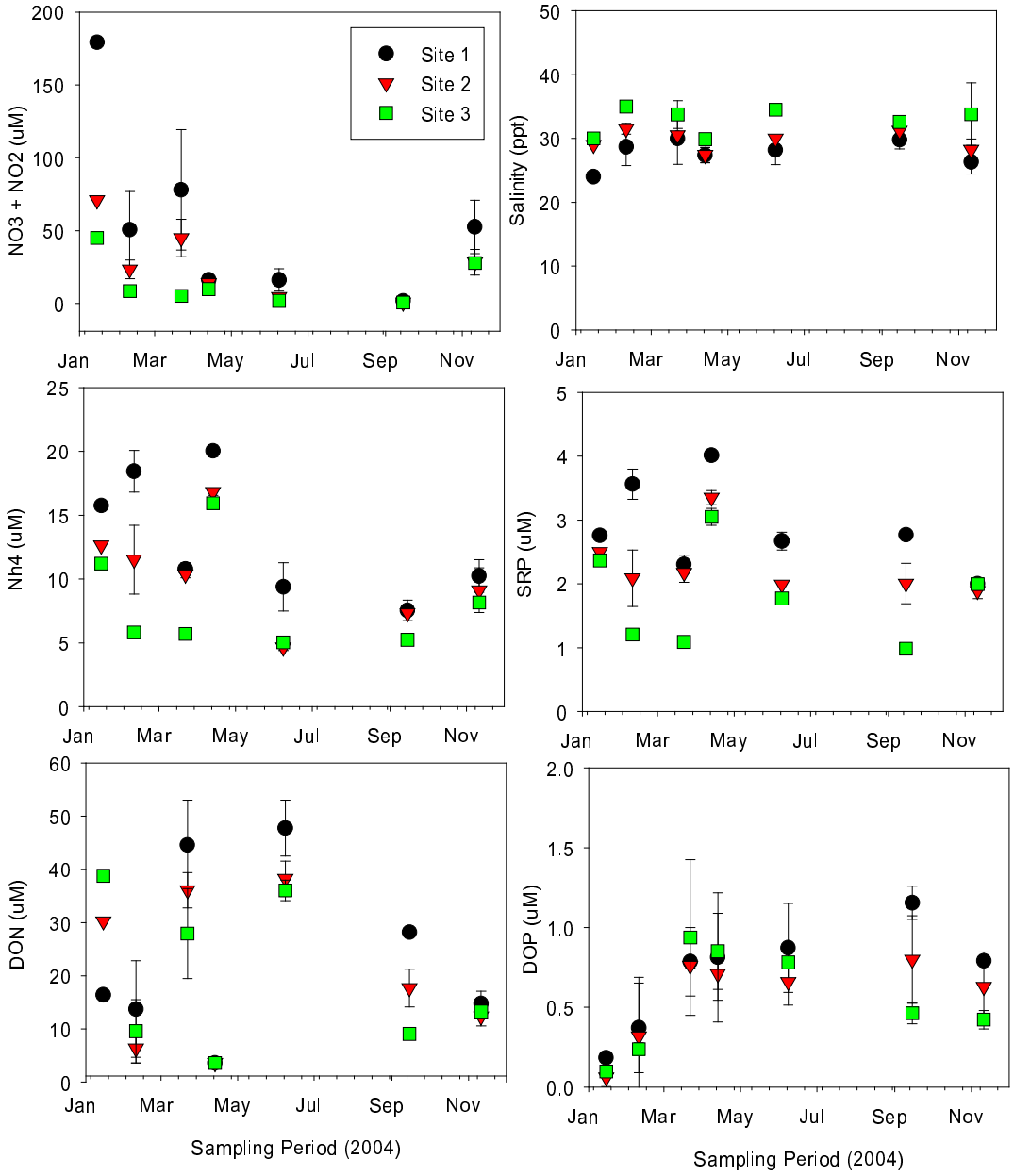


**Figure 2-3. Mean and standard deviation of surface and bottom water salinity and nutrient concentrations by sampling period.**

Little stratification of the water column was observed with respect to salinity (Figure 2-4). Thus the minor differences in nutrient concentrations observed between surface and bottom waters were likely due to incomplete mixing of the water column (Figure 2-4). Differences between

surface and bottom waters were most noticeable with respect to $NO_3^-$ + $NO_2^-$ during wet season sampling periods where surface samples were higher than bottom waters. Surface water DON also tended to be slightly higher than bottom waters, although not consistently for every site, throughout all sampling periods.

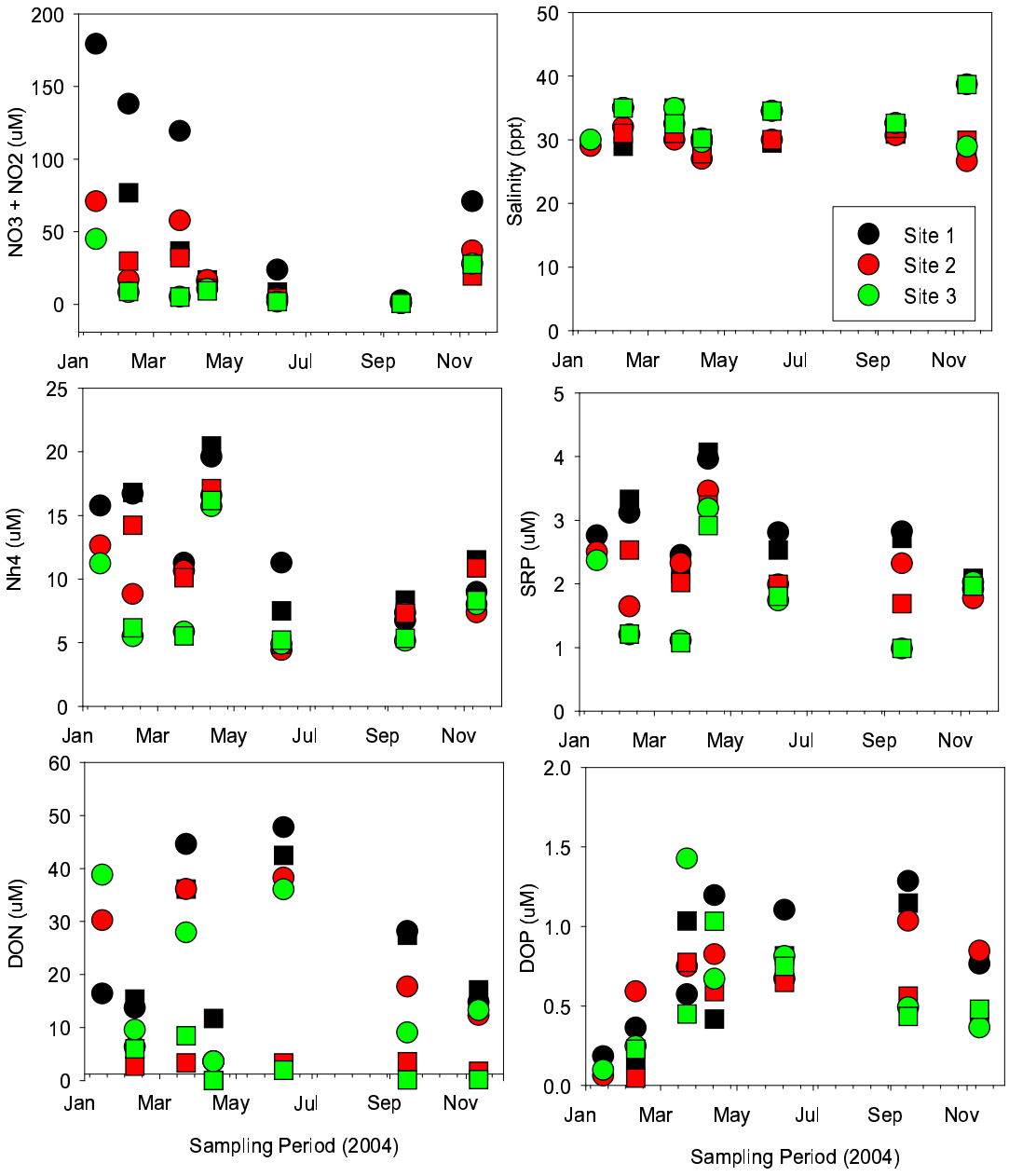


**Figure 2-4. Surface and bottom water salinity and nutrient concentrations by sampling period. Circles represent surface water; squares represent bottom water.**

*Algal Biomass, Speciation, and Tissue Nutrient Content*

Surface water chlorophyll *a* (CHLA) was also low throughout all periods sampled (mean ± S.D. of 2.8 ± 1.9 µg $L^{-1}$). No significant difference was found between wet and dry seasons (p-value$_{\alpha=0.05}$ =0.27, n=73); however, concentrations were significantly different by site (p-value$_{\alpha=0.05}$ = 0.002, n=73), with Site 1 showing the highest concentration (3.66 µg $L^{-1}$ CHLA) and decreasing downstream to a value of 1.7 µg $L^{-1}$ CHLA at Site 3.

Macroalgal biomass ranged from 13 to 240 g dry wt $m^{-2}$ and was highly variable spatially throughout all sampling periods (Figure 2-5). The greatest amount of macroalgae was found in February 2004 at Site 3; none was found in March and April; and moderate amounts were found in June and September at Sites 1 and 2. *Enteromorpha* and *Ulva spp.* were the dominant macroalgae in February 2004. In June 2004, *Enteromorpha*, *Ulva,* and the red alga *Ceramium sp.*were present. In September 2004, *Ulva* and a green macroalgal species tentatively identified as *Cladophora sp*. were recorded. Benthic microalgae were observed at all sites during all sampling periods, but no measurement of biomass was made.

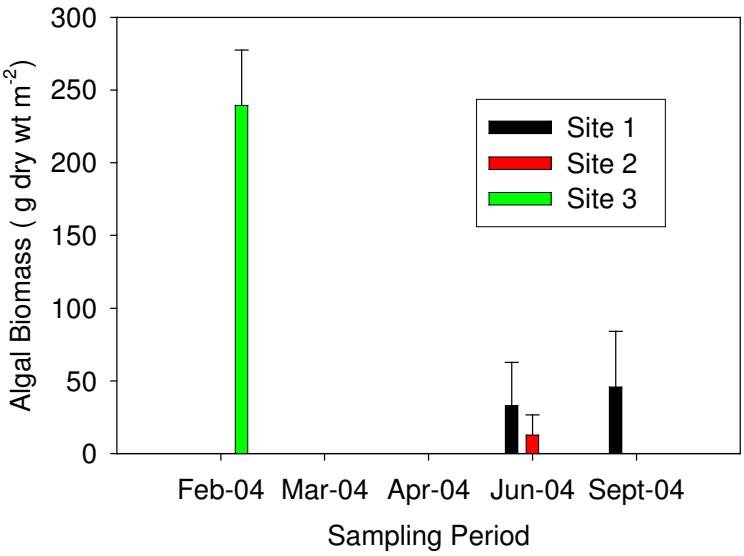


**Figure 2-5. Mean total macroalgal biomass and standard deviation per site and sampling period. Where bars are not shown, biomass was zero.**

Table 2-4 shows the mean tissue N and P content of the three macroalgal species sampled during the study. Regressions of tissue N and P with sediment TN and TP showed that *Enteromorpha* tissue P was positively correlated to sediment P ($r^2$= 0.63, p-value$_{\alpha=0.05}$ = 0.001,

n=21). *Enteromorpha* and *Ulva* tissue N were also positively correlated to sediment N ($r^2$= 0.41, p-value$_{\alpha=0.05}$ = 0.002, n=21).

**Table 2-4. Mean ± standard deviation of macroalgal tissue nutrients.**

| Species | Sample Size (n) | Tissue N (%dry wt N) | Tissue P (%dry wt P) |
|---|---|---|---|
| Enteromorpha sp. | 18 | 2.5 ± 0.8 | 0.23 ± 0.07 |
| Ulva sp. | 11 | 2.7 ± 0.7 | 0.23 ± 0.03 |
| Ceramium sp | 4 | 3.8 ± 0.2 | 0.32 ± 0.28 |

### *2.4.2 Patterns and Rates of Sediment Deposition and Resuspension*

Plots of total $^7$Be inventory with sediment depth can be used to estimate the rate of seasonal sediment deposition and understand the extent of deposition processes versus removal processes occurring at the site. Total inventories integrate new deposition to the bed with the residual $^7$Be remaining ed from a previous depositional event. Figures 2-6a and b present $^7$Be inventories as a function of sediment depths, over seven sampling periods, for intertidal and subtidal locations respectively. Higher inventories in the upper centimeters of a core indicate new deposition, while the decreasing inventories with depth indicate decay of older $^7$Be. At sites where an increase in $^7$Be appeared at depth, such as Site 3-subtidal in September, it may indicate either a rapid sedimentation event or increased sediment mixing downcore from physical events or bioturbation.

Vertical profiles of $^7$Be inventories in the sediments show a distinct pattern related to the wet season input of sediment into UNB (Figure 2-6a, b). Core locations that were measured in January show a residual $^7$Be inventory, indicating that sediment deposition had occurred during the early wet season before sampling began. The depth of detected $^7$Be inventories peaked during the March and April 2004 sampling events: periods coinciding with highest precipitation and runoff from the watershed. These inventories were observed to depths of > 6 cm at Site 1 intertidal and subtidal locations and at Site 3 intertidal locations (Figure 2-6a, b). $^7$Be was detected to depths of 3-4 cm at Site 2 intertidal and subtidal locations and Site 3 subtidal locations.

The sum of the total inventories over time show the largest deposition of sediments in the subtidal area of Site 1 (119.97 dpm/cm$^2$), a near equal deposition of sediment at the intertidal and subtidal areas at Site 2 (45.7 and 43.5 dpm/cm$^2$ respectively), and a larger deposition of sediment at the intertidal area of Site 2 (81.6 dpm/cm$^2$).

The total inventories for each sampling event were divided into residual and new inventories in order to elucidate the removal or deposition of sediment for any given time period and location (Figure 2-7). A residual inventory larger than the total inventory indicated a removal event. A positive new inventory indicates a deposition event; these values were used to calculate a mass accumulation for each site. Data showing large removals from April to June 2004 sampling interval for the Site 2 subtidal area and for the Site 3 intertidal area are likely to be overestimates (Figure 2-7); however, these numbers were not used in subsequent calculation of dry season and annual sedimentation rates.

Net sediment accumulation was the highest in the January–April 2004 time period: a period coinciding with the greatest rainfall (Table 2-5). The magnitude of the deposition was highest at Site 1, where the subtidal location was slightly higher than the intertidal location, and decreased downstream to values of 5.3-5.6 g wet wt sediment cm$^{-2}$). Based on wet-bulk densities of approximately 1.3-1.4 g wet wt sediment cm$^{-3}$ for the three sites, these values translate to a range of 3.6 cm (Site 3) to 8.9 cm (Site 1) deposited during this two-month period.

In general, the sites show variable patterns of deposition and erosion occurring throughout both wet and dry seasons. Net erosion occurred at the intertidal zone of Site 1. An erosion event apparently occurred between the months of April and June 2004, resulting in consistent removal of sediment from all sites. Notably, net deposition also occurred at all sites between June and September 2004, despite expectations of low sediment input for this period. Mass accumulation during this period increased downstream from a low of 4.0 g wet wt sediment cm$^{-2}$ at Site 1, to a high of 8.9 g wet wt sediment cm$^{-2}$, at Site 3. In spite of this period of apparent deposition, the net rate over the 5-month dry season was negative for Site 1 and Site 2 intertidal locations, with removals ranging from –0.6 to -10.5 g wet wt sediment cm$^{-2}$.

At times, the magnitude of net sediment deposition rates also appeared to be lagged or offset from the timing of the precipitation events that may have caused them. One example of this was Site 1, where it was anticipated that the February – March 2004 period would have the

highest mass accumulation rate coinciding in response to the largest rainfall events of this year (Figures 2-6, 2-7). Instead, net sediment deposition was highest from late March to mid-April. Another example was lower than expected $^{7}$Be inventories in November 2004 following an unusually high rain event occurring in October 2004.

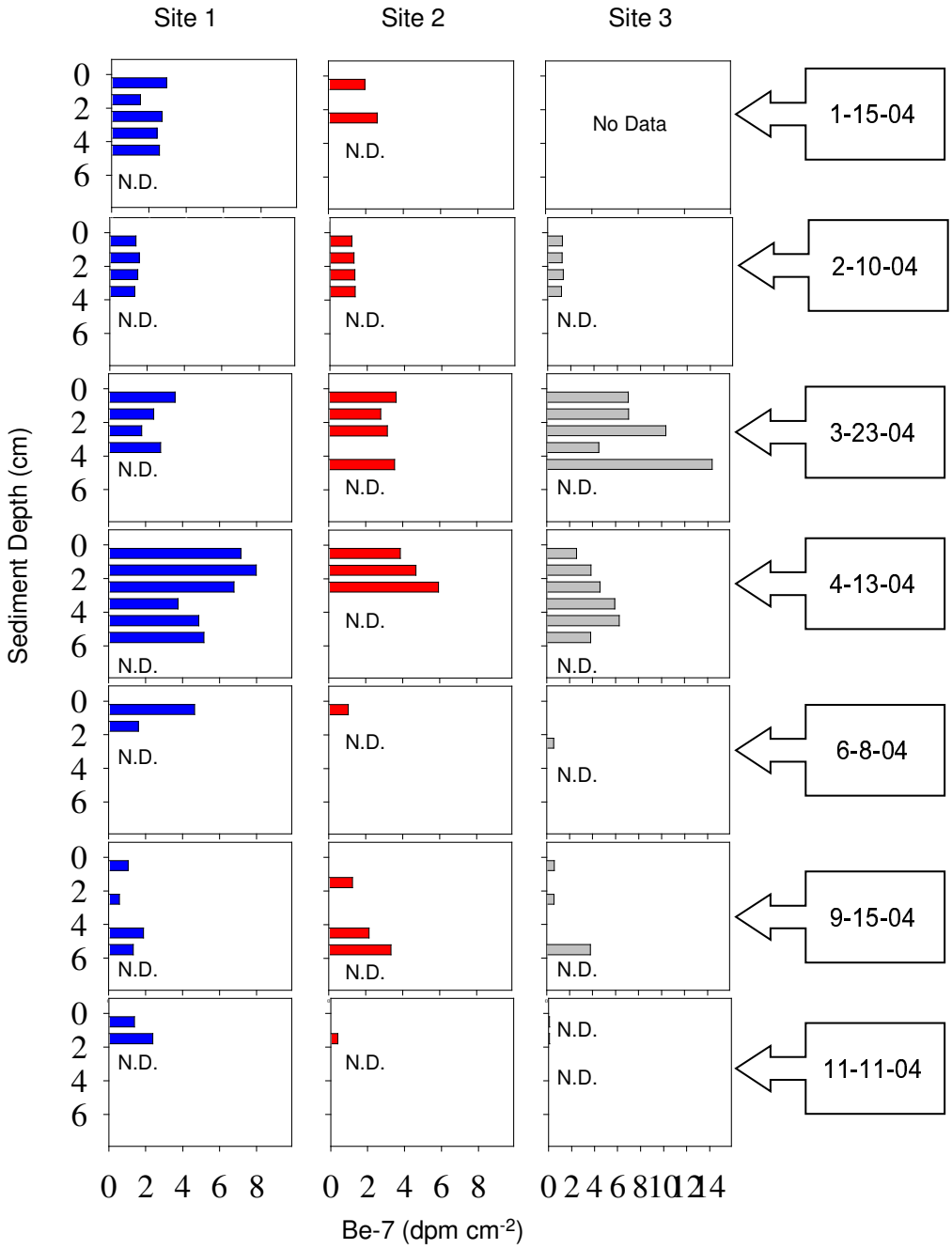


**Figure 2-6a. $^{7}$Be inventories as a function of sediment depth for intertidal locations of Sites 1-3 for the seven sampling periods. N.D. = non-detect.**

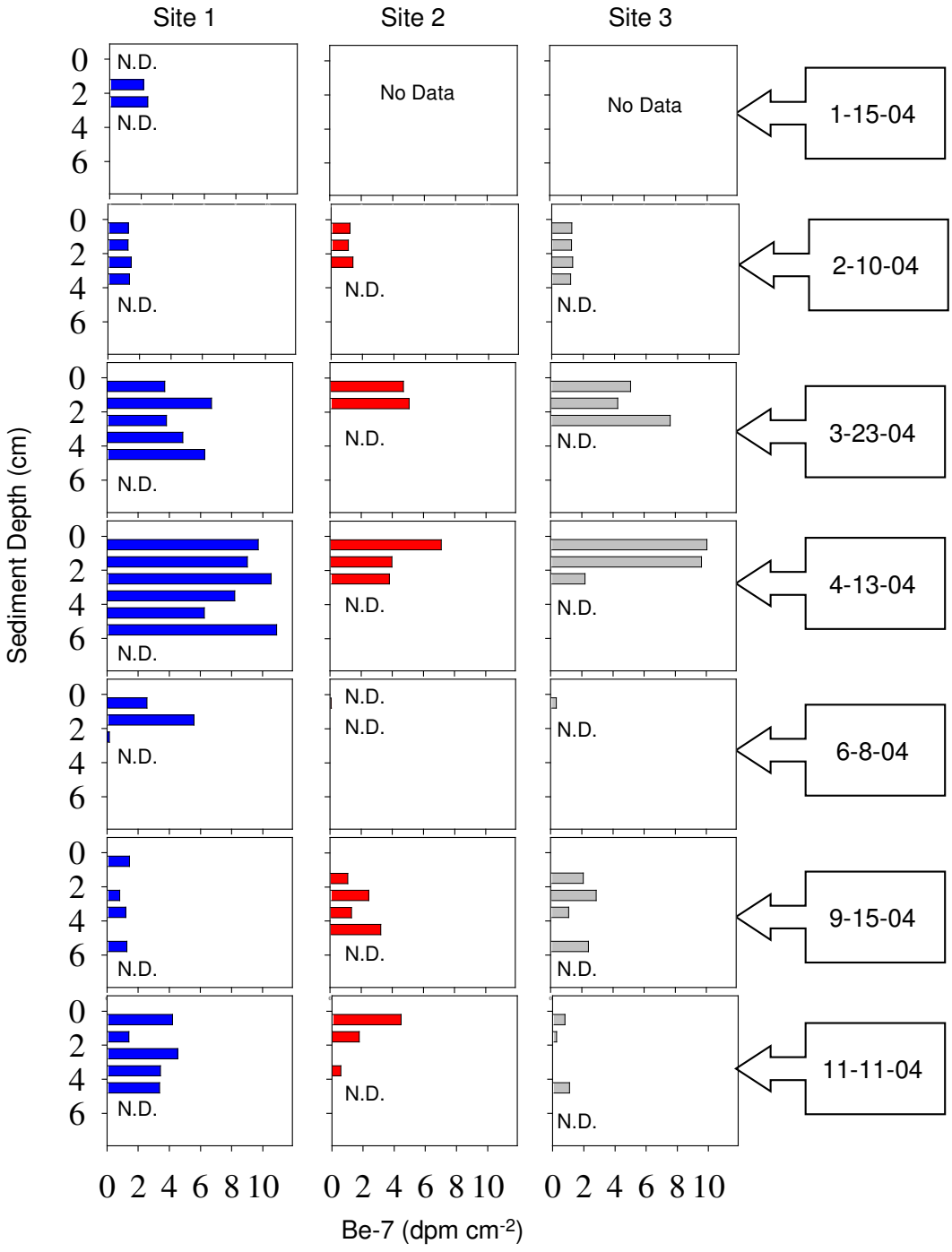


**Figure 2-6b. $^{7}$Be inventories as a function of sediment depth for subtidal locations of Sites 1-3 for the seven sampling periods. N.D. = non-detect.**

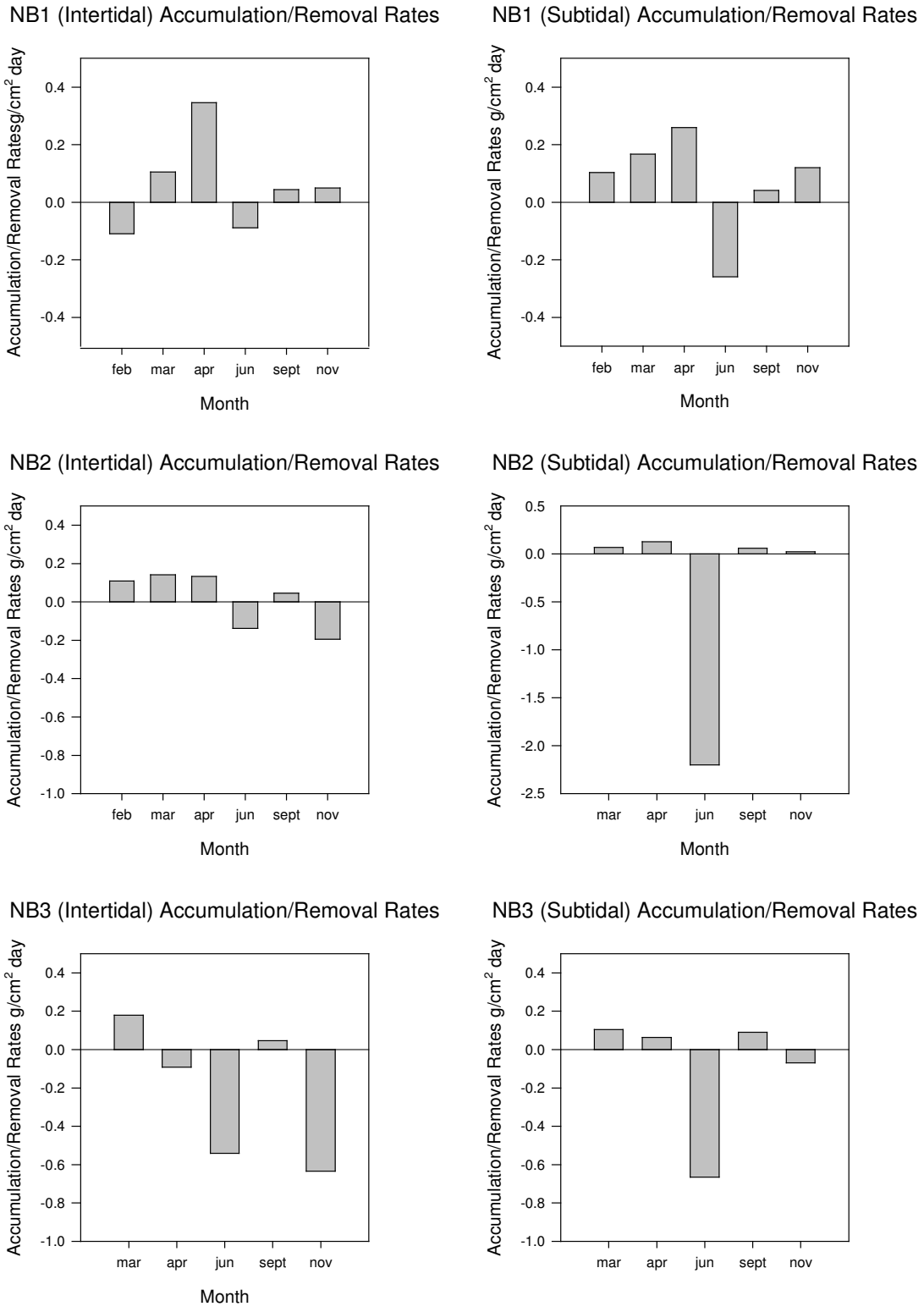


**Figure 2-7. Deposition/removal rates in UNB are distinctly seasonal and highly controlled by location with respect sediment loading areas.**

**Table 2-5. Net sediment accumulation (positive values) or removal rates (negative values) for wet and dry seasons by core location. Large removal rates calculated for the April-June 2004 sampling interval for Site 2 subtidal locations ,as well as for Site 3 intertidal and subtidal Site locations were considered erroneous and therefore omitted from calculations in this table (see Figure 2-7). For this reason, total sediment deposited is only given for cores obtained during the dry season (Jun-Sept) and a sediment deposition rate was not calculated for Sites 2 and 3.**

| Season | Site | Subsample Location | Sample Period Used in Calculation | Total Sed Deposition (g $cm^{-2}$) | Sediment Deposition Rate (mg wet wt $cm^{-2}$ $d^{-1}$) |
|---|---|---|---|---|---|
| Wet | 1 | Intertidal | Jan-April | 8.7 | 10.0 |
| | | Subtidal | Jan-April | 14.9 | 17.2 |
| | 2 | Intertidal | Jan-April | 11.4 | 13.1 |
| | | Subtidal | Feb-April | 5.34 | 8.8 |
| | 3 | Intertidal | Feb-April | 5.42 | 8.9 |
| | | Subtidal | Feb-April | 5.59 | 9.2 |
| | All | Intertidal | Mean ± StdDev | | 10.7±1.8 |
| | | Subtidal | | | 12.2±1.9 |
| | Mean All Sites | | | | 11.2 ±3.1 |
| Dry | 1 | Intertidal | Apr-Sept | -0.6 | -0.7 |
| | | Subtidal | Apr-Sept | -10.5 | -12.1 |
| | 2 | Intertidal | Apr-Sept | -3.2 | -3.7 |
| | | Subtidal | Jun-Sept | 5.34 | -- |
| | 3 | Intertidal | Jun-Sept | 5.42 | -- |
| | | Subtidal | Jun-Sept | 5.59 | -- |
| | All | Intertidal | Mean ± StdDev | | -2.2 ± 2.1 |
| | | Subtidal | | | -12.1 ± 4.9 |
| | Mean All Sites | | | | -7.7 ± 7.0 |

### *2.4.3. Wet-season and Long-Term Annual Deposition Rates*

Due to a delay in the scheduled start of field sampling, a pre-wet season baseline of $^{7}Be$ inventories was not captured, nor were the first 2 months of the wet season sampled. Consequently, $^{7}Be$ data could only be used with confidence to yield a net deposition rate for the 2-3 month time period of the wet season for which data was available. These rates, averaged over the 3 sites, ranged from 10.7±1.8 mg wet wt sediment $cm^{-2}$ $d^{-1}$ at the intertidal sites to 12.2±1.9 mg wet wt sediment $cm^{-2}$ $d^{-1}$ at subtidal sites, with an overall mean sediment deposition rate of 11.2 ±3.1 mg wet wt sediment $cm^{-2}$ $d^{-1}$. Assuming that the total combined intertidal and subtidal areas equal 449.8 acres (ACOE 2000), that the average moisture content of the sediments for this study was 44%, and the occurance of a 181-day wet season indicated

that this sediment-deposition rate would yield approximately $22.7X10^3$ tons of sediment deposited in UNB during the wet season.

$^7$Be data can also be used to derive an annual sedimentation rate for the 2003-2004 period covered in this study. Addition of wet- and dry-season rates yielded $^7$Be-derived annualized sedimentation rates for intertidal tidal and subtidal areas, as well as a rate for the two habitat types combined (0.91 ± 2.00 cm $y^{r-1}$; Table 2-6). This rate was approximately five times the long-term annual sedimentation rate calculated from $^{210}$Pb (0.166 ± 0.019 cm $y^{r-1}$), which covered a period of approximately 40 years worth of sedimentation at Site 4 (Figure 1-1).

**Table 2-6. Comparison of annual sedimentation rates derived from $^7$Be (for 2003-2004) versus $^{210}$Pb-derived long-term annual sedimentation rates.**

| Method | Habitat Type | Mass Accumulation Rate (mg wet wt $cm^{-2}$ $d^{-1}$) | | Annual Sedimentation Rate (cm $yr^{-1}$) | |
|---|---|---|---|---|---|
| | | Mean | Std Dev | Mean | Std Dev |
| $^7$Be- Annual Sedimentation Rate (Sites 1-3) | Intertidal | 8.50 | 2.77 | 2.22 | 0.72 |
| | Subtidal | 0.10 | 5.26 | 0.026 | 1.37 |
| | Overall Mean | 3.50 | 7.66 | 0.91 | 2.00 |
| $^{210}$Pb Long-Term Average Annual Rate (Site 4) | Subtidal | -- | -- | 0.166 | 0.019 |

### *2.4.4 Patterns in Sediment Characteristics and Wet Season N and P Deposition*

*Spatial and Temporal Trends in Bulk Sediment Characteristics*

The sediment bulk characteristics (grain size, SN, and SP) showed clear spatial andseasonal trends in UNB. One such trend was a significant increase in downstream grain size, from a mean of 41 ±1.5 % sand at Site 1 to a mean of 70 ±1.5 % sand at Site 3 (Figure 2-8). Correspondingly, grain size appeared to exert a major control on SN and SP concentrations. Percent sand showed a significant negative correlation with both SN ($r = 0.40$, p-value $_{\alpha = 0.05} = 0.0001$) and SP ($r^2 = 0.41$, p-value $_{\alpha = 0.05} = 0.0001$). Both SN and SP decreased downstream from mean values of 0.12 % dry wt N and 0.054 % dry wt P at Site 1 to 0.08 % dry wt N and 0.048% at Site 3. SN was significantly higher in subtidal locations than in intertidal locations (p-value $_{\alpha = 0.05} = 0.0001$, n=248), while SP exhibited no significant difference in values (p-value $_{\alpha = 0.05} = 0.12$, n=248).

Calculation of atomic SOC:SN (C:N ratio) and SOC:SP ratios (C:P ratio) are useful to control for the effects of grain size on SN and SP content, allowing an estimation of the extent to which sediment is enriched with respect to N or P. C:N ratios at all three sites were relatively high, ranging from an overall mean of 11.6:1 at Site 2 to 12.8:1 at Site 1, with a significant difference between these two sites (p-value $_{\alpha = 0.05} = 0.0002$, n=248). C:P ratios were also high, ranging from 47:1 at Site 2 to 60:1 at Site 1, with a significant difference between Sites 2 and 3 versus 1 (p-value $_{\alpha = 0.05} = 0.0001$, n=248). These values indicate that Site 1 had the most organic content of the three sites, but was the least enriched with respect to N and P-- in spite of the fact that these sites had the highest SN and SP concentrations of all three sites.

Seasonal trends were modest with respect to sediment bulk characteristics (Figure 2-9). Mean SN increased over the duration of the wet season, then decreased to its lowest point during the dry season. However only mean values for the late wet season (0.12 % dry wt N) and the late dry season (0.08 % dry wt N) were significantly different (p-value $_{\alpha = 0.05} = 0.002$, n=248). C:N ratios, reflecting N enrichment, were lowest during the mid-late wet season and early dry season. The late dry season had a mean C:N ratio (13.8:1), which was significantly higher than the mid-late wet-season mean , indicating sediment that was the most depleted with respect to N. (p-value $_{\alpha = 0.05} = 0.0001$, n=248). In contrast, SP appeared to peak in the late dry season, although seasonal SP values were only significantly different between the early and late dry

seasons (0.049 and 0.55 % dry wt P; p-value $_{\alpha = 0.05}$ = 0.002, n=248). Seasonal C:P ratios showed that the late wet season had a significantly higher mean value relative to the other three periods (60:1, p-value $_{\alpha = 0.05}$ = 0.002, n=248), suggesting that the sediments were most depleted with respect to P during this time period.

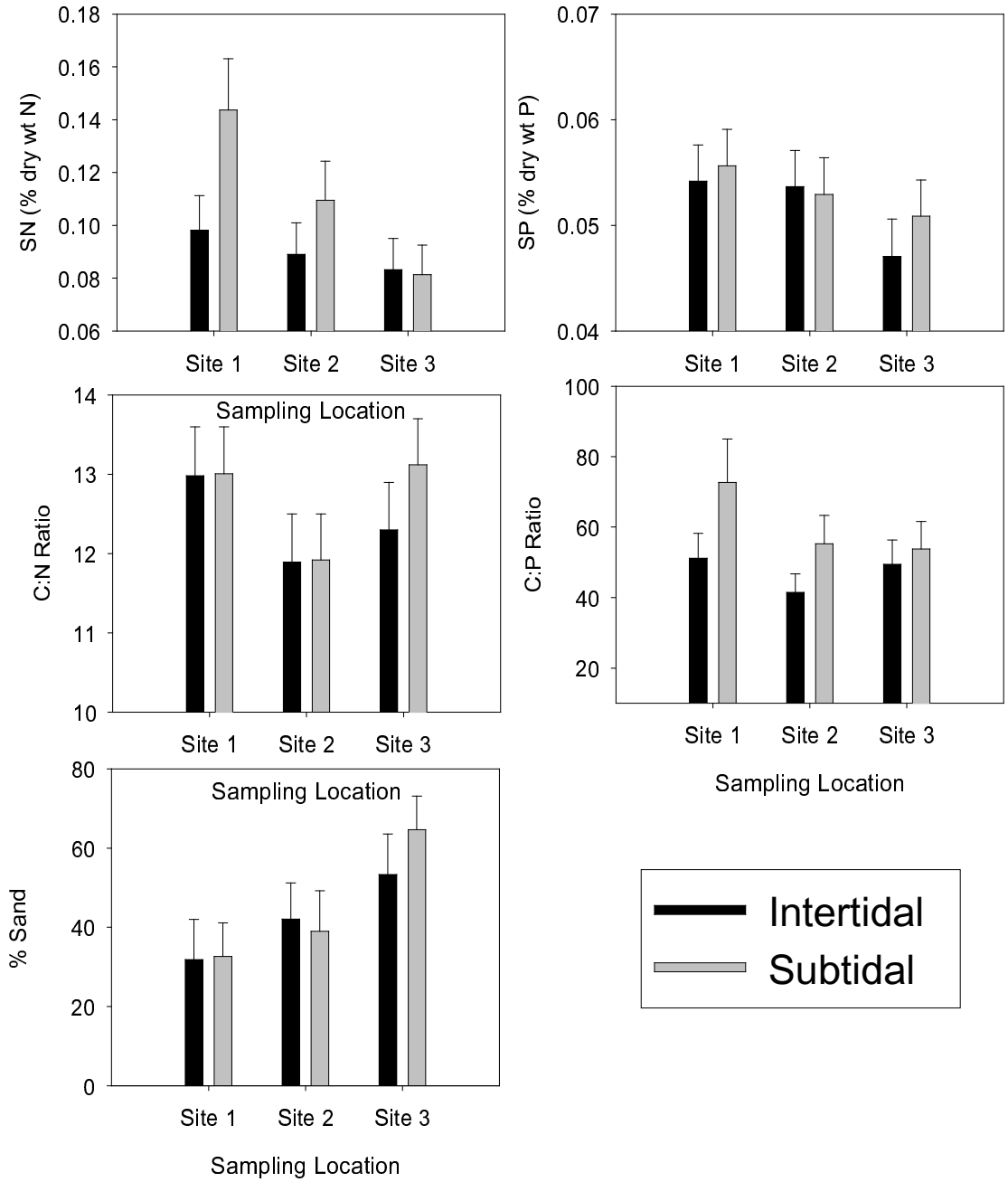


**Figure 2-8. Mean bulk sediment characteristics for each site and subsample location, averaging the 0-6 cm in depth over all sampling periods. Error bars represent upper confidence intervals.**

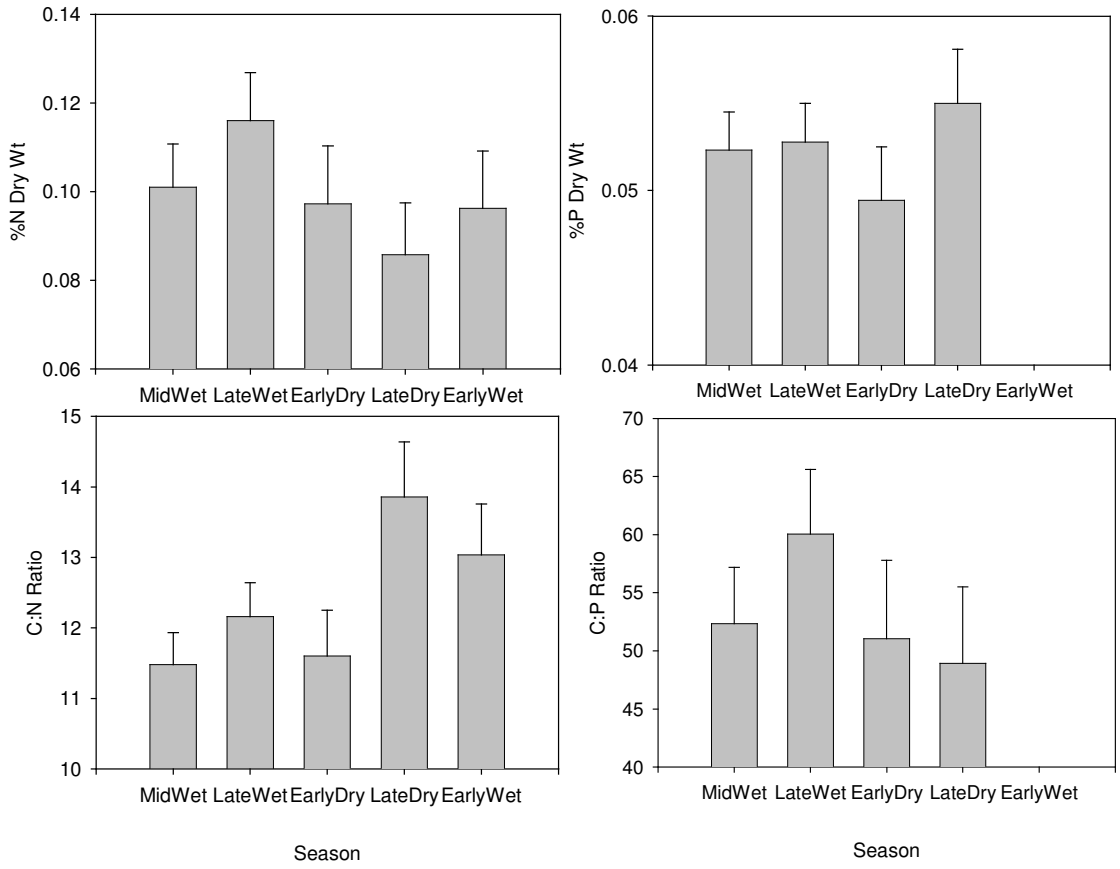


**Figure 2-9. Mean bulk sediment characteristics for each seasonal period, averaging 0-6 cm in depth over all sites. MidWet = Jan-Feb 2004, LateWet = Mar – Apr 2004, EarlyDry = Jun 2004, LateDry = Sept 2004, and Early Wet = Nov 2004. Error bars represent the upper confidence. interval.**

*Estimation of Newly Deposited N and P During Wet Season*

Quantities and rates of net sediment deposition by sampling period were used estimate the total amount of SN and SP deposited at each site for the wet season period for which data were available. These rates are given in Table 2-7. Mean SN and SP deposition rates, averaged over all sites for the period sampled, were 81 ± 27 µg N $cm^{-2}$ $d^{-1}$ and 32 ± 11 µg P $cm^{-2}$ $d^{-1}$. Assuming that intertidal mudflat and subtidal areas in UNB represent a combined surface area of 449.8 acres and that this rate reflects average deposition over a 181-day wet season, the total particulate N and P deposited during the 2003-2004 wet season was 121± 40 $x10^3$ lb TN and 48± 16 $x10^3$ lb TP.

**Table 2-7. N and P deposition rates during the wet season. A detailed explanation of calculations used to derive these estimates is given in Section 2.3.**

| Site | Subsample Location | Sample Period Used in Calculation | Total Sed Deposition (g wet wt $cm^{-2}$) | Total N Deposition (mg dry wt N $cm^{-2}$) | Total P Deposition (mg dry wt P $cm^{-2}$) | N Deposition Rate (µg dry wt N $cm^{-2}$ $d^{-1}$) | P Deposition Rate (µg dry wt P $cm^{-2}$ $d^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | Intertidal | Jan-April | 8.70 | 5.60 | 2.68 | 64 | 31 |
| | Subtidal | Jan-April | 14.94 | 11.56 | 4.45 | 133 | 51 |
| 2 | Intertidal | Jan-April | 11.41 | 6.73 | 3.64 | 77 | 42 |
| | Subtidal | Feb-April | 5.34 | 3.53 | 1.54 | 58 | 25 |
| 3 | Intertidal | Feb-April | 5.42 | 6.01 | 1.62 | 99 | 27 |
| | Subtidal | Feb-April | 5.59 | 3.41 | 1.16 | 56 | 19 |
| All | Intertidal | Mean ± StdDev | | | | 80 ± 14 | 33 ± 6 |
| | Subtidal | | | | | 82 ± 36 | 32 ± 14 |
| Total | | | | | | 81 ± 27 | 32 ± 11 |

### *2.4.5 Seasonal and Spatial Trends in Sediment Pore Water Profiles*

*$NO_3^-$*

Pore water $NO_3^-$ concentrations generally ranged from <0.01 to 3 µM in the early to late dry season (June and November 2004), when overlying surface water concentrations averaged 5 µM (Figures 2-3, 2-10). During the wet season (February, March, April, and November), when overlying surface water ranged from 5 to 180 µM (mean of 25 µM), pore water $NO_3$ concentrations increased up to 20 µM in surficial sediments, but typically declined rapidly with depth to concentrations ranging from <0.01 to 1 µM. No clear spatial trends in pore water $NO_3$ were observed with respect to site or subsample location (intertidal or subtidal); concentrations were generally low but highly variable with depth so that no spatial trends were discernable.

*$NH_4^+$ and SRP*

In general, pore water $NH_4^+$ and SRP concentrations behaved similarly with respect to both spatial and temporal trends (Figures 2-10, 2-12). Concentrations were lowest in surficial sediments, but usually higher (5-500 µM $NH_4^+$ and 1-200 µM SRP)) than found in overlying surface waters (1 – 20 µM $NH_4^+$ and 1-4 µM SRP; Figure 2-3). Pore water concentrations of both species increased with depth to values of 100 - 3500 µM $NH_4^+$ and 10-400 µM SRP.

In general, pore water $NH_4^+$ and SRP concentrations were highest in mid-late wet season and then declined in the late dry season by a factor of 40-50. Peak concentrations of pore water

$NH_4^+$ and SRP were found in strikingly similar depth profiles in March 2004. In early wet season (November 2004), concentrations were also low, but slightly higher than found during the late dry season.

Consistent spatial trends were also found for $NH_4^+$ and SRP. Site 2 had lower $NH_4^+$ and SRP concentrations than those for Sites 1 and 3regardless of sampling period. Site 1 subtidal locations typically had the highest concentrations of all six coring locations during most sampling periods, with the exception of February 2004, for $NH_4^+$, and February and September 2004, for SRP. For Site 1, $NH_4^+$ was consistently higher at the subtidal locations than at the intertidal location. $NH_4^+$ and SRP were comparable at the intertidal and subtidal Site 2 locations. At Site 3, $NH_4^+$ was slightly higher at the intertidal location, while SRP was slightly higher at the subtidal location.

$S^{-2}$

Pore water $S^{-2}$ concentrations, indicative of the microbially-remediated reduction of $SO_4^{-2}$ to $S^{-2}$, are used as an indicator of some important biogeochemical processes that can affect nutrient cycling in sediments (see Discussion in section 2.5 for further details).

Pore water $S^{-2}$ concentrations were low in surficial sediments, with typical concentrations ranging from below detection limit – 40 μM (Figure 2-13). Concentrations generally increased mid-depth, at times declining towards the bottom of the core.

Pore water $S^{-2}$ concentrations were highest at subtidal Site 1 during all sampling periods (Figure 2-12). Intertidal Site 3 concentrations were also high during late wet season sampling periods, while subtidal $S^{-2}$concentrations for this site were higher than intertidal during dry season months. Site 2 intertidal and subtidal sites were typically low (below detection limit to 10 μM), with the exception of February and September 2004, where concentrations of 1000-1500 μM were observed.

$S^{-2}$ concentrations were highest during the wet season sampling periods, with peak concentrations of up to 0.4 M $S^{-2}$ found at subtidal Site 1 and 0.2 M $S^{-2}$ found at intertidal Site 3 during March 2005. These concentrations were 2-3 orders of magnitude higher than observed at any other site or sampling period throughout the remainder of the study. During the early wet season sampling period (November 2004), pore water $S^{-2}$ at the lowest concentration range

observed for all sites. The magnitude and shape of the pore water $S^{-2}$ depth profile covaried with pore water $NH_4^+$ and SRP concentrations for Sites 1 and 3 for all sampling periods, indicating that elevated $NH_4^+$ and SRP concentrations could be linked to $SO_4^{-2}$ reduction in sediments.

*DON and DOP*

Pore water DON and DOP were minor components (~2-10%) of the total dissolved nutrient concentration in pore waters. Concentrations of these species were more highly variably and showed less consistent spatial and temporal trends than the dissolved inorganic constituents (Figures 2-14 and 2-15). The range of pore water DON concentrations was generally higher in the mid-late wet-season months (non-detect -200 μM N) than during the dry season or early wet season (non-detect -50 μM N). DOP was generally in the range of non-detect -5 μM P for all seasons except the early wet season when peak concentrations were 2.5 μM P.

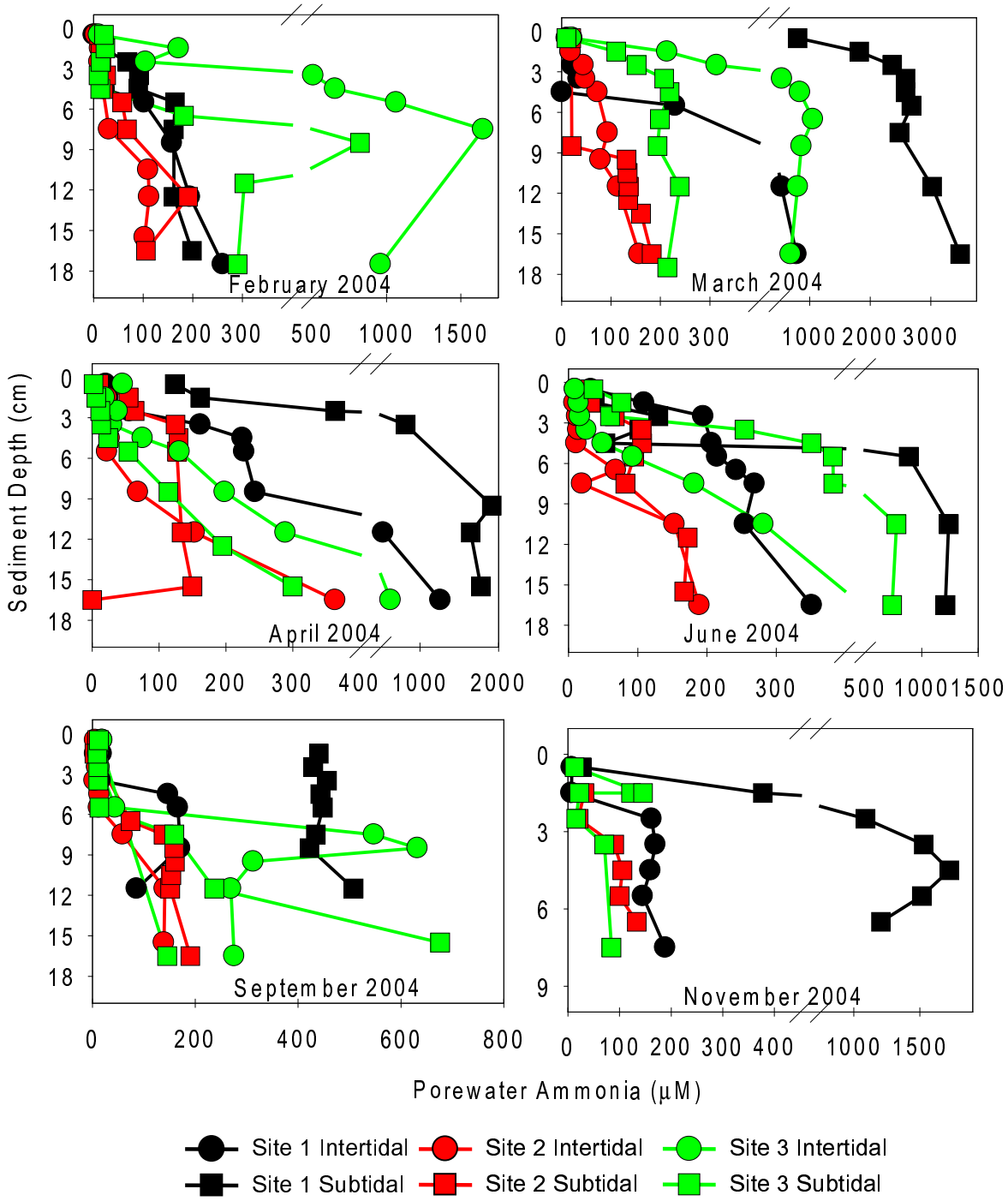


**Figure 2-10. Vertical profile of pore water $NH_4^+$ concentration by site and sampling period.**

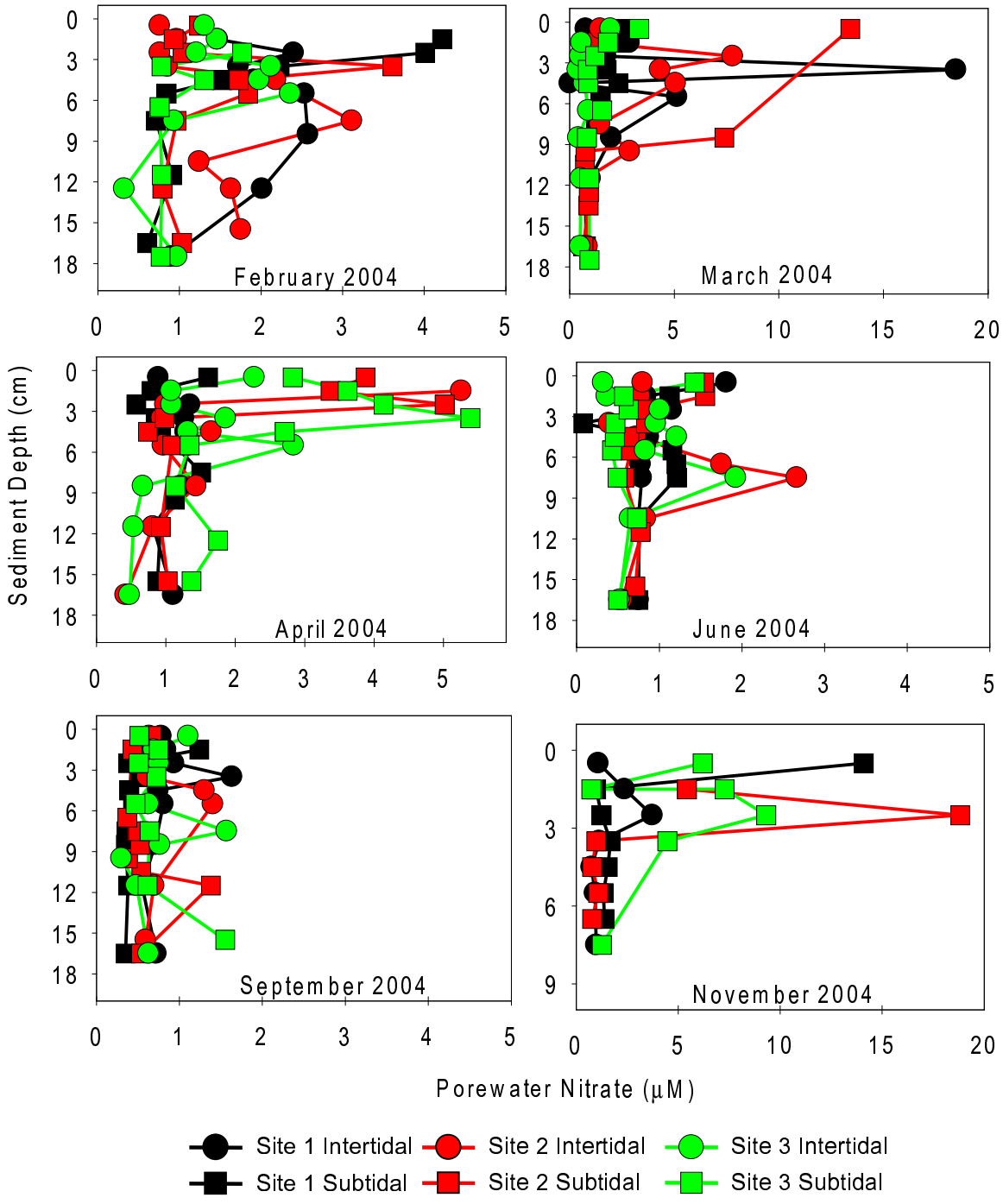


**Figure 2-11. Vertical profile of pore water $NO_3$ concentration by site and sampling period.**

.

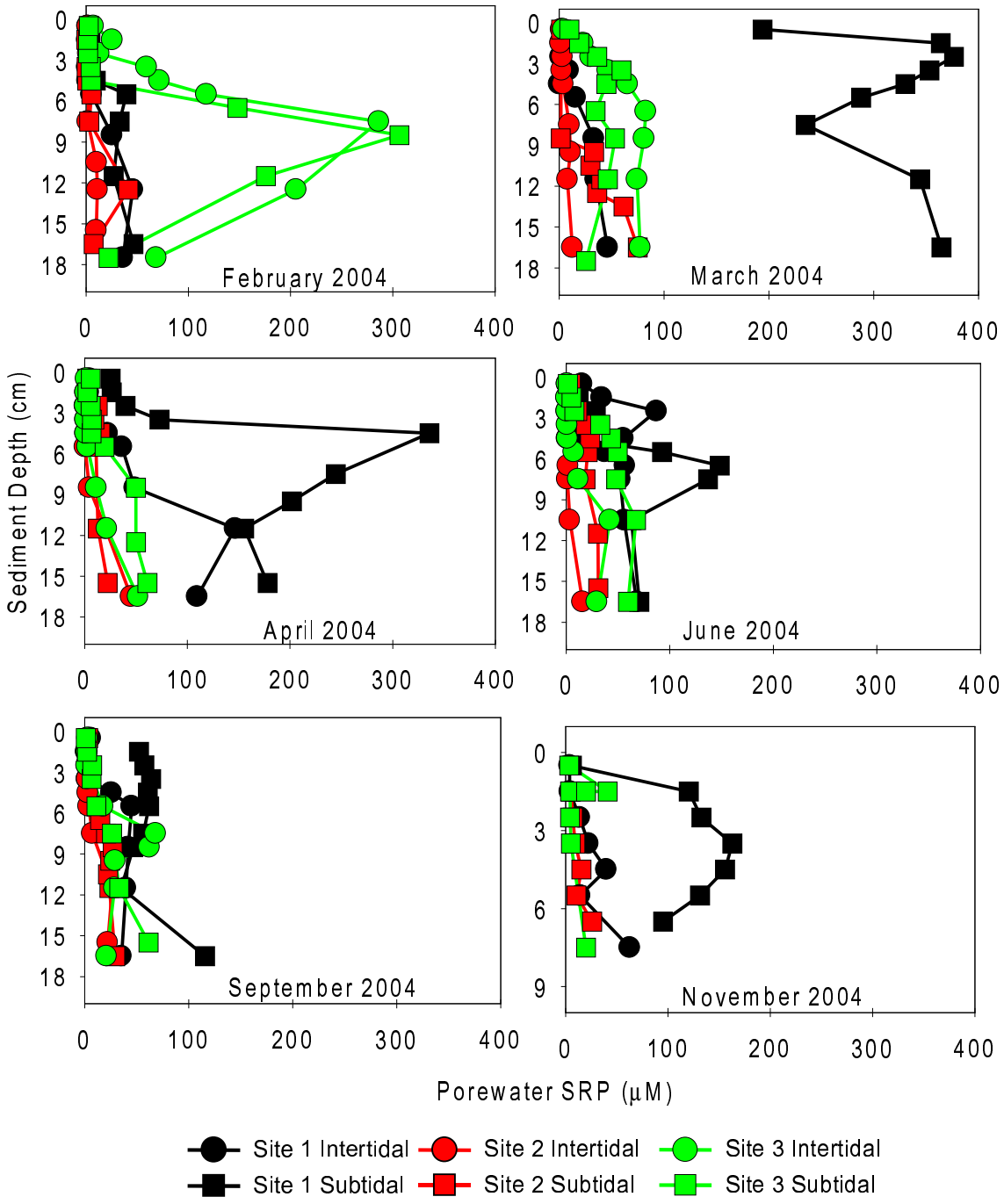


**Figure 2-12. Vertical profile of pore water SRP concentration by site and sampling period.**

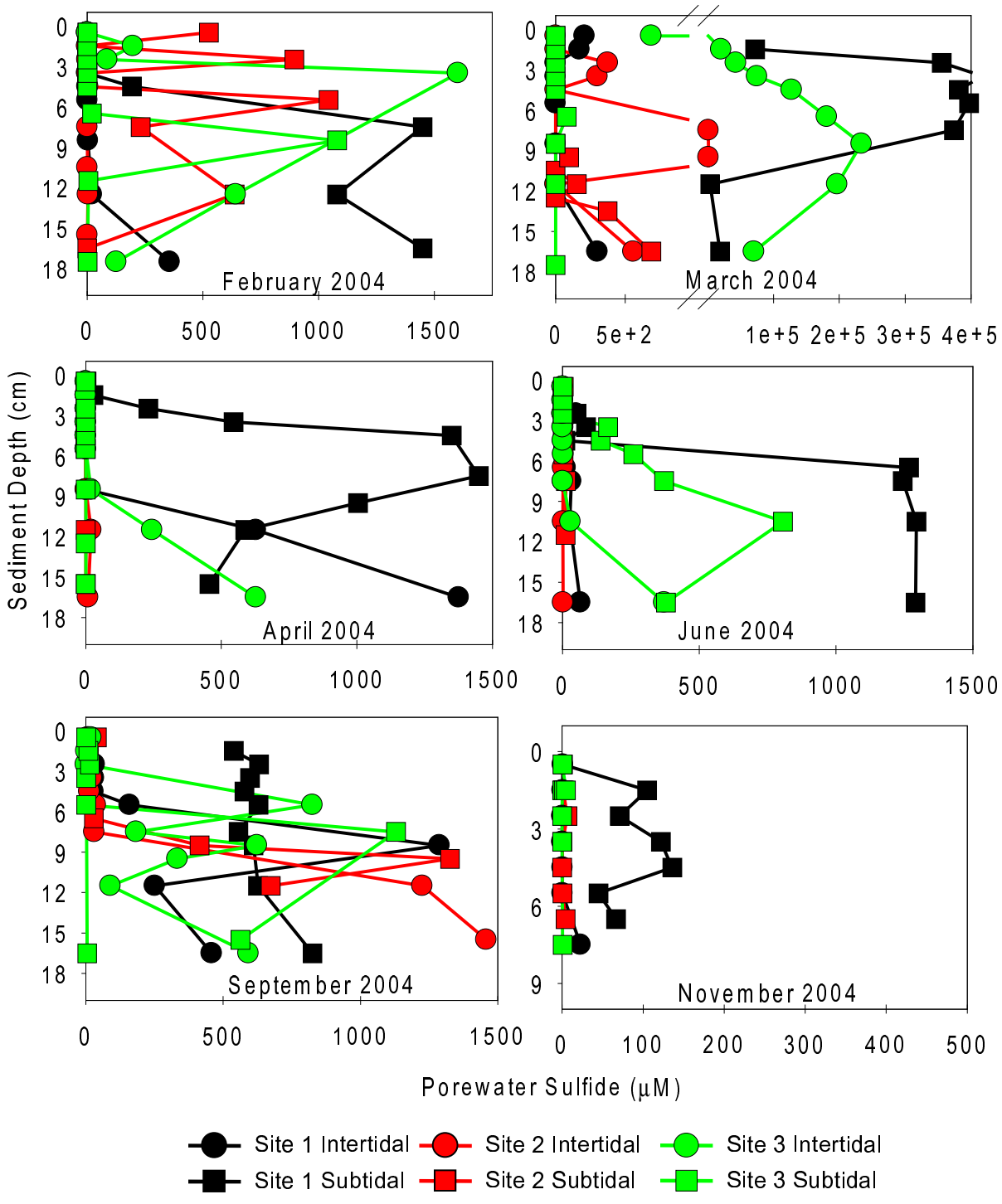


**Figure 2-13. Vertical profile of pore water $S^{-2}$ concentration by site and sampling period.**

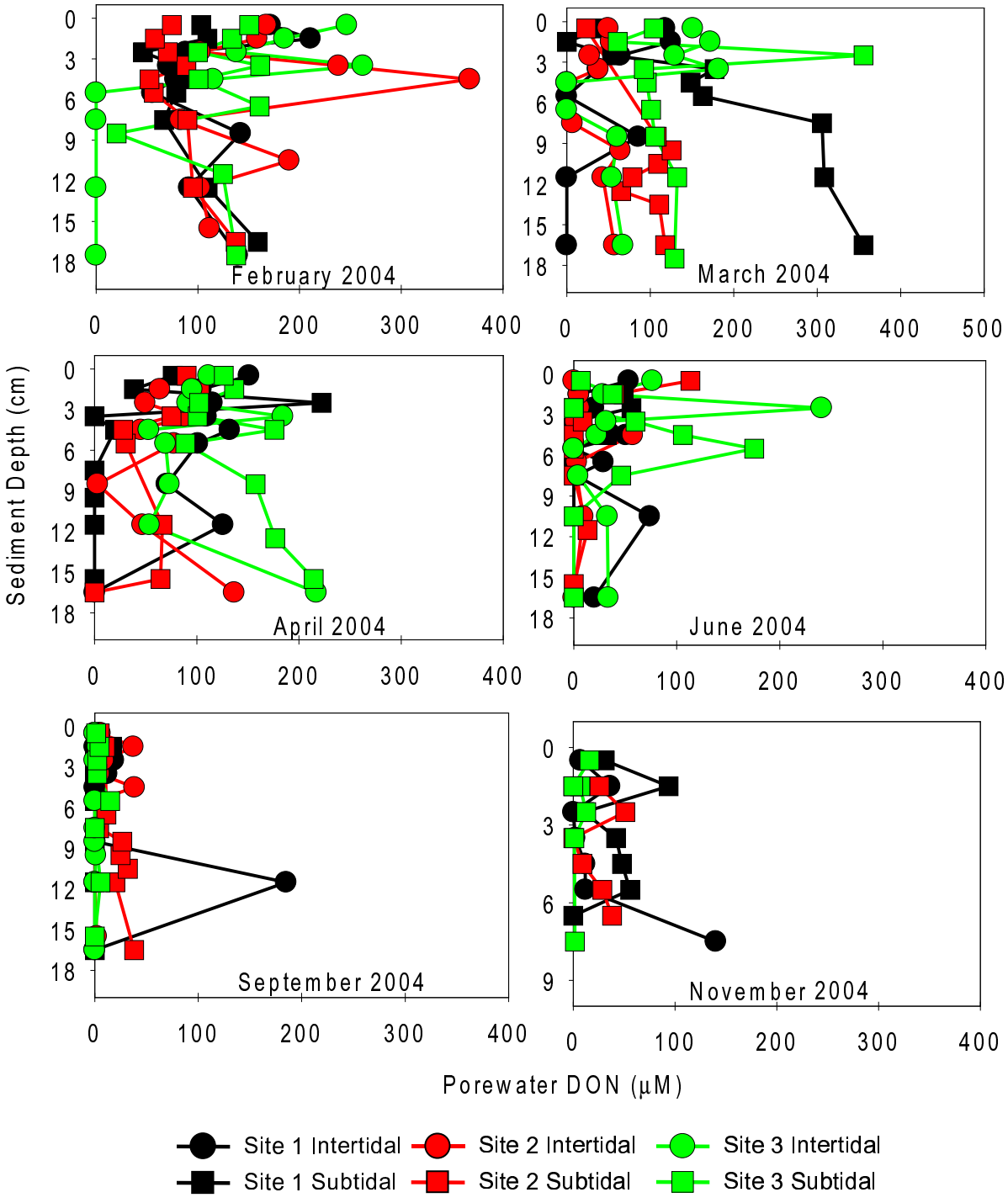


**Figure 2-14. Vertical profile of pore water DON concentration by site and sampling period.**

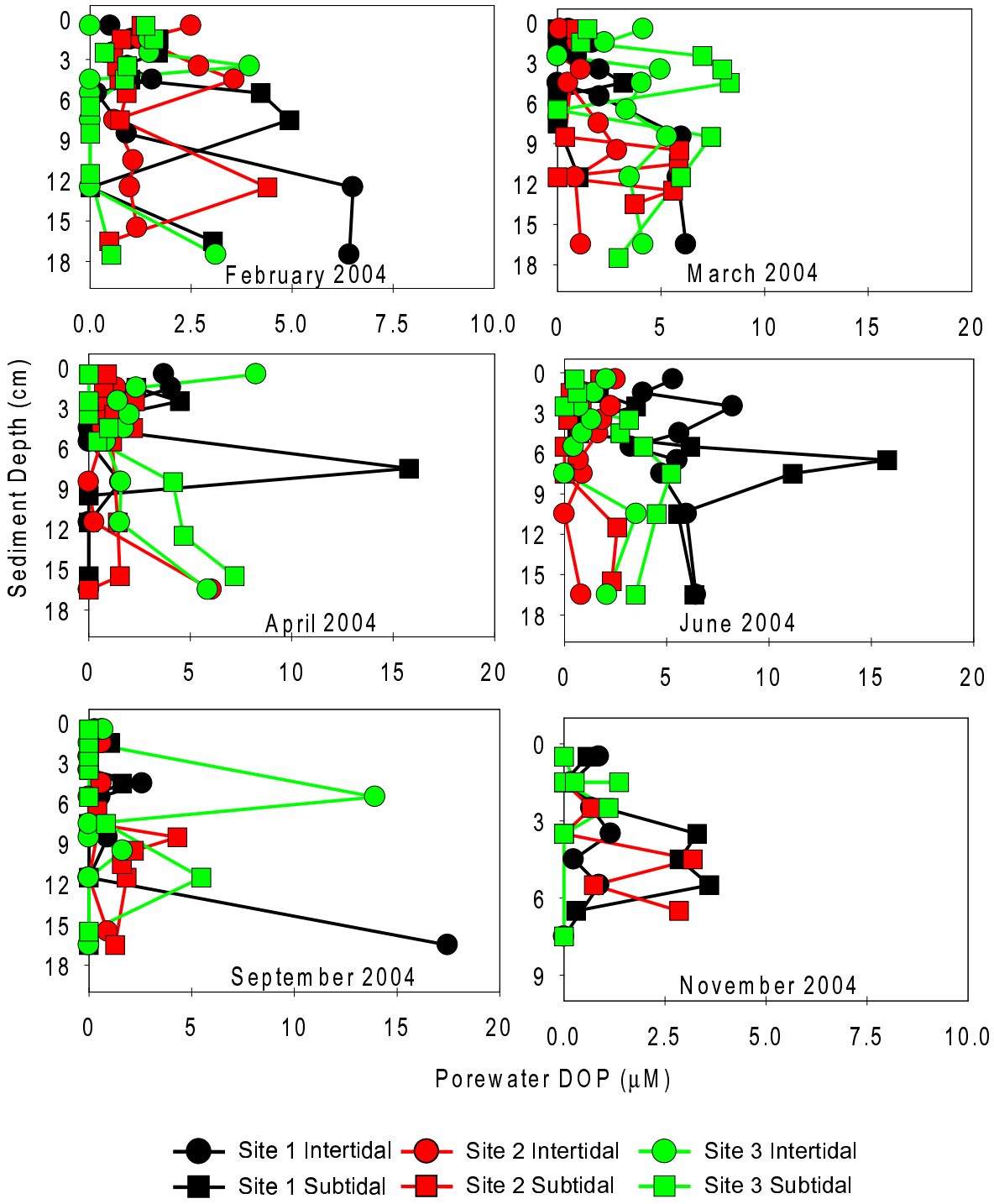


**Figure 2-15. Vertical profile of pore water DOP concentration by site and sampling period.**

### *2.4.6 Diffusive Transport Between Sediments and Surface Waters*

*Temporal Trends in Diffusive Flux Estimates*

Predictions of diffusive flux at UNB sites generally showed a positive flux of $NH_4^+$ and SRP, as well as a negative flux of $NO_3^-$, from the sediments into the surface waters (Figures 2-16, 2-17, and Tables 2-8, 2-9). When rates were averaged over all sites, $NH_4^+$ and SRP fluxes were highest March and April, with a range of 0.4 – 21.7 µmol $NH_4^+$ and 0.4 – 11.4µmol SRP $m^{-2}$ $hr^{-1}$. The variability in these rates was high, with the magnitude of the flux principally driven by the estimates from subtidal Site 1. Mean $NH_4^+$ and SRP flux was lowest in February 2004 (Table 2.8, 2.9). $NO_3^-$ flux into the sediments was highest in the mid-late wet season (-20.2 to –5.6 µmol NO3 $m^{-2}$ $hr^{-1}$) and lowest during the dry season (-0.01 to –1.8 µmol NO3 $m^{-2}$ $hr^{-1}$).

**Table 2-8. Mean ± standard deviation of nitrogen diffusive flux estimates by subsample location and sampling period. All values are in µmol $m^{-2}$ $hr^{-1}$.**

| Species | Location | Feb-2004 | Mar-2004 | Apr-2004 | Jun-2004 | Sept-2004 | Nov-2004 |
|---|---|---|---|---|---|---|---|
| $NH_4^+$ | Intertidal | -0.9 ± 4.2 | 5.0 ± 3.4 | 5.4 ± 6.2 | 5.6 ± 5.4 | 0.9 ± 2.7 | -0.7 |
| | Subtidal | 1.7 ± 7.2 | 38.4 ± 47.0 | 21.4 ± 38.5 | 16.0 ± 6.7 | 6.2 ± 5.0 | 15.6 ± 18.0 |
| | All Sites | 0.4 ± 6.0 | 21.7 ± 37.3 | 13.4 ± 28.7 | 10.8 ± 8.0 | 3.5 ± 4.9 | 11.5 ± 17.1 |
| NO3 | Intertidal | -20.6 ± 14.9 | -10.5 ± 6.7 | -5.7 ± 3.2 | -1.6 ± 1.0 | 0.01 ± 0.09 | -3.9 |
| | Subtidal | -19.8± 15.0 | -11.7 ± 7.5 | -5.5 ± 3.0 | -2.1 ± 1.8 | -0.02 ± 0.03 | -3.0 ± 2.4 |
| | All Sites | -20.2 ± 15.0 | -11.1 ± 7.1 | -5.6 ± 3.1 | -1.8 ± 1.5 | -0.01 ± 0.07 | -3.2 ± 2.1 |
| DON | Intertidal | 34.5 ± 10.2 | 9.8 ± 5.8 | 15.8 ± 9.2 | 1.2 ± 3.9 | 1.1 ± 2.1 | 1.0 |
| | Subtidal | 21.0 ± 7.5 | 12.1 ± 8.1 | 14.9 ± 1.6 | 2.9 ± 7.1 | -1.2 ± 0.6 | 0.8 ± 1.5 |
| | All Sites | 27.7 ± 11.2 | 10.9 ± 7.1 | 15.5 ± 8.7 | 5.3 ± 6.3 | -0.1 ± 1.9 | 0.8 ± 1.3 |
| TDN | Intertidal | 12.9 ± 25.4 | 4.3 ± 13.2 | 19.4 ± 12.8 | 6.7 ± 7.9 | 2.0 ± 2.5 | -1.8 ± 1.8 |
| | Subtidal | 2.9 ± 27.5 | 38.8 ± 36.4 | 30.8 ± 34.2 | 16.7 ± 1.5 | 5.0 ± 5.0 | 13.4 ± 14.7 |
| | All Sites | 7.9 ± 27.0 | 21.5 ± 32.4 | 23.2 ± 26.1 | 11.0 ± 7.3 | 3.5 ± 4.2 | 7.3 ± 13.6 |

**Table 2-9. Mean ± standard deviation of P diffusive flux estimates by subsample location and sampling period. All values are in μmol $m^{-2}$ $hr^{-1}$.**

| Species | Location | Feb-2004 | Mar-2004 | Apr-2004 | Jun-2004 | Sept-2004 | Nov-2004 |
|---|---|---|---|---|---|---|---|
| SRP | Intertidal | 0.6 ± 1.0 | 2.0 ± 2.3 | 1.2 ± 1.7 | 1.2 ± 1.2 | 0.6 ± 0.3 | 0.1 |
| | Subtidal | 0.1 ± 0.3 | 20.9 ± 16.8 | 2.3 ± 3.0 | 1.2 ± 1.2 | 5.2 ± 6.2 | 3.8 ± 2.7 |
| | All | 0.4 ± 0.8 | 11.4 ± 15.2 | 1.7 ± 2.5 | 1.2 ± 1.2 | 2.9 ± 5.0 | 2.9 ± 2.8 |
| DOP | Intertidal | 0.1 ± 0.2 | 0.1 ± 0.3 | 0.5 ± 0.4 | 0.3 ± 0.2 | 0.04 ± 0.1 | -0.03 |
| | Subtidal | 0.3 ± 0.0 | 0.3 ± 0.4 | -0.1 ± 0.1 | 0.1 ± 0.1 | 0.01 ± 0.2 | -0.01 ± 0.01 |
| | All | 0.2 ± 0.2 | 0.2 ± 0.4 | 0.3 ± 0.5 | 0.3 ± 0.2 | 0.05 ± 0.20 | -0.02 ± 0.02 |
| TDP | Intertidal | 0.8 ± 0.9 | 2.1 ± 2.2 | 1.7 ± 1.3 | 1.6 ± 1.4 | 0.6 ± 0.3 | 0.1 |
| | Subtidal | 0.4 ± 0.3 | 21.2 ± 16.5 | 2.3 ± 2.9 | 1.3 ± 1.3 | 5.2 ± 6.4 | 3.8 ± 2.6 |
| | All | 0.6 ± 0.7 | 11.6 ± 15.2 | 2.0 ± 2.3 | 1.4 ± 1.4 | 2.9± 5.1 | 2.8 ± 2.8 |

Mean DON fluxes were positive and highest in mid-late wet season sampling periods, with means ranging from 15.5 to 27.7 μmol DON $m^{-2}$ $hr^{-1}$ (Table 2-8, Figure 2-17). During the dry season and early wet season sampling periods, mean rates were small and at times negative (-0.1 to 5.3 μmol DON $m^{-2}$ $hr^{-1}$). Typically, $NH_4^+$ dominated TDKN fluxes, although during the February and April sampling periods, DON fluxes equaled or exceed that of $NH_4^+$.

DOP fluxes were also generally positive but typically an order of magnitude lower or higher than SRP fluxes. The magnitude of DOP flux was highest during the mid-late wet season and early dry season sampling periods (0.2 – 0.3 μmol DOP $m^{-2}$ $hr^{-1}$) and lowest during late dry season and early wet season sampling periods (-0.02 – 0.05 μmol DOP $m^{-2}$ $hr^{-1}$).

*Spatial Trends in Diffusive Flux Estimates*

Some spatial trends were apparent in predicted fluxes for the dissolved inorganic nutrient species; however, these trends were not consistent for each sampling period (Figures 2-15 and 2-15). $NH_4^+$ fluxes were typically highest at Site 1 and lowest at Site 2, with subtidal estimates usually exceeding those for intertidal locations. $NH_4^+$ flux estimates for subtidal Site 1 greatly exceed other sites, with the exception of February 2004, when intertidal Site 3 was highest and

Site 1 fluxes were negative. SRP fluxes from the sediments were typically the highest at Site 1 and lowest at Site 3, again with estimates for subtidal locations typically exceeding intertidal locations. For $NO_3^-$ flux, Sites 1 and 2 had the highest predicted fluxes into the sediment, but no consistent trend existed between subtidal and intertidal locations. For DON and DOP, few consistent spatial trends with respect to site or subsample location were evident in the flux estimates.

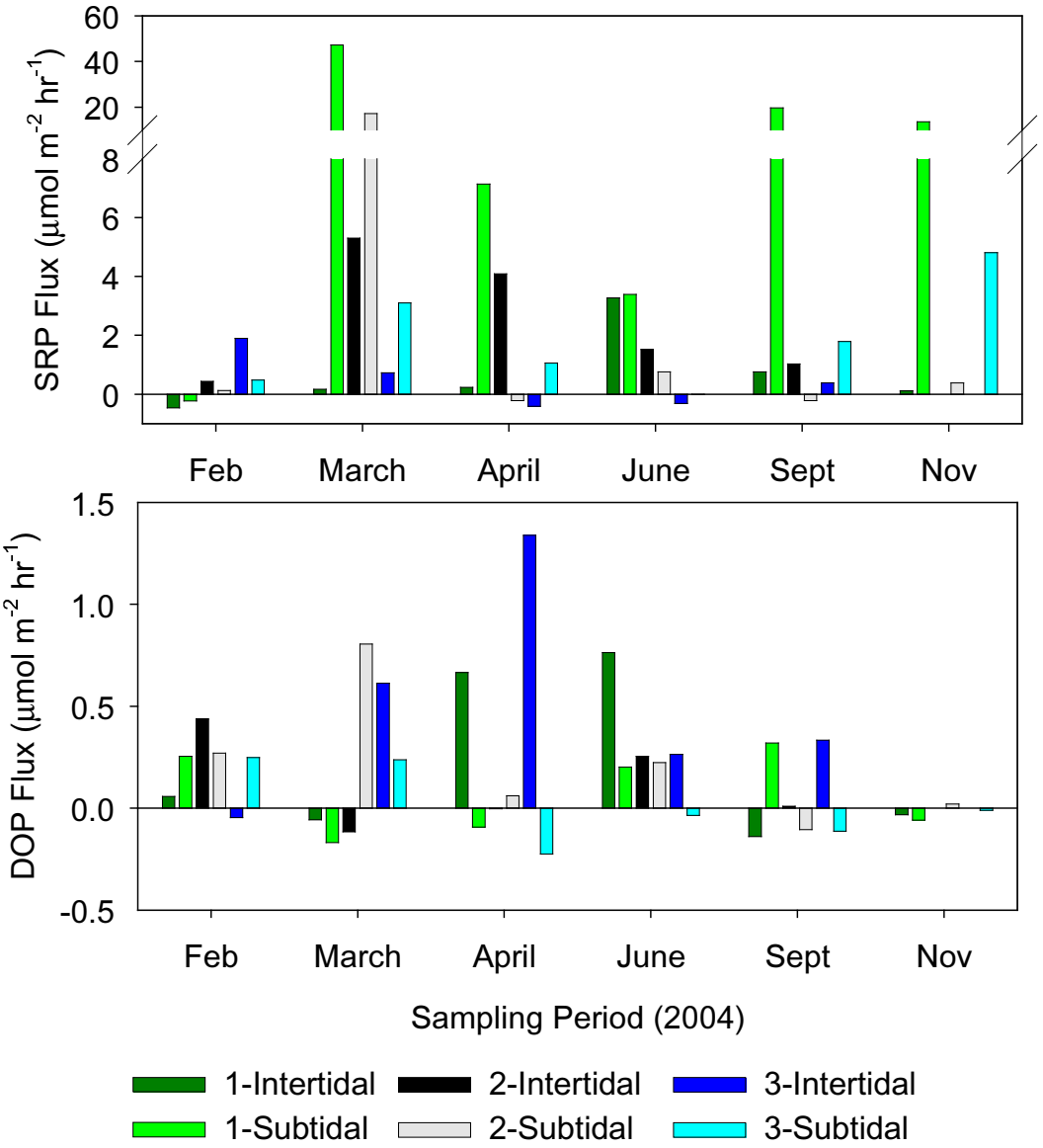


**Figure 2-16. Diffusive flux estimates for SRP and DOP by site and sampling period. Fluxes for intertidal sites in November 2004 sampling period were not estimated because pore waters were not sampled.**

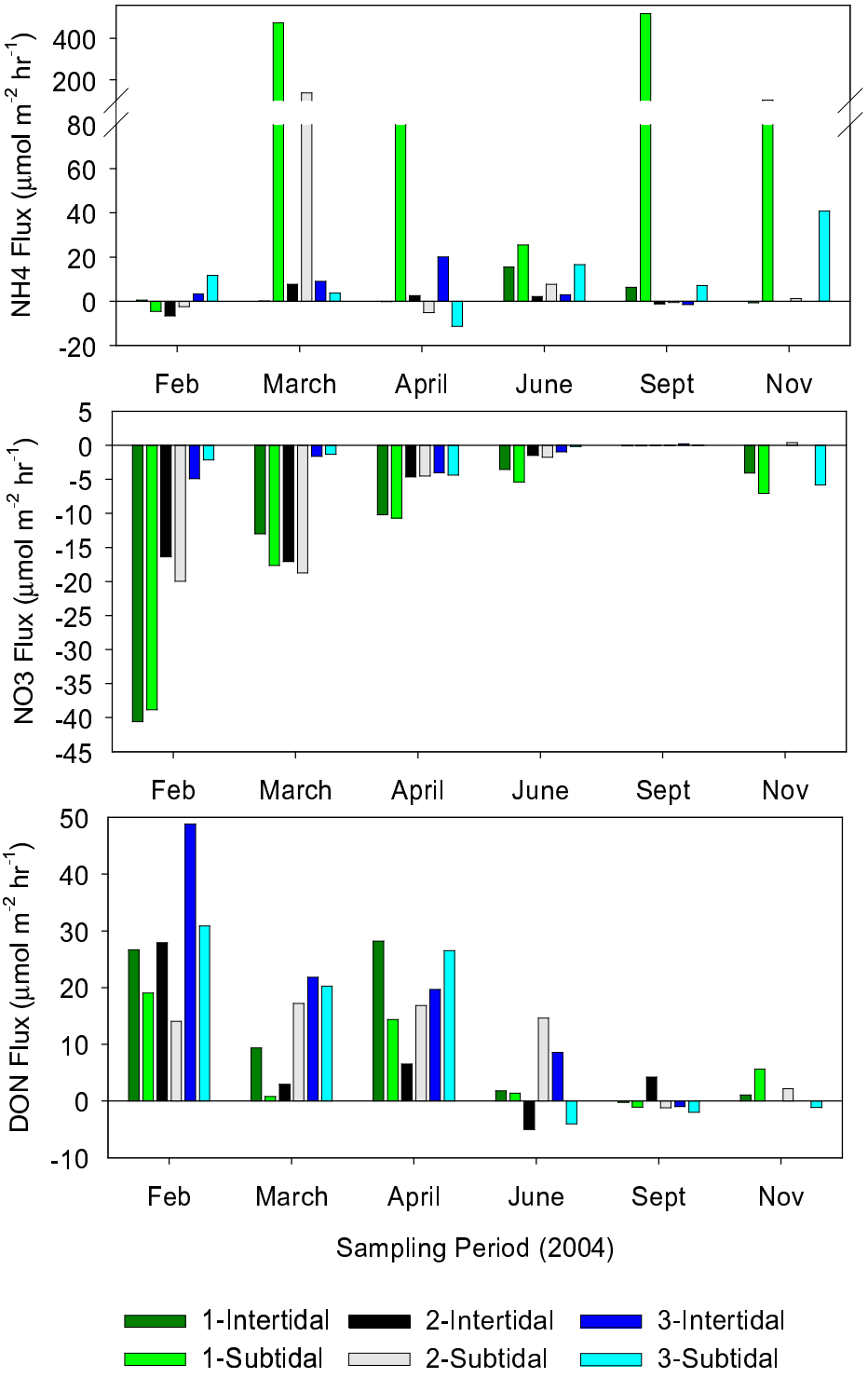


**Figure 2-17. Diffusive flux estimates for $NH_4^+$, $NO_3$, and DON by site and sampling period. Estimates for intertidal sites in November 2004 sampling period were not estimated because pore waters were not sampled.**

## 2.5 Discussion

In this component of the study, the N and P particulate load associated with sediment deposited in UNB during the 2003-2004 wet season were documented. Through processes of sediment diagenesis (organic matter decomposition, oxidation-reduction reactions, etc.), this newly-deposited particulate N and P was mineralized, resulting in pore water nutrient concentrations that were elevated relative to surface water levels. Through processes such as diffusion as well as sediment resuspension and advective flow of water through sediments from tidal currents and bioirrigation, these pore waters were exchanged with the surface waters. Estimates of predicted diffusive flux showed a net release of dissolved inorganic and organic nutrients from the sediments to the surface waters throughout the year. This release provides a source of nutrients for growth of primary producers such as macroalgae in UNB. It can also sustain eutrophic conditions in wetlands even when external loads are curtailed (Fisher and Reddy 2001). These findings are discussed in detail below.

### *2.5.1 Seasonal and Long-term Annual Sediment Deposition in UNB and Associated N and P Particulate Load*

In this study, $^{7}$Be and $^{210}$Pb radioisotopic data provided a means of constraining estimates of sediment deposition in UNB for the 2003-2004 wet season and estimating a long-term annual sedimentation rate for a period of approximately 50 years. Radioisotopes such as $^{7}$Be, $^{210}$Pb, and $^{137}$Cs have been successfully used in combination to study short-term and long-term sedimentation processes such as deposition, resuspension, and accumulation of sediments within shallow water environments (Giffen and Corbett 2000, Sutula et al. 2004). Sutula et al. (2004) used $^{7}$Be to estimate the loading of N and P to Malibu Lagoon from wet season watershed sources. $^{7}$Be-derived sedimentation rates calculated for the 2003-2004 wet season yielded estimates of 11.2 g wet wt sediment cm$^{-2}$ d$^{-1}$: a rate that translates to 27x10$^{3}$ tons dry wt of sediment deposited in the intertidal and subtidal areas of UNB during the wet season. This figure appears reasonable, given that the average sediment load into UNB during 1985 – 1997 was 60x10$^{3}$ tons (ACOE 2000) and that the rainfall for the wet season during which the study took place (11.2 cm) was approximately one-half of the average rate from 1971 – 2000 (24 cm). In addition, sedimentation was not estimated in the vegetated marsh areas, which represents approximately one-third of the surface area of UNB (ACOE 2000).

The temporally and spatially-variable nature of sediment delivery to UNB is also highlighted by comparison of $^{7}$Be-derived annual sedimentation rate (0.91 $\pm$ 2.00 cm yr$^{-1}$) for the November

2003-September 2004 study year, with the long-term annual sedimentation rate calculated using $^{210}$Pb (0.166 ± 0.019 cm $y^{r-1}$). The $^{7}$Be-derived rate (measured over a year) would be expected to be higher than the $^{210}$Pb rate (measured over 50 years) because of the compaction that occurs in sediments over time. Even so, there is a great deal of interannual variability in rainfall and therefore in sediment delivery to UNB (ACOE 2000); consequently, a rate measured over a year would not reflect the long-term average for the site. $^{7}$Be data suggest that intertidal mudflat areas within UNB are accreting faster than the subtidal areas, in part because subtidal areas are more subject to erosion during storm flows or peak tidal velocities.

Calculations of the N and P loading from the nutrient content of this newly-deposited sediment resulted in an estimated 121± 40 $x10^3$ lb TN and 48± 16 $x10^3$ lb TP deposited in UNB over the November 2003 – April 2004 wet season. The SN and SP content of this newly-deposited sediment during April 2004 (0.13 ± 0.03 % dry wet N) indicate that UNB is lower than the most hypereutrophic estuaries cited in the literature. Higher SN have been found in Venice Lagoon, Italy (0.27-0.53%; Marcomini et al. 1995, Sfriso et al. 1995), the Peel-Harvey Inlet, Australia- (0.45% dry wt; McComb et al. 1998), and values found in local estuaries (0.341 ± 0.228 % in Malibu Lagoon; Sutula et al. 2004; 0.3% dry wt TN in Carpinteria Salt Marsh Reserve and Mugu Lagoon; Kennison et al. 2003). Similarly, UNB SP (0.053 ± 0.002 % dry wt P) was lower than average SP in the top 2 cm of Malibu Lagoon (0.081 ± 0.032 %; Sutula et al. 2004), Mugu Lagoon (0.13% dry wt, Kennison et al. 2003), and Venice Lagoon and Peel-Harvey Inlet (0.07% dry wt for each, Marcomini et al. 1995, McComb et al. 1998). For this study, mean SN and SP content was consistent with previous research that measured these constituents in UNB (0.05-0.07 % SP, 0.05 – 0.15 % SN; Boyle et al. 2002). Sediment N and P from Los Penasquitos Lagoon and Tijuana Estuary overlap with UNB sediment SN and SP values (Kennison et al. 2003).

N and P content for estuarine sediment is known to vary as a function of nutrient loading from the watersheds and distance from the source (Boyle et al. 2002, Kennison et al. 2003). A slight, but significant, enrichment in SN content was observed from January – April 2004 (0.02%) without significant increase in SP content. However, since it was not practicable to obtain a pre-wet-season baseline, it is likely that pre-wet-season sediment N and P concentrations were different than those first measured in January 2004, and that enrichment of SN and SP occurred prior to January 2004. It is also possible that nutrient loads to UNB had been reduced to a point where minimal sediment nutrient enrichment occurs (Orange County TMDL Monitoring Report,

2002), or that nutrient loading to UNB via surface water and sediments was lower than average because of reduced rainfall during the particular hydrologic year sampled (Sutula et al. 2003).

Spatial trends observed in SN and SP content for UNB along the longitudinal axis of the estuary were influenced by distance from San Diego Creek, primary nutrient sources and hydrodynamic controls on sediment particle size sorting. Both SN and SP concentration decreased downstream from mean values of 0.12 % dry wt N and 0.054 % dry wt P at Site 1 to 0.08 % dry wt N and 0.048% dry wt P at Site 3. This trend was documented in a previous study of UNB (Kennison et al. 2003). Confounding similar trends with nutrient loading, grain size is known to exert a strong control on nutrient content; clays and silts tend to have higher matter content and thus a higher organic N and P content (Sutula et al. 2003). In addition, clays and silts typically have a surficial armoring of reactive iron and aluminum hydroxyoxides and thus a higher capacity for adsorbing P (Carritt and Goodgal 1954, Froelich 1988, Mclaughlin et al. 1981). C:P and C:N ratios, which help to control for grain size effects (Sutula et al. 2003), also generally decreased downstream, indicating that nutrient loading from San Diego Creek influenced sediment nutrient content in UNB.

### *2.5.2 Particulate N and P in Lagoon Sediments are Mineralized and Provide a Source of Nutrients to Surface Waters*

In this study, "mineralization[1]" refers to the process by which N and P bound up in organic matter are broken down and released in dissolved, more biologically available forms (Schlesinger 1997). After deposition, the sediments of estuaries and coastal lagoons undergo a series of transformations that control the mineralization and release of N and P to surface waters. Organic matter decomposes, proceeding through a well-established sequence of terminal electron acceptors: $O_2$, $NO_3^-$, $MnO_2$, FeOOH, $SO_4^{2-}$, and $CO_2$ (Froelich and Klinhammer 1979). During this process, the decomposition of organic matter results in the build-up of $NH_4^+$, DON, SRP, and DOP in pore waters. SRP can also be desorbed and released from iron precipitates (Fe(II)-hydroxide-$PO_4$ complexes and/or Fe(II)-$PO_4$ minerals) commonly found in clay and silt sediments in anoxic conditions as the Fe(III) is reduced to (Fe(II) (Roden and Edmonds 1997). Peaks in UNB sediment pore water SRP, DOP, $NH_4^+$ and DON concentrations during the wet season, followed by decreases to the lowest concentrations during the late dry season, indicate the occurrence of these transformations. The build-up of

[1] The use of the *mineralizatio*n differs from the usage in the literature of geology, in which *mineralization* refers to various processes that result in the deposition of metal oxides.

$NH_4^+$, DON, SRP, and DOP in UNB sediment pore waters relative to surface waters is responsible for the predicted net release of these constituents to the surface waters throughout the year, as predicted by Ficke's law of diffusive transport (Berner 1980). The majority of TDN and TDP flux is comprised of $NH_4^+$ and SRP, the most biologically reactive forms of nutrients.

Overall, pore water $NO_3^-$ decreased with depth to non-detectable levels; a trend that can be explained by the conversion of $NO_3^-$ to nitrogen gas through microbially-mediated denitrification (Seitzinger 1988). Thus, predicted diffusive fluxes during the wet season were negative when surface water $NO_3^-$ concentrations were highest, indicating an influx into the sediment. This influx of $NO_3^-$ into surficial sediments would explain why pore water $NO_3^-$ concentrations in the first 6 cm were generally higher than concentrations at greater depths. During the dry season, when $NO_3^-$ concentrations in surface waters were low, pore water $NO_3^-$ was very low, probably due to the combined of effect of denitrification and the lack of a significant source of surface water $NO_3^-$, that could diffuse into the sediments. Thus, predicted flux of $NO_3^-$ during the dry season, while still negative, was of very small magnitude relative to wet season rates.

The remobilization and net release of TDN and TDP from pore waters to surface waters would predict a gradual decline in SN and SP content in newly-deposited sediments from the wet season to the dry season. SN follows this predicted trend, decreasing 25% from the late wet season (0.12 % dry wt N) to the late dry season (0.08 % dry wt N). C:N ratios rose over this time period, indicating that sediments become progressively less-enriched with N over the dry season. Conversely, in spite of the positive flux of TDP from sediments, SP increases peaked in the late dry season. No ancillary data are available to explain this trend. As is the case in many tidally dominated estuaries, radioisotope tracer data also showed that the processes of sediment deposition and resuspension are highly dynamic (Woodruff et al. 2001). In UNB, $^7$Be data indicate that depositional and erosional events are occurring in both the wet and dry seasons, making the interpretation of the fate of newly-deposited particulate N and P over time difficult to track. Sediment that was deposited during the interval between sampling periods may have been partially or completely removed by hydrodynamic processes (Corbett and Reid 2003), or reworked by benthic infauna or birds. It is therefore uncertain whether this trend in increased SP is due to biological processing of P in the estuary during the dry season, or P transported from another source.

Spatial trends observed for SN and SP concentrations generally held for pore water nutrient profiles, as well as for predicted diffusive fluxes. Site 1, with the highest sediment concentrations, generally had higher pore water $NH_4^+$ and SRP concentrations than Sites 2 and 3. The exception to this was Site 2, which had higher bulk sediment nutrient concentrations than Site 3, but had consistently lower pore water $NH_4^+$, SRP, DON, and DOP concentrations. Several factors could be responsible for this deviation. Site 2 was located along a straight channel, as opposed to being located along a curved shoreline or point bar, as was the case with Sites 1 and 3. Tidal currents could be stronger at Site 2, causing advective mixing and dilution of pore waters with surface waters. Another possible explanation is differences in the types and abundances of benthic infauna inhabiting Sites 1-3. Benthic fauna, such as bivalves, tube worms, and crabs, permeate the sediment with burrows and actively force the exchange of sediment pore waters with overlying surface water (Boudreau and Marinelli 1994). Qualitatively, Site 1 sediments appeared to be dominated by polychaete and oligochaete worms, with few tubes visible on surficial sediments. Site 3 sediments supported tube worms (*Asychis sp*), while Site 2 supported a high density of both tube worms and bivalves. It is possible that the high density of burrow forming benthic infauna observed at Site 2 caused a greater exchange with surface waters, thus diluting pore water nutrient concentrations. Because the fluxes estimated in this component of the study do not account for possible advective transport through tidal currents or bioirrigation, the predicted diffusive fluxes do not reflect this potentially for greater flux that could be occurring at Site 2.

$SO_4^{-2}$ reduction is often a dominant process in eutrophic systems, occurring only after the aerobic bacteria have removed dissolved $O_2$, and other bacteria responsible for denitrification, Mn, and Fe reduction have consumed the available electron receptors (i.e. $NO_3^-$, Mn(II) and Fe(II)) from the sediment (Skyring 1987). The consequences of $SO_4^{-2}$ reduction for nutrient cycling, particularly for P cycling, are important. Roden and Edmonds (1997) found that direct microbial Fe(III) reduction solubilized only 3-25% of initial sediment-bound P during sulfate-free sediment incubation experiments, and that much of the phosphate ($PO_4^{-3)}$ released was re-captured and loosely bound by solid-phase reduced iron compounds (Fe(II)-hydroxide- $PO_4$ complexes and/or Fe(II)- $PO_4$ minerals). During $SO_4^{-2}$ reduction, Fe(II) is converted to iron-sulfides via reaction with $S^{-2}$ produced by $SO_4^{-2}$ reduction (Roden and Edmonds 1997). Because iron-sulfides cannot bind SRP, approximately 2-5 times the amount of P is released to pore waters and overlying surface waters. $NH_4^+$ is also released from organic matter during degradation from $SO_4^{-2}$ reduction. $S^{-2}$ was found in UNB sediment pore waters, indicating that

$SO_4^{-2}$ reduction was taking place. Spatially, the highest concentrations were found at Site 1 throughout most sampling periods, indicating that this is the most eutrophic of the sites. $S^{-2}$ concentrations were highest during the wet season sampling periods, with peak concentrations of up to 0.4 M $S^{-2}$ found at subtidal Site 1 and 0.2 M $S^{-2}$ found at intertidal Site 3 observed during March 2005. These peak concentrations of $S^{-2}$ in sediments were coincident with peak concentration of SRP and $NH_4^+$, particularly at Site 1. Thus, when $SO_4^{-2}$ reduction occurred in UNB sediments, the potential for remobilization of nutrients to pore waters and the overlying water column was higher. The particularly high concentrations of SRP, $NH_4^+$, and $S^{-2}$in sediments at Site 1 at Site 3 during wet season sampling periods were likely indicative of degradation of fresh organic matter recently deposited at these locations. Predicted positive diffusive fluxes of SRP and $NH_4^+$ from the Site 1 subtidal sediments were reflective of these extremely high pore water concentrations.

Confidence is low that the diffusive flux rates are predictive of actual *in situ* flux rates. Many studies have found that advective transport of water through the sediments, which includes processes such as groundwater seepage, tidal pumping and bioturbation, are dominant factors relative to diffusive transport in controlling benthic flux (Watson and Frickers 1995, Giffen and Corbett 2003). Comparative studies of fluxes predicted by diffusion versus those measured *in situ* with benthic chambers indicate that diffusive fluxes typically underestimate flux by several orders of magnitude (Sinke et al. 1990, Devol 1987, Hopkinson 1987, Callender and Hammond, 1982). Chapter 5 of this report compares the predicted diffusive fluxes with the *in situ* flux measurements detailed in Chapter 4.

### *2.5.3 Relationship of Algal Biomass and Nutrient Content with Sediment Nutrient Content and Predicted Fluxes*

The association between increased anthropogenic nutrient loads and nuisance blooms of macroalgae has been documented in many locations (Kamer et al. 2001, Valiela et al. 1992). Seasonal blooms of macroalgae are common in coastal estuaries subject to pulses of high nutrients. While macroalgae are a natural component of southern California estuaries, excessive biomass can have negative ecosystem wide-effects, including low water column dissolved $O_2$, shifts in benthic infaunal communities and excessive organic matter input into the sediment. These primary impacts can lead to acute and chronic impacts on estuarine fish, invertebrate, and bird communities (Raffaelli et al. 1989). During this 2004 study of UNB, maximum combined macroalgal biomass of *E. intenstinalis*, *U. expansa*, and *Ceramium spp*.

was high during one sampling period (240 g dry wt $m^{-2}$ in February 2004) in comparison with previous reports of greater than 150 g dry wt $m^{-2}$ documented in 1997 by Kamer et al. (2001). With the exception of the February 2004 sampling period, when the maximum biomass was recorded, total macroalgal biomass was generally less than 100 g dry wt $m^{-2}$ and in two sampling periods no algal biomass was visible. Peak algal biomass in February at Site 3 coincided with the lowest predicted positive fluxes of $NH_4^+$ and SRP and the highest predicted fluxes of DON. Water column $NO_3$ and SRP-$NO_3$ concentrations were at measured at their peak at Site 3 during February, suggesting that the macroalgal bloom observed during this period at this site was responding to wet season nutrient loading from the watershed.

In estuarine systems, macroalgal tissue is known to reflect the ambient N and P conditions that the alga recently experienced (Bjornsater and Wheeler 1990). Macroalgal tissue nutrients (2.3 – 3.4 % dry wt N and 0.23 – 0.28 % dry wt P) were comparable to previous values for UNB (2-4% dry wt N and 0.11-0.30% dry wt P; Kamer et al. 2001). This study found a significant correlation of *E. intestinalis* tissue nutrients with SN and SP and a correlation between *U. expansa* tissue N with SN. Other studies have found similar links between tissue and sediment nutrient content. Birch et al. (1981) found that Cladophora tissue N and P were positively correlated to sediment N and P. Kamer et al. (2004) showed that *E. intestinalis* was positively correlated to sediment P in laboratory experiments.

## 2.6 References

ACOE 2000. Upper Newport Bay Ecosystem Feasibility Restoration Study Final Report. U.S. Army Corps of Engineers, Los Angeles District. September 2000.

APHA. 1992. Standard methods for the examination of water and wastewater. 18th Edition. American Public Health Association.

Appleby, P. G., and F. Oldfield. 1992. Application of lead-210 to sedimentation studies. In M. Ivanovich and R. Harmon [eds.], Uranium-Series Disequilibrium: Applications to Earth, Marine and Environmental Sciences. Claredon Press.

Banse, K., C. P. Falls, et al. (1963). A gravimetric method for determining suspended matter in sea water using Millipore filters. Deep-sea Research 10: 639-642.

Berner, R.A., 1980. Early Diagenesis: A Theoretical Approach: Princeton, NJ (Princeton Univ. Press).

Birch, P. B., D. M. Gordon, and A. J. McComb. 1981. Nitrogen and phosphorus nutrition of Cladophora in the Peel-Harvey estuarine system, western Australia. Botanica Marina 24: 381-387.

Bjornsater B.R. and P.A. Wheeler. 1990. Effect of nitrogen and phosphorus supply on growth and tissue composition of Ulva Fenestrata and Enteromorpha Intestinalis. Journal of Phycology. 26 (4): 603-611

Boudreau, B.P. (1997) Diagenetic Models and their Implementation. Springer-Verlag.

Boudreau, B.P. and R.L. Marinelli. 1994. A modelling study of discontinuous biological irrigation. Journal of Marine Research 52: 947-968.

Boyle, K. A., K. Kamer, and P. Fong. 2004. Spatial and temporal patterns in sediment and water column nutrients in a eutrophic southern California estuary. Estuaries 27(3): 378-388.

Brandl and Hanselmann1991).

Burnett, W. C., J. Chanton, J. Christoff, E. Kontar, S. Krupa, M. Lambert, W. Moore, D. O'Rourke, R. Paulsen, C. Smith, L. Smith and M. Taniguchi (2002). "Assessing methodologies for measuring groundwater discharge to the ocean." EOS 83: 117-123.

Callender, E. and D. Hammond (1982) Nutrient exchange across the sediment-water interface in the Potamac River Estuary. Esturarine, Coastal and Shelf Science, 15, 395-413.

Canuel, E.A., C.S. Martens, and L.K. Benninger. 1990. Seasonal variations in 7Be activity in the sediment of Cape Lookout Bight, North Carolina. Geochimica et Cosmochimica Acta 54: 237-245.

Carritt, D. E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep Sea Research 1: 224-243.

DeMaster, D. J., B. A. McKee, C. Nittrouer, Q. Jiangchu, and C. Guodang. 1985. Rates of sediment accumulation and particle reworking based on radiochemical measurement from continental shelf deposits in the East China Sea. Continental Shelf Research 4: 143-158.
Devol, A.H. 1987. Verification of flux measurements made with in situ benthic chambers. Deep Sea Res. 34:1007–1026.

Fisher M.M. and K.R. Reddy. 2001 Phosphorus Flux from Wetland Soils Affected by Long-Term Nutrient Loading. Journal of Environmental Quality 30:261-271

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta, 43:1075-1090.

Froelich, P. N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. Limnology and Oceanography 33: 649-668.

Giffin, D. and Corbett, D.R., 2003, Evaluation of sediment dynamics in coastal systems via short-lived radioisotopes, Journal of Marine Systems 42: 83-96.

Hesslein, R.H. 1976. An in situ sampler for close interval porewater studies. Limnology and Oceanography 21:912–914.

Hopkinson, C.S. 1987. Nutrient regeneration in shallow water sediments of the estuarine plume region of the nearshore Georgia Bight, USA. Marine Biol. 94:127–142.

Huettel, M., W. Ziebis and S. Forster, 1996, Flow-induced uptake of particulate matter in permeable sediments, Limnology and Oceanography 41(2): 309-322.

Kamer, K., K. A. Boyle, and P. Fong. 2001. Macroalgal bloom dynamics in a highly eutrophic southern California estuary. Estuaries 24(4): 623-635.

Kamer, K., P. Fong, R. L. Kennison, and K. Schiff. 2004. The relative importance of sediment and water column supplies of nutrients to the growth and tissue nutrient content of the green macroalga Enteromorpha intestinalis along and estuarine resource gradient. Aquatic Ecology 38: 45-56.

Kennison, R. L., K. Kamer, and P. Fong. 2003. Nutrient dynamics and macroalgal blooms: a comparison of five southern California estuaries. # 416. Southern California Coastal Water Research Project. Westminster, CA. 79 pp.

Koike, I. and Mukai, H., 1983, Oxygen and inorganic nitrogen contents and fluxes in burrows of the shrimps Callianassa japonica and Upogebia major, Marine Ecology Progress Series 12: 185-190

Marcomini, A., A. Sfriso, B. Pavoni, and A. A. Orio. 1995. Eutrophication of the Lagoon of Venice: nutrient loads and exchanges, p. 59-79. In A. J. McComb [ed.], Eutrophic shallow estuaries and lagoons. CRC Press.

Martin, J., Cable, J., Swarzenski, P., and Lindenberg, M., 2004, Enhanced submarine groundwater discharge from mixing of pore water and estuarine water, Ground Water (special Oceans issue) 42: 1001-1010.

McComb, A. J., S. Qiu, R. J. Lukatelich, and T. F. McAuliffe. 1998. Spatial and temporal heterogeneity of sediment phosphorus in the Peel-Harvey estuarine system. Estuarine Coastal and Shelf Science 47: 561-577.

McKee, B. A., C. A. Nittrouer, and D. J. DeMaster. 1983. The concepts of sediment deposition and accumulation applied to the continental shelf near the mouth of the Yangtze River. Geology 11: 631-633.

McLaughlin, J. R., J. C. Ryden, and J. K. Syers. 1981. Sorption of inorganic phosphate by iron-containing and aluminum-containing components. Journal of Soil Science 32: 365-377.

Meyer, G. A. and P. N. Keliher. 1992. An overview of analysis by inductively coupled plasma-atomic emission spectrometry. p. 473-505. In: A. Montaser and D.W. Golightly (ed.) Inductively coupled plasmas in analytical atomic spectrometry. VCH Publishers Inc. New York, NY.

Milner, H. B. 1962. Sedimentary Petrography. New York, MacMillan Company.

Nedwell, D. B., A. S. Sage, and G. J. C. Underwood. 2002. Rapid assessment of macroalgal cover on intertidal sediments in a nutrified estuary. Science of the Total Environment 285: 97-105.

Nittrouer, C. A., R. W. Sternberg, R. Carpenter, and J. T. Bennett. 1979. The use of Pb210 geochronology as a sedimentological tool: Application to the Washington coastal shelf. Marine Geology 31: 297-316.

Orange County 2002. Report of the Regional Monitoring Program for the Newport Bay/San Diego Creek Watershed Nutrient TMDL (Resolution 98-9, as Amended by 98-100). November 2002.

Raffaelli D, S. Hulls, and H. Milne. 1989. Long-term changes in nutrients, weed-mats, and shorebirds in an estuarine system. Cahiers de Biologie Marine 30 (2): 259-270 1989

Rizzo, W. M., and R. R. Christian. 1996. Significance of subtidal sediments to heterotrophically-mediated oxygen and nutrient dynamics in a temperate estuary. Estuaries 19(2B): 475-487.

Roden, E. E. and J. W. Edmonds 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction versus iron-sulfide formation. Archives fur Hydrobiologie 139(3): 347-378.

Sah, R. N. and R. O. Miller. 1992. Spontaneous reaction for acid dissolution of biological tissues in closed vessels. Analytical Chemistry. 64:230-233.

Schelsinger, W. 1997. Biogeochemistry: An Analysis of Global Change. 2nd Edition. Academic Press, San Diego California.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnology and Oceanography 33(4, part 2): 702-724.

Sfriso, A., B. Pavoni, and A. Marcomini. 1995. Nutrient distributions in the surface sediment of the central lagoon of Venice. Science of the Total Environment 172: 21-35.
Sinke et al., 1990

Skyring, GW, 1987, Sulfate reduction in coastal ecosystems: Geomicrobiology Journal, 5, 295–374

Solorzano, l. and J. H. Sharp 1980 "Determination of total dissolved phosphorus and particulate phosphorus in natural waters." Limnology and Oceanography 25: 745-758.

Sutula M, T.S. Bianchi, B.A. McKee. Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico. Limnology and Oceanography 49 (6): 2223-2235

Sutula, Martha, K.Kamer and J.Cable. 2004. Sediments as a non-point source of nutrients to Malibu Lagoon, California (USA). Southern California Coastal Water Research Project, Westminster, CA. Technical Report #441.

Valiela, I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-Andreson, C. D'Avanzo, M. Babione, C. H. Sham, J. Brawley, and K. Lajtha. 1992. Couplings of watersheds and coastal waters sources and consequences of nutrient enrichment in Waquoit Bay Massachusetts. Estuaries 15(4): 443-457.

Watson PG and Frickers T. 1995 Sediment-water exchange of nutrients in the southern North Sea adjacent to the Humber estuary. Ophelia 41: 361-384 1995

Woodruff JD, Geyer WR, Sommerfield CK, and N.W. Driscoll 2001. Seasonal variation of sediment deposition in the Hudson River estuary. Marine Geology 179 (1-2): 105-119

# 3 SEDIMENT NUTRIENT FLUX IN UNB: IN SITU ESTIMATES AND INVESTIGATION OF FACTORS CONTROLLING EXCHANGE

William Berelson, Martha Sutula, Jeff Mendez, and Jaye Cable

## 3.1 Abstract

In this component of the study, benthic chambers and additional methods were utilized to: 1) measure *in situ* fluxes of nutrients during two seasons, and 2) explore factors controlling exchange of nutrients between sediments and surface waters. Benthic chamber data were used to assess flux values of dissolved inorganic and organic nutrients, TCO2 (a measure of total respiration), silic acid (silicate; ($Si(OH)_4$)), $O_2$, and trace metals across the sediment-water interface. A conservative tracer, Br was used in chamber studies to measure total rate of pore water exchange with the overlying water column. This technique was complemented by the use of a multisampler pieziometer to assess pore water advection and exchange at depths up to 80 cm in sediments. These techniques aided in determining the importance of diffusive versus advective transport in controlling the magnitude of benthic nutrient fluxes.

Based on flux data, UNB is a eutrophic estuary. Fluxes of TC02 (107 ± 81 mmol $m^{-2}$ $d^{-1}$), $O_2$ (-43 ± 20 mmol $m^{-2}$ $d^{-1}$), nutrients (5.7 ± 2.7 mmol $NH_4^+$ and 0.36 ± 0.52 mmol SRP $m^{-2}$ $d^{-1}$) and metals were among the highest values reported for *in situ* benthic flux measurements and comparable to the most anthropogenically-impacted estuaries. $SO_4^{-2}$ reduction, common in eutrophic estuaries, was a dominant process occurring in sediments, particularly for the site at the mouth of the San Diego Creek. The high rate of TCO2, as well as nutrient efflux and sediment $O_2$ demand in UNB indicate that a high rate of sediment and organic matter loading from the watershed is occurring and that this organic matter is also degraded very quickly in this system. The efficiency of organic matter degradation in this system can be attributed to several factors, including: 1) abundant supply of terminal electron acceptors (e.g. $NO_3$, Fe (III), Mn(IV), and $SO_4^{-2}$) that fuel oxidation-reduction reactions (e.g. denitrification and $SO_4^{-2}$ reduction) and the degradation of organic matter in sediments; and 2) significant reworking of sediments by physical or hydrodynamic mixing, including bioturbation and bioirrigation. All of these factors were shown to be significant in UNB during this study component and that of Chapter 2. The combination of these factors causes reincorporation of fresh organic matter and terminal electron acceptors into the sediments, where repetitive oxidation/ reduction reactions result in the efficient decomposition of organic carbon.

This study found that one of the major factors controlling benthic flux of nutrients in UNB is advective transport—most likely to be caused by bioirrigation from benthic infauna. Br in benthic chambers was diluted by 40% or more, indicating very high rates of exchange with pore waters. If diffusion alone were responsible for exchange, this rate of loss would have been <10%. Br loss rates were also comparable among the April and October 2005 field season, suggesting that the advective processes controlling exchange are fairly constant; trends in Br loss among sites suggest that advective transport may be greater in areas below the salt dike than around the mouth of San Diego Creek. Two additional lines of evidence corroborate the importance of advective transport in UNB. First, pore water advection estimated with multisamplers at the site near Shellmaker Island showed a high rate of advection exchange, with rates ranging from 8 - 65 cm $d^{-1}$. Second, Worsnopp et al. (2004) used radioisotopes to determine rates and major processes responsible for advective transport in UNB synoptically using the chamber work in this study. Although their work is preliminary and not presented in this report, their work suggests that advective transport enhances solute fluxes by a factor of 3-5 times that of diffusion. The major process responsible for this advective transport is not definitive, although evidence points to certain dominant mechanisms such as bioirrigation and/or tidal pumping, rather than groundwater input.

SRP, Fe, and Mn fluxes were higher at the site closest to the mouth of San Diego Creek versus lower sites in the estuary. These findings are consistent with the concept of San Diego Creek as the source of particulate trace metals and P loading into UNB. Low $O_2$ in bottom waters at this site enhance $SO_4^{-2}$ reduction and SRP fluxes from sediments. In contrast, site differences in $O_2$ uptake, as well as TCO2 and $NH_4^+$ fluxes were unexpected based on spatial gradients in particulate matter deposition, bulk sediment characteristics, and pore water nutrient concentrations, which were highest at the site nearest the creek mouth. This may have been due to higher density of benthic infauna (tube worms and bivalves) at sites below the salt dike versus the site near the creek mouth. Increased bioirrigation at these sites would result in larger fluxes of bioavailable nutrients.

## 3.2 Introduction

Benthic exchange, or the flux between solutes in the overlying water column and solutes in sediment pore waters, may be studied using a variety of approaches. Typically, pore water concentration gradients are determined and models describing transport of these solutes are applied to estimate fluxes (Berner 1980). This approach suffers due to uncertainties in

formulating an accurate transport model (diffusion and advection must be considered and are likely to vary spatially and temporally as well as with respect to the ability of standard pore water extraction techniques to accurately determine solute gradients near the sediment-water interface. Pore water extraction using conventional core processing methods (sectioning and centrifugation) or via the use of pore water peepers (as in this study) requires that either cores be removed from the natural environment, or that the sediment be disturbed when inserting the peeper. This can introduce potential artifact and further uncertainties in data interpretation.

Benthic flux chambers have been used in a wide variety of environments to assess rates of solute exchange (e.g. rivers (Callender and Hammond, 1982), estuaries and embayments (Hammond et al. 1985, McNichol et al. 1988, Berelson et al. 1998), and open ocean environments (Jahnke et al. 2000, Berelson et al. 2002)). A benthic flux chamber approach to making flux determinations has certain advantages over pore water profiling: a) a direct determination is available from assessing the change in chamber concentration versus time, b) chambers integrate the net reactions occurring within the sediments enclosed by the chamber, and c) a wide variety of flux determinations are possible. However, chambers also introduce potential artifact when the natural hydrodynamics of the sea-bed are perturbed. Further, although chambers allow for estimates of net flux, these measurements do not indicate the location within the sediment column where solutes may be produced or consumed. A major advantage of *in situ* chamber flux determinations over other methods is that a solutetransport model is not required and any process that moves solutes across the sediment-water interface will be detected by concentration changes measured in a chamber. Also, *in situ* chambers also allow for certain ambient conditions, such as ambient temperatures, light conditions and sediment biological communities, to remain relatively undisturbed during flux experiments.

In this study, benthic chambers were utilized to: 1) measure *in situ* benthic fluxes of nutrients during two seasons, and 2) explore factors controlling exchange of nutrients between sediments and surface waters. As discussed below, the benthic chamber data were used to assess flux values of dissolved inorganic and organic nutrients, $TCO_2$, $Si(OH)_4$ , $O_2$, and trace metals across the sediment-water interface. $TCO_2$, which is the sum of dissolved $CO_2$, bicarbonate, and carbonate ions, is a measure of all processes that respire $CO_2$ in the water column and sediments. Further, a conservative tracer spike (Br) injected into the chamber was used to measure the total rate of pore water exchange with the overlying water column. In addition, a multisampler pieziometer was used to assess pore water advection and exchange at depths up

to 80 cm. Both benthic chambers and multisamplers pieziometers were used to determine the importance of diffusive versus advective transport in controlling benthic nutrient fluxes.

## 3.3 Methods

### *3.3.1 Study Approach and Field Methods*

The study approach involved several components designed to estimate *in situ* sediment fluxes of several nutrients and trace metals while investigating the relative importance of factors that control the magnitude and direction of benthic exchange. Benthic flux chambers were used to measure rates of nutrients, trace metals (uranium (U), Fe and Mn), TCO2, and $O_2$ flux over time periods ranging from 4-8 hours. Measurements of $O_2$, TCO2, and trace-metal fluxes were used to help interpret patterns observed in nutrient flux. The Br flux was modeled to assess the degree of bio-irrigation, a component of advective transport, occurring at each site. Water column sampling was conducted along the salinity gradient in the Bay in order to determine the presence of zones of production or consumption of nutrients in surface waters of UNB. Specific methodologies employed for each of these sampling components are described in detail in subsequent sections below.

Sediment flux of nutrients is controlled by a host of physical, chemical, and biological factors that are known to vary substantially throughout the year. However, because of the intensive effort involved in obtaining *in situ* flux estimates with benthic chambers, it was only possible to conduct this sampling twice. Two index periods were chosen as optimal to constrain the magnitude of nutrient fluxes in UNB: 1) mid-wet season, which represented a period of greatest freshwater influence, maximal physical disturbance to sediments from storm flows, and the input of new organic matter and nutrients from the watershed; and 2) mid-dry season, which characterized a period of low freshwater input and physical disturbance and high biological productivity. However, because of delays in contracting and logistical constraints due to endangered species breeding season in UNB, sampling occurred during early dry season (April 2004) and early wet season (November 2004). Table 3-1 shows the conditions that occurred during these sampling periods.

**Table 3-1. Summary of environmental conditions during benthic flux sampling periods.**

| Sampling Period | Days From Last Rainfall | Surface Water Temperature Range | Range of Ambient DO During Chamber Deployment |
|---|---|---|---|
| April 20-22, 2004 | 9 | 15-20°C | 10-80% |
| October 29-30, 2004 | 1 | 13-18°C | 75-100% |

*Benthic Flux Chambers*

Two identical benthic chambers designed and built as described by Berelson and Hammond (1986) were used for this study (Figure 3-1a). The chamber is made of polyvinyl carbonate (PVC); it is cylindrical with a 30 cm diameter and has a clear acrylic lid (Figure 3-1b). This chamber is mounted in an approximately 5'x2'x2' aluminum frame, weighing approximately 25 lbs in water. When properly implanted in the sediment, the chamber captures a volume of approximately 7 liters.

The chamber is 'plumbed' with teflon and tygon tubing leading to nylon sample tubes (15 and 30 ml) and then to sample draw mechanisms (Figure 3-1c). There are 6 sample draw mechanisms: 3 are spring-loaded syringes which draw 100 ml and 3 are flexible bulbs, coupled to springed hinges, which draw 200 ml. When a draw is activated, de-ionized water fills the tubing and sample tubes, draws into the syringe or bulb, and chamber water flushes the sample tube until the draw is complete. Typically, the flushing of the sample tube with chamber water is effective in providing a sample that is >99% pure chamber water.

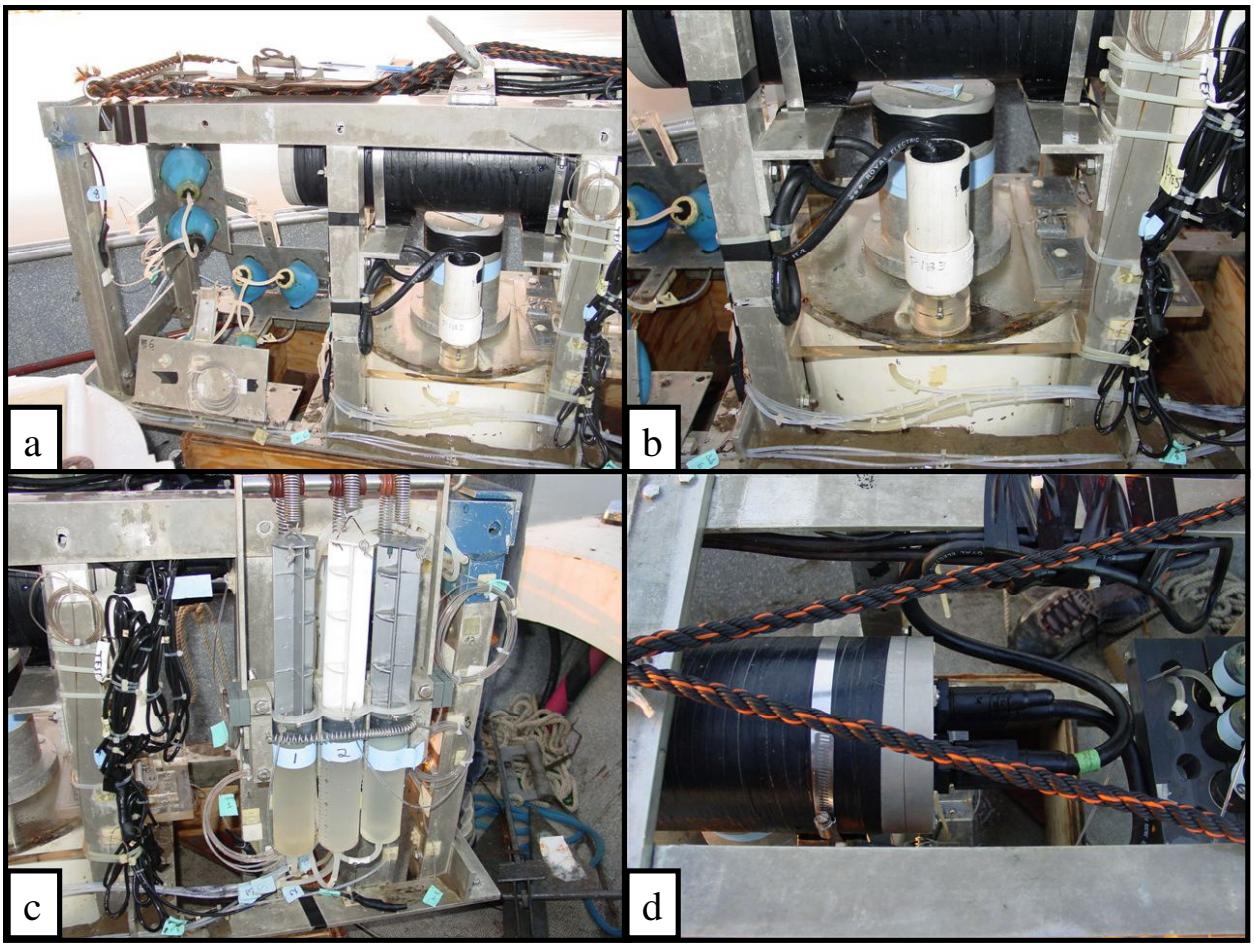


**Figure 3-1. Photos of the benthic chamber apparatus mounted on an aluminum frame (a). The chamber body is constructed of polycarbonate with a clear acrylic lid; $O_2$ and temperature are measured directly within the chamber (b). Samples are drawn from chamber via spring-loaded syringes and flexible bulbs that are coupled to springed hinges (c). A data logger, contained within a pressure case (d), records all ambient data as well as all chamber mechanical operations.**

Each chambers was continuously stirred with a rotating paddle to impede the development of a benthic boundary layer that would alter the benthic-flux rate. The effect of rotation rate on benthic boundary layer thickness has been studied (Berelson et al. 1990). Paddles were set to rotate at a rate of 5-7 revolutions per minute, affecting a benthic boundary layer of 200-300 µm.Each chamber is equipped with a pulsed-oxygen electrode that monitors $O_2$ tension within the chamber every 6 minutes (Figure 3-1b). A second electrode was mounted outside the chamber to monitor $O_2$ in the ambient water for the duration of the deployment. Each pulsed-oxygen electrode used on the chambers had been calibrated in the laboratory prior to fieldwork. The pulsed-oxygen electrodes were also coupled to a thermistor temperature recorder. All electrode data were transmitted to a data-logger contained within a pressure case mounted on the chamber frame (Figure 3-1d). The data-logger also controlled all mechanical operations in

the chamber by allowing current to flow to specific 'burn-wires' at pre-programmed times. Mechanisms controlled by the chamber computer include: 1) springed hinges force the closure of an acrylic lid to seal against a silicone gasket, 2) syringe springs activate injection of a Br spike solution, 3) springed syringes tigger draws 1-3, 4) springed hinges open bulbs for draws 4-6, and 5) tubing pinch-off device seals all samples to prevent accidental contamination during chamber recovery. The chamber pressure case was sealed with a microprocessor and batteries providing enough power for 6 deployments. This microprocessor can be programmed by computer connection without opening up the case. The timing of each chamber operation was fed into the computer and the device was set for deployment.

Benthic-chamber samples were collected into nylon syringe tubes specially constructed for this purpose. Each tube was labeled with respect to sample a draw number which corresponded to the time elapsed between chamber lid closure and sample draw. Using an electrode, water from these sample tubes was split, with an unfiltered portion dedicated to pH measurement, according to analytical needs. Other portions were filtered through 0.45 µm acetate filters into clean polyethylene bottles for subsequent aliquot extraction and nutrient analysis. Splits of this sample water were divided for the following analyses: TCO2, trace elements, Br, $NH_4^+$, $NO_3^-$, $NO_2^-$, SRP, $Si(OH)_4$, DON, and DOP. During the April deployments, separate sample vessels (5-ml glass ampoules) were dedicated for $O_2$ analysis. A 25 µm pulsed-oxygen electrode tip was inserted the sample vessels and $O_2$ tension was determined. Samples designated for nutrient analysis were frozen immediately. Samples designated for trace element analysis were acidified with nitric acid solution and stored in acid cleaned vials for analysis by ICPM at Caltech. TCO2 was analyzed shortly after recovery and processing of chamber samples.

During the April and October field seasons, benthic chambers were deployed at a depth of 1 m from the mean lower low water line for Sites 1-3 subtidal locations Figure 1-1) . Some chambers were deployed in the morning, for day incubation; then recovered, sampled, turned-around, and redeployed in the evening for a night incubation (Table 3-2). Typical sampling interval was 1-2 hours.

**Table 3-2. Summary of chamber deployments for April and October 2004 sampling periods. Deployments designated with an "*" for unsuccessful chamber height and not included in the data analysis.**

| Sampling Period | Site No. | Deployment Date | Deployment No. | Incubation Time (Hrs) | Day or Night | Chamber Ht. (± Uncertainty) (cm) |
|---|---|---|---|---|---|---|
| April 2004 | 1 | 21-Apr | 1-1 | 5 | Day | 10 (1) |
| | | 21-Apr | 1-2 | 6 | Night | 11.3 (1) |
| | 2 | 20-Apr | 2-1 | 5 | Day | 14.5 (3) |
| | | 20-Apr | 2-2 | 8 | Night | 12.2 (1.5) |
| | | 22-Apr | 2-3 | 4 | Day | 13.3 (3) |
| | | 22-Apr | 2-4 | 8 | Night | 13.3 (3) |
| | 3 | 20-Apr | 3-1 | 5 | Day | 13.4 (2) |
| | | 20-Apr | 3-2 | 8 | Night | 11.9 (2) |
| October 2004 | 1 | 29-Oct | 1-1 | 8 | Night | 10 (2) |
| | | 30-Oct | 1-2 | 8 | Night | 9 (2) |
| | 2 | 28-Oct | 2-1 | 5 | Day | * |
| | | 28-Oct | 2-2 | 8 | Night | 10 (2) |
| | | 30-Oct | 2-3 | 8 | Night | 10 (2) |
| | 3 | 27-Oct | 3-1 | 8 | Night | * |
| | | 29-Oct | 3-2 | 8 | Night | * |

*Groundwater Sampling and Analysis*

Advective processes such as sediment resuspension and hydraulic transport of pore waters through such mechanisms as groundwater input (water derived from aquifers on land), bioirrigation, or tidal pumping have been identified as a means through which nutrients may be transported to surface waters (e.g., Burnett et al. 2002, Giffin and Corbett 2002, Martin et al. 2004). Pore water advection is the total flux including recirculated seawater and ground water. Knowledge of the fraction associated with aquifer-derived ground water can often be resolved from the total flux to elucidate the "new" nutrient sources. Pore water advection (or mixing) rates have been estimated by measuring radioisotopes, such as $^{222}$Rn in sediments, pore waters, and surface waters and back-calculating the advection rate required to maintain the measured surface water concentration.

To quantify pore water advection and examine whether or not evidence exists that a component of this process may be due to groundwater input, multi-level piezometers ("multisamplers") were installed at Site 3 for pore water collection down to 230-cm depth in the sediments (Figures 1-1,

3-2; Martin et al. 2003). At Sites 1 and 2 the permeability was too low in clay-rich bay sediments to extract any pore water; consequently, multisamplers were not installed. At Site 3, d pore waters were extracted from the upper 80 cm in the sediments; however, low permeability of the deeper sediments prevented pore water extraction down to 230 cm. The ports at depths of 10, 30, 50, and 80 cm in the Site 3 multisampler were developed by pumping until the pore water had low turbidity and dissolved $O_2$ was stable (<0.9 mg/L). Pore waters and overlying water column were sampled for $^{222}Rn$, $^{226}Ra$, chloride ($Cl^-$), conductivity, temperature, salinity, dissolved $O_2$, and pH whenever possible. Samples of approximately 15 mL of pore water were collected in HDPE bottles for measurement of $Cl^-$ concentrations. Using a glass syringe, 10-mL samples were quantitatively transferred from the overflow container to a 20-mL clear glass scintillation vial that had been prefilled with 10 mL of a mineral-oil scintillation cocktail for $^{222}Rn$ extraction ($t_{1/2}$ = 3.83 days). Geochemical tracers were analyzed at Louisiana State University via liquid scintillation counting (Rn) on a Packard Tri-Carb 3100TR with alpha-beta discrimination or by $AgNO_3$ titration (Cl; Clesceri et al. 1989).

At all sites, 1-m cores were collected and sectioned in the field. Sections were separated for either centrifugation, to extract pore waters for $Cl^-$ titrtation (Clesceri et al. 1989) or quickly and carefully transferred into gas-tight glass jars, for $^{222}Rn$ analysis by cryogenic extraction (e.g. Smethie et al. 1981, Hammond et al. 1977). This approach was utilized for Sites 1 and 2, where permeabilities were too low for direct porewater sampling, and dulplicated at site 3 for cross-calibration with the direct sampling method.

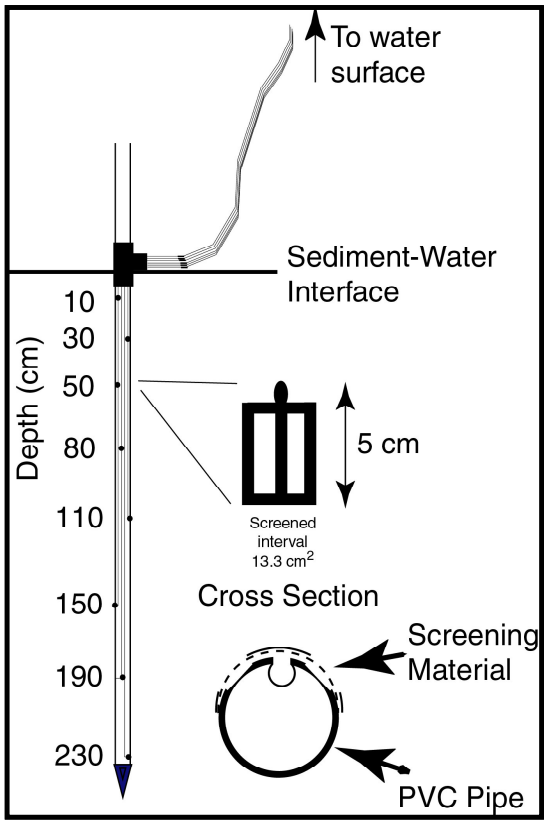


**Figure 3-2. Multi-level piezometers each contained eight sampling ports screened to 200 cm and connected to the surface via individual sampling tubes. The ports were sampled gently using a peristaltic pump (Martin et al. 2003).**

*Sampling of Surface Water Nutrients and Trace Metals Along Salinity Gradient*

A transect of surface water (0-1 m water depth) was completed during a 2-3 hour cruise April 21, October 29, and October 30, 2004, which allowed for sampling during both high and low tides. Sampling sites were selected based on salinity measurements continuously monitored using a conductivity probe with an internal salinity calibration. Sampling sites resulted in a wide range of salinity; several identical locations for both the high and low tide transects. Samples were collected in 250-mL HDPE bottles attached to the end of a fiberglass pole with tygon tubing and plastic tie wraps. The pole and bottle assembly was held over the bow of a whaler moving at minimum speed in order to ensure that sampling was conducted in water that had not been contaminated by the boat. Sampling during low tide and in locations with low salinity, required sampling from the banks of the river using nearly the same procedure. Sample bottles were uncapped and submerged upside down, breaking through the surface micro-layer and inverted approximately 30 cm below the water. This was repeated three times to rinse the bottle of all remaining acid from the leaching process and then filled in the same manner replacing the cap immediately upon surfacing after the fourth filling. Samples were secured in clean plastic

bags and placed on ice. Upon collection of all samples, a split or independent sample was allocated for analysis of nutrients and TCO2; other water was filtered and acidified for trace-metal analysis.

### *3.3.2 Analytical Methods*

Chamber and salinity-transect surface water samples were analyzed for dissolved inorganic nutrients ($NH_4^+$, SRP, $Si(OH)_4$, $NO_3^-$, and $NO_2^-$) at the University of California at Santa Barbara Marine Sciences Laboratory using an Alpkem Autoanalyzer (APHA 1992). TP was digested by combustion and hydrolysis, as in Solorzano and Sharp (1980), then analyzed as SRP by autoanalyzer (APHA 1992). TN was analyzed at the Chesapeake Biological Laboratory (University of Maryland) using the persulfate method for digestion, followed by $NO_2^-$ analysis of using an Alpkem Autoanalyzer (APHA 1992). DON and DOP were calculated by subtracting the DON or DOP concentrations from TN or TP respectively.

Total dissolved Fe and Mn were analyzed in the chamber and salinity-transect surface waters at the California Institute of Technology using ICP-MS.

TCO2 was analyzed within two days of sample collection using a Coulemetrics coulometer (Johnson et al. 1985, 1987); Br was analyzed by ion selective electrode analysis using a standard solution made up in water adjusted to the correct salinity.

.

Sediment samples were acidified, using a CHNS-O Elemental Analyzer, to remove carbonates and analyzed for SOC and SN. Sediment TP was digested with microwave acid digestion and analyzed using inductively coupled atomic emission spectroscopy (ICP-AES; Sah and Miller 1992, Meyer and Keliher 1992). Sediment dry grain density was determined by taking pre-weighed sample of sediment and measuring the volume displaced by that sample in a graduated cylinder filled with water. Sand, silt, and clay grain-size fractions were determined by wet sieving each sample through a 62 mm sieve in order to separate coarse and fine fractions; the fine fraction were then analyzed using the pipette method (Milner 1962).

### *3.3.3 Data Analysis*

*Chamber Fluxes*

Br serves as both a measure of the initial volume enclosed by the chamber and, as the incubation proceeds, as a means to estimate the advective mixing of chamber water with

sediment pore water or ambient water (Berelson et al. 1999). The procedure for determining chamber volume from Br measurements is as follows. The initial spike volume ($V_{SPIKE}$) and Br concentration ($C_{SPIKE}$) added to a chamber was known. The amount of Br in the chamber prior to the spike injection was determined from the concentration of Br in ambient water ($C_{AMB.H20}$), given that water with salinity 35 ppt has [Br]=860 µM and water with salinity 0 ppt has 0 µM [Br]. The solution to chamber volume is determined by Eq. 3-1:

$$V_{CHAMBER} = \frac{V_{SPIKE} * C_{SPIKE}}{(C_{CHAMBER} - C_{AMB.H20})} \qquad \textbf{Eq. 3-1}$$

where $C_{CHAMBER}$ represents the Br concentration extrapolated to the time when the lid first closed ($t_0$). Approximately one hour elapsed between the time when the Br spike was injected and thetime when the first sample was obtained; thus an extrapolation of the Br versus time trend allows prediction of the concentration at $t_0$. Chamber volume divided by chamber area (730 $cm^2$) yields the effective chamber height (h), a parameter used in calculation of fluxes.

The loss of Br spike from a chamber over the deployment period follows an exponential function and permits the calculation of pore water exchange. In this case we use the excess Br (that Br injected into the chamber in excess of the ambient Br concentration present in bay water) versus time and used to find that an exponential function provides a good fit to the data. The exponent represents a time constant (1/time) and is a measure of how rapidly Br is lost from the chamber water. Excess Br concentrations ($C_{Br}$) was fit with the Eq. 3-2:

$$C_{Br} = A \exp(-bt) \qquad \textbf{Eq. 3-2}$$

where A (concentration units) and b ($hr^{-1}$) are constants and t is incubation time (hours).

Flux rates (F) for each constituent measured (e.g. nutrients, TCO2, and $O_2$) are the product of chamber height (h) and change in solute concentration within a chamber versus incubation time (dC/dt), as given in Eq. 3-3:

$$F = h * dC/dt. \qquad \textbf{Eq. 3-3}$$

Concentration versus time was plotted as a linear gradient using all data that passed a quality assurance check. Use of a linear gradient assumes that the flux of a constituent is constant during the incubation interval.

Corrections can be applied to account for the dilution of chamber water by ambient water, which occurs during a sample draw. However, for chamber data from this study, this correction was not applied. This decision was made because the ambient water chemistry was changing regularly and no measure of the ambient water value at the time of sample draw was available. This correction has a 10-20% impact on flux calculations, so it is unlikely that neglecting this correction significantly skews the flux data.

Chambers deployed in April had faulty sample-draw mechanisms, resulting in samples that were a mixture of chamber water and up to 40% DIW. The DIW was used to fill the sample tubes prior to deployment, and a poor sample draw results in much of the DIW left remaining in the sample tube. A normal sample draw leaves no more than 0-7% DIW mixed with sample water. Assuming the DIW nutrient concentration was negligible, a correction was applied to samples affected by dilutions of <7% DIW. However, a decision was made to exclude data from the flux calculation if it was subjected to a larger DIW correction. A comparison of fluxes determined using DIW-corrected samples; after dropping these samples indicated that fluxes were within 20% agreement.

Chambers deployed in October faced an unusual hydrodynamic regime. Heavy rainfall occurred just prior to the October deployments. Estuarine flow was dramatically stratified and high current velocities were observed. Because a recently-deployed chamber would acclimate with an open lid approximately 30 minutes before closing, initial ambient water that filled the chamber at the time of deployment may have may freshened due to changing tidal regime. This could serve to stratify the chamber water such that saltier water remained in contact with the sediment and less salty water filled the upper parts of the chamber. Chamber mixing is effective in breaking down this stratification, but sometimes the first two samples drawn showed this stratification effect; the condition of the chamber in which stratification occurred was noted.

As desired, some chambers behaved as closed systems for the duration of the incubation; others showed signs that chamber water was being exchanged with ambient water. A signal of this exchange is often picked up in the pulsed-oxygen electrode data, as $O_2$ concentration is

quite sensitive to small sources and sinks. Notations were made when a chamber was considered to have been breached by tidal current scour during the deployment period. Flux data from chambers exhibiting questionable indicators were eliminated from consideration for this study. Chamber 2-1 from the October deployment was the most enigmatic chamber; there were some indications that the chamber worked properly and other indications that is was leaky, consequently this chamber's data was eliminated from the summary table.

*Calculation of Pore Water Advection Rate From Multisampler Data*

In the shallow pore water zone beneath surafce waters, $^{222}$Rn concentrations varied between 15 and 596 dpm/L. Overlying waters were approximately 7 dpm/L. Pore water inventories ($I_{pw}$) were calculated for each sampling trip by integrating the pore water activities with depth in the sediments (Tables 3-5, 3-6). A predicted $^{222}$Rn total flux ($J_{pred}$), which will include both advective and diffusive components, could then be calculated based on equation 3-4 (Corbett et al. 2000):

$$J_{pred} = I_{pw} \Big/ \left(1 - e^{-\lambda t} / \lambda\right) \qquad \textbf{Eq. 3-4}$$

where $\lambda$ is the decay constant for $^{222}$Rn (0.1809 day$^{-1}$) and t is time (days). While sediment spatial heterogeneities may produce variations in $^{222}$Rn production along a pathlength, the input of $^{222}$Rn to pore waters is assumed to be constant in time. Spatial variations in production are accounted for by sampling multiple depths within nearshore pore waters to assess radon activity. The total predicted flux, $J_{pred}$, is then corrected for diffusion using Fick's First Law (Eq. 3-5):

$$J_{diff} = -\phi * D_s * \left(\frac{\partial [C]}{\partial z}\right) \qquad \textbf{Eq. 3-5}$$

where $\phi$ is sediment porosity, $D_s$ is the diffusion coefficient of radon in sediments (2.03 x 10$^{-5}$ m$^2$/day), z is depth, $\frac{\partial [C]}{\partial z}$ is the vertical concentration gradient of $^{222}$Rn, $D_s$ is obtained by correcting the free-water radon diffusion coefficient for both temperature and tortuosity, $D_o$ is 1.4 x 10$^{-5}$ cm$^2$/sec at the mean pore water temperature of 27.2ºC (Peng et al. 1974), tortuosity is accounted for using the empirical relationship $D_s = \phi^2 D_o$ (Ullman and Aller, 1980), and $\phi$ = 0.41.

Under conditions where advection is assumed to be absent, a maximum concentration gradient is used to calculate the maximum expected diffusive flux using near-bottom water column

concentrations and $^{222}$Rn pore water concentrations where they become constant with depth or are at the deepest sampled concentration. Even when a maximum concentration gradient is assumed, the diffusive flux calculated from equation 2 is a minor component of radon transport (less than 3% of the total flux, $J_{pred}$). A net $^{222}$Rn flux, $J_{net}$, was calculated from the difference between the total predicted and diffusive fluxes (Eq. 3-6):

$$J_{net} = J_{pred} - J_{diff} \qquad \textbf{Eq. 3-6}$$

$J_{net}$ represents the sum of advective exchange processes across the sediment-water interface due to meteoric (fresh) groundwater and recirculated seawater driven by local biology and physics (e.g. waves, tides, convective mixing). Dividing $J_{net}$ by the fresh porewater $^{222}$Rn concentration yields an advective rate for interstitial fluids in nearshore sediments of UNB (e.g. Corbett et al. 2000). Rates ranged from 3 to 11 cm/day based on this approach (Table 3-6).

## 3.4 RESULTS

### *3.4.1 In Situ Flux Measurements*

*Success of Chamber Deployments*

During the April sampling event (April 22-24, 2004), two chambers were deployed at Site 1, four at Site 2, and two at Site 3; Table 3-3 summarizes all chamber flux data and indicates whether the deployments occurred during the day or at night. Sampling occurred during a neap tidal cycle. All eight chamber deployments provided useable data (Table 3-3).

In the fall sampling event (October 29-30, 2004), chambers were deployed at Sites 1-3. However, there was a large rainfall just prior to the first chamber deployments, so that the fresh water input was strong and UNB surface waters were strongly salinity stratified. In addition, because sampling occurred during a spring tide, tidal currents were much greater than had been the case in April. Thus, this sampling event captured conditions in which sediments had been recently disturbed following a strong rain event. Work conditions were not optimal for obtaining benthic flux measurements because the system had been recently disturbed. Hence all of the flux data presented for October had greater uncertainties than April flux values.

**Table 3-3. *In situ* flux estimates. All values in mmol $m^{-2}$ $d^{-1}$, except for U and Fe fluxes, which are in µmol $m^{-2}$ $d^{-1}$. ND = no data generated due to insufficient sample volume or problems with laboratory analysis.**

| 2004 Date | Day/ Night | ID | $O_2$ | SRP | DOP | $SI(OH)_4$ | $NO_2^-$ | $NO_3^-$ | TCO2 | $NH_4^+$ | DON | Mn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4/21 | D | 1-1 | -21 | 1.09 | ND | 5.9 | 0.19 | -1.3 | 73 | ND | ND | 0.41 | 60 |
| 4/21 | N | 1-2 | -56 | 0.89 | -0.01 | 3.8 | 0.40 | -4.8 | 78 | ND | ND | 0.55 | 15 |
| **April Site 1 Mean ± sd** | | | **-38±25** | **0.99±0.14** | **-0.01** | **4.8±1.5** | **0.29±0.16** | **-3.0±2.4** | **76±4** | **ND** | **ND** | **0.48±0.10** | **37±32** |
| 4/20 | D | 2-1 | -56 | 0.22 | -0.14 | 6.1 | 0.16 | -2.8 | na | ND | ND | 0.20 | -2 |
| 4/20 | N | 2-2 | -51 | 0.45 | ND | 7.4 | 0.30 | 1.3 | 104 | ND | ND | 0.40 | 41 |
| 4/22 | D | 2-3 | -53 | 0.62 | 0 | 3.2 | 0.45 | -0.3 | 177 | ND | ND | 0.04 | -40 |
| 4/22 | N | 2-4 | -36 | 0.42 | -0.29 | 9.1 | 0.34 | 2 | 173 | ND | ND | 0.30 | 28 |
| **April Site 2 Mean ± sd** | | | **-49±8.9** | **0.43±0.16** | **-0.14±0.15** | **6.4±2.5** | **0.31±0.12** | **0.05±2.1** | **151±41** | **ND** | **ND** | **0.24±0.15** | **7±36** |
| 4/20 | D | 3-1 | -42 | 0.26 | -0.49 | 5.3 | 0.34 | -5.4 | na | ND | ND | -0.08 | -60 |
| 4/20 | N | 3-2 | -77 | 1.1 | ND | 13.6 | 0.29 | 3.2 | 266 | ND | ND | 0.28 | 60 |
| **April Site 3 Mean ± sd** | | | **-59±25** | **0.68±0.59** | **-0.49** | **9.5±5.9** | **0.32±0.04** | **-1.1±6.1** | **266** | | | **0.10±0.25** | **0±85** |
| **April Mean ± sd** | | | **-49 ± 16** | **0.63±0.35** | **-0.19±0.21** | **6.8±3.3** | **0.31±0.10** | **-1.0±3.2** | **145± 75** | | | **0.26±21** | **13±44** |
| 10/29 | N | 1-1 | -19 | -0.17 | -0.67 | -3.9 | -0.05 | -4.8 | 110 | 6.4 | -23.9 | 0.89 | 287 |
| 10/30 | N | 1-2 | -10 | -0.51 | -0.24 | -14.9 | -0.23 | -15.6 | -15.7 | 2.1 | -10.2 | 1.11 | -96 |
| **October Site 1 Mean ± sd** | | | **-15±6.4** | **-0.34±0.24** | **-0.46±0.30** | **-9.4±7.8** | **0.14±0.13** | **-10.2±7.6** | **47±89** | **4.2±3.0** | **-17.1±9.7** | **1.0±0.2** | **95±270** |
| 10/28 | D | 2-1 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 10/28 | N | 2-2 | -32 | 0.29 | -0.31 | 6.3 | 0.25 | 1.1 | 25 | 5.6 | -10.4 | 0.03 | -30 |
| 10/30 | N | 2-3 | -63 | -0.31 | -0.02 | -3.3 | 0.46 | -8.9 | 77 | 8.6 | -0.3 | 0.46 | 78 |
| **October Site 2 Mean ± sd** | | | **-47±22** | **-0.01±0.42** | **-0.17±0.21** | **1.5±6.8** | **0.36±0.15** | **-3.9±7.1** | **51±37** | **7.1±2.1** | **-5.4±7.1** | **0.24±0.30** | **24±76** |
| 10/27 | N | 3-1 | na | na | na | na | na | na | na | na | | na | na |
| 10/29 | N | 3-2 | na | na | na | na | na | na | na | na | | na | na |
| **October Mean ± sd** | | | **-31±23** | **-0.18±34** | **-0.31±0.27** | **-4.0±8.7** | **0.11±0.31** | **-7.1±7.0** | **49±56** | **5.7±2.7** | **-11.2±9.7** | **0.62±0.49** | **60±188** |
| **Overall Mean ± sd** | | | **-43±20** | **0.36±0.52** | **-0.24±0.23** | **3.2±7.5** | **0.24±0.20** | **-3.0±5.3** | **107±81** | | | **0.38±0.35** | **3±10** |

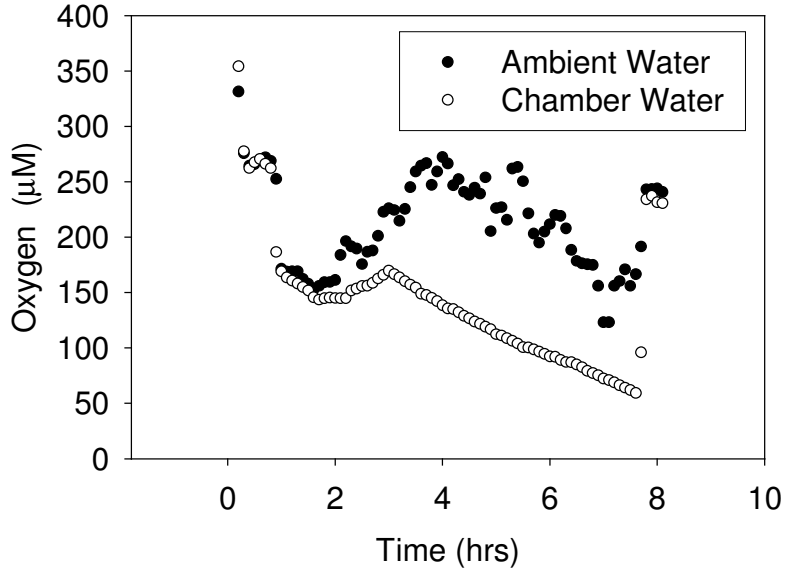


**Figure 3-3. Typical time series of $O_2$ concentration relative to DO in ambient surface water (outside the chamber) in Deployment 2-3 at Site 2 (April 2004). $O_2$ trend at close of chamber lid (at 3-hour mark) shows linear decrease over time.**

Seven chambers were deployed during the October field season. However, data from 3 of the 7 were severely influenced by dilution and contamination by ambient water entering the chamber, thus, only 4 flux determinations are presented here. Culling the data in this manner, fluxes for Sites 1 and 2 were obtained, but none were collected for Site 3, located on a point bar that generated high current flow past the chamber, which was ultimately breached. That is, the sediment in which the chamber was planted got eroded such that the bottom of the chamber was exposed to ambient bay water.

*$O_2$ and TC02 Fluxes*

The sediments from all three sites consistently showed $O_2$ consumption during the April and October 2004 sampling periods. Figure 3-3 shows a typical time series of $O_2$ concentration relative to DO in ambient surface water (outside the chamber) during Deployment 2-3 (April 2004) at Site 2. The chambers at Site 1 show oxygen-uptake rates of -21 and -56 mmol $m^{-2}day^{-1}$, chambers at Site 2 showed $O_2$ uptake at rates between -36 and -56 mmol $m^{-2}day^{-1}$, and Site 3 chambers showed oxygen uptake rates of –42 and -77 mmol $m^{-2}day^{-1}$ (Figure 3-3). The mean $O_2$ flux rate for Sites 1-3 was -49 ± 16 (sd) mmol $m^{-2}$ $d^{-1}$ (negative values indicating a net uptake or fluxes into the sediments). This indicates that the sediment regime was net heterotrophic and $O_2$ consumption occurred at all sites.

During the October sampling event, $O_2$ fluxes were into the sediments, with uptake rates ranging from -19 to -63 mmol $m^{-2}day^{-1}$ (Figure 3-4). Oxygen-uptake rates were higher at Site 2 compared to values obtained at Site 1. The average rate of $O_2$ uptake for both sites was -31 ± 23 mmol $m^{-2}day^{-1}$.

When $O_2$ consumption within surface waters and sediments outweighs $O_2$ production, the system demonstrated net respiration or heterotrophy during that time period. Net respiration or heterotrophy often results in net production of TCO2 and a resultant flux of TCO2 from the sediments to the overlying water column. During April and October sampling events, net TCO2 was positive, indicating that UNB surface waters and sediments are heterotrophic. The average TCO2 efflux from sediments during April 2004 was 145 ±75 mmol $m^{-2}day^{-1}$, with fluxes ranging from 73-266 mmol $m^{-2}day^{-1}$. The largest flux was at Site 3; the lowest mean fluxes were at Site 1. Two chamber deployments had unreliable TCO2 data and yielded no flux value for this sampling period. During the October sampling period, total $CO_2$ fluxes were of smaller magnitude than April TCO2 fluxes from the same sites. Site 1 fluxes varied from -15.7 to110 mmol $m^{-2}day^{-1}$. The average TCO2 flux was + 49 ± 56 mmol $m^{-2}day^{-1}$.

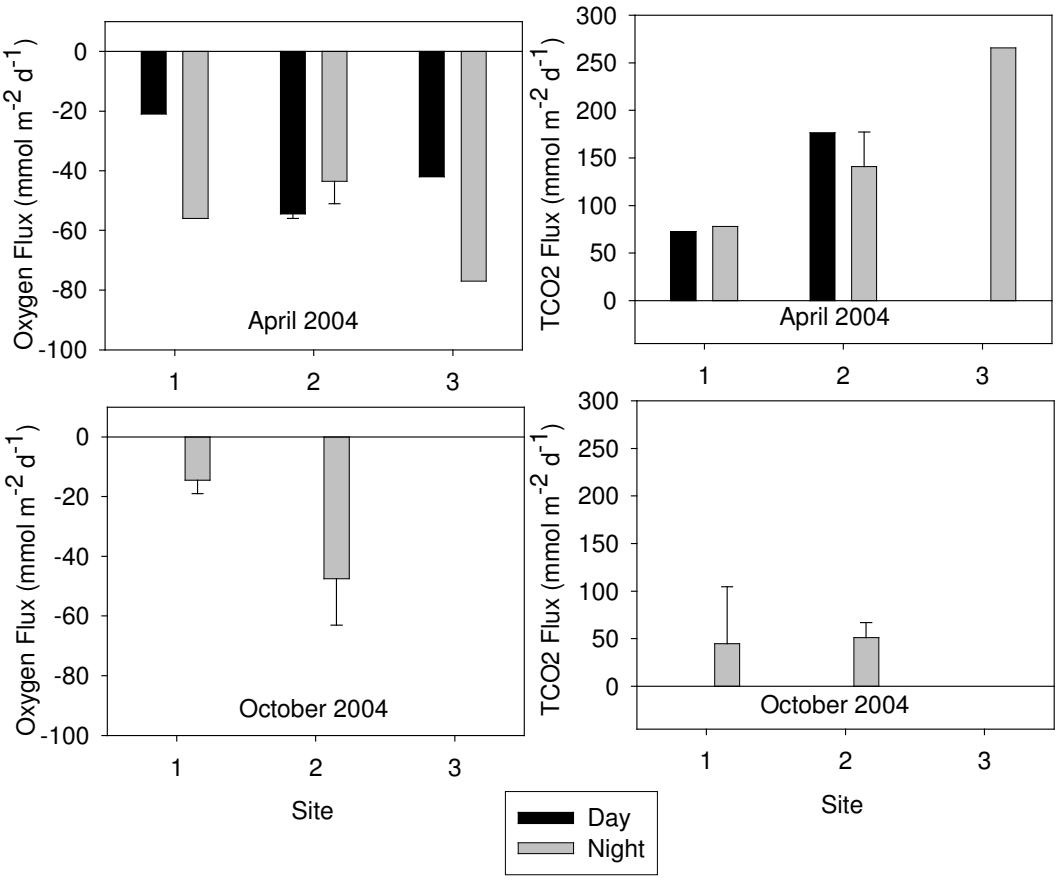


**Figure 3-4. $O_2$ and TCO2 fluxes for April and October 2004 sampling periods. Values for April Site 2 represent mean and standard deviation of two measurements during day and nighttime at that site. Values for October represent mean and standard deviation of two flux measurements taken at nighttime for Sites 1 and 2. Deployments were not successful for Site 3 for this sampling period. All other values are single measurements.**

$NO_3^-$ *and* $NO_2^-$

In April 2004, 5 of the 8 deployments showed a negative $NO_3$ flux (into the sediments; Figure 3-5). However, two chambers deployed at Site 2 and one at Site 3 showed a net efflux of $NO_3$. Fluxes ranged from -5.4 –to 3.2 mmol $m^{-2}day^{-1}$ and the overall mean rate of $NO_3$ flux for this system was –1.0 ± 3.2 mmol $m^{-2}day^{-1}$. Some systematic and positive relationships were observed between $NO_3$ flux into the sediment during the daytime, and flux out of the sediments at night for Sites 2 and 3.

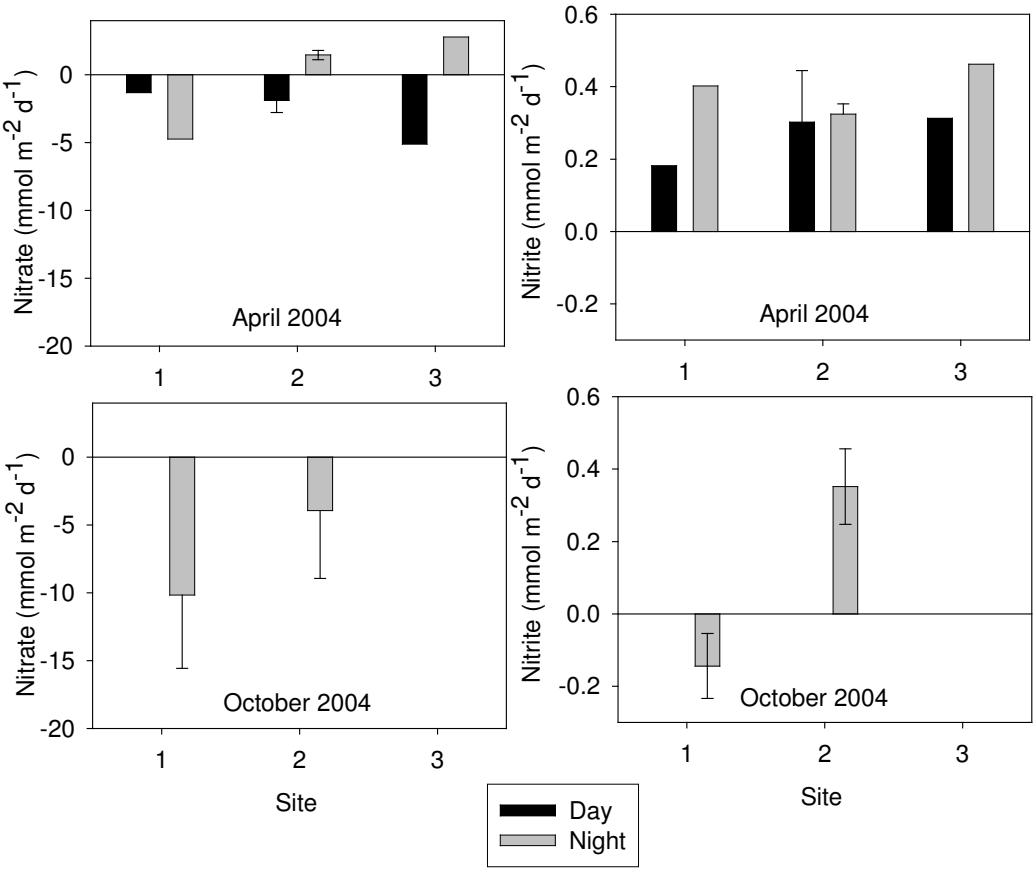


**Figure 3-5. $NO_3^-$ and $NO_2^-$ fluxes for April and October 2004 sampling periods. Values for April Site 2 represent mean and standard deviation of two measurements during day and nighttime at that site. Values for October represent mean and standard deviation of two flux measurements taken at nighttime for Sites 1 and 2. October deployments were not successful. All other values are single measurements.**

During this time period, $NO_2^-$ consistently fluxed from bay sediments; the fluxes ranged from 0.2 to 0.5 mmol $m^{-2}d^{-1}$ with a mean flux of 0.31 ± 0.10 mmol $m^{-2}d^{-1}$ (Figure 3-5). $NO_3^-$ fluxes were largest and negative at Sites 1 and 3, yet $NO_2$ fluxes were always positive and consistent in magnitude between all three sites. In October 2004, $NO_3^-$ fluxes were highly variable with sites but generally negative, ranging from -15.6 to1.1 mmol $m^{-2}day^{-1}$; the mean $NO_3^-$ flux was –7.1± 7.0 mmol $m^{-2}day^{-1}$. When $NO_2^-$ fluxes were small compared to $NO_3^-$ fluxes, $NO_2^-$ fluxes ranged from –0.23 to 0.46 mmol $m^{-2}day^{-1}$ with an overall mean of 0.11 ± 0.31 mmol $m^{-2}day^{-1}$.

*Ammonia and DON*

Neither ammonia nor DON flux data were generated for the April field period due to problems with analyses. Ammonia fluxes in October 2004 were positive (Figure 3-6), ranging from 2.1 to

8.6 mmol $m^{-2}d^{-1}$. The mean value of ammonia efflux from UNB sediments was 5.7 ± 2.7 mmol $m^{-2}d^{-1}$, with Site 2 fluxes slightly higher than Site 1 flux. DON fluxes during this time period were highly variable, but negative for all deployments, and higher at Site 1 than Site 2. DON, when combined with NO3 fluxes, represented larger sinks of N than $NH_4^+$ fluxes. Thus, during the October 2004 sampling period, TDN flux at Site 1 and 2 was negative, with mean values ranging from –17 to –5 mmol $m^{-2}$ $d^{-1}$ (Figure 3-7).

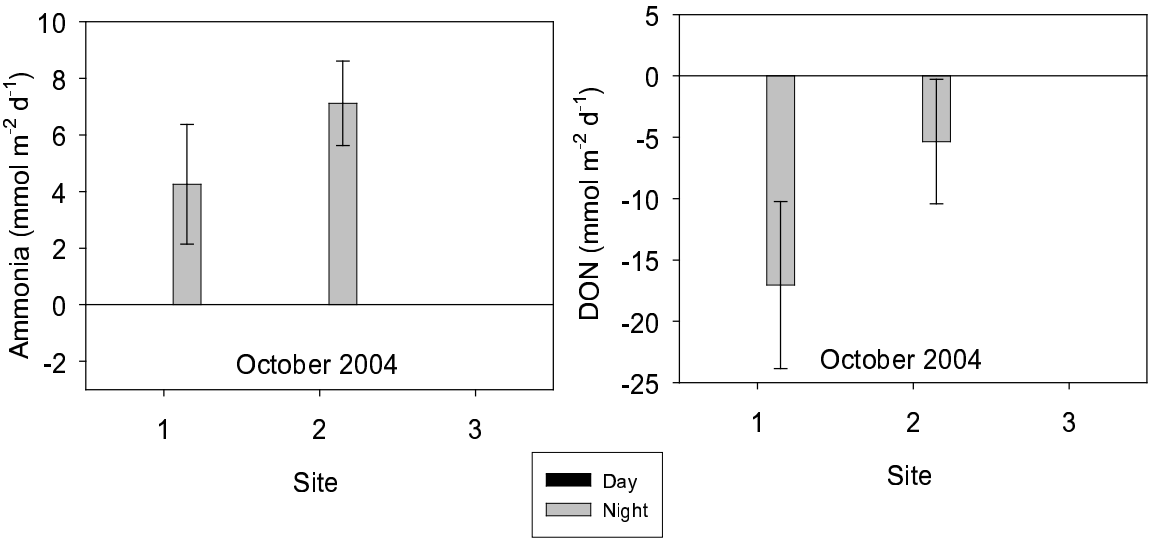


**Figure 3-6. $NH_4^+$ and DON fluxes for October 2004 sampling periods. Values for October represent mean and standard deviation of two flux measurements taken at night for Sites 1 and 2. Deployments were not successful for Site 3 for this sampling period. No data for ammonia and DON are available for April 2004.**

*SRP and DOP*

In April 2004, all sites showed a release of SRP from the sediments to the overlying water (Figure 3-8). SRP flux ranged between 0.2 and 1.1 mmol $m^{-2}d^{-1}$, with a mean of 0.62 ± 0.35 mmol $m^{-2}d^{-1}$. SRP fluxes were largest at Site 1 and Site 3 (night). DOP fluxes were consistently negative, indicating uptake within the sediments. Generally, these fluxes were smaller than the SRP fluxes; however, at Site 3 during the day, one chamber had a larger negative DOP flux than positive SRP flux. Thus TDP flux during April was generally positive with a mean DOP flux was -0.18 ± 0.19 mmol $m^{-2}d^{-1}$ (Figure 3-7).

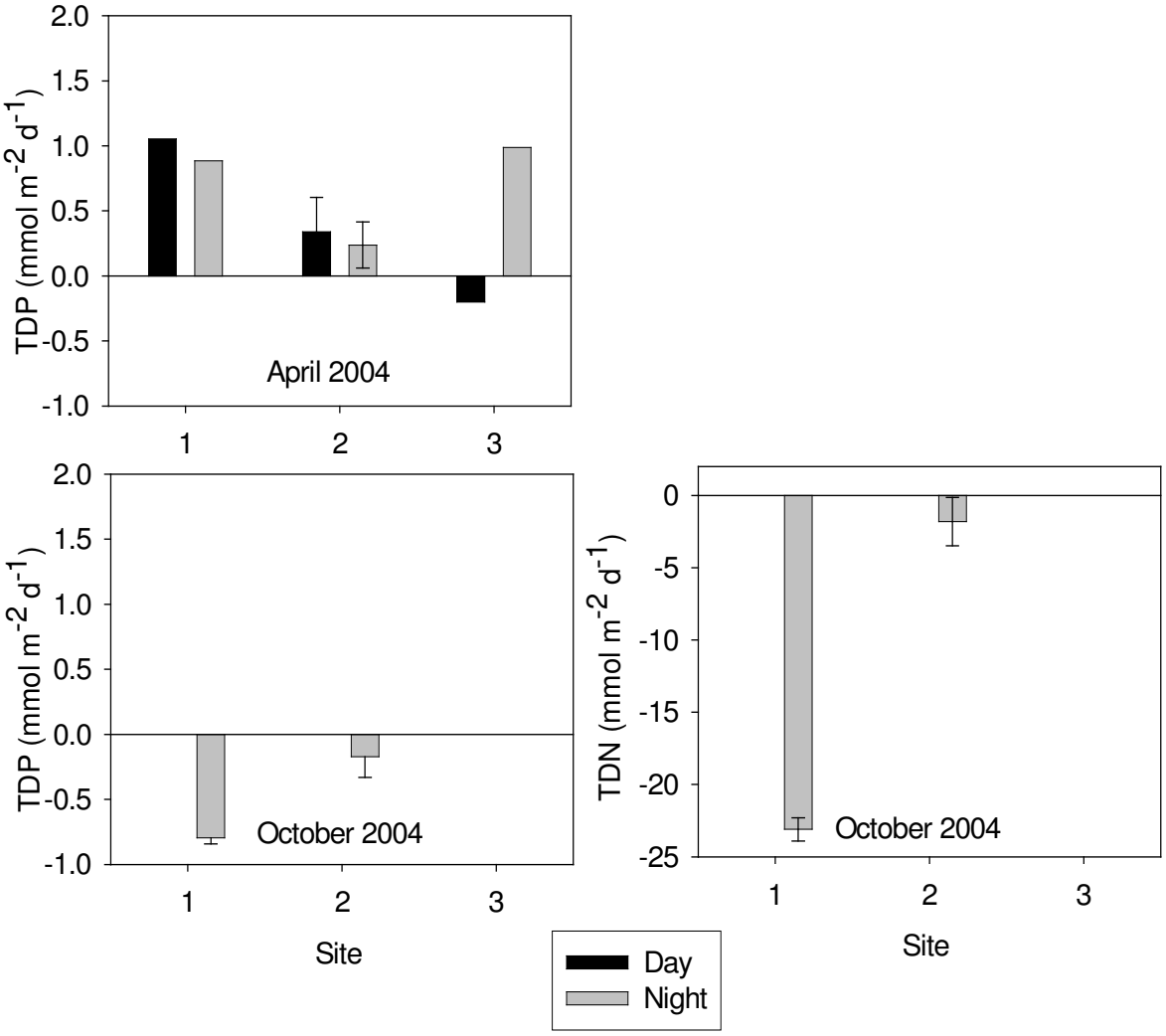


**Figure 3-7. TDN and TDP fluxes for April and October 2004 sampling periods. Values for April Site 2 represent mean and standard deviation of two measurements during the day and at night for that site. Values for October represent mean and standard deviation of two flux measurements taken at nighttime for Sites 1 and 2. October deployments were not successful for Site 3. All other values are single measurements. Because $NH_4^+$ and DON estimates were not available for April 2004, TDN estimates for this period are not reported.**

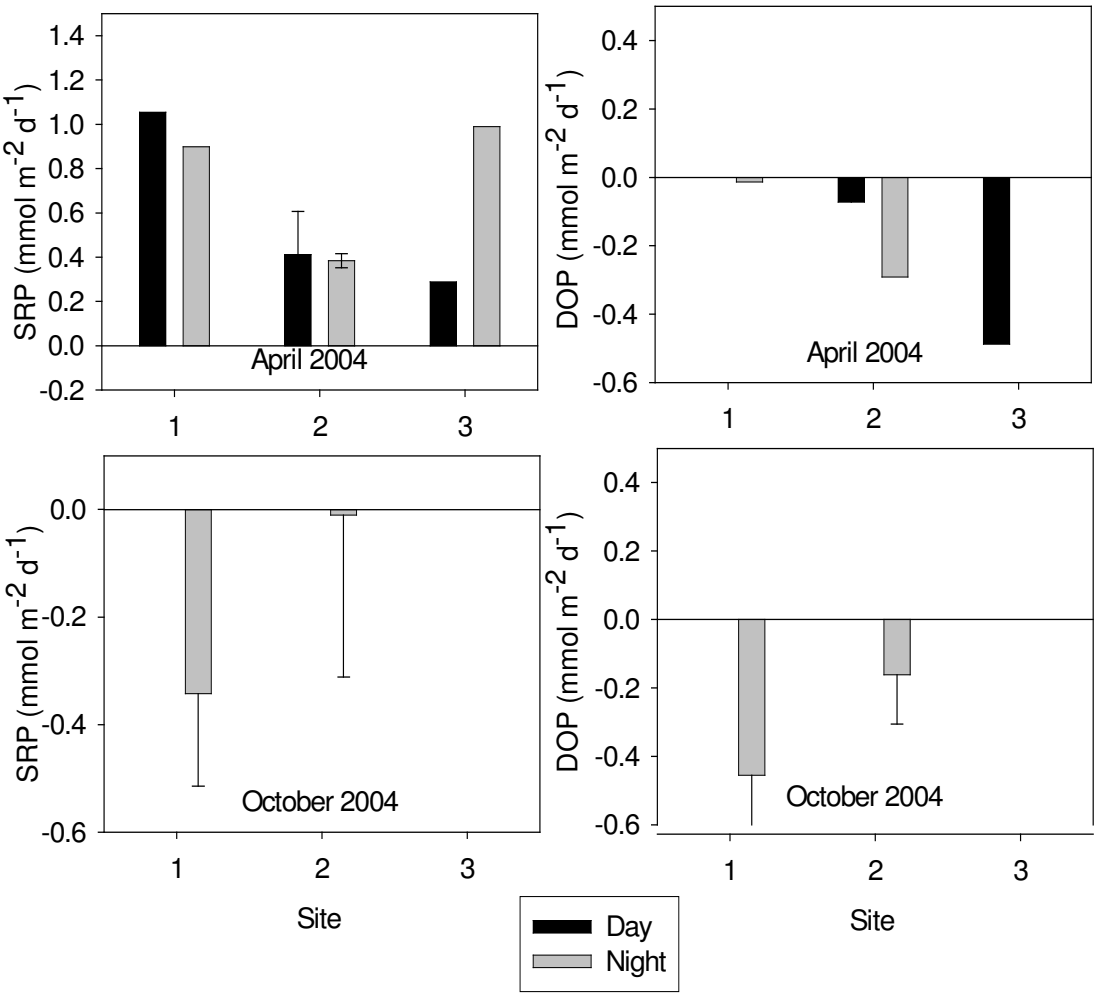


**Figure 3-8. SRP and DOP fluxes for April and October 2004 sampling periods. Values for April Site 2 represent mean and standard deviation of two measurements during the day and at night for that site. Values for October represent mean and standard deviation of two flux measurements taken at nighttime for Sites 1 and 2. Deployments were not successful for Site 3 during this sampling period. All other values are single measurements.**

In October 2004, SRP fluxes were generally negative, representing a flux into the sediments and removal from the overlying water column. Three of the four chamber fluxes indicate SRP uptake; the range in fluxes was -0.51 to 0.29 mmol SRP $m^{-2}day^{-1}$, with a mean of -0.18 ± 0.34 mmol SRP $m^{-2}day^{-1}$. DOP fluxes in October were negative and of the same magnitude as, or larger than, SRP fluxes. The average DOP flux was -0.31 ± 0.27 mmol $m^{-2}d^{-1}$. TDP flux for Sites 1 and 2 ranged from – 0.1 to to 0.8 mmol $m^{-2}d^{-1}$

*Trace Metals and $Si(OH)_4$ Fluxes*

During April 2004 and October 2004, sediments were generally a source of dissolved Mn (II) to the overlying water (Figure 3-9). During both sampling periods, flux was highest at Site 1 and decreased in magnitude at sites lower in UNB. In April 2004, fluxes ranged from -0.1 to 0.55 mmol $m^{-2}day^{-1}$ and the average of eight flux determinations was 0.26 ± 0.21. In October 2004, Mn flux values ranged from 0.03 to 1.1mmol $m^{-2}day^{-1}$, with a mean of 0.62 ± 0.48 mmol $m^{-2}day^{1}$.

During April 2004, Fe fluxes ranged from –0.06 to 0.06 mmol $m^{-2}day^{-1}$., with a mean flux of 0.013 ± 0.044 mmol $m^{-2}day^{-1}$. As with Mn, Fe efflux was greater at Site 1. During October, Fe fluxes were highly variable and bidirectional; flux values ranged from –0.10 to 0.29 mmol $m^{-2}day^{-1}$. The average Fe flux was 0.06 ± 0.17 mmol $m^{-2}day^{-1}$.

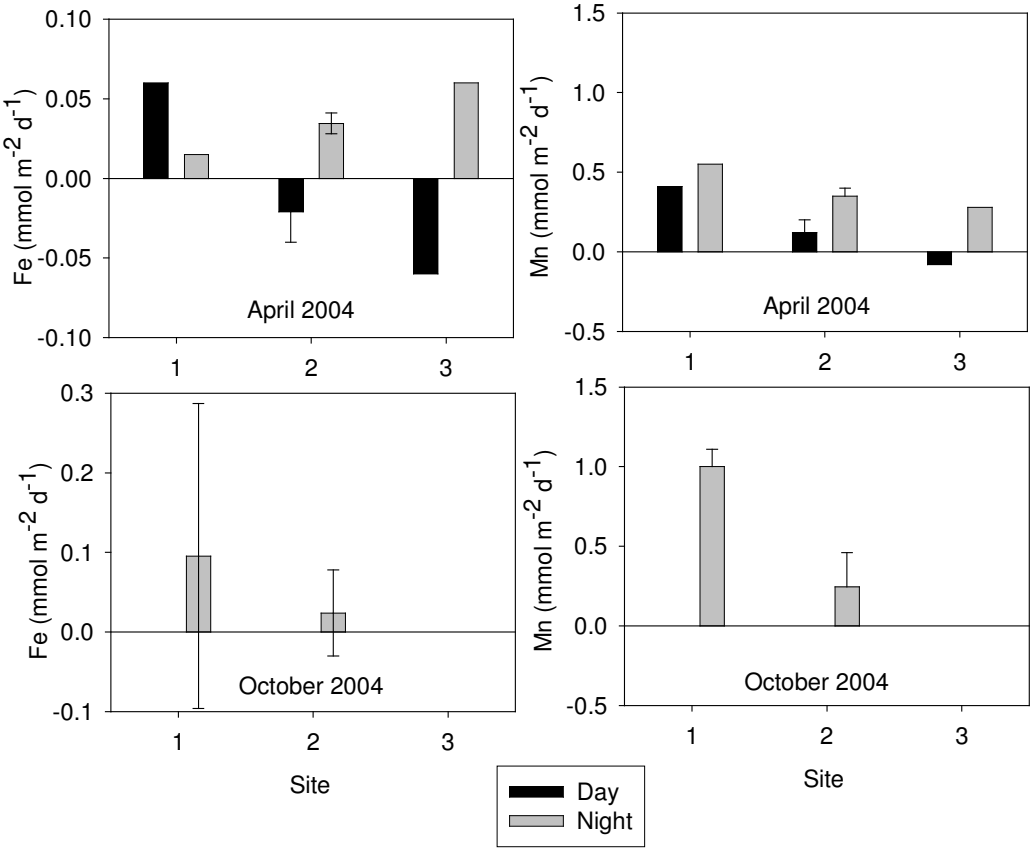


**Figure 3-9. Total dissolved Fe and Mn fluxes for April and October 2004 sampling periods. Values for April Site 2 represent mean and standard deviation of two measurements during day and nighttime at that site. Values for October represent mean and standard deviation of two flux measurements taken at nighttime for Sites 1 and 2. Deployments were not successful for Site 3 for this sampling period. All other values are single measurements.**

$Si(OH)_4$) is formed in pore waters as biogenic opal, commonly found in diatom tests, dissolves. During the April field season, $Si(OH)_4$ was found to flux from the sediment and pore waters to the overlying bay water at all sites. $Si(OH)_4$ efflux ranged from 3 to 14 mmol $m^{-2}day^{-1}$, with an average of 6.8 ± 3.3 mmol $m^{-2}day^{-1}$. Spatial trends in $Si(OH)_4$ flux were subtle, but it appeared that more dissolution and flux occurred s at downstream sites. $Si(OH)_4$ flux in three of four chambers during the October 2004 sampling event indicated and unusual net uptake. Silicone fluxes ranged from -14.9 to 6.3 mmol $m^{-2}day^{-1}$, with average flux of –4.0 ± 8.7.

### *3.4.2 Br Tracer Loss From Chambers*

For all sites in April and October 2004, the rate of Br spike decrease versus time was much larger than diffusive loss alone would predict. Figure 3-10 illustrates loss of Br from chamber 2-2 in April 2004. Table 3-4 gives the Br loss rates (b) for all chamber deployments. These rates of Br spike loss are indicative of very high rates of exchange between chamber water and either sediment pore water or ambient surface water. Chamber deployments that were considered leaky based on behavioral evidence (e.g. behavior of dissolved oxygen in the chamber) are designated with an asterisk in Table 3-4.

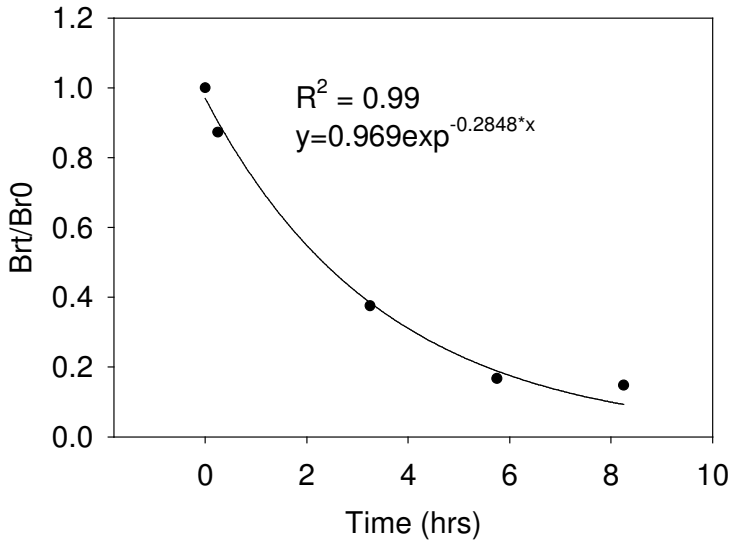


**Figure 3-10. Br loss rate in chamber 2-2 (Site 2, April 2004), illustrating fitting of data with exponential decay curve y = A*exp(-b*t).**

For the chamber deployments not designated by an asterick in Table 3-4, b (as defined by Eq. 3-2 indicates high rates of bioirrigation by benthic infauna. The average value of the b constant for 6 chamber deployments in April was 0.17 ± 0.10 $hr^{-1}$ (Table 3-4). The b value for

four chamber deployments in October (excluding chambers considered to be leaky) was 0.19 ± 0.05 $hr^{-1}$. There was no significant difference between mean b values for April or October sampling events (p-$value_{\alpha=0.05}$ = 0.62). Although the number of chamber deployments is too small to determine significant differences between sites, the b exponent may be greater at Site 3 relative to Sites 1 and 2.

**Table 3-4. Br loss rate (b, as defined by Eq. 3-2). An asterisk (*) denotes chambers that were determined to have leaks. ND = no spike injected. Higher b values indicate higher loss rates.**

| Time Period | Site | Deployment Number | Br Loss Rate (b) ($hr^{-1}$) |
|---|---|---|---|
| April 20-22, 2004 | 1 | 1-1 | 0.20 |
| | | 1-2 | 0.05 |
| | 2 | 2-1 | 0.08 |
| | | 2-2 | 0.25 |
| | | 2-3 | ND |
| | | 2-4 | ND |
| | 3 | 3-1 | 0.16 |
| | | 3-2 | 0.30 |
| October 29-30, 2004 | 1 | 1-1 | 0.16 |
| | | 1-2 | 0.16 |
| | 2 | 2-1* | 0.26* |
| | | 2-2 | 0.16 |
| | | 2-3 | 0.11 |
| | 3 | 3-1* | 0.59* |
| | | 3-2* | 0.12* |

### *3.4.3 Trends In Nutrients and Metals Along Salinity Transects*

Plots of nutrient and trace metals versus salinity illustrate the extent to which the constituent is produced, consumed, or conserved along the longitudinal axis of the estuary (Figure 3-110a,b). Surface-water concentrations that indicate production (convex line) or consumption (concave line) along the salinity gradient are the result of processes that can be occurring in the sediments or water column or both. Plots of $NH_4^+$, SRP, and Mn from the April 2004 samplings show a convex shape, indicating production of these species through a salinity gradient of 15 – 24 ppt. $NO_3$, $Si(OH)_4$, DOP, DON, and dissolved Fe show a linear trend, indicating conservative mixing (neither production or consumption). As was the case in April, October $NH_4^+$ and Mn mixing diagrams showed production and DOP, DON, and Fe show conservative behavior within a salinity gradient of 3 – 33 ppt, but $Si(OH)_4$ and $NO_3$ diagrams show consumption.

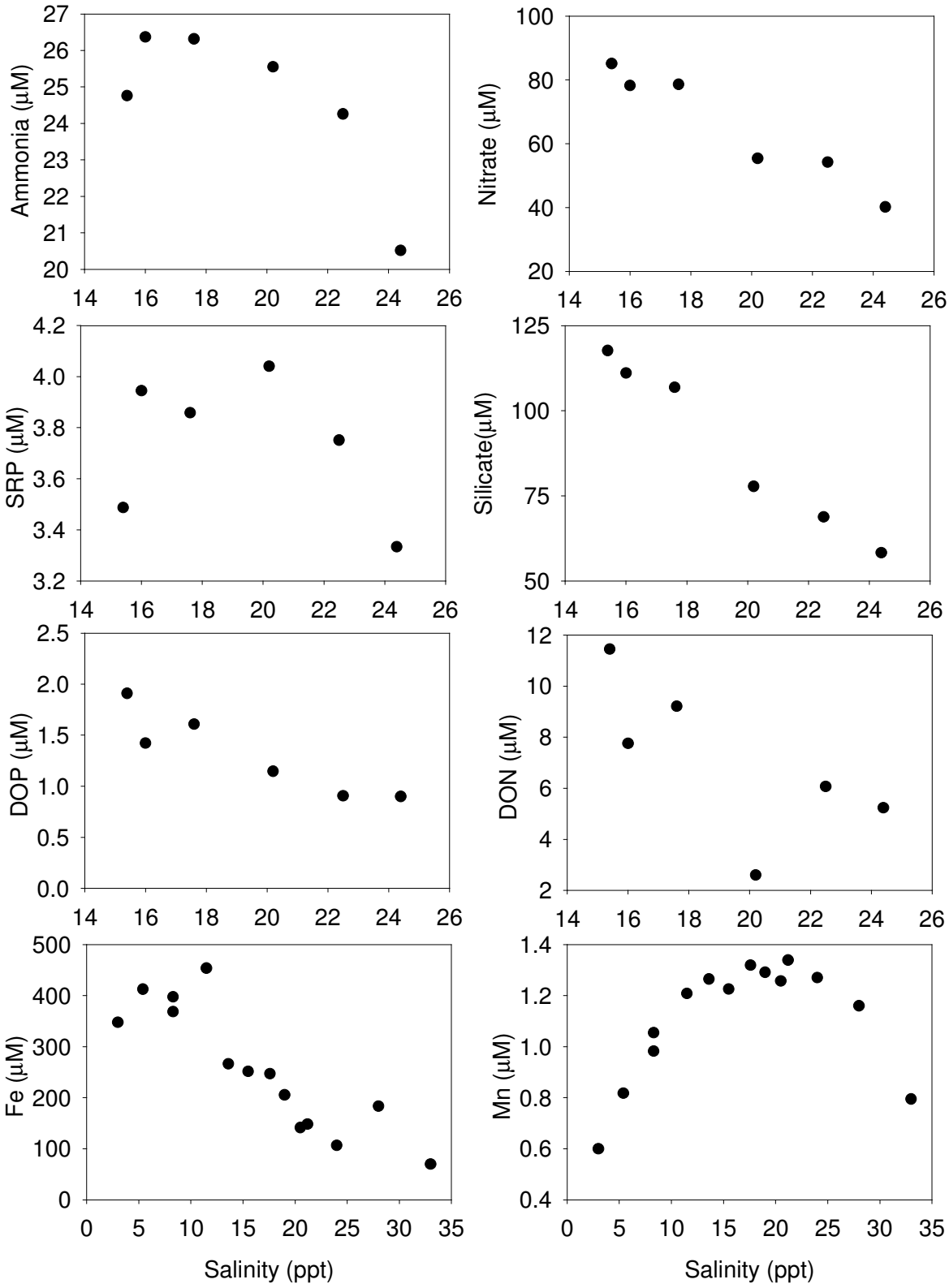


**Figure 3-11a. Mixing diagrams showing behavior of dissolved inorganic and organic nutrients and trace metals along salinity transect in April 2004.**

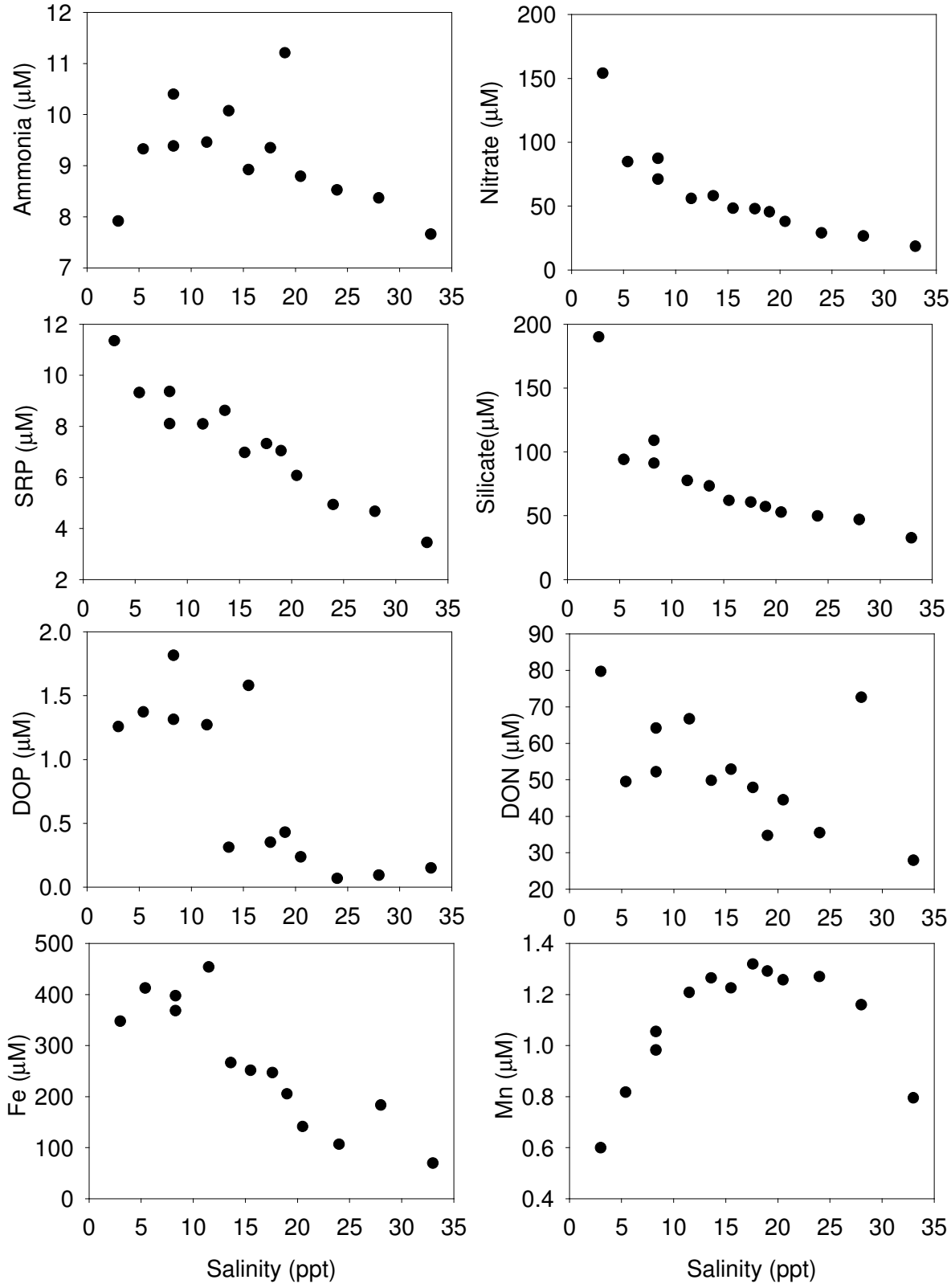


**Figure 3-11b. Mixing diagrams showing behavior of dissolved inorganic and organic nutrients and trace metals along salinity transect on October 30, 2004.**

### *3.4.4 Determination of Pore Water Advection Rates and Influence of Groundwater*

Transport rates estimated above provide an idea of the magnitude of porewater advection or seepage but do not distinguish fresh and marine sources. Using the $Cl^-$ concentrations (or salinity) in UNB surface and pore waters, a simple mass balance calculation can provide information about the relative composition of water seeping into UNB. Thus, a mixing equation between the subsurface and bay waters can be written as:

$$\left(1 - f_{fw}\right)C_{sw} + f_{fw}C_{fw} = C_{pw} \qquad \textbf{Eq. 3-7}$$

where $f_{fw}$ is the fraction of freshened pore water entering the UNB via seepage, $C_{sw}$ is the salinity in the overlying bay water column, $C_{fw}$ is the salinity of fresh pore water, and $C_{pw}$ is the salinity in the freshest intermediate mixing zone of the pore waters.

Selection of $C_{pw}$ is very important, because this term exerts the most control on the fraction of freshwater, $f_{fw}$, derived from the above mass balance. In all pore water profiles collected at the Newport study site, a fresh zone was not present in the sediments. Rearranging equation 3-7 allows calculation of the fraction of the fresh groundwater end-member associated with pore water advection:

$$f_{fw} = \frac{C_{pw} - C_{sw}}{C_{fw} - C_{sw}} \qquad \textbf{Eq. 3-8}$$

Using this approach for pore waters collected during 2004, it was estimated that fresh component of pore water seepage across the sediment-water interface ranged from 6% in March to 21% in February (Table 3-6).

However, a very important point to note here is the source of freshened waters. Since pore waters were always brackish to saline, and the lowest salinities were typically observed near the sediment-water interface, any decrease in salinity is generally assumed to be derived from the surface waters. UNB receives surface discharge from San Diego Creek as well as substantial precipitation in the spring (February to April 2004). These freshwater inputs lower the overall estuarine salinity and could be mixed into pore waters during resuspension events (Collis et al. 2006) or through bioirrigation (e.g. Worsnopp et al. 2006). Worsnopp et al. (2006) estimated the groundwater discharge to UNB was likely less than 3 mm/year. It is likely that the attributed the excess source of $^{222}Rn$ in the UNB was derived from burrowing organisms (see further discussion in next section).

**Table 3-5. Pore water $^{222}$Rn activities and physicochemical parameters from the Site 3 multisampler. $^{223,224}$Ra activities were determined by Madeline Worsnopp and Dr. Doug Hammond, USC.**

| Sampling Period | Depth | Rn-222 (dpm $L^{-1}$) ± Stdev (n=3) | DO (mg $L^{-1}$) | Cond (mS $cm^{-1}$) | Sal | Temp ($^{o}$C) | Ra-223 (dpm $m^{-3}$) | Ra-224 (dpm $m^{-3}$) | Advective Exchange Rate (cm $d^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| February 2004 | SW +30 | 7.1 ± 0.1 | 6.83 | 47.36 | 23.8 | 14.1 | 111 | 760 | |
| | 10 | 63.0 ± 11.7 | 5.68 | 28.67 | 22.1 | 15.4 | | | |
| | 30 | 719.7 ± 0 | 0.22 | 37.62 | 29.8 | 15.4 | 1847 | 19610 | 8 |
| | 50 | 596.3 ±153.4 | 0.89 | 37.77 | 29.5 | 16 | | | |
| | 80 | 366.3 ±37.1 | 0.75 | 37.25 | 29 | 16.1 | | | |
| March 2004 | SW +30 | 7.5 ±2.8 | 9.08 | 41.14 | 30.90 | 18.30 | | | |
| | 10 | 15.7 ±3.6 | 7.85 | 41.39 | 30.80 | 18.90 | | | |
| | 30 | 300.5 ±157.5 | 0.76 | 40.29 | 30.50 | 17.80 | | | 65 |
| | 50 | 269.7 ±56.2 | 1.11 | 38.77 | 29.30 | 17.80 | | | |
| | 80 | 112.7 ±3.3 | 0.81 | 38.83 | 29.40 | 17.40 | | | |
| August 2004 | -30 | 7.5 ± 2.8 | 4.76 | 49.30 | 32.10 | 22.80 | | | |
| | 10 | 27.7 ±4.0 | 3.07 | 49.14 | 32.20 | 22.60 | | | |
| | 30 | 190.7 ±15.4 | 0.27 | 46.28 | 30.10 | 22.50 | | | 25 |
| | 50 | 197.3 ±22.5 | 0.66 | 45.85 | 29.80 | 22.30 | | | |
| | 80 | 110.4 ±6.1 | 0.43 | 44.93 | 29.10 | 22.40 | | | |

**Table 3-6. Pore water transport based on $^{222}$Rn inventory, predicted flux from sediments, and $Cl^-$ mass balance of the freshwater fraction**.

| Date 2004 | $I_{pw}$ (dpm/m$^2$) | $J_{pred}$ (dpm/m$^2$/day) | $J_{diff}$ (dpm/m$^2$/day) | $J_{net}$ (dpm/m$^2$/day) | Transport Rate (cm/day) | Fresh Fraction |
|---|---|---|---|---|---|---|
| Feb | 415,200 | 74,915 | 509 | 74,407 | 11 | 21% |
| Mar | 164,475 | 29,677 | 150 | 29,527 | 4 | 6% |
| Aug | 126,125 | 22,757 | 146 | 22,611 | 3 | 7% |

## 3.5. DISCUSSION

The trophic status of an estuary refers the rate at which organic matter is supplied to it (Nixon 1995). Eutrophication is defined as an increase in the rate at which organic matter is supplied (Eyre 2002). Comparison of UNB benthic fluxes with that of a variety of other estuarine systems allows for a better understanding of UNB's trophic status and consideration of the magnitude of UNB's nutrient and metal fluxes within a broader context.

As organic matter decomposes, microbially-mediated redox reactions occur in a process referred to as "sediment diagenesis", proceeding through a well-established sequence of terminal electron acceptors: $O_2$, $NO3^-$, $MnO_2$, FeOOH, $SO_4^{2-}$, and $CO_2$. During these diagenetic processes, $O_2$ and NO3 are consumed via aerobic decomposition and denitrification, releasing TCO2, $NH_4^+$, DON, SRP, and DOP through the breakdown of organic matter (Froelich and Klinhammer 1979). SRP can also be desorbed and released from iron precipitates (Fe(III)-hydroxide-$PO_4$ complexes and/or Fe(III)-$PO_4$ minerals), commonly found in clay and silt sediments under anoxic conditions, as the Fe(III) is reduced to (Fe(II) (Roden and Edmonds 1997). $SO_4^{-2}$ reduction, the dominant process in eutrophic estuaries, further enhances SRP release from reduced Fe complexes by forming an insoluble $FeS_2$ precipitate (Rodens and Edmonds 1997). Thus the magnitude of TCO2, $NH_4^+$, SRP, Fe, and Mn efflux out of UNB sediments and the O2 and NO3 influx into UNB sediments, relative to other systems, illustrate the degree to which these diagenetic processes are resulting in the efficient decomposition of this organic matter into TCO2 and bioavailable nutrients. These processes also indicate the magnitude of organic matter and associated particulate-nutrient loading occurring within this system.

If $O_2$ consumption within surface waters and sediments outweighs $O_2$ production, the system has net respiration during that time period. Net respiration often results in net production of

TCO2 and a resultant flux of TCO2 from the sediments to the overlying water column. During the April and October sampling events, net TCO2 was positive, indicating that UNB surface waters and sediments are heterotrophic. One basic principal of sediment diagenesis is that during the aerobic decomposition of organic matter or respiration, 1.3 moles of $O_2$ consumption will drive the release of 1.0 moles of CO2 (Froelich et al. 1979). In UNB sediments, TCO2 flux was 2-3 times higher than the rate of $O_2$ uptake, indicating that other processes, mainly $SO_4^{-2}$reduction, are responsible for the majority of the TCO2 flux. The presence of hydrogen sulfide ($H_2S$) in pore waters at all sites is clear indication that $SO_4^{-2}$ reduction is occurring at these sites (Chapter 2).

Fluxes of TC02, $O_2$, nutrients, and trace metals were among the highest values reported for *in situ* benthic flux measurements and comparable to the most anthropogenically-impacted estuaries (Table 3-7). The mean TCO2 flux for UNB (107 ± 81 mmol $m^{-2}$ $d^{-1}$) is considered eutrophic (where eutrophic = 96 – 144 mmol TCO2 $m^{-2}$ $d^{-1}$, Eyre 2002). These estimates were among the higher values reported for anthropogenically-impacted enclosed bays and estuaries such as the Chesapeake Bay, San Francisco Bay, Tomales Bay, and Plum Island Sound, where mean TCO2 fluxes ranged from 24 to 167 mmol TCO2 $m^{-2}$ $d^{-1}$ (Dollar et al. 1991, Hopkinson et al 1999, Hammond et al. 1985). Similarly, mean $O_2$ demand of UNB sediments (-43 ± 20 mmol $m^{-2}$ $d^{-1}$) and mean fluxes of $NH_4^+$ and SRP (5.7 ± 2.7 mmol $NH_4^+$ and 0.36 ± 0.52 mmol SRP $m^{-2}$ $d^{-1}$) are among the highest shown in Table 3-7 and comparable to estuarine systems noted for eutrophication (Chesapeake Bay, Plum Island Sound, and the Danube Delta of the Balck Sea. Mixing diagrams of surface water $NH_4^+$, SRP, and dissolved Mn suggest that the magnitudes of these fluxes from the sediments are significant enough to affect surface water concentrations (Figure 3-10).

The high rate of TCO2, nutrient efflux, and sediment-$O_2$ demand in UNB indicate that a high rate of sediment and organic matter loading from the watershed is occurring and that this organic matter is respired very quickly in this system. The efficiency of organic matter degradation in this system can be attributed to several factors, including: 1) abundant anthropogenic supply of terminal electron acceptors (e.g. $NO_3$) that fuel oxidation-reduction reactions (e.g. denitrification) in sediments and 2) significant reworking of sediments by physical or hydrodynamic mixing, including bioturbation and bioirrigation. These factors were shown to be significant in UNB

**Table 3-7. Summary of benthic fluxes from various environments. All fluxes in mmol $m^{-2}$ $d^{-1}$ except Fe, which has units µmol $m^{-2}$ $d^{-1}$. The Monterey Bay site is in 100 m water depth and serves as an open shelf environment against which the estuarine data may be compared. An asterick (*) designates a value which is the sum of $NO_3^-$ + $NO_2^-$ fluxes.**

| Site | $O_2$ | TCO2 | SRP | DOP | $NH_4^+$ | $NO_3^-$ | DON | $Si(OH)_4$ | Mn | Fe |
|---|---|---|---|---|---|---|---|---|---|---|
| Newport Bay (This study) | -43±20 | 107±81 | 0.36 ±0.52 | -0.24 ±0.23 | 5.7 ± 2.7 | -3.0±5.3 | -11.2±9.7 | 3.2±7.5 | 0.38 ±0.35 | 30±100 |
| Los Angeles Harbor (Berelson unpublished) | -18.9± 6.3 | 39±29 | 0.33± 0.40 | | 3.9±2.9 | -0.19± 0.18 | | 3.9±1.5 | 0.25± 0.13 | -4.0±3.4 |
| San Francisco Bay (Hammond et al. 1985) | -30±7 | 24±8 | 0.10± 0.50 | | 1.1±0.1 | -0.5±0.6* | | 5.9±1.3 | | |
| Monterey Bay (Berelson et al. 2003) | -9.1±2.4 | 9.9±2.7 | 0.113± 0.073 | | 0.56± 0.24 | -0.57± 0.48 | | 7.4 | 0.010± 0.006 | 5.2±3.2 |
| Chesapeake Bay (Callendar & Hammond 1982, Cowan & Boynton 1996) | -49 | | 0.8 | | 10.2 | -2.9 - 0.2* | -4.8 - 14.4 | 7.8 | | |
| Danube and Dinestre River Mouths, Black Sea (Friedl et al. 1998) | 0 - (-33) | | 0.5 | | 2.6 - 4.4 | | | 5.2 - 6.4 | 0.18-2.3 | 500 - 2100 |
| San Quintin Bay, Baja California (Ibarra-Obando et al. 2004) | -23.4 +/- 10.7 | 31.0 +/- 22.9 | 0.114 +/- 0.140 | | 2.15 +/- 1.39 | | | | | |
| Tomales Bay (Dollar et al. 1991) | -9.37 ±9.56 | 20.7±24.4 | 0.24± 0.40 | -0.18 +/ 1.39 | 1.96 ± 2.39 | -0.01 ±0.17 | -1.22±7.63 | 3.6±3.4 | | |
| Plum Island Sound (Hopkinson et al. 1999) | -33 – (-170) | 23 - 167 | -0.25 - 1.5 | | 4.8 – 21.2 | | -10 - 15 | | | |

during this study component and the study component found in Chapter 2. The combination of these factors causes reincorporation of fresh organic matter and terminal electron acceptors into the sediments. This continuously resets the cycle of sediment diagenesis, where repetitive oxidation and reduction reactions (redox) result in the efficient decomposition of organic carbon (Aller 1998).

The fluxes of Mn and Fe from UNB sediments are comparable to those from the Danube and Dinestre River mouths (Friedl et al. 1998), which are influenced by the deposition of Fe and Mn-rich terrigenous sediment borne by these rivers. UNB metal fluxes were larger than those in Galveston Bay, where they ranged from 6 to 34 µmol Fe $m^{-2}$ $d^{-1}$)- an anthropogenically-influenced estuary in Texas (Warnken et al. 2001). Metal fluxes decreased with distance from river mouths in both UNB and Galveston Bay, further supporting the concept that sedimentation of Fe and Mn-rich material is a likely factor in the high fluxes of metals at Site 1.

*Factors Controlling Benthic Flux in UNB: Importance of Advective Transport*

When overlying surface water nutrient concentrations are in disequilibrium with pore water concentrations, a net exchange of constituents can occur through the process of diffusion (Berner 1980). Thus, when there is a difference in concentration between sediment pore waters and the overlying water column, diffusion will occur in a direction that decreases the concentration gradient. *Advective transport* refers to a collection of processes by which water is moved through the sediments and surface waters (Koike and Mukai 1983; Huettel et al. 1996), causing a physical mixing and net transfer of nutrients between pore waters and surface waters. Advection can enhance diffusion transport, often up to several orders of magnitude higher than diffusion alone. Examples of advective transport processes include physical mixing (caused by erosion, scouring, or bioturbation) and hydraulic transport through sediment caused by groundwater inputs, bioirrigation from benthic infauna, or high velocity currents from tidal forcing or storm events.

Conservative tracers such as Br and $^{137}Cs$ have been used in previous benthic-chamber studies to track the transport of solutes from chamber water to unspiked water reservoirs (Berelson et al. 1998). In a chamber well planted in sediments and closed to surface water exchange, the loss of Br from the chamber water occurs as water and/or solutes are exchanged with sediment pore water. If diffusive transport were controlling the rate of Br loss from the chamber, an incubation of 6-8 hours would change the Br spike concentration within the chamber by <10%

(Townsend, 1998). Hence, measurements of Br loss from a chamber can define the transport mechanism as solely diffusive alone, or diffusive transport enhanced by advective processes. In all chamber deployments, Br was diluted by 40% or more, indicating very high rates of exchange with pore waters. Similar tracer loss rates have been measured in San Francisco Bay (Berelson, unpublished data). Br loss rates were also comparable among the April and October 2005 field season, suggesting that the advective process controlling exchange is fairly constant. Although the number of chamber deployments is too small to determine accurate statistics, the trends in Br loss among sites suggest that advective transport may be greater at Sites 2 and 3 than at Site 1.

Two additional lines of evidence corroborate the importance of advective transport in controlling benthic fluxes in UNB. Pore water advection estimated with multisamplers at Site 3 showed a high rate of advection exchange, with rates ranging from 3 - 11 cm $d^{-1}$. Worsnopp et al. (2004, 2006) used $^{222}Rn$ and $^{233,\ 234}Ra$ to determine rates and major processes responsible for advective transport in UNB synoptically with the chamber work conducted in this study. The rate at which the flux of $^{222}Rn$ in a benthic chamber is enhanced over the flux predicted by modeling sediment $^{226}Ra$ distributions suggests that advective transport enhances solute fluxes by a factor of 3-5 times. Evidence from previous studies supports the importance of advective relative to diffusive transport. Callender and Hammond (1982) found that the rates of nutrient fluxes measured *in situ* using benthic chambers were a factor of 1-10 times higher than rates driven by potential diffusive flux alone, and that these rate increases were attributed to irrigation of sediments by macrofauna.

Although the primary process responsible for this advective transport has not been definitively determined, evidence points to bioirrigation and/or tidal pumping, rather than groundwater input, as dominant mechanisms. No freshening of down-core pore waters was observed in the mulitisampler at Site 3, indicating that groundwater is not a major factor in controlling advection at this location. This observation is supported by Worsnopp et al. (2004, 2006), which found that groundwater inputs are likely to contribute < 3 mm $yr^{-1}$ – a rate much less than that of total advective flux estimated using multisampler technique at Site 3 (3 - 11 cm $d^{-1}$). Bioirrigation has been shown in previous sites to be a major controlling factor in recirculating estuarine waters through the sediments. Physical mechanisms for pumping water into and out of sediments usually have depth ranges less than 20 to 30 cm due to the increased friction of the pore networks. Huettel et al. (1996) found that currents in a wave tank produced pore water

exchange down to 30 cm for 3-cm high ripple mounds. In contrast, sediment ventilation by burrowing shrimp, while generally episodic, has been shown to create pumping rates ranging from 340 to 2100 $cm^{3} \cdot s^{-1}$ through their tubes (Koike and Mukai 1983), with burrows as deep as 50 to 250 cm in the eastern coastal United States (Griffis and Suchanek, 1991). In estuaries such as UNB, with sediments containing high clay/silt content and low permeability, tidal pumping may be less important than bioirrigation.

*Factors Controlling Spatial Gradients in Benthic Flux*

SRP, Fe and Mn fluxes were higher at Site 1 versus than Sites 2 and 3, supporting the assumption of San Diego Creek as the source of particulate trace-metal and P loading into UNB (Friedl et al. 1998, Meybeck 1982, Sutula et al. 2003). Notably, site differences in $O_2$ uptake, as well as TCO2 and $NH_4^+$ fluxes were unexpected based on spatial gradients in particulate matter deposition, bulk sediment characteristics, and pore water nutrient concentrations. The magnitude of these fluxes were higher at Sites 2 and 3 – sites which had lower wet season sediment deposition, lower organic carbon and nutrient content, and generally lower pore water nutrient concentrations than Site 1.

Several factors controlling diagenetic processes may differ among the sites and may be responsible for this trend. First, based on visual observations of sediments at the three sites, it was clear that Sites 2 and 3 support a greater density of benthic infauna: tube worms were observed at Site 3, while tube worms as well as filter feeders were observed at Site 2 (Sutula, personal observation; Chapter 2). As suggested in the previous section, bioirrigation by benthic infauna in this estuary can increase the rate of benthic flux by as much as 3-5 times the rate of diffusion alone. Also, as noted in Chapter 2 pore water nutrients were lower at Site 2 relative to Sites 1 and 3, possibly due to the effect of greater observed density of infauna at this site. Site 1 sediments appeared to have lower infaunal densities and were dominated by stress-tolerant polychaete and oligochaete worms. Sediment characteristics indicate that Site 1 is generally a more hostile environment to infauna and that bioirrigation is not likely to be as an important factor for diagenetic processes at this site. Previous studies have noted that O2 consumption and TCO2 production can be greatly increased by benthic infauna (Hopkinson and Smith 2004). Thus in spite of greater pore water $NH_4^+$ concentrations; higher SOC, SN and SP content; and higher sediment-deposition rates at Site 1; the influence of benthic infauna may be driving higher than expected benthic nutrient fluxes at Sites 2 and 3.

Another factor that can control the fluxes of $O_2$, TCO2, and nutrients is the presence of algae – either macroalgae or benthic diatoms. The presence of benthic microalgae have been shown to mediate dissolved organic and inorganic nutrient fluxes from sediments in estuaries (Tyler et al. 2003, Sundback et al. 2000). In the case of nutrients, benthic algae can modify biogeochemical gradients and thereby reduce the actual flux of nutrients across the sediment water interface. If present within the benthic chamber, macroalgae can also efficiently strip the water column of dissolved inorganic nutrients – thus altering the estimated flux within the chamber. $O_2$ fluxes from April 2004 samplings showed higher $O_2$ consumption for night incubations than day incubations at Sites 1 and 3, indicating that autotrophic $O_2$ production (from algae) may be mitigating net flux during the daytime. Experiments to stimulate autotrophic response in sediments obtained in April showed that shining light directly on sediments greatly increased photosynthetic activity and O2 production, particularly for Sites 2 and 3 (W. Ziebis, unpublished data). However, expected decreases in $O_2$ uptake coupled with decreased TCO2 production during the day did not occur in the April 2004 chamber studies. Thus, while benthic microalgae may not have been present, it is not likely that this condition had a significant impact on benthic fluxes during this time period. It was presumed suspect that because of high turbidity and recent sediment deposition from rainfall occurring within 10 days of the sampling periods, that autotrophic impacts on nutrient $O_2$ and TCO2 were minimal. It is possible, however, that autotrophic impacts play an important role during other parts of the year not characterized by these two sampling events.

Another factor that may contribute to differences in flux values between sites within UNB is the spatial pattern of $O_2$ concentration within bay bottom waters. Measurements from this study indicate that the upper basin at the mouth of San Diego Creek (Site 1) had consistently had lower bottom water $O_2$ concentrations. The likely explanation for this observation is that the residence time of water in the upper basin of UNB is longer than residence time in the lower bay, with benthic respiration lowering the $O_2$ concentration in the upper basin (ACOE 2000). Particles that travel to UNB from the San Diego Creek watershed are likely subjected to oxic conditions given the shallow depth of the creek. However, upon entering UNB, these particles are subject to a lower redox environment and the transformation of SRP adsorped to particles and freely-dissolved into pore waters may occur. The consistently high $SO_4^{-2}$reduction occurring at Site 1, as evidenced by high $S^{-2}$ in pore waters, indicates the low redox state of these sediments and also may be responsible for high concentrations of SRP in pore waters at this site. Roden and Edmonds (1997) found that direct microbial Fe(III) reduction solubilized

only 3-25% of initial sediment-bound P during sulfate-free sediment incubation experiments, and that much of the $PO_4^{-3}$ released was re-captured and loosely bound by solid-phase reduced iron compounds (Fe(II)-hydroxide-$PO_4$ complexes and/or Fe(II)-$PO_4$ minerals). During $SO_4^{-2}$ reduction, Fe (II) is converted to iron-sulfides via reaction with $S^{-2}$ produced by $SO_4^{-2}$reduction (Roden and Edmonds 1997). Because iron-sulfides cannot bind SRP, approximately 2-5 times the amount of P is released to pore waters and overlying surface waters. Thus, it is likely that the predominance of $SO_4^{-2}$ reduction at this site, coupled with high rates of organic and inorganic P loading to sediments, result in Site 1 having the highest magnitude of SRP fluxes of the three sites.

*Factors Affecting Temporal Variability in Benthic Nutrient Fluxes*

A number of factors have been cited as important in determining the temporal variability in benthic nutrient fluxes (Cowan and Boynton 1996). These factors include temperature, salinity, light, variability in organic-matter loading, surface-water nutrient concentrations, $O_2$concentrations, biomass, productivity of primary producer and benthic infaunal communities, sediment-bulk characteristics, variability in estuarine hydrodynamics, sediment deposition, and resuspension. To adequately constrain variability in benthic flux rates, a great number of deployments measured throughout the year would be necessary—but cost-prohibitive. Thus it is important to interpret flux data in terms of the conditions captured during the chamber deployments, and not to over-interpret how applicable these conditions are to the estuary during other times of the year not measured.

While the original intention of the two sampling events was to characterize fluxes during the wet and dry seasons, the April and October 2004 sampling events were characterized more by the time lapse from an antecedent storm event (10 days versus 1 day). Data from the October chamber studies should be interpreted carefully given that fluxes measured during this time period represent transitory and very unusual conditions. Because a sizeable storm event occurred one day prior to the beginning of storm-chamber deployment, it is conceivable that chambers were capturing water in contact with sediments that had not fully equilibrated with ambient conditions. A chamber placed over sediment that has been recently eroded will yield strongly time-dependent fluxes (Will Berelson, experiments in Los Angeles Harbor, unpublished data). Such a condition would only be assessed if fluxes at a given site were determined on a time-series basis; this study obtained no more than two consecutive measurements at any given site.

The difference between April and October benthic fluxes was more dramatic than between-site differences. Oxygen-uptake rates and TCO2 fluxes were lower in October than April. $P0_4^{-3}$ and $Si(OH)_4$ fluxes were negative during October, but positive during April. Nitrate uptake by sediments was higher in October than in April. DOP fluxes were, on average, larger and more negative in October compared to April. Average Mn and Fe fluxes were larger in October than April, however greater uncertainties were noted.

One hypothesis that could explain the difference in the magnitude of fluxes between the two sampling events is that October fluxes characterize a recently disturbed sediment regime. Physical mixing of sediments could, under this scenario, lower $O_2$ uptake and TCO2 production, in addition to limiting the effects of bioirrigation. In October, primary-producer and benthic-infaunal communities were clearly disturbed. Unlike in April, experiments in which light was shined on UNB sediments conducted in October failed to stimulate photosynthetic activity and an increase in pore water DO concentrations (W. Ziebsis, unpublished data). Pore water nutrient concentrations were much lower in November than in April 2004—possibly due to advective flushing and dilution with surface water or by precipitation (SRP) during redoxidation of Fe and $S^{-2}$. Studies of storm-driven advective flushing of pore water nutrients and trace metals have been documented in several estuarine systems (Kozlowski et al. 2003, Giffen and Corbett 2003). Kozlowski et al. (2003) found that trace metal pore water concentrations in Lake Ponchartrain, Louisiana, typically took approximately a week to reach pre-storm levels. At the same time, nutrient concentrations (particularly $NO_3^-$ and SRP) in the days following the storm event increased due to anthropogenic inputs from the watershed. Thus, diffusive transport processes may be more important in controlling the direction and magnitude of benthic fluxes in periods just following storm events. This concept is supported by diffusive fluxes predicted from pore water profiles in November 2004, which in most cases correctly predicted the direction of the flux of dissolved inorganic and organic nutrients at Sites 1 and 2.

Benthic fluxes are also known to vary on time scales of days to hours. In April 2004, chamber deployments during the dayt and at night were made in an attempt to capture this variability. Chamber deployments during the day captured benthic fluxes while the sediments were exposed to light. However, although the lid of each benthic chamber is made of clear acrylic the walls of the chamber are opaque and the amount of light penetrating each chamber was not measured. The question of the opacity of these particular chambers was addressed in a paper

by Nicholson et al (1999) in which fluxes determined using these chambers were compared to fluxes determined using chambers made entirely of clear acrylic. Results showed that there was no significant difference in flux values. The turbidity of the water within the chamber inhibits light penetration to the benthos, thus diminishing any effects from autotrophic organisms; it was noted that during both field seasons, water turbidity was high.

Phosphate fluxes (dissolved inorganic phosphorus (DIP), DOP or DIP+DOP) show no systematic relationship to day or night, suggesting that autotrophy during the day and heterotrophy at night may not be occurring or may not be significant with respect to overall net heterotrophy. $Si(OH)_4$ flux shows some trend toward lower effluxes during the day compared with the night, except at Site 1. This would be predicted if benthic diatoms were taking up silica during daylight hours. However, $NO_3^-$ fluxes suggest higher rates of denitrification during the day and lower net denitrification at night. Again, Site 1 was the exception. At all three sites sampled during the April field season, the Mn flux was smaller, or negative, during the day and larger and/or positive during the night. Iron flux followed this pattern as well, except for Site 1.

The pattern of fluxes during the day and at night were intriguing, but not easily interpreted. The sensitivity of Mn and Fe fluxes to day versus night does suggest lower fluxes during the daytime. It is possible that benthic photosynthesis was a source of $O_2$ at or very near the sediment-water interface and the oxidation of Mn and Fe may provide the sink for the soluble, redox-sensitive metals. However, if benthic photosynthesis were occurring, the net effect of this $O_2$ production was not apparent in oxygen-flux determinations. In April, in spite of deploying four chambers for day incubations, chamber $O_2$ uptake always indicated net consumption. Notably, at Site 2, where replicate deployments allowed statistical comparison, the oxygen-uptake rates during both day and night deployments were not significantly different ($p\text{-value}_{\alpha=0.05} = 0.87$). At Sites 1 and 3, daytime $O_2$ consumption was less than nighttime consumption, but TCO2 production did not follow the same trend. Further, it is likely that $O_2$ production near the sediment-water interface would enhance the rate of nitrification and the rate of $NO_3^-$ flux out of sediments, however this increase was not observed. It is possible that the redox sensitivity of trace metals and nitrogen species could be decoupled if the sedimentary region generating or consuming $NO_3^-$ were spatially separated from the region where trace metal recycling occur.

## 3.6 REFERENCES

ACOE 2000. Upper Newport Bay Ecosystem Feasibility Restoration Study Final Report. U.S. Army Corps of Engineers, Los Angeles District. September 2000.

Aller, R. 1998. Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. Marine Chemistry 61: 143-155

APHA. 1992. Standard methods for the examination of water and wastewater. 18th Edition. American Public Health Association.

Berelson, W. M. and D. E. Hammond (1986). The calibration of a new free vehicle benthic flux chamber for use in the deep sea, Deep Sea Research, v. 33, 1439-1454.

Berelson, W. M., D. E. Hammond and G. Cutter (1990) In situ measurements of calcium carbonate dissolution in deep-sea sediments. Geochimica. Cosmochimica Acta, v. 54, 3013-3020.

Berelson, W., D. Heggie, A. Longmore, T. Kilgore, G. Nicholson and G. Skyring (1998). Benthic nutrient recycling in Port Phillip Bay, Australia. Estuarine, Coastal and Shelf Science, v. 46, 917-934.

Berelson, W., T. Townsend, D. Heggie, P. Ford, A. Longmore, G. Skyring, T. Kilgore and G. Nicholson (1999). Modeling bioirrigation rates in sediments of Port Phillip Bay. Marine and Freshwater Research., v. 50, 573-579.

Berelson, W., K. Johnson, K. Coale and H-C. Li (2002) Organic matter diagenesis in the sediments of the San Pedro Shelf along a transect affected by sewage effluent. Continental Shelf Research, v. 22, 1101-1115.

Berelson, W., J.McManus, K. Coale, K. Johnson, D. Burdige, T. Kilgore, D. Colodner, F. Chavez, R. Kudela and J. Boucher (2003) A time series of benthic flux measurements from Monterey Bay, CA. Continental Shelf Research, 23, 457-481.

Berner, R.A., 1980. Early Diagenesis: A Theoretical Approach: Princeton, NJ (Princeton Univ. Press).

Burnett, W. C., J. Chanton, J. Christoff, E. Kontar, S. Krupa, M. Lambert, W. Moore, D. O'Rourke, R. Paulsen, C. Smith, L. Smith and M. Taniguchi (2002). "Assessing methodologies for measuring groundwater discharge to the ocean." EOS 83: 117-123.

Cable, J., W. Burnett, J. Chanton, and G. Weatherly. 1996. Estimating ground water discharge into the northeastern Gulf of Mexico using radon-222. Earth and Planetary Science Letters 144: 591-604.

Cai, W-J. and Clare Reimers (1995) Benthic oxygen flux, bottom water oxygen concentrations and core top organic carbon content in the deep NE Pacific Ocean. Deep-Sea Research, 42, 1681-1699.

Callender, E. and D. Hammond (1982) Nutrient exchange across the sediment-water interface in the Potamac River Estuary. Esturarine, Coastal and Shelf Science, 15, 395-413.

Clesceri, L., Greenberg, A., Trussell, R., Franson, M. 1989. *Standard methods for the examination of water and wastewater*: Washington DC: American Public Health Association, American Water Works Association, Water Pollution Control Federation.

Collis, H., Cable, J.E., and Sutula, M.A., in press, Evaluating sediment depositional patterns using $^{7}$Be in Upper Newport Estuary, California, *Hydrological Science and Technology, Proc. American Institute of Hydrology*

Corbett, R., Dillon, K., Burnett, W., Chanton, J. 2000. Estimating the groundwater contribution into Florida Bay via natural tracers, $^{222}$Rn and $CH_4$, *Limnology and Oceanography* 45: 1546-1557.

Cowan J.W. and W.R. Boynton. !996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors and ecological significance. Estuaries 19 (3): 562-580

Craig, H. 1969. Abyssal carbon and radiocarbon in the Pacific. Journal of Geophysical Research, 74(23): 5491-5506.

Dollar S.J., S.V. Smith, S.M. Vink, S. Obreski, and J.T. Hollibaugh. 1991. Annual cycle of benthic nutrient fluxes in Tomales Bay, California and contribution of benthos to total ecosystem metabolism. Marine Ecology Progress Series, 79 (1-2): 115-125

Eyre, B. and A.J.P. Ferguson 2002. Sediment biogeochemical indicators for defining sustainable nutrient loads to coastal ecosystems, Proceedings of Coast to Coast 2002 - "Source to Sea", Tweed Heads, pp. 101-104.

Fisher, T.R., J.D. Hagy, and E. Rochelle-Newall. 1998. Dissolved and particulate organic carbon in Chesapeake Bay. Estuaries 21:215–229

Friedl G., C. Dinkel C, and B.Wehrli . 1998. Benthic fluxes of nutrients in the northwestern Black Sea. Marine Chemistry 62 (1-2): 77-88

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta, 43:1075-1090.

Giffin, D. and Corbett, D.R., 2003, Evaluation of sediment dynamics in coastal systems via short-lived radioisotopes, Journal of Marine Systems 42: 83-96.

Giordani, P., D. E. Hammond, W. M. Berelson, R. Poletti, G. Montanari, A. Milandri, M. Frignani, L. Langone, M. Ravaioli and E. Rabbi (1992) Benthic fluxes and nutrient budgets for sediments in the Northern Adriatic Sea: Burial and recycling efficiencies. Science of the Total Environment (suppl.). pp. 251-269.

Griffis, R. and Suchanek, T., 1991, A model of burrow architecture and trophic modes in thalassinidean shrimp (Decapoda: Thalassinidea), Marine Ecology Progress Series 79: 171-183

Hammond, D. E., C. Fuller, D. Harmon, B. Hartman, M. Korosec, L. Miller, R. Rea, S. Warren, W. Berelson and S. Hager (1985) Benthic fluxes in San Francisco Bay. Hydrobiologia, 129, 69-90.

Hammond, D. E., H. J. Simpson, and G. Mathieu. 1977. $^{222}$Radon distribution and transport across the sediment-water interface in the Hudson River estuary. Journal of Geophysical Research **82:** 3913-3920.

Hopkinson, C. S. J., A. E. Giblin, J. Tucker, and R. H. Garritt. 1999. Benthic metabolism and nutrient cycling along an estuarine salinity gradient. Estuaries 22(4): 863-881.

Hopkinson, Jr., C.S. and E.M. Smith (2004). Estuarine respiration: An overview of benthic, pelagic, and whole system respiration. *In:* P. del Giorgio and P.J. Williams. Respiration of Aquatic Ecosystems of the World, Academic Press, NY. 328 pp, pp. 122-146, 2004 WHOI-R-04-005

Huettel, M., W. Ziebis and S. Forster (1996) Flow-induced uptake of particulate matter in permeable sediments. Limnology and Oceanography, 41, 309-322.

Ibarra-Obando SE, S.V. Smith, T. Poumian-Tapia, V. Camacho-Ibar, J.D. Carriquiry, and H. Montes-Hugo. Benthic metabolism in San Quintin Bay, Baja California, Mexico. Marine Ecology Progress Series 283: 99-112 2004

Jahnke, R., J. R. Nelson, R. L. Marinelli and J. E. Eckman (2000) Benthic flux of biogenic elements on the SE US continental shelf. Contintential Shelf Research, 20, 109-127.

Johnson, K.M., A.E. King, and J. McN. Sieburth (1985): Coulometric DIC analyses for marine studies: An introduction. Marine Chemistry, 16, 61-82.

Johnson, K.M., P.J. Williams, L. Brandstrom, and J. McN. Sieburth (1987): Coulometric total carbon analysis for marine studies: Automation and calibration. Marine Chemistry, 21, 117-133.

Koike, I. and Mukai, H., 1983, Oxygen and inorganic nitrogen contents and fluxes in burrows of the shrimps Callianassa japonica and Upogebia major, Marine Ecology Progress Series 12: 185-190.

Kozlowski, G. J.; B.A. McKee; R.T. Powell and D.A. Duncan, 2003. Rates of redox driven processes in a shallow estuarine environment. Estuarine Research Federation Conference Abstracts, New Orleans Louisiana September 2003.

Martin, J., Cable, J., Swarzenski, P., and Lindenberg, M., 2004, Enhanced submarine groundwater discharge from mixing of pore water and estuarine water, Ground Water (special Oceans issue) 42: 1001-1010.

Martin, J. B., K. M. Hartl, D. R. Corbett, P. W. Swarzenski and J. E. Cable (2003). A multilevel pore water sampler for permeable sediments. Journal of Sedimentary Research 73: 128-132.

McNichol, A. P., C. Lee and E. R. M. Druffel (1988) Carbon cycling in coastal sediments: A quantitative estimate of the remineralization of organic carbon in the sediments of Buzzards Bay, MA. Geochimica Cosmochimica Acta, 52, 531-1543.

Meybeck, M. 1982. Carbon, nitrogen, and phosphorus transport by the world rivers. American Journal of Science 282: 824-834.

Meyer, G. A. and P. N. Keliher. 1992. An overview of analysis by inductively coupled plasma-atomic emission spectrometry. p. 473-505. In: A. Montaser and D.W. Golightly (ed.) *Inductively coupled plasmas in analytical atomic spectrometry*. VCH Publishers Inc. New York, NY.

Milner, H. B. 1962. Sedimentary Petrography. New York, MacMillan Company.

Nichholson, G. J., A. R. Longmore and W. M. Berelson (1999) Nutrient fluxes measured by two types of benthic chamber. Marine and Freshwater Research, 50, 567-572.

Peng, T.-H., Takahashi, T., Broecker, W. 1974. Surface radon measurements in the north Pacific station Papa, Journal of Geophysical Research 79: 1772-1780.

Roden, E. E. and J. W. Edmonds 1997. Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction versus iron-sulfide formation. Archives fur Hydrobiologie 139(3): 347-378.

Sah, R. N. and R. O. Miller. 1992. Spontaneous reaction for acid dissolution of biological tissues in closed vessels. Analytical Chemistry. 64:230-233.

Smethie, W., C. Nittrouer, and R. Self. 1981. The use of radon-222 as a tracer of sediment irrigation and mixing on the Washington continental shelf, *Marine Geology* 42: 173-200.

Solorzano, l. and J. H. Sharp 1980 "Determination of total dissolved phosphorus and particulate phosphorus in natural waters." Limnology and Oceanography 25: 745-758.

Sundback K, Miles A, and E. Goransson. (2000). Nitrogen fluxes, denitrification and the role of microphytobenthos in microtidal shallow-water sediments: an annual study. Marine Ecology Progress Series, 200, 59-76

Sutula M, T.S. Bianchi, B.A. McKee. Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico. Limnology and Oceanography 49 (6): 2223-2235

Townsend, T. (1998) Numerical simulations of tracer loss from benthic chambers: An investigation of bio-irrigation rates and patterns in marine sediments. MS Thesis, USC, 173 pp.

Tyler AC, McGlathery KJ, and IC Anderson. 2003. Benthic algae control sediment-water column fluxes of organic and inorganic nitrogen compounds in a temperate lagoon. Limnology and Oceanography 48(6): 2125-2137

Ullman, W. and Aller, R. 1981. Diffusion coefficients in nearshore marine sediments, *Limnology and Oceanography* 27(3): 552-556.

Warnken, K. W., G. A. Gill, L. L. Griffin and P. H. Santschi (2001) Sediment-water exchange of Mn, Fe, Ni and Zn in Galveston Bay, Texas. Marine Chemistry, 73, 215-231.

Worsnopp, M., Hammond, D.E., Cable, J.E., Colbert, S., Berelson, W., and Sutula, M. 2006, Using Ra and Rn to Quantify Solute Exchange Across System Boundaries in an Estuary: Evaluating Irrigation, Groundwater Flow, and Tidal Pumping, AGU/ASLO Ocean Sciences Meeting, Honolulu, Hawaii, 20-24 Feb 2006.

Worsnopp, M.B., Hammond, D.E., and Cable, J.E. (2004) Radium and radon as tracers of ground water flow into Upper Newport Bay, CA, EOS Transactions, American Geophysical Union, 85 (47), Fall Meet. Suppl., Abstract H21B-1013, San Francisco, CA, 13-17 December 2004.

# 4 CONTROLS OF $O_2$, NUTRIENT CONCENTRATIONS AND MACROALGAE ON SEDIMENT NUTRIENT FLUX IN A CONTROLLED LABORATORY SETTING

Krista Kamer, Martha Sutula, and Emily Briscoe

## 4.1 Abstract

In this component of the study, a laboratory experiment was conducted using intact sediment cores to examine the interaction of varying levels of DON and DOP concentrations, water column $O_2$ availability, and the presence or absence of the macroalga *E. intestinalis* on the magnitude and direction of sediment nutrient flux.

This component of the study found that the gradient in nutrient concentration between surface waters and sediment pore waters exerted a major control on the magnitude and direction of benthic flux in batch-incubated sediments. $NO_3^-$ and SRP fluxes into sediments increased in a linear proportion to increases in overlying water concentrations. Flux of $NH_4^+$ into the sediments also increased in response to higher overlying water column concentrations, but the behavior was not linear. Rates of flux measured in this experiment were of the same order of magnitude as those measured *in situ* with benthic chambers, resulting in estimates that were 1-2 orders of magnitude higher than those predicted by Ficke's law of diffusion (Chapter 3). In a laboratory setting, where physical mixing processes such as tidal pumping, scouring by strong currents, and groundwater influx were largely absent. It is likely that bioirrigation from benthic infauna was the major advective transport process affecting flux.

$O_2$ availability in surface waters affected the flux of dissolved inorganic nutrients in several different ways. First, hypoxia promoted $NO_3^-$ flux into sediments and SRP flux out of sediments. Increased $NO_3^-$ flux was most likely due to enhanced denitrification ($NO_3^-$ conversion to $N_2$ gas) in pore waters. Second, oxic conditions promoted $NH_4^+$ flux into sediments, although this trend was highly variable and not significant. Under oxic conditions, nitrifying bacteria transform $NH_4^+$ to $NO_3^-$, thus reducing the concentration of $NH_4^+$ in pore waters of surficial sediments. In sediments that have low available $NO_3^-$ in surface waters but maintain an oxic surface layer, coupled nitrification-denitrification is enhanced, providing a pathway for permanent loss of N from the estuary. Third, increased SRP flux under hypoxic conditions was due to desorption of P from Fe(III) hydroxyoxides precipates when dissolved during Fe reduction in hypoxic

sediments. Released SRP is further enhanced by $SO_4^{-2}$ reduction as sediments become completely anoxic.

This study component also found that green macroalgae, such as *E. intestinalis*, known for its capacity to quickly and dramatically deplete a water column of inorganic nutrients, can potentially affect benthic nutrient flux and nutrient cycling in several ways. First, macroalgal uptake of dissolved inorganic nitrogen can reduce the importance of denitrification as a permanent mechanism for N removal from the estuary. The presence of *E. intestinalis* reduced the amount of $NO_3^-$ and $NH_4^+$ available in the water column that might diffuse into sediments, and be permanently lost through coupled nitrification-denitrification to $N_2$ gas. However, once in macroalgal tissue, the nutrients can follow several pathways that would recycle them within the system. Through these different pathways, uptake of nutrients by macroalgae rather than by sediments can lead to increased recycling and retention of N within the system. Second, the flux of nutrient species such as SRP or $NH_4^+$, which typically have high pore water concentrations relative to surface waters (Chapter 2), would be enhanced by the presence of macroalgae. In this experiment, nutrient uptake by *E. intestinalis* prevented accumulation of inorganic nutrients in the water column, thus enhancing the concentration gradient and diffusive transport from pore waters to surface waters.

Finally, this component found that the rates of inorganic nutrient flux measured in this study were up to two orders of magnitude higher than rates measured in other estuarine studies, supporting evidence from Chapters 2 and 3 that identify UNB as a eutrophic system. Also, the findings of this study have significant relevance to nutrient cycling in natural estuarine systems, particularly those systems already suffering from eutrophication. Increases in nutrient loads resulting in elevated water column concentrations may be retained within the system temporarily via flux into the sediments and subsequent storage. When water-column nutrient concentrations decrease, often occuring during the summer when nutrient inputs are low and primary productivity is high, flux from sediments may be promoted. This regeneration of overlying water column nutrients has the potential to significantly enhance primary production and extend the duration of an algal bloom.

## 4.2 Introduction

Rates of sediment-nutrient flux in estuaries can vary as a function of factors including, but not limited to, water column nutrient concentrations, $O_2$ availability, and primary producer

community. The nutrient concentration gradient between the water column and sediment pore waters determines the rate of diffusive flux, an important component of benthic flux (Vanderborght and Billen 1975, Boynton and Kemp 1985, Rizzo and Christian 1996, Trimmer et al. 1998). The presence of $O_2$ at the sediment-water interface affects the rate of biogeochemical processes occurring there and can either enhance or reduce nutrient flux (Sundback and Graneli 1988). The presence of microphytobenthos often reduces flux to the overlying water column when illuminated (Rizzo 1990, Rysgaard et al. 1995, Sundback et al. 2000). In comparison to microalgae, the role of macroalgae in benthic flux has been relatively uninvestigated. In particular, high nutrient uptake rates of macroalgae (Harlin 1978, O'Brien and Wheeler 1987, Fujita 1985) can deplete the water column of nutrients, thus maintaining the concentration gradient and promoting nutrient efflux. The mechanisms by which varying nutrient and water column $O_2$ concentration can alter sediment nutrient flux have been fairly well studied in the eastern United States and western Europe (e.g. Boynton et al. 1980, Seitzinger et al. 1991, Rysgaard et al. 1995, Trimmer et al. 2000). Rates derived from these studies could be used for dynamic simulation water quality models may not be applicable to southern California estuaries, where with Mediterranean climate, physical characteristics, and predominance of green macroalgae, factors that control sediment nutrient flux may be very different from from those found in larger estuaries in temperate climates.

The objective of this experiment was to examine the interaction of varying levels of DIN and DIP concentrations, water-column $O_2$availability, and the presence or absence of the macroalgae *E. intestinalis* with respect to the magnitude and direction of sediment nutrient flux. The ultimate purpose in conducting this experiment was to produce data that can serve to develop the sediment exchange component of the UNB water quality model.

## 4.3 Methods

### *4.3.1 Experimental Methods*

In this study, sediment nutrient flux was estimated with respect to varying water column concentrations of dissolved inorganic N and P, $O_2$, and the presence or absence of macroalgae (*E. intestinalis*). Three levels of nutrient availability (ambient or low), medium and high) were fully crossed with two levels of $O_2$ availability (oxic and hypoxic). The third factor, the presence or absence of macroalgae, was fully crossed with nutrients within the oxic treatments, for a total of 9 experimental treatments (Table 4-1). Regrettably, limited resources prevented the full crossing of macroalgae with $O_2$ availability. Thus, this component effectively tested only two

different hypotheses with one experimental design: interactions of nutrient concentration and $O_2$ availability on nutrient flux, and interactions of nutrient concentrations and macroalgae on nutrient flux.

**Table 4-1. Nine experimental treatment combinations. Nutrient-level designations are as follows : Low Nutrient ($N_L$), Medium Nutrient ($N_M$), High Nutrient ($N_H$), Low Oxygen ($O_L$), High Oxygen ($O_H$), With Algae (+Algae), Without Algae (-Algae)**

| | Nutrient Level | | |
|---|---|---|---|
| $O_2$ Availability and Macroalgae | $N_L$, $O_L$, -Algae | $N_M$, $O_L$, -Algae | $N_H$, $O_L$, -Algae |
| | $N_L$, $O_H$, -Algae | $N_M$, $O_H$, -Algae | $N_H$, $O_H$, -Algae |
| | $N_L$, $O_H$, +Algae | $N_M$, $O_H$, +Algae | $N_H$, $O_H$, +Algae |

*E. intestinalis* was collected from UNB on July 7, 2005, 10 days prior to the beginning of the experiment. Algae were transported to SCCWRP where they were maintained according to batch culture in order to expose each batch to the same nutrient levels, thus equalizing internal nutrient stores (Fong et al. 1994). Algae were placed in a shallow pan filled with low-nutrient seawater. The pan was covered with window screening to reduce incident light (2,200–2,500 µmoles $m^{-2}$ s at mid-day) by ~30% to simulate coastal levels (1,405–1,956 µmoles $m^{-2}$ s, Arnold and Murray 1980) and placed in a temperature controlled water bath (20 ± 2°C). The algal cultures were mixed daily and temperature, as well as salinity, was checked. Salinity was maintained between 25 and 30 PSU through the addition of DIW when salinity exceeded 30 PSU. After 10 days, tissue N levels were 2.22 ± 0.08 % dry wt (mean ± SE) and P levels were 0.18 ± 0.01 % dry wt.

On the morning of the experiment (July 17, 2005), 40 sediment cores (10.16 cm internal diameter, 10 cm depth of sediment, 1 cm overyling water) and water were collected from UNB at low tide at approximately 7:00 am from Site 2 (Figure 1-1). All cores were collected from areas without macroalgal cover at the same elevation over a horizontal distance of ~50 m in four blocks of 10 to account for any spatial gradients. Cores were wrapped with black electrical tape from the bottom up to the height of the sediment-water interface, then placed in the dark for transportation back to SCCWRP. Immediately upon return to SCCWRP, the sediment cores were placed in an outdoor water bath to control temperature (20 ± 2°C) and covered with a layer of window screening to reduce incident light. One sediment core from every collection block

was vertically sectioned in 1-cm intervals down to 3 cm for analysis of initial characteristics. Each section was wet weighed, dried at 60°C to constant weight, re-weighed to calculate percent solid, and analyzed for percent organic carbon, organic nitrogen and total phosphorus. The results of these analyses are presented in Table 4-2. Means with SE are presented, as there were no apparent spatial gradients over the area from which the cores were collected.

**Table 4-2. Initial sediment characteristics. Means with SE are presented as no spatial gradients were apparent.**

| Depth | % Solids | TOC | TON | TP |
|---|---|---|---|---|
| | | (% dry weight) | | |
| 0-1 | 76.32 ± 7.13 | 1.241 ± 0.171 | 0.102 ± 0.017 | 0.0575 ± 0.003 |
| 1-2 | 46.37 ± 6.07 | 1.616 ± 0.130 | 0.157 ± 0.023 | 0.0625 ± 0.005 |
| 2-3 | 56.69 ± 8.50 | 1.243 ± 0.184 | 0.122 ± 0.025 | 0.0625 ± 0.006 |

The seawater was divided into six aliquots to make solutions of different nutrient levels. Solutions were mixed in large, pre-cleaned plastic containers and kept in the dark at 4°C. Inorganic salts of $NO_3^-$, $NH_4^+$, and $PO_4^{-3}$ were added to the seawater to increase $NO_3^-$ concentrations by 50 µM and 250 µM in the "Medium" and "High" solutions, respectively, with target nutrient ratios of 10:1 $NO_3^-$and $NH_4^+$, and 16:1 $NO_3^-$+ $NH_4^+$ and SRP; no nutrients were added to the solutions designated as "Ambient". These concentrations and ratios are representative of conditions in southern and central California estuaries (Caffrey et al. 2002, Kennison et al. 2003, Boyle et al. 2004). Actual nutrient concentrations are shown in Table 4-3. Solutions designated as "Oxic" were bubbled with compressed air and solutions designated as "Hypoxic" were bubbled with nitrogen gas. Each solution was bubbled for three hours prior to the experiment.

Experimental treatments were assigned to cores using a randomized block design: each of the nine experimental treatments contained one randomly chosen sediment core from each collection block. Replication was four-fold for a total of 36 sediment cores. Two parallel water blanks were also run for each of the 9 experimental treatments, for a total of 54 experimental units. Water blanks were used to control for processes that occur exclusively in the water column that alter nutrient concentrations and thus have the potential to confound calculations of benthic flux. Water blanks were identical to experimental units except for the absence of

sediments. Thus, the water blanks for –Algae units consisted of water only; water blanks for +Algae units contained water and algae.

**Table 4-3. Mean nutrient concentrations of solutions used to fill experimental units at the beginning of the experiment. All units are in µM. Values shown are mean ± 1 SE.**

| Nutrient Level | $O_2$ Availability | $NO_3^-$ | $NH_4^+$ | DON | SRP | DOP |
|---|---|---|---|---|---|---|
| Ambient | Oxic | 1.60 ± 0.01 | 3.80 ± 0.34 | 21.20 ± 3.91 | 1.53 ± 0.00 | 0.38 ± 0.09 |
| Ambient | Hypoxic | 2.17 ± 0.13 | 1.72 ± 1.46 | 19.71 ± 1.46 | 1.56 ± 0.02 | 0.29 ± 0.13 |
| Medium | Oxic | 54.09 ± 0.61 | 8.55 ± 1.63 | 27.16 ± 8.77 | 5.04 ± 0.03 | 0.39 (n=1) |
| Medium | Hypoxic | 52.33 ± 0.01 | 9.41 ± 1.09 | 19.16 ± 1.09 | 4.93 ± 0.02 | 0.32 (n=1) |
| High | Oxic | 265.09 ± 0.34 | 25.53 ± 2.30 | 10.19 ± 2.30 | 24.65 ± 0.08 | 0.53 ± 0.20 |
| High | Hypoxic | 253.63 ± 0.83 | 26.95 ± 1.32 | 5.19 ± 2.26 | 24.67 ± 0.00 | 0.00 ± 0.00 |

Each experimental unit had an air-tight transparent lid with a number of ports: an air line to bubble compressed air or nitrogen gas, a sampling port to remove water samples throughout the experiment, and a port to measure DO, temperature and pH. A stir bar was suspended from each lid and rotated freely at mid-depth in the water column. Units were randomly assigned to one of nine arrays in the water bath. Each array consisted of six experimental units clustered around an empty central tube. The central tube had a motor that powered a large stir bar fastened to a stainless steel shaft. The electromagnetic field from this central stir bar powered smaller stir bars in each of the six experimental units around it.

To initiate the experiment, the overlying water of each sediment core was carefully siphoned off, minimizing disturbance of the sediment surface. One liter of the appropriate treatment solution was carefully added to each experimental unit. Ten grams wet wt *E. intestinalis* were added to each unit designated to receive algae (+Algae). The *E. intestinalis* floated at the surface of the water column. Each experimental unit was capped and the time recorded.

The experiment ran for a total of 12 hours (6 h light, 6 h dark). A 60-ml sample was taken for nutrient analysis from each unit at each of the following time intervals: 45, 90 (1.5 h) 180 (3 h), 270 (4.5 h), 360 (6 h), 450 (7.5 h), 540 (9 h), 630 (10.5 h) and 720 (12 h) minutes. The

sampling port was flushed before each sample was taken. Immediately after each 60-ml sample was taken, the volume was replaced by adding 60 ml of the same solution that was initially used to fill the experimental unit. The sampling port was flushed after the 60 ml were added. Each time the solutions were used to replace water in the experimental units, a sub-sample was taken for nutrient analysis; these values were used in flux calculations as described below. All water samples were filtered (Whatman GF/F) and frozen for subsequent analysis. DO, temperature and pH in each unit were measured at 1.5 h, 3 h and 7.5 h. Only one DO measurement in the oxic units was < 5 mg $l^{-1}$.

### *4.3.2 Analytical Methods*

Water samples were analyzed for $NO_3^-$, $NO_2^-$, $NH_4^+$, SRP, and TP by the Marine Science Institute Analytical Laboratory at UCSB and for total Kjeldahl nitrodgen (TKN), which is $NH_4^+$ and organic nitrogen, by the Department of Agriculture and Natural Resources Analytical Laboratory at UC Davis. Dissolved inorganic nutrients where determined using an Alpkem Autoanalyzer for the analysis of $NO_3^-$, $NO_2^-$, $NH_4^+$, SRP (APHA 1992). TP was digested by combustion and hydrolysis as in Solorzano and Sharp (1980), then analyzed as SRP by autoanalyzer (APHA 1992). TKN was determined by the micro-kjeldahl method (APHA 1992). DON was calculated by subtracting $NH_4^+$ from TKN. DOP was calculated by subtracting SRP from TP. If $NH_4^+$ values exceeded TKN values, or SRP values exceeded TP values, then the calculated values were set to 0.

Algal samples were individually rinsed briefly in freshwater to remove external salts, dried in a forced air oven at 60°C to a constant weight, ground with mortar and pestle and analyzed for tissue N and P by the DANR Analytical Laboratory at UC Davis. N was determined using an induction furnace and a thermal conductivity detector (Dumas 1981). P was determined by atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) following a nitric acid/hydrogen peroxide microwave digestion (Meyer and Keliher 1992). N and P content of algae are reported as total mass $unit^{-1}$, which is calculated by multiplying the nutrient concentration of a sample (% dry wt) as a proportion by the dry wt of that sample where mg N or P $unit^{-1}$ = [% tissue N or P/100] * dry wt (g) * 1000 mg/g

### *4.3.3 Data analysis*

The change in water column concentration over each time interval was used to calculate a flux rate (F) for that time interval (time = t to time= t + 1) for each replicate sediment core and water blank (R). The procedure to calculate the flux rate for each time interval was as follows. The flux rate $F_{i+1}$ that occurs over any time interval *i* ($\delta t_{i+1}$) is the product of the change in mass of the constituent over the time interval i + 1 ($\delta M_{i+1}$) divided by the product of the area of the sediment core (A) and the duration of the time interval $\delta t_{i+1}$ (Eq. 4-1):

$$F_{i+1} = \delta M_{i+1}/(A*\delta t_{i+1}) \quad \text{Eq. 4-1}$$

During the first time interval (i=1), the change in mass ($\delta M_{i=1}$) is given by Eq. 4-2:

$$\delta M_{i=1} = (C_{i=1} - C_{TREAT,\ i=o})*V_0 \quad \text{Eq. 4-2}$$

where $C_{i=1}$ is the concentration of the constituent in the core at the end of the interval, $C_{i=1}$, $C_{TREAT,\ i=o}$ is the concentration in the treatment solution at time zero, and $V_0$ is the initial volume of water in the core. During subsequent intervals, $\delta M_{i+1}$ (Eq. 4-3), is given by the change in mass of the constituent from the beginning ($M_i$; Eq. 4-4) to the end of the interval ($M_{i+1}$; Eq. 4-5). The mass of the constituent at the beginning of the interval ($M_i$) was corrected for the mass of the constituent removed in each 60 ml analytical sample and the mass added in the replacement volume, where $C_i$ and $V_i$ are the concentration of the constituent and volume remaining at the end of the previous interval, $V_{SAMPLE,\ i}$ is the volume removed at the end of the previous interval for the analytical sample, and $V_{REPLACE,\ i}$ is the volume of the treatment solution of concentration $C_{TREAT}$ with which it was replaced.

$$\delta M_{i+1} = M_{i+1} - M_i \quad \text{Eq. 4-3}$$

$$M_{i+1} = C_i*(V_i - V_{SAMPLE,\ i} + V_{REPLACE,\ i}) \quad \text{Eq. 4-4}$$

$$M_i = C_{i+1}*(V_{i+1} - V_{SAMPLE,\ i+1}) - C_{TREAT,\ i+1} * V_{REPLACE,\ i+1} \quad \text{Eq. 4-5}$$

Positive values indicate release of the nutrient from the sediment; negative values indicate uptake of the nutrient by the sediment.

Net flux rates for each replicate (R) sediment core for the first 6 hours of the experiment (light, $F_{0\text{-}6,}$), the last 6 hours of the experiment (dark, $F_{6\text{-}12}$), and for the total duration of the experiment, (total, $F_{0\text{-}12}$) were calculated by summing the flux rates for each time interval and correcting for the average changes in the two parallel water blanks. Eq. 4-6 gives the net flux for the light time period as an example of this calculation.

$$F_{0\text{-}6,\,R} = \left(\sum_{i=1}^{6} F_{SED,\,i,\,R}\right) - \left(\sum_{i=1}^{6} F_{H20,\,i,\,R}\right) \qquad \text{Eq. 4-6}$$

Suspect data identified as outliers with the Grubbs test were removed from statistical analyses. To test for differences in flux rates among treatments for the integrated time period (0-12 h), 2-factor ANOVA was used to test for the effects of nutrients and $O_2$availability in the units without algae. In the units supplied with $O_2$, 2-factor ANOVA was used to test for the effects of nutrients x macroalgae. In order to limit experiment-wise error, we did not test for among treatment differences in the individual light and dark periods. Because we ran two ANOVAs simultaneously for each nutrient, a Bonferroni correction was applied to the alpha level to ensure that the overall chance of making a Type I error was still less than 0.05. Therefore, significance was determined at the p=0.025 level. The data sets were often not normally distributed or had unequal variance and were rank-transformed prior to analysis. Significant interactions did not occur unless otherwise noted.

To test for differences in end of experiment mass of N and P in algal tissue, 2-factor ANOVA was used to test for the effects of nutrients X sediments (present or absent). Significance was determined at the p=0.05 level. Significant interactions did not occur unless otherwise noted.

## 4.4 Results

When *E. intestinalis* was present, water column $NO_3^-$ decreased to near 0 µM in all treatments by the end of the experiment (Figure 4-1). Without *E. intestinalis*, $NO_3^-$ decreased in all units containing sediment cores compared to water-blank units, indicating flux into the sediments. For all nutrient concentrations, the decreases were greater in the hypoxic cores. Under both

medium and high nutrients with algae, the decrease in $NO_3^-$ was greater in sediment cores than in water blanks, indicating flux into sediments even with rapid algal uptake.

When *E. intestinalis* was present, water column $NH_4^+$ decreased dramatically for all treatments within the first 45 minutes of the experiment (Figure 4-2). Without *E. intestinalis*, water column $NH_4^+$ either increased or decreased in sediment cores depending on nutrient concentration. Under ambient nutrients without algae, sediment core and water blank $NH_4^+$ fluctuated slightly and variability was high (Figure 4-2). Under medium nutrients without algae, $NH_4^+$ increased in oxic sediment cores throughout the experiment and variability was high; in hypoxic cores, $NH_4^+$ decreased during the first half of the experiment and then increased during the second half (Figure 4-2). Under high nutrients without algae, $NH_4^+$ decreased in sediment cores during the first half of the experiment, indicating flux into the sediment (Figure 4-2c). $NH_4^+$ in hypoxic sediment cores increased during the second half of the experiment, indicating flux out of the sediments, but variability was high.

Whether SRP increased or decreased in the water column varied with nutrient concentration (Figure 4-3). *E. intestinalis* reduced SRP concentrations over the course of the experiment, but changes were not as dramatic as they were for DIN. Under ambient nutrients without algae, SRP increased in hypoxic sediment cores, particularly during the second half of the experiment when it was dark (Figure 4-3), while concentrations remained relatively stable in water blanks and oxic sediment cores. At the 3 h mark and after, SRP was slightly higher in sediment cores with algae compared to water blanks, perhaps due to flux out of sediments. Under medium nutrients without algae, SRP decreased in sediment cores during the first half of the experiment, indicating flux into sediments (Figure 4-3). In the second half of the experiment, when it was dark, SRP in hypoxic sediment cores increased. Under high nutrients, SRP decreased in oxic and hypoxic sediment cores, indicating flux into sediments (Figure 4-3). In sediment cores with algae, SRP was lower than in water blanks, indicating flux into sediments.

Changes in water column DON fluctuated greatly and were highly variable through time in most of the individual treatments (data not shown). Algae did not appear to significantly take up DON. DON was generally higher in sediment core treatments than in water blanks; this pattern was less consistent under medium nutrients. Changes in water column DOP fluctuated greatly and were highly variable through time in most of the individual treatments (data not shown). Algae did not appear to significantly take up DOP.

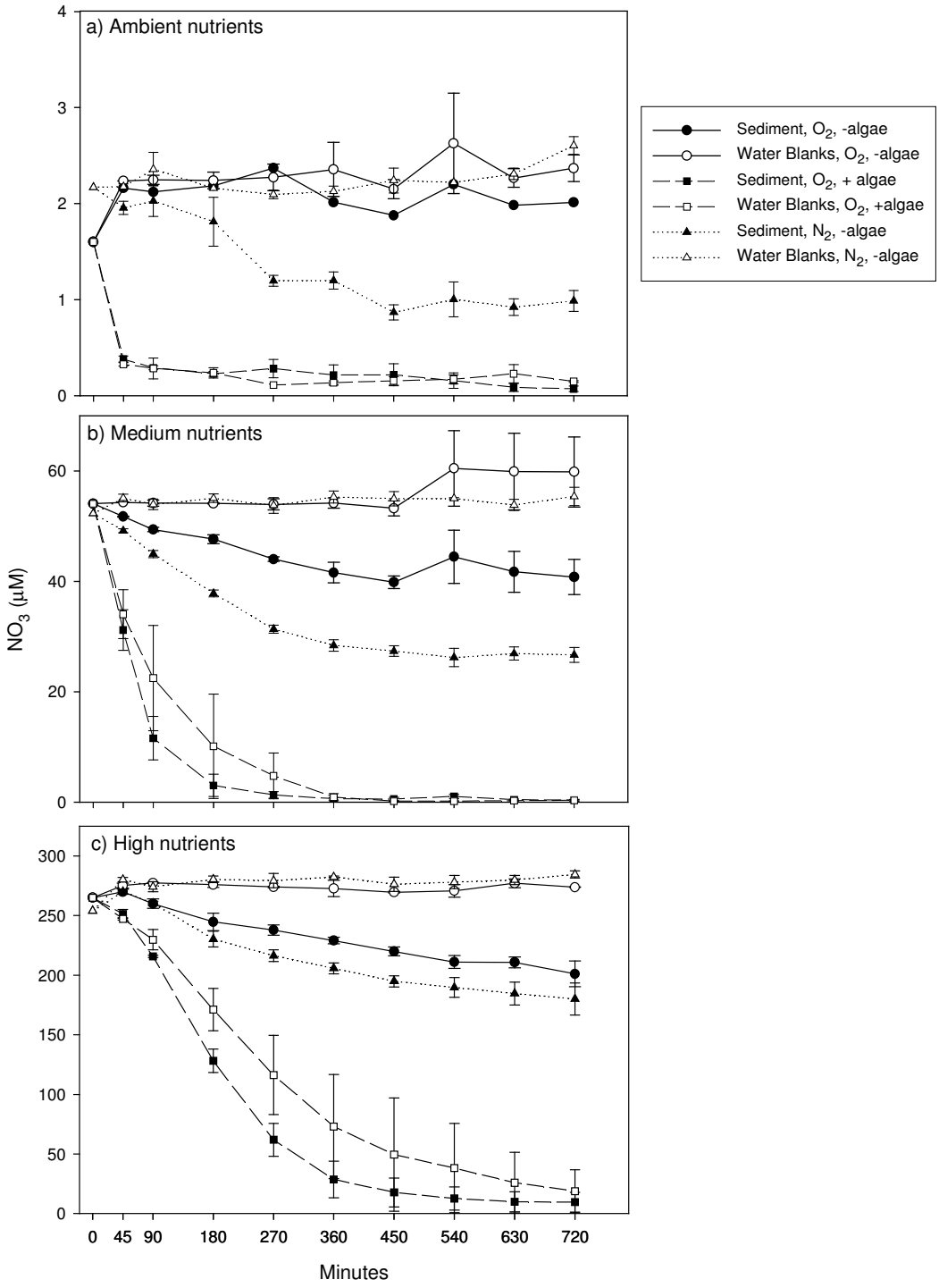


**Figure 4-1. Mean water column $NO_3^-$ over time in experimental units containing sediments and in water blanks under oxic and hypoxic conditions, with and without algae. Bars are ± 1 SE.**

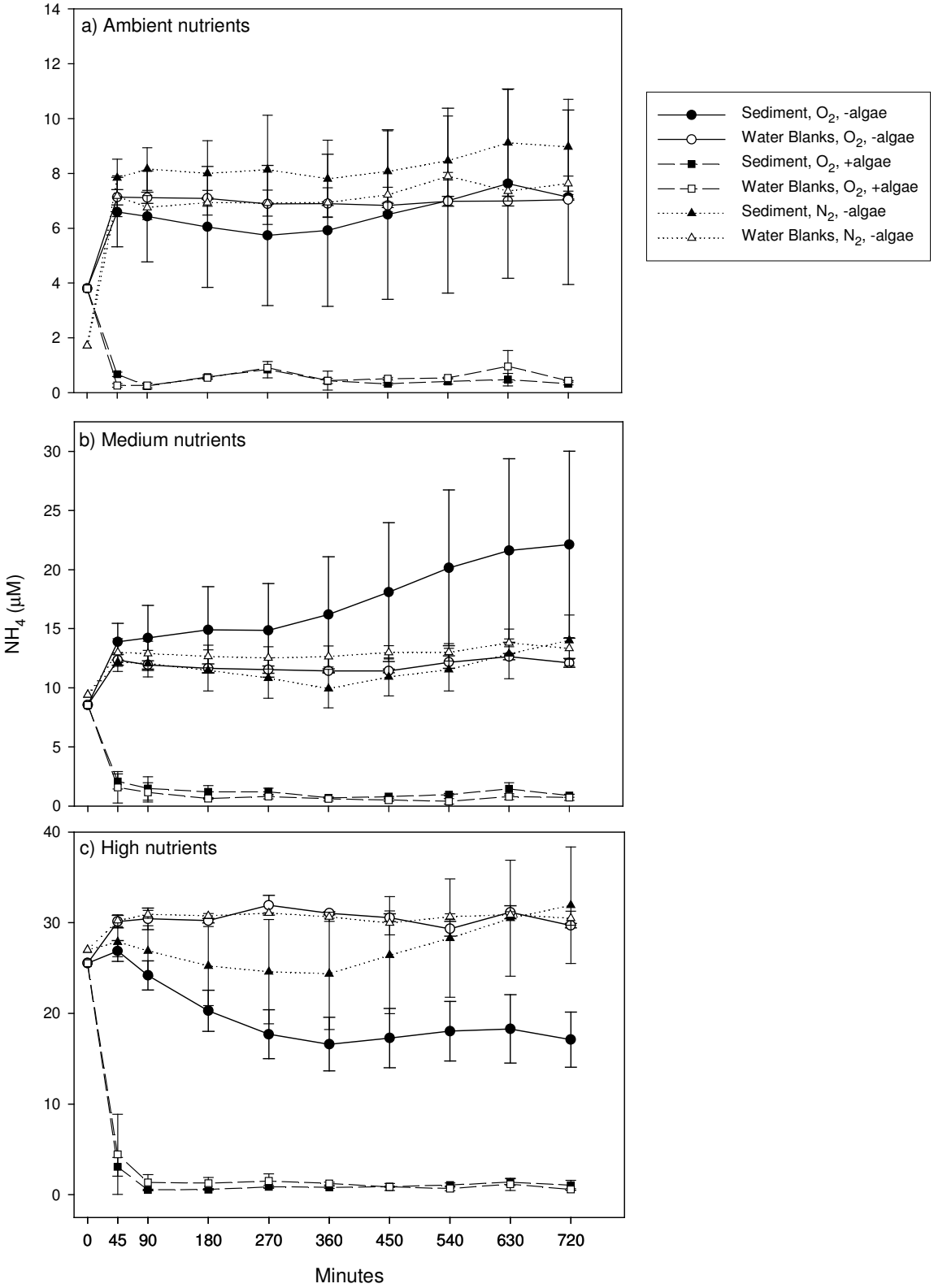


**Figure 4-2. Mean water column $NH_4$ over time in experimental units containing sediments and in water blanks under oxic and hypoxic conditions, with and without algae. Bars are ± 1 SE.**

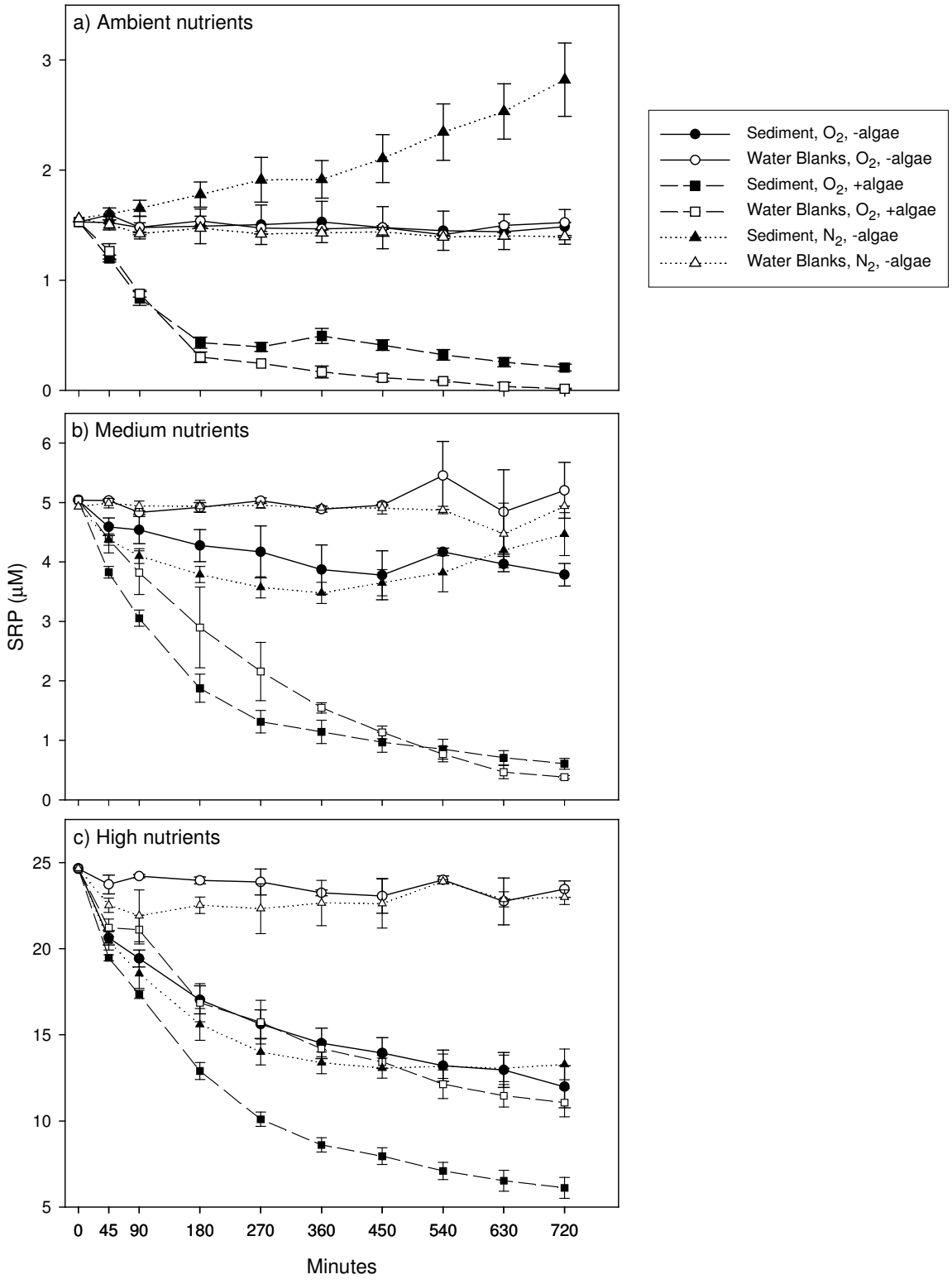


**Figure 4-3. Mean water column SRP over time in experimental units containing sediments and in water blanks under oxic and hypoxic conditions, with and without algae. Bars are ± 1 SE.**

Nutrients and $O_2$ availability both affected total net $NO_3^-$ flux in cores without algae ($p<0.001$ for both factors), and nutrients and algae affected total net flux in oxic cores (nutrients: $p<0.001$, algae: $p=0.025$). $NO_3^-$ fluxed into sediments under all conditions (Figure 4-4). Overall, flux into sediments increased with increasing nutrients, and total net flux was roughly three times greater under high nutrients than under medium nutrients. Hypoxia increased flux into sediments during the light period by 35-260%, which was reflected in the total flux. Algae reduced flux into sediments. Flux was greater during the first half of the experiment compared to the second half, probably because concentration gradients were stronger in the beginning.

Total net $NH_4^+$ flux was not affected by nutrients, $O_2$ availability, or algae ($p>0.025$ in all cases). Flux was highly variable and in both directions during the light period, but flux was generally positive in the dark period (Figure 4-4). Oxic conditions promoted flux into sediments under high nutrient concentrations. Measured fluxes were very low when algae were present due to rapid algal uptake that prevented $NH_4^+$ from accumulating in the water column. Integrated net fluxes were strongly influenced by the light period, but the magnitudes were different due to the dark period.

Total net DON flux was not affected by nutrients, $O_2$ availability, or algae ($p>0.025$ in all cases). DON flux was generally positive with a few exceptions, and variability was high in many of the treatments (Figure 4-4). $O_2$ availability affected the direction of flux under medium nutrient concentrations during the light period. Patterns of flux under medium nutrients were very different for both light and dark periods. Under high nutrient levels, DON fluxed out of sediments in the light, whereas flux was either into the sediments or minimal in the dark. The direction of integrated net DON fluxes was strongly influenced by the light period.

Nutrient levels affected total net SRP flux in cores without algae ($p<0.001$) but $O_2$ availability did not following Bonferroni correction ($p=0.034$). Nutrients ($p<0.001$) and algae ($p=0.004$) affected total net flux in oxic cores. Net SRP flux into sediments increased as nutrients increased (Figure 4-4). This effect was clear in the light and integrated periods though not as strong in the dark period. Hypoxia promoted positive flux. The presence of algae reduced flux to the sediments under high nutrients. Total net flux was roughly 8-9 times greater under high nutrients than under medium nutrients.

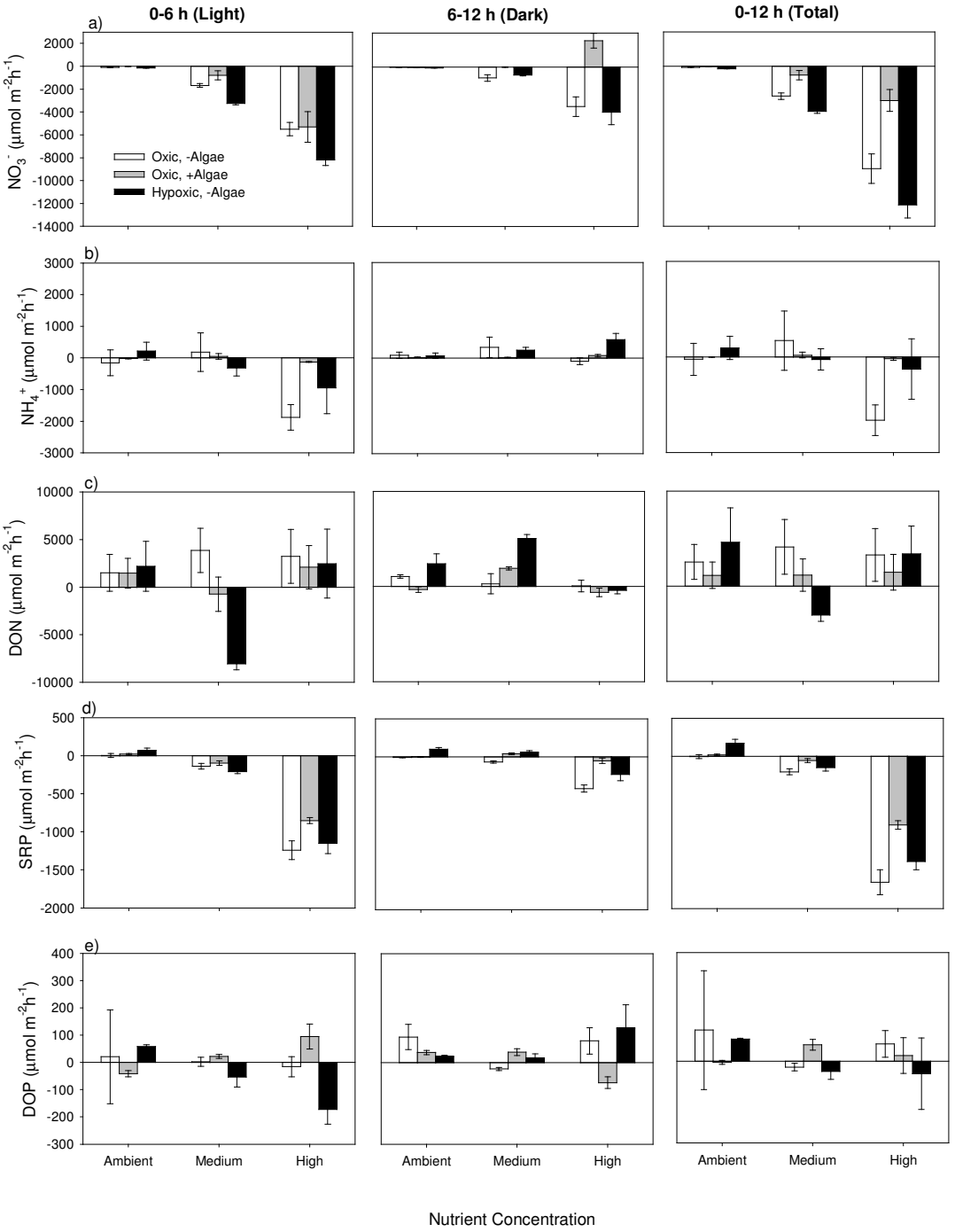


**Figure 4-4. Mean net flux of a) $NO_3^-$, b) $NH_4^+$, c) DON, d) SRP, and e) DOP over a 12 h incubation period for sediment cores under oxic and hypoxic conditions. Rates are corrected for changes in water blanks. Bars are ± 1 SE.**

Total net DOP flux was not affected by nutrients, $O_2$ availability or algae ($p>0.025$ in all cases). Patterns in net DOP flux were inconsistent and highly variable in some cases (Figure 4-4). Fluxes occurred in both directions during the light period. During the dark period, DOP flux was generally positive but there were exceptions. Total net flux did not vary consistently with nutrients, $O_2$, or macroalgae.

The presence of sediments generally increased tissue nutrient concentrations (Figure 4-5). The effect of sediments on algal tissue nutrients was significant for P ($p=0.010$) but not for N ($p=0.085$). Nutrient concentrations significantly affected both tissue N and P ($p<0.001$ in both cases).

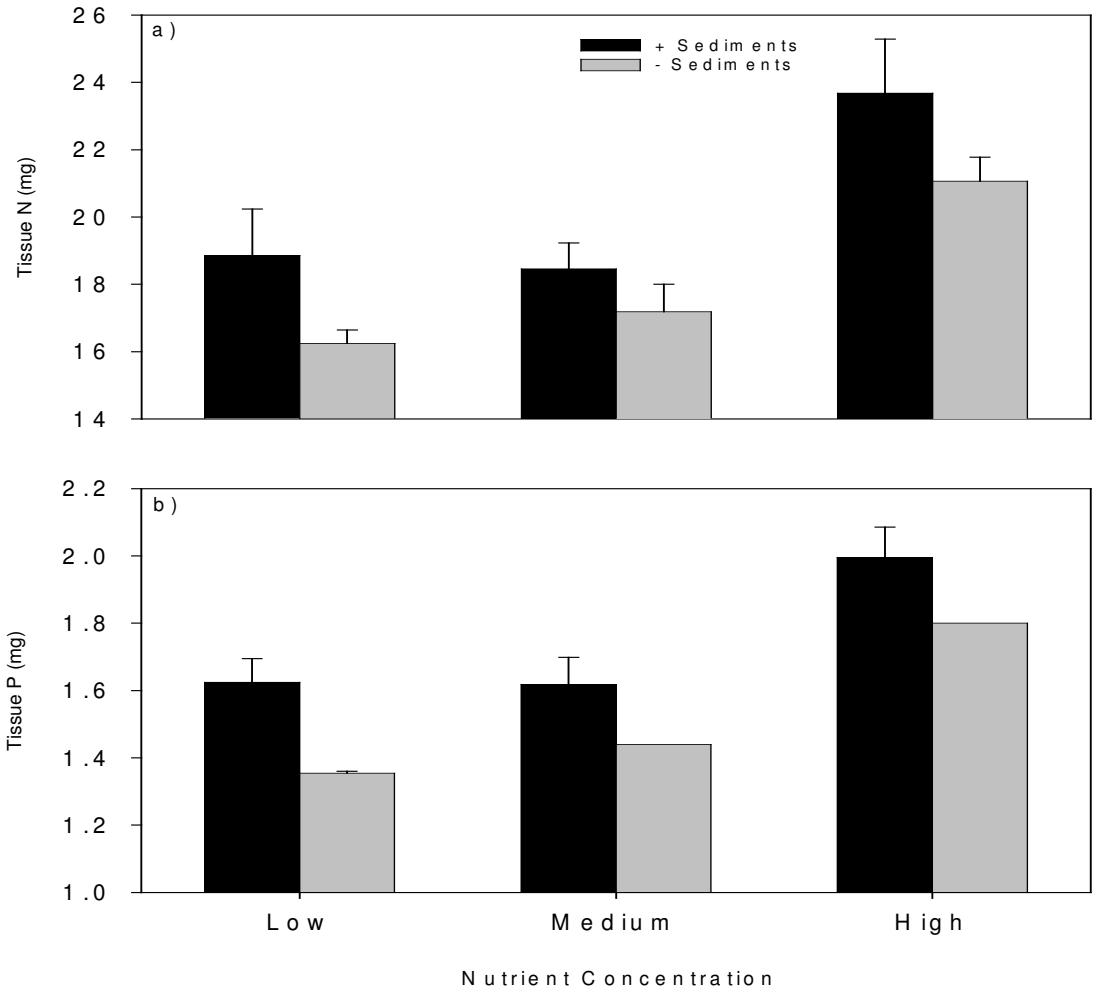


**Figure 4-5. Mass of a) N and b) P in *E. intestinalis* tissue at the end of the experiment.**

Overall, *E. intestinalis* was highly efficient at removing N and P from the water column (Table 4-4). *E. intestinalis* took up over 90% of the $NO_3^-$ in the water column, regardless of initial concentration, reducing the amount available for flux into sediments. $NH_4^+$ flux was highly variable, but again *E. intestinalis* took up most of the available $NH_4^+$. This process kept the water column $NH_4^+$ concentration low and drove the efflux from the sediment seen when algae were not present. *E. intestinalis* removed significant amounts of SRP from the water column, even when SRP concentrations were high.

**Table 4-4. Changes in nutrient concentrations due to uptake by sediments under different conditions and uptake by E. intestinalis.**

| Nutrient Treatment | Initial Concentration (µM) | Changes in Nutrient Concentration (% of initial) by In Situ Processes | | | |
|---|---|---|---|---|---|
| | | Exchange with Sediments | | | Macroalgal Uptake |
| | | Oxic -Algae | Hypoxic -Algae | Oxic +Algae | |
| $NO_3^-$ | | | | | |
| Ambient | 2 | -36 ± 7 | -75 ± 5 | -5 ± 2 | -91 ± 1 |
| Medium | 53 | -39 ± 5 | -55 ± 3 | -0 ± 0 | -99 ± 0 |
| High | 260 | -27 ± 4 | -41 ± 5 | -4 ± 3 | -93 ± 7 |
| $NH_4^+$ | | | | | |
| Ambient | 2.5 | +2 ± 84 | +79 ± 102 | -3 ± 1 | -88 ± 0 |
| Medium | 9 | +58 ± 81 | +7 ± 23 | +2 ± 2 | -92 ± 3 |
| High | 26 | -49 ± 12 | +5 ± 24 | +2 ± 2 | -98 ± 0 |
| SRP | | | | | |
| Ambient | 1.5 | -2 ± 10 | +91 ± 21 | +13 ± 2 | -99 ± 0 |
| Medium | 5 | -32 ± 4 | -10 ± 7 | +5 ± 2 | -92 ± 1 |
| High | 24 | -47 ± 5 | -39 ± 4 | -20 ± 2 | -55 ± 3 |

## 4.5 DISCUSSION

*Diffusive transport* refers to the process by which solutes (in this case nutrients) move from an area of higher concentration to lower concentration (Berner 1980). When there is a difference in concentration between sediment pore waters and the overlying water column, diffusion will occur to decrease the concentration gradient. *Advective transport* processes can enhance the magnitude of the flux by forcing the mixing of pore waters and surface waters.

In this experiment, the gradient in nutrient concentration between surface waters and sediment pore waters exerted a major control on the magnitude and direction of benthic flux in batch-incubated sediments. During the first 6 hours of the experiment, $NO_3^-$, $NH_4^+$ and SRP fluxes into sediments increased as overlying water concentrations increased. The relationships were linear for $NO_3^-$ and SRP (Figure 4-6); a linear relationship did not describe $NH_4^+$ dynamics well because the data were highly variable. Boynton and Kemp (1985) and Eriksson et al. (2003) also found that $NO_3^-$ fluxes into sediment were directly proportional to $NO_3^-$ concentrations in overlying water. Magalhaes et al. (2002) found the same mechanism to govern sediment P uptake as well. Rates of flux measured in this experiment were of the same order of magnitude as those measured *in situ* with benthic chambers. In both cases the measured fluxes were 1-2 orders of magnitude higher than those predicted by Ficke's law of diffusion (Chapter 3). In a laboratory setting, where physical mixing processes such as tidal pumping, scouring by strong currents, groundwater influx, etc. were largely absent; bioirrigation from benthic infauna was likely the major advective transport process affecting flux.

$O_2$ availability affected flux of dissolved inorganic nutrients in several different ways. First, hypoxia promoted $NO_3^-$ flux into sediments. Denitrification, the microbially-remediated process of $NO_3^-$ conversion to $N_2$ gas, is the likely reason for the observed increase in $NO_3^-$ flux. Denitrification, which is enhanced under anoxic conditions in sediments (Seitzinger 1988), can reduces pore water $NO_3^-$ concentrations to near non-detectable levels (Chapter 2). This would increase the concentration gradient across the sediment-water interface and promote greater flux into the sediment relative to oxic conditions. Second, oxic conditions promoted $NH_4^+$ flux into sediments. Under oxic conditions, nitrifying bacteria transform $NH_4^+$ to $NO_x^-$ (Rysgaard et al. 1994, 1995), thus reducing the concentration of $NH_4^+$ in pore waters of surficial sediments. This can reduce the flux of $NH_4^+$ out of sediments when ambient concentrations are low or cause a greater influx of $NH_4^+$ into sediments when ambient $NH_4^+$ concentrations are high. In sediments that have low available $NO_3^-$ in surface waters but maintain an oxic surface layer, couple nitrification-denitrification is enhanced (An and Joye 2001), providing a pathway for permanent loss of ammonia-N from the estuary.

Second, hypoxia enhanced SRP efflux. The mechanism for this has been well-studied in estuaries, lakes and wetlands. SRP is known to adsorb to or be incorporated into the mineral lattice of iron (III) hydroxyoxides, which precipate under oxic conditions in the sediments (Carritt and Goodgal 1954, Froelich 1988). When $O_2$ and $NO_3^-$ in the sediments are no longer available

and microbially-mediated reduction of Fe(III) begins, these precipitates dissolve and release SRP to pore waters. In estuarine sediments that are anoxic at some depth and have elevated pore water SRP concentrations. However, if surficial sediments are maintained oxic by exchange with a well-oxygenated water column or by the presence of benthic microalgae, SRP will not flux from the sediments because it is trapped and absorbed by Fe(III) precipitates in this surficial layer. When surface waters and sediments become anoxic, $PO_4^{-3}$ efflux from sediments is enhanced (Sundby et al. 1992).

The regressions between flux rate and water column nutrient concentrations indicate whether the relationship between these two variables are linear and also indicate how the response to increasing water column nutrient concentrations, represented by the b coefficient, (L $m^{-2}$ $hr^{-1}$; Table 4-4), varies under oxic and hypoxic conditions. Regressions for $NO_3^-$ and SRP were linear and statistically significant, while the relationship between $NH_4^+$ flux rate and nutrient level was not (Table 4-5). For $NO_3^-$, the slope for treatments without algae is greater under hypoxic versus oxic by 30%; for SRP, these slopes where only slightly, but not significantly different.

**Table 4-5. Results of linear regression of flux rate against water column nutrients. See Figure 4-6 for NO3-, NH4+, and SRP.**

| Nutrient and Treatment | | Slope | Intercept | $r^2$ | p |
|---|---|---|---|---|---|
| $NO_3^-$ | Oxic, -algae | -19.8 | -291 | 0.9213 | <0.001 |
| | Oxic, +algae | -20.5 | 140 | 0.7367 | <0.001 |
| | Hypoxic, -algae | -29.3 | -925 | 0.9325 | <0.001 |
| $NH_4^+$ | Oxic, -algae | -91.8 | 531 | 0.5619 | 0.013 |
| | Oxic, +algae | -6.3 | 46 | 0.2502 | 0.098 |
| | Hypoxic, -algae | -43.7 | 193 | 0.1998 | 0.168 |
| SRP | Oxic, -algae | -54.7 | 110 | 0.9447 | <0.001 |
| | Oxic, +algae | -37.9 | 85 | 0.9854 | <0.001 |
| | Hypoxic, -algae | -50.7 | 92 | 0.9216 | <0.001 |

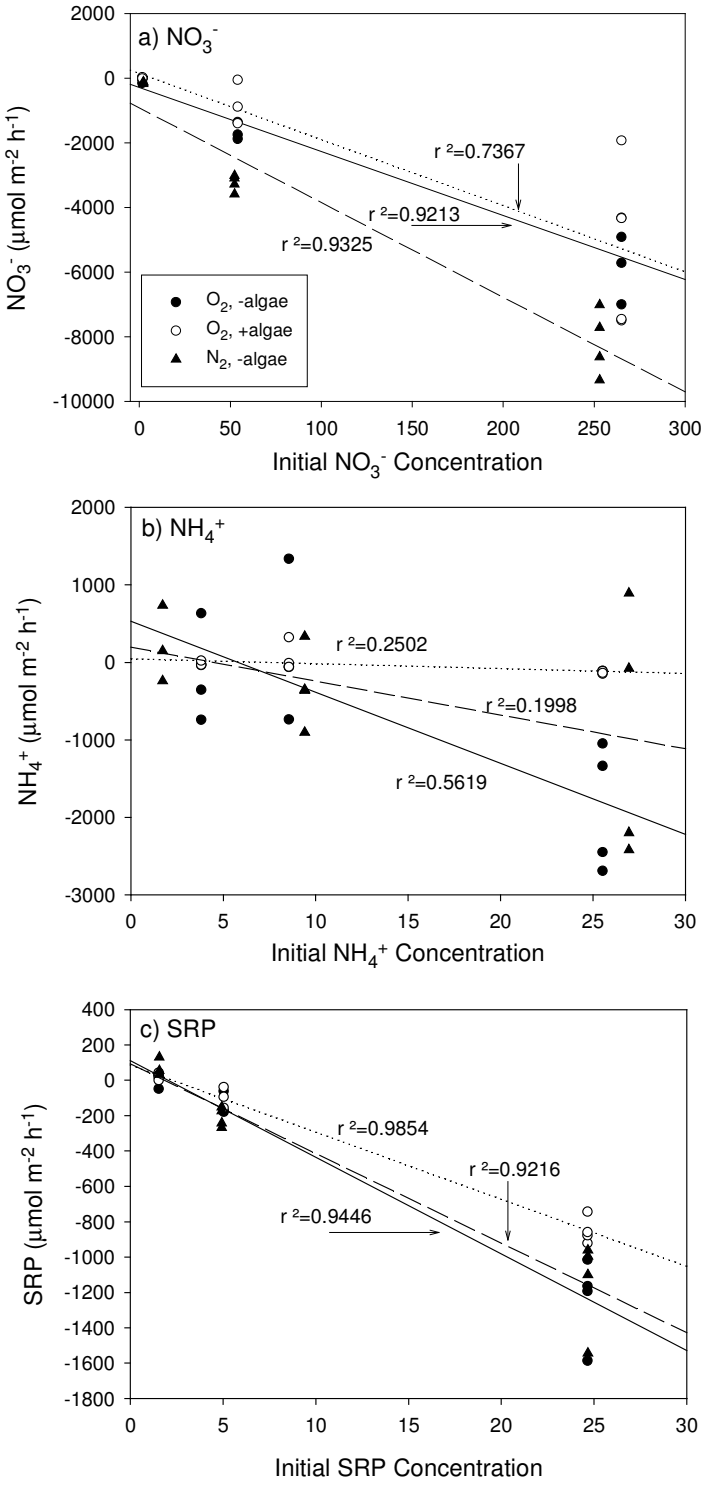


**Figure 4-6. Nutrient flux rates versus initial nutrient concentrations.**

*Interactions of Macroalgae and Water Column Nutrient Concentrations on Nutrient Flux*

As observed in this experiment, green macroalgae, such as *E. intestinalis* is known for its capacity to quickly and dramatically deplete the water column of inorganic nutrients (Kamer et al. 2001). High macroalgal nutrient uptake rates can potentially affect benthic nutrient flux and nutrient cycling in several ways. First, macroalgal uptake of dissolved inorganic nitrogen can reduce the importance of denitrification as a permanent mechanism for N removal from the estuary. The presence of *E. intestinalis* reduces the amount of nutrients available in the water column that might diffuse into and be transformed in the sediment. As demonstrated in Chapter 2, pore water $NO_3^-$ is generally very low relative to surface water concentrations due to active denitrification in the sediments – a process that converts $NO_3^-$ to nitrogen gas (Seitzinger 1988). Thus $NO_3^-$ is predicted to consistently flux into the sediments during most conditions observed (Chapter 2). Rather than move into the sediments and be denitrified and therefore permanently removed from the system, $NO_3^-$ was taken up by *E. intestinalis*. Similarly, in the absence of algae, $NH_4^+$ diffused into sediments under high concentrations. This $NH_4^+$ would potentially undergo couple nitrification-denitrification, a process which converts $NH_4^+$ to $NO_3^-$, which is then subsequently transformed into nitrogen gas and permanently removed from the system (An and Joye 2001). Once in macroalgal tissue however, the nutrients can follow several pathways that would recycle them within the system. Inorganic N and P and DON can leak out of *E. intestinalis* and *Ulva* spp. (Kamer et al. 2002, Tyler et al. 2003). The inorganic nutrients are immediately biologically available again and the DON can be taken up directly by macroalgae (Tyler et al. 2003) or mineralized to inorganic N (Seitzinger and Sanders 1997). Alternatively, when macroalgae senesces, it often sinks to the bottom of the estuary where it decomposes and its nutrients are mineralized to inorganic forms and are biologically available. Through these different pathways, uptake of nutrients by macroalgae rather than by sediments can lead to increased recycling and retention of N within the system.

Second, the flux of nutrients species such as SRP or $NH_4^+$, which typically have high pore water concentrations relative to surface waters (Chapter 2), would be enhanced by the presence of macroalgae. In this experiment, nutrient uptake by *E. intestinalis* prevented accumulation of inorganic nutrients in the water column. In the absence of algae, the magnitude of $NH_4^+$ and SRP efflux from the sediment was smaller when water column concentrations were higher. When *E. intestinalis* was present, water column $NH_4^+$ and SRP concentrations remained low, thus maintaining a strong concentration gradient between the water column and sediment pore waters; based on Ficke's Law of Diffusion (Berner 1980), this would increase the flux of $NH_4^+$

and SRP from the sediments to the surface waters. Applying this paradigm to an estuarine setting, it can be concluded that the presence of macroalgae with a high affinity for nutrients may lead to increased efflux of bioavailable $NH_4^+$ and SRP.

The effect of benthic algae on nutrient flux, namely the reduction of efflux of $NH_4^+$ and SRP, is a widely accepted model (Henriksen et al. 1980, Rizzo 1990, Rysgaard et al. 1995, Thornton et al. 1999, Sundback et al. 2000). In each of these cases, the algae are truly benthic and a component of the substrate. Macroalgae, such as *Enteromorpha* and *Ulva* spp., function differently because they do not rest on the benthos when submerged. They form floating, detached mats (Thybo-Christesen et al. 1993, Duarte 1995, Young et al. 1998, Kamer et al. 2001) or if they are attached to the benthos, the thalli extend up into the water column (Sfriso et al. 1987, 1992). In both situations, the algae are a component of the water column. In this study, *E. intestinalis* reduced the accumulation of nutrients in the water column, similar to the effects of benthic microalgae.

*Comparison of Laboratory Ambient Flux Rates With Estimates from other Estuarine Systems.*
Patterns of inorganic nutrient flux found in this study were similar to patterns found in other studies. In both estuarine and coastal ocean systems, sediments are commonly a source of $NH_4^+$, a sink for $NO_3^-$ (Boynton et al. 1980, Laima et al. 2002, Eriksson et al. 2003, Gregoire and Friedrich 2004) and a temporary reservoir for P (Boynton et al. 1980, Sutula et al. 2004). Measurements of dissolved organic nutrients fluxes are less common, and the limited published data show DON and DOP flux into and out of sediments erratically (Boynton et al. 1980, Cowan and Boynton 1996, Tyler et al. 2001, 2003).

Rates of inorganic nutrient flux measured in this study were up to two orders of magnitude higher than rates measured in other estuarine studies (Table 4-6). Only rates from treatments without algae were included in Table 4-5. $NO_3^-$, $NH_4^+$, and SRP flux rates from the ambient nutrient treatments were comparable to rates from other studies, most of which had water column dissolved inorganic water column nutrient concentrations in the range of our ambient and medium treatments. Even in systems with water column nutrient levels as high as those in our high nutrient treatment (Caffrey et al. 2002), benthic flux measurements were lower.
The importance of benthic nutrient regeneration to primary production is well known (Boynton et al. 1980, Blackburn and Henriksen 1983, Boynton and Kemp 1985, Trimmer et al. 1998, 2000, Kamer et al. 2004). The findings of this study also have significant relevance to nutrient cycling

**Table 4-6. Nutrient flux rates from selected estuarine studies. Values with * are approximations because they were not presented in text but are interpreted from graphs. Rates presented are for treatment means, not individual replicates, and only treatments without algae were included from this study.**

| Site | Flux rates (µmol $m^{-2}$ $h^{-1}$) | | | Reference |
|---|---|---|---|---|
| | $NO_3^- \pm NO_2^-$ | $NH_4^+$ | P (SRP unless otherwise noted) | |
| UNB | | | | |
| Ambient, oxic | -86 to -10 | -155 to +84 | -8 to +4 | This study |
| Ambient, hypoxic | -223 to -79 | +71 to +287 | +72 +172 | |
| Medium, oxic | -2623 to -954 | +180 to +516 | -204 to -66 | |
| Medium, hypoxic | -3944 to -694 | -320 to +244 | -209 to +59 | |
| High, oxic | -8968 to -3474 | -1986 to -103 | -1655 to -415 | |
| High, hypoxic | -12152 to -3972 | -951 to +571 | -1381 to -230 | |
| Patuxent River | -674 to +100* | -50* to +1577 | -10* to +34 (DOP) +1* to +295 (DIP) | Boynton et al. 1980 |
| York River | -45* to +25* | -162 to +364 | -6 to +80 | Rizzo 1990 |
| Chesapeake Bay | -120 to +35 | -35 to +506 | -16.5 to +148 | Cowan and Boynton 1996 |
| | -125* to +288 | +35.6 to +821 | -5* to +40* | Boynton and Kemp 1985 |
| Neuse River | -150* to +100* | -30* to +120* | -5* to +40* | Rizzo and Christian 1996 |
| Randers Fjord, Denmark | | 0 to +500 | | Rysgaard et al. 1999 |
| Venice Lagoon, Italy | -285* to +7* | -142* to +429* | | Eriksson et al. 2003 |
| Elkhorn Slough | -305 to 76 ($NO_3^-$) -300 to +179 ($NO_{3^-+2}^-$) | -42 to + 575 | -231 to +51 | Caffrey et al. 2002 |
| S. San Francisco Bay | -300 to +259 | -8 to + 216 | | Caffrey and Miller 1995 |
| Potter Pond, RI | -95* to +80* | 0 to +440 | -10 to +50 (DIP) -20 to +40 (DOP) | Nowicki and Nixon 1985 |
| Great South Bay, NY | +40 to +2600 | | | Dietz 1982 (cited in Nowicki and Nixon 1985 |

in natural estuarine systems, particularly those already suffering from eutrophication. Increases in nutrient loads that result in elevated water column concentrations may be retained within the system temporarily via flux into the sediments and subsequent storage. When water column nutrient concentrations decrease, often occurring during the summer when nutrient inputs are low and primary productivity is high (Boynton et al. 1980, Hopkinson et al. 1999, Kennison et al. 2003), flux from sediments may be promoted. This regeneration of overlying water column nutrients could significantly enhance primary production and extend the duration of an algal bloom.

## 4.6 References

An S. and S.B. Joye 2001. Enhancement of coupled nitrification-denitrification by benthic photosynthesis in shallow estuarine sediments. Limnology and Oceanography 46(1): 62-74

APHA. 1992. Standard methods for the examination of water and wastewater. 18th Edition. American Public Health Association.

Anderson, I. C., K. J. McGlathery, and A. C. Tyler. 2003. Microbial mediation of 'reactive' nitrogen transformations in a temperate lagoon. Marine Ecology Progress Series 246: 73-84.

Arnold, K. E., and S. N. Murray. 1980. Relationships between irradiance and photosynthesis for marine benthic green algae Chlorophyta of differing morphologies. Journal of Experimental Marine Biology and Ecology 43(2): 183-192.

Berner, R.A., 1980. Early Diagenesis: A Theoretical Approach: Princeton, NJ (Princeton Univ. Press).

Blackburn, T. H., and K. Henriksen. 1983. Nitrogen cycling in different types of sediments from Danish waters. Limnology and Oceanography 28(3): 477-493.

Boyle, K. A., K. Kamer, and P. Fong. 2004. Spatial and temporal patterns in sediment and water column nutrients in a eutrophic southern California estuary. Estuaries 27(3): 378-388.

Boynton, W. M., and W. M. Kemp. 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Marine Ecology Progress Series 23: 45-55.

Boynton, W. R., W. M. Kemp, and C. G. Osborne. 1980. Nutrient fluxes across the sediment-water interface in the turbid zone of a coastal plain estuary, p. 533. In V. S. Kennedy [ed.], Estuarine Perspectives. Academic Press.

Caffrey, J. M., N. Harrington, and B. Ward. 2002. Biogeochemical processes in a small California estuary. 1. Benthic fluxes and pore water constituents reflect high nutrient freshwater inputs. Marine Ecology Progress Series 233: 39-53.

Carritt, D. E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep Sea Research 1: 224-243.

Cowan J.W. and W.R. Boynton. !996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors and ecological significance. Estuaries 19 (3): 562-580

Duarte, C. M. 1995. Submerged aquatic vegetation in relation to different nutrient regimes. Ophelia 41(0): 87-112.

Eriksson, P. G., J. M. Svensson, and G. M. Carrer. 2003. Temporal changes and spatial variation of soil oxygen consumption, nitrification and denitrification rates in a tidal salt marsh of the Lagoon of Venice, Italy. Estuarine Coastal and Shelf Science 58: 861-871.

Froelich, P. N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. Limnology and Oceanography 33: 649-668.

Fong, P., R. M. Donohoe, and J. B. Zedler. 1994. Nutrient concentration in tissue of the macroalga Enteromorpha as a function of nutrient history: An experimental evaluation using field microcosms. Marine Ecology Progress Series 106(3): 273-281.

Fujita, R. M. 1985. The role of nitrogen status in regulating transient ammonium uptake and nitrogen storage by macroalgae. Journal of Experimental Marine Biology and Ecology 92: 283-301.

Gregoire, M., and J. Friedrich. 2004. Nitrogen budget of the northwestern Black Sea shelf inferred from modeling studies and in situ benthic measurements. Marine Ecology Progress Series 270: 15-39.

Harlin, M. M. 1978. Nitrate uptake by Enteromorpha spp. (Chlorophyceae): applications to aquaculture systems. Aquaculture 15: 373-376.

Henriksen, K., J. I. Hansen, and T. H. Blackburn. 1980. The influence of benthic infauna on exchange rates of inorganic nitrogen between sediment and water. Ophelia Suppl 1: 249-256.

Hopkinson, C. S. J., A. E. Giblin, J. Tucker, and R. H. Garritt. 1999. Benthic metabolism and nutrient cycling along an estuarine salinity gradient. Estuaries 22(4): 863-881.

Kamer, K., K. A. Boyle, and P. Fong. 2001. Macroalgal bloom dynamics in a highly eutrophic southern California estuary. Estuaries 24(4): 623-635.

Kamer, K., P. Fong, R. L. Kennison, and K. Schiff. 2004. The relative importance of sediment and water column supplies of nutrients to the growth and tissue nutrient content of the green macroalga Enteromorpha intestinalis along and estuarine resource gradient. Aquatic Ecology 38: 45-56.

Kamer, K., K. Schiff, R. L. Kennison, and P. Fong. 2002. Macroalgal nutrient dynamics in Upper Newport Bay. # 365. Southern California Coastal Water Research Project. Westminster, CA. 98 pp.

Kennison, R. L., K. Kamer, and P. Fong. 2003. Nutrient dynamics and macroalgal blooms: a comparison of five southern California estuaries. # 416. Southern California Coastal Water Research Project. Westminster, CA. 79 pp.

Laima, M., D. Brossard, P.-G. Sauriau, M. Girard, P. Richard, D. Gouleau, and L. Joassard. 2002. The influence of long emersion on biota, ammonium fluxes and nitrification in intertidal sediments of Marennes-Oleron Bay, France. Marine Environmental Research 53: 381-402.

Magalhaes, C. M., A. A. Bordalo, and W. J. Wiebe. 2002. Temporal and spatial patterns of intertidal sediment-water nutrient and oxygen fluxes in the Douro River estuary, Portugal. Marine Ecology Progress Series 233: 55-71.

Miller-Way, T., G. S. Boland, G. T. Rowe, and R. R. Twilley. 1994. Sediment oxygen consumption and benthic nutrient fluxes on the Louisiana continental shelf: a methodological comparison. Estuaries 17(4): 809-815.

O'Brien, M. C., and P. A. Wheeler. 1987. Short term uptake of nutrients by Enteromorpha prolifera (Chlorophyceae). Journal of Phycology 23: 547-556.

Rizzo, W. M. 1990. Nutrient exchanges between the water column and a subtidal benthic microalgal community. Estuaries 13(3): 219-226.

Rizzo, W. M., and R. R. Christian. 1996. Significance of subtidal sediments to heterotrophically-mediated oxygen and nutrient dynamics in a temperate estuary. Estuaries 19(2B): 475-487.

Rysgaard, S., P. B. Christensen, and L. P. Nielsen. 1995. Seasonal variation in nitrification and denitrification in estuarine sediment colonized by benthic microalgae and bioturbating infauna. Marine Ecology Progress Series 126: 111-121.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnology and Oceanography 33(4, part 2): 702-724.

Seitzinger, S. P., W. S. Gardner, and A. K. Spratt. 1991. The effect of salinity on ammonium sorption in aquatic sediments: implications for benthic nutrient recycling. Estuaries 14(2): 167-174.

Seitzinger, S. P., and R. W. Sanders. 1997. Contribution of dissolved organic nitrogen from rivers to estuarine eutrophication. Marine Ecology Progress Series 159: 1-12.

Sfriso, A., A. Marcomini, and B. Pavoni. 1987. Relationships between macroalgal biomass and nutrient concentrations in a hypertrophic area of the Venice Lagoon Italy. Marine Environmental Research 22(4): 297-312.

Sfriso, A., B. Pavoni, A. Marcomini, and A. A. Orio. 1992. Macroalgae, nutrient cycles, and pollutants in the Lagoon of Venice. Estuaries 15(4): 517-528.

Solórzano, l., and J. H. Sharp. 1980. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. Limnology and Oceanography 25: 745-758.

Sundback, K., and W. Graneli. 1988. Influence of microphytobenthos on the nutrient flux between sediment and water: a laboratory study. Marine Ecology Progress Series 43: 63-69.

Sundback, K., A. Miles, and E. Goransson. 2000. Nitrogen fluxes, denitrification and the role of microphytobenthos in microtidal shallow-water sediments: an annual study. Marine Ecology Progress Series 200: 59-76.

Sundby, B., C. Gobeil, N. Silverberg, and A. Mucci. 1992. The phosphorus cycle in coastal marine sediments. Limnology and Oceanography 37(6): 1129-1145.

Sutula, Martha, K.Kamer and J.Cable. 2004. Sediments as a non-point source of nutrients to Malibu Lagoon, California (USA). Southern California Coastal Water Research Project, Westminster, CA. Technical Report #441.

Thornton, D. C. O., G. J. C. Underwood, and D. B. Nedwell. 1999. Effect of illumination and emersion period on the exchange of ammonium across the estuarine sediment-water interface. Marine Ecology Progress Series 184: 11-20.

Thybo-Christesen, M., M. B. Rasmussen, and T. H. Blackburn. 1993. Nutrient fluxes and growth of Cladophora sericea in a shallow Danish bay. Marine Ecology Progress Series 100: 273-281.

Trimmer, M., D. B. Nedwell, D. B. Sivyer, and S. J. Malcolm. 1998. Nitrogen fluxes through the lower estuary of the river Great Ouse, England: the role of the bottom sediments. Marine Ecology Progress Series 163: 109-124.

Trimmer, M., D. B. Nedwell, D. B. Sivyer, and S. J. Malcolm. 2000. Seasonal organic mineralisation and denitrification in intertidal sediments and their relationship to the abundance of Enteromorpha sp. and Ulva sp. Marine Ecology Progress Series 203: 67-80.

Tyler, A. C., K. J. McGlathery, and I. C. Anderson. 2003. Benthic algae control sediment-water column fluxes of organic and inorganic nitrogen compounds in a temperate lagoon. Limnology and Oceanography 48(6): 2125-2137.

Vanderborght, J.-P., and G. Billen. 1975. Vertical distribution of nitrate concentration in interstitial water of marine sediments with nitrification and denitrification. Limnology and Oceanography 20(6): 953-961.

Young, D. R., D. T. Specht, P. J. Clinton, and H. I. Lee. 1998. Use of color infrared aerial photography to map distributions of eelgrass and green macroalgae in a non-urbanized estuary of the Pacific northwest U.S.A. Proceedings of the Fifth International Conference on Remote Sensing for Marine and Coastal Environments 2: 37-45.

# 5 INTERNAL LOADS OF NITROGEN AND PHOSPHORUS FROM SEDIMENTS IN UNB: ANNUAL ESTIMATES AND COMPARISON WITH OTHER SOURCES

## 5.1 Abstract

This component of the study integrates data from Chapters 2 through 4, for the purpose of: 1) understanding the extent to which predicted diffusive fluxes are comparable to the magnitude and direction of fluxes measured *in situ* or by incubation of sediment cores, 2) using the estimates of benthic flux to derive an annual estimate of benthic nutrient exchange with UNB surface waters, and 3) compare the relative importance of this exchange with other sources of nutrients to UNB.

Comparison of diffusive fluxes predicted from pore water peeper data with fluxes measured *in situ* and by incubating sediment cores showed that diffusive fluxes underpredicted measured fluxes by roughly 1-2 orders of magnitude, a result supported by numerous studies in the literature. This is not surprising, given the results of Chapter 2, which show that benthic exchange in UNB is driven by advective transport – perhaps by a factor of 3-5 times above what diffusion alone may be contributing (Worshnapp et al. 2004; Chapter 3). Thus, if used to estimate annual internal loading of nutrients from the sediments, uncorrected diffusive fluxes greatly underestimate the magnitude of this source of nutrients to UNB.

For this reason, seasonal and annual nutrient loads from benthic exchange were estimated from corrected fluxes. This correction was based on a linear regression between flux rates measured *in situ* in April and October 2004 and diffusive fluxes predicted from pore water profiles during those time periods. These loading estimates are reasonable in terms of the order of magnitude and direction of benthic nutrient exchange, and are useful for interpreting the importance of benthic exchange of nutrients relative to other nutrient sources to UNB. Notably, this study found less confidence in the precise accuracy of these estimates, for the following reasons. First, the calculations were based on the assumption that the derived rates are constant for the time period during which the load is being estimated. Water column concentration of nutrients can change dramatically on time scale of hours to season, so static rates applied to an entire month introduce a great deal of uncertainty into the loading estimate. Second, the simplifying assumption was made that surface water covers the intertidal mudflat area approximately one-half the time; consequently, loads were divided by a factor of two to compensate for this

assumption. Both of these issues can be addressed through the development of a benthic nutrient exchange component of the UNB water quality model. A dynamic simulation model would allow diffusive flux rates to change as a function of overlying surface water concentration and give an integrated estimate of intertidal mudflat loading of nutrients based on an integration of available surface area over a tidal cycle.

This study found that internal loading of nutrients from the sediments to the surface waters represents a significant proportion of total annual and dry season loading to UNB. Total annual load of TN from the sediments (102,685 lbs), estimated for the period of October 2003 – September 2004, represents approximately 10% of estimated average-annual load from the San Diego Creek watershed during years 1990-1997. This studyestimated that approximately 48,000 lbs of particulate P were deposited in UNB during the 2003-2004 wet season. This number is within the range of the wet season TP load measured in San Diego Creek at Campus Drive (65,400 lbs TP). Annual benthic release of TP to surface waters (18,302 lbs) represents approximately 40% of the total wet season TP deposition to UNB. Benthic release of nutrients will have the most significant biological effect during the dry season, when other factors such as light availability and temperature enhance the growth of macroalgal blooms. During this period, benthic release of TN and TP (40,300 lbs TN and 18,000 lbs TP) is a significant portion of summertime watershed nutrient loads –equivalent to N loads from San Diego Creek during this period. It also represents approximately 20% of the allocated summertime TMDL for N and P to UNB for 2002.

## 5.2 Introduction

Calculations of allocations of total maximum daily nutrient loads (TMDL) for a watershed are based in part on the understanding of the total loading to the receiving basin. Previous calculations of total nutrient loads to UNB have not included estimates of the internal loading of nutrients from sediments. In this chapter, estimates of benthic nutrient flux are used to derive seasonal and annual estimates of nutrient loading from sediments to surface watersand then compare these estimates to existing documentation of other nutrient sources to UNB.

In this study, three methods were employed to estimate benthic nutrient flux: 1) diffusive fluxes predicted from concentrations gradients between pore waters and surface waters, 2) measured from incubation of sediment cores with manipulations of nutrient concentrations and $O_2$ content in overlying surface water, and 3) *in situ* measurements of flux with benthic chambers.

Of these three methods, it is generally accepted that *in situ* measurements with benthic chambers provide the most accurate estimates of benthic flux because they reflect field conditions that affect both diffusive and advective exchange of nutrients between sediments and surface waters (Callendar and Hammond 1982). Batch incubation of sediment cores results in the disturbance of sediments as the core is removed, thus potentially changing the biogeochemistry of the core and impacting flux. It also isolates sediments from ambient-field conditions; thus so while the impacts of bioirrigation on flux may be captured, advective exchange from other physical processes (sediment resuspension, tidal pumping, etc.) will not be captured. Prediction of diffusive fluxes from concentration gradients between surface and pore waters does not capture how surficial chemistry of sediments may alter predicted fluxes (e.g. redox status or effect of biological communities at the sediment-water interface). Nor does it capture advective transport – which in this study as well as other appears to be a dominant force in controlling benthic flux (Chapter 3, Callendar and Hammond 1982, Huettel et al. 1996, Koike and Mukai 1983).

In spite of this, *in situ* measurements are not the most widely used to estimate benthic flux. One reason for this is that the indirect measures of sediment nutrient flux are much less labor/cost-intensive than *in situ* estimates, and therefore provide a means of exploring how nutrient flux magnitude and direction could change over temporal and spatial time scales. It is also recognized that both *in situ* and batch incubation of intact sediment cores provide an estimate of flux under *ambient* surface water nutrient concentrations. Since surface water nutrients concentrations and important physiochemical parameters such as $O_2$and temperature, can change dramatically over times scales from a tidal cycle to seasons, the capacity to *predict* flux based on changes in overlying surface water nutrient concentration is very useful. Use of Ficke's Law of Diffusive Transport provides a theoretical basis to predict fluxes and therefore has an undisputed applicability in dynamic simulation modeling of benthic nutrient exchange. The difficulty exists in adding additional terms to the equation in order to account for advective flux, which varies greatly over time and space, or finding a means to correct diffusive fluxes based on *in sit*u measurements.

The objectives of this chapter are to:

1. Understand the extent to which predicted diffusive fluxes are comparable to the magnitude and direction of *in situ* measurements or batch incubation of intact soil cores,

2. Use the estimates of benthic flux to derive an annual estimate of benthic nutrient exchange with UNB surface waters, and
3. Compare the relative importance of this exchange with other sources of nutrients to UNB.

Application of this study's estimates of benthic flux requires assumptions about how well these measurements represent the annually averaged conditions in the estuary. These assumptions are explicitly stated and their validity explored below.

## 5.3 Methods

### *5.3.1 Approach*

The superior means of determining annual internal loading of nutrients to UNB from benthic exchange is the utilization of a dynamic simulation model with a benthic exchange component that predicts how fluxes change in response to overlying water column concentrations. In the absence of a calibrated model of this type for UNB, seasonal and annual estimates of benthic nutrient loads to surface waters using the benthic flux data were generated for this study (Chapter 2—diffusive flux, Chapter 3 – *in situ* measured flux, Chapter 4 – flux from incubated sediment cores).

In order to estimate annual internal nutrient loads from sediments, it is useful to understand to what degree diffusive flux predicted from pore water peeper data correlate with fluxes measured either *in situ* or from incubated sediments cores. In this study, these three types of flux estimates were compared to one another in order to determine the degree to which diffusive fluxes predict direction and magnitude of measured flux.

Based on the comparisons between diffusive and *in situ* fluxes, correction factors were then developed to apply to the diffusive fluxes. This was done to compensate for *in situ* estimates available only for April and October sampling periods. Because of the paucity of *in situ* measurements and the recognition that these ambient fluxes can vary greatly in response to changes in water column concentrations, a methodology derived from a theoretical basis to predict fluxes was selected (ie. Ficke's Law of Diffusion) to estimate annual loads. Because limited data were available to add additional terms to the equation in order to account for advective flux, an empirical correction factor that could be applied to the diffusive flux estimates was developed for this study. These corrected estimates were annualized, as explained in

detail below. These numbers were then compared to existing load estimates for TN and TP to place the importance of these loads for UNB in perspective.

### *5.3.2 Data Analysis and Assumptions*

*Comparisons of Diffusive Fluxes versus Fluxes Measured In Situ and from Incubated Sediment Cores*

To compare diffusive fluxes versus *in situ* fluxes (Chapter 3), the diffusive flux estimates were first generated by utilizing the pore water concentration profiles and related parameters (% moisture, porosity) from the April and November sampling periods (Chapter 2). However, instead of using the nutrient concentration in the overlying bottom waters at the time the pore water peepers were pulled, the concentration of the ambient surface water measured at the start of the benthic chamber deployment was used to determine the concentration gradient (dC/dz; see Eq. 2-6 in Section 2.3.4). The diffusive flux estimates were generated for each successful deployment at each of the three sites in April and October (Chapter 3).

Similarly, to predict diffusive fluxes under the ambient, medium, and high nutrient concentrations employed in the incubations of sediment cores (Chapter 4), the study utilized the pore water concentration profiles and associated bulk sediment characteristics generated under the June 2004 sampling period for Site 2 – the location where the cores for the batch incubation were taken. Since no pore water profiles were generated in July, the time period of the experiment, the June pore water profiles were used. As with the comparison with *in situ* fluxes, the concentration gradient (dC/dz; see Eq. 2-6 in Section 2.3.4) was generated by the difference between the pore water concentration for that particular constituent and the concentration of the oxic treatments for nutrients under ambient, medium, and high nutrient levels (Chapter 4, Table 4-3).

The predicted diffusive fluxes were regressed against the measured fluxes of both types (*in situ* and batch incubated), assuming a linear relationship defined by Eq. 5-1, where $F_{MEAS}$ and $F_{PRED}$ are the measured flux (*in situ* or from incubated sediment cores) and predicted diffusive fluxes respectively, and *b* and *a* are slope and intercept of the linear regression respectively.

$$\mathbf{F_{MEAS} = F_{PRED}*b + a} \qquad \textbf{Eq. 5-1}$$

*Estimation of Annual Loading of Nutrients from Benthic Sources*

Two estimates of annual loading of nutrients from benthic sources were generated for UNB. The first was based on uncorrected diffusive flux rates; the second was based on corrected flux rates, using the linear relationship developed between the diffusive and *in situ* measured fluxes.

To determine the annual loading for uncorrected diffusive fluxes, the following assumptions were made:

- Exchange between the sediments and surface waters occurred at steady state;
- Overlying water column nutrient concentrations and mean flux rate for intertidal and subtidal zones do not vary over the period in which the load was calculated;
- Respective mean flux rates for Sites 1-3 are representative of the spatially-averaged rates for intertidal and subtidal zones of UNB.
- Average rates for months in which pore water peeper data are not available can be interpolated from the mean of the previous and next month for which data were available.

To estimate annual nutrient loads, the mean rates for subtidal and intertidal for each month for each constituent (Table 5-1) in μmoles $m^{-2}$ $hr^{-1}$ were converted to a load (lbs) by using Eq. 5-2:

$$L = F*A*t \qquad \text{Eq. 5-2}$$

where L is monthly load, A is area, and t is time.

A conversion factor of $3.086X10^{-8}$ μmoles per lb N and $6.832 X10^{-8}$ μmoles per lb P was used to convert μmoles to pounds. The surface area of the intertidal and subtidal portions of UNB (240.4 and 209.4 acres, respectively; ACOE 2000) were converted into square meters by multiplying by a factor of 4046.86 $m^2$ per acre. For months in which pore waters were not sampled, an average rate was interpolated from the previous and next months for which data were available (Table 5-1). For November 2003, the rates derived from November 2004 pore water profiles. Each monthly load was then summed to yield a seasonal or annual load. For the intertidal zone, made a simplifying assumption that the surface area would be covered by water, and therefore would be subject to benthic exchange, only one-half the time. Therefore, monthly loads were divided by two to correct for this.

Corrected fluxes were derived using the linear regression relationships shown in Table 5-4. Calculation of annual and seasonal loads followed the same procedure as was done with the uncorrected diffusive fluxes.

**Table 5-1. UNCORRECTED diffusive flux rates for each nutrient species by habitat type (subtidal and intertidal) and month used in calculation of seasonal and annual fluxes. All fluxes are given in μmol $m^{-2}$ $hr^{-1}$. An asterick (*) designates months for which rates were interpolated by averaging previous and next months during which pore water sampling occurred. November 2003 rate is rate derived from November 2004 pore water profile.**

| Month | No Days | NH4 | | N03 | | DON | | SRP | | DOP | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Subtidal | Intertidal | Subtidal | Intertidal | Subtidal | Intertidal | Subtidal | Intertidal | Subtidal | Intertidal |
| Oct-03 | 31 | 17.89 | -0.75 | -4.15 | -4.07 | 2.24 | 1.08 | 6.26 | 0.12 | -0.02 | -0.03 |
| Nov-03* | 30 | 9.74 | -0.83 | -12.23 | -12.35 | 11.79 | 17.78 | 3.19 | 0.37 | 0.12 | 0.06 |
| Dec-03* | 31 | 9.74 | -0.83 | -12.23 | -12.35 | 11.79 | 17.78 | 3.19 | 0.37 | 0.12 | 0.06 |
| Jan-04* | 31 | 9.74 | -0.83 | -12.23 | -12.35 | 11.79 | 17.78 | 3.19 | 0.37 | 0.12 | 0.06 |
| Feb-04 | 28 | 1.59 | -0.90 | -20.31 | -20.63 | 21.34 | 34.48 | 0.12 | 0.62 | 0.26 | 0.15 |
| Mar-04 | 31 | 41.9 | 5.61 | -12.57 | -10.58 | 12.77 | 11.39 | 22.56 | 2.06 | 0.29 | 0.15 |
| Apr-04 | 30 | 22.48 | 7.50 | -6.52 | -6.29 | 19.24 | 18.14 | 2.66 | 1.30 | -0.09 | 0.67 |
| May-04 | 31 | 19.55 | 7.20 | -4.48 | -4.14 | 11.62 | 9.97 | 2.02 | 1.40 | 0.02 | 0.55 |
| Jun-04 | 30 | 16.62 | 6.89 | -2.44 | -1.99 | 3.99 | 1.79 | 1.38 | 1.49 | 0.13 | 0.43 |
| Jul-04* | 31 | 9.26 | 4.04 | -1.24 | -0.98 | 1.29 | 1.40 | 4.23 | 1.11 | 0.08 | 0.25 |
| Aug-04* | 31 | 9.26 | 4.04 | -1.24 | -0.98 | 1.29 | 1.40 | 4.23 | 1.11 | 0.08 | 0.25 |
| Sep-04 | 30 | 7.8 | 1.18 | -0.03 | 0.03 | -1.42 | 1.01 | 7.09 | 0.72 | 0.03 | 0.07 |

**Table 5-2. CORRECTED flux rates for each nutrient species by habitat type (subtidal and intertidal) and month used in calculation of seasonal and annual fluxes. All fluxes are given in μmol $m^{-2}$ $hr^{-1}$. An asterick (*) designates months for which rates were interpolated by averaging previous and next months during which pore water sampling occurred. November 2003 rate is derived from November 2004 pore water profile.**

| Month | No Days | NH4 | | N03 | | DON | | SRP | | DOP | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Subtidal | Intertidal | Subtidal | Intertidal | Subtidal | Intertidal | Subtidal | Intertidal | Subtidal | Intertidal |
| Oct-03 | 31 | 570.7 | -253.2 | -5.4 | -4.6 | -166.7 | -203.0 | 29.9 | -6.6 | -4.2 | -5.3 |
| Nov-03* | 30 | 210.5 | -256.4 | -81.0 | -82.1 | 133.8 | 322.2 | 11.6 | -5.2 | 4.6 | 0.6 |
| Dec-03* | 31 | 210.5 | -256.4 | -81.0 | -82.1 | 133.8 | 322.2 | 11.6 | -5.2 | 4.6 | 0.6 |
| Jan-04* | 31 | 210.5 | -256.4 | -81.0 | -82.1 | 133.8 | 322.2 | 11.6 | -5.2 | 4.6 | 0.6 |
| Feb-04 | 28 | -149.6 | -259.6 | -156.6 | -159.5 | 434.3 | 847.4 | -6.6 | -3.7 | 13.3 | 6.4 |
| Mar-04 | 31 | 1631.8 | 28.1 | -84.2 | -65.5 | 164.6 | 121.3 | 126.8 | 4.9 | 15.4 | 6.2 |
| Apr-04 | 30 | 773.7 | 111.8 | -27.6 | -25.4 | 368.1 | 333.5 | 8.5 | 0.4 | -8.6 | 39.4 |
| May-04 | 31 | 644.2 | 98.1 | 3.0 | -5.3 | 128.3 | 76.4 | 4.6 | 1.0 | -1.7 | 31.8 |
| Jun-04 | 30 | 514.8 | 84.5 | 33.5 | 14.8 | -111.5 | -180.7 | 0.8 | 1.5 | 5.1 | 24.1 |
| Jul-04* | 31 | 229.2 | -41.6 | 33.3 | 24.3 | -196.6 | -193.0 | 17.8 | -0.8 | 2.1 | 12.6 |
| Aug-04* | 31 | 229.2 | -41.6 | 33.3 | 24.3 | -196.6 | -193.0 | 17.8 | -0.8 | 2.1 | 12.6 |
| Sep-04 | 30 | 69.3 | -167.6 | 33.2 | 33.8 | -281.8 | -205.3 | 34.8 | -3.0 | -1.0 | 1.2 |

## 5.4 Results

### *5.4.1 Comparison of Predicted Diffusive Flux Versus Measured Fluxes*

Table 5-3 presents the results of predicted diffusive versus measured *in situ* flux estimates by nutrient species, while Table 5-4 presents the results of linear regression of these two estimates.

**Table 5-3. Comparison of predicted diffusive flux versus measured *in situ* flux estimates. All rates are given in units of mmol $m^{-2}$ $d^{-1}$.**

| Date | ID | Day (D)/ Night (N) | Estimate Type | SRP | DOP | $NO_3^-$ | $NH_4^+$ | DON |
|---|---|---|---|---|---|---|---|---|
| 4/21/04 | 1-1 | D | In Situ | 1.09 | ND | -1.30 | ND | ND |
| | | | Diffusive | 0.15 | -- | -0.12 | -- | -- |
| 4/21/04 | 1-2 | N | In Situ | 0.89 | -0.01 | -4.80 | ND | ND |
| | | | Diffusive | 0.17 | -0.03 | -0.23 | -- | -- |
| 4/20/04 | 2-1 | D | In Situ | 0.22 | -0.14 | -2.80 | ND | ND |
| | | | Diffusive | 0.001 | 0.00 | -0.26 | -- | -- |
| 4/20/04 | 2-2 | N | In Situ | 0.45 | ND | 1.30 | ND | ND |
| | | | Diffusive | 0.01 | -- | -0.09 | --- | -- |
| 4/22/04 | 2-3 | D | In Situ | 0.62 | 0.000 | -0.30 | ND | ND |
| | | | Diffusive | 0.002 | 0.001 | -0.15 | -- | -- |
| 4/22/04 | 2-4 | N | In Situ | 0.42 | -0.29 | 2.00 | ND | ND |
| | | | Diffusive | 0.01 | 0.01 | -0.07 | -- | -- |
| 4/20/04 | 3-1 | D | In Situ | 0.26 | -0.49 | -5.40 | ND | ND |
| | | | Diffusive | 0.03 | -0.005 | -0.26 | -- | -- |
| 4/20/04 | 3-2 | N | In Situ | 1.10 | ND | 3.20 | ND | ND |
| | | | Diffusive | 0.04 | -- | -0.06 | -- | -- |
| 10/29/04 | 1-1 | N | In Situ | -0.17 | -0.67 | -4.80 | 6.40 | -23.90 |
| | | | Diffusive | -0.02 | -0.01 | -1.06 | 0.29 | -0.44 |
| 10/30/04 | 1-2 | N | In Situ | -0.51 | -0.24 | -15.60 | 2.10 | -10.20 |
| | | | Diffusive | -0.02 | -0.005 | -1.56 | 0.19 | 0.07 |
| 10/28/04 | 2-2 | N | In Situ | 0.29 | -0.31 | 1.10 | 5.60 | -10.40 |
| | | | Diffusive | 0.01 | -0.01 | -0.49 | 0.26 | -0.22 |
| 10/30/04 | 2-3 | N | In Situ | -0.31 | -0.02 | -8.90 | 8.60 | -0.30 |
| | | | Diffusive | 0.003 | -0.001 | -0.55 | 0.25 | -0.11 |

**Table 5-4. Linear regression statistics between predicted diffusive flux and measured *in situ* fluxes. All rates are given in units of mmol $m^{-2}$ $d^{-1}$.**

| Nutrient Species | Sample Size (N=) | Regression Equation | $R^2$ |
|---|---|---|---|
| SRP | 12 | $F_{MEAS} = 5.94*F_{PRED} - 0.176$ | 0.51 |
| DOP | 8 | $F_{MEAS} = 63.85*F_{PRED} - 0.076$ | 0.48 |
| $NO_3^-$ | 12 | $F_{MEAS} = 9.36*F_{PRED} + 0.837$ | 0.65 |
| $NH_4^+$ | 4 | $F_{MEAS} = 44.20*F_{PRED} – 5.277$ | 0.49 |
| DON | 4 | $F_{MEAS} = 31.45*F_{PRED} – 5.6893$ | 0.48 |

Diffusive fluxes performed fairly well in predicting the direction, but not magnitude, of fluxes measured *in situ* or from incubating sediment cores (i.e. into or out of the sediment), (Table 5-4, 5-5). In particular, this was the case for *in situ* NH4, DON and SRP, where 92–100% of the predicted estimates in the correct direction. For DOP and N03, these values were less (80 and 60% respectively). Diffusive fluxes were much less predictive of the magnitude of flux than the direction. All diffusive flux estimates underpredicted *in situ* flux by up to two orders of magnitude (Figure 5-1, Table 5-4). SRP and N03 performed the best, with measured values generally within a factor of 5-10 times that of predicted. Diffusive fluxes for DON, NH4, and DOP under predicted *in situ* fluxes by approximately two orders of magnitude.

**Table 5-5. Linear regression statistics between predicted diffusive flux and measured batch incubation fluxes under ambient, medium, and high nutrient concentrations (for nutrient concentrations used, see Chapter 4, Table 4-3). Medium and high DON and DOP concentrations were not included in the experiment, thus the designation of N/A = not applicable. Numbers with astericks represents division of the $F_{MEAS}$ by $F_{PRED}$.**

| Species | Flux Rates (mmol $m^{-2}$ $d^{-1}$) | | | | Regression Equation | $R^2$ |
|---|---|---|---|---|---|---|
| | Type | Ambient | Medium | High | | |
| N03 | Predicted | -0.0009 | -0.80 | -4.00 | $F_{MEAS} = 31.41*F_{PRED} - 7.67$ | 0.99 |
| | Measured | -1.84 | -40.06 | -131.88 | | |
| SRP | Predicted | 0.0200 | -0.0045 | -0.15 | $F_{MEAS} = 176.16*F_{PRED} - 3.16$ | 0.99 |
| | Measured | 0.10 | -3.32 | -29.76 | | |
| NH4 | Predicted | 0.20 | 0.12 | -0.18 | $F_{MEAS} = 122.1*F_{PRED} - 20.67$ | 0.87 |
| | Measured | -3.73 | 4.32 | -45.17 | | |
| DON | Predicted | 0.41 | N/A | | 87.5* | N/A |
| | Measured | 36.05 | | | | |
| DOP | Predicted | 0.0060 | | | 83.6* | |
| | Measured | 0.50 | | | | |

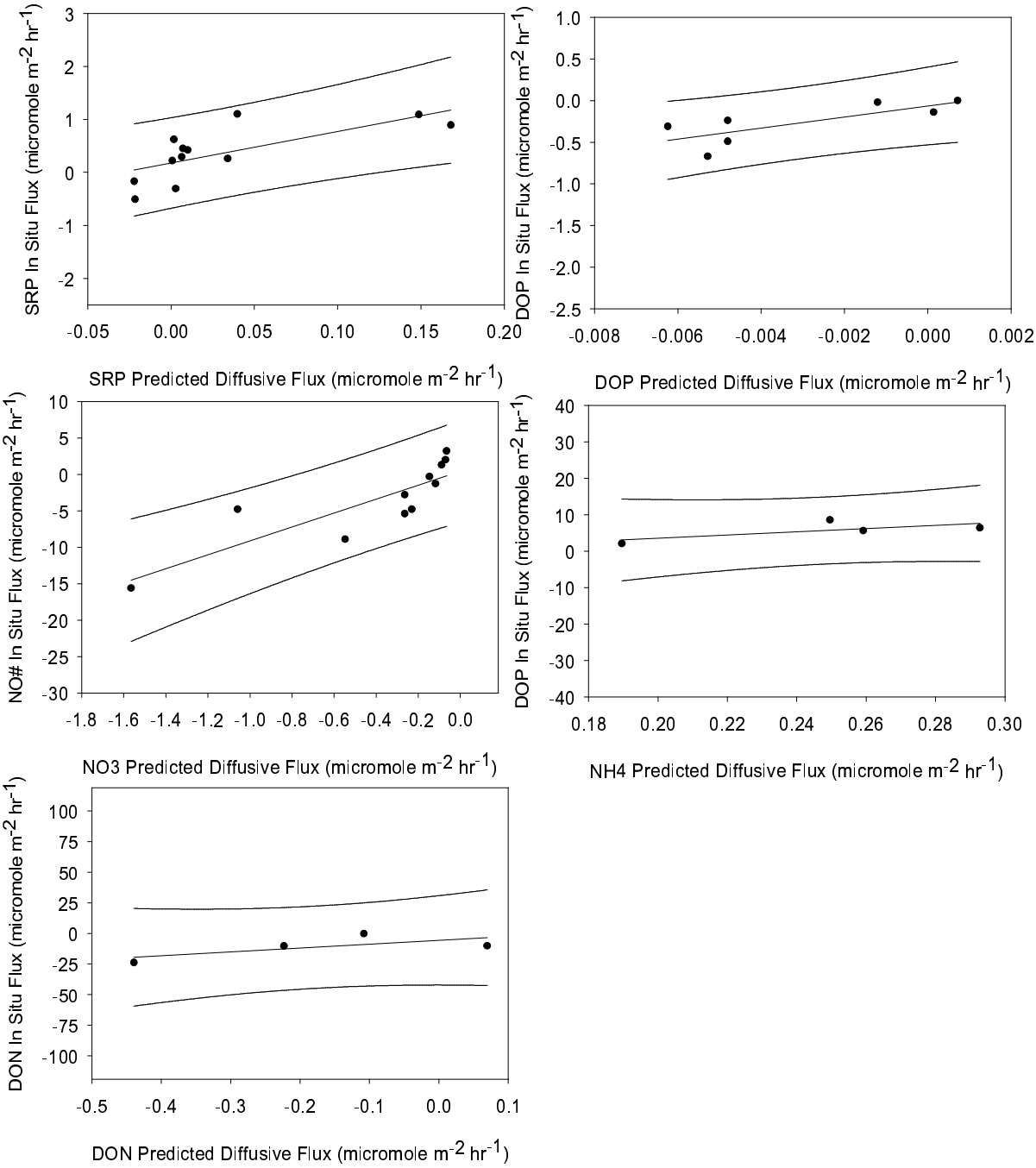


**Figure 5-1. Linear regressions of predicted diffusive flux versus measured *in situ* fluxes for SRP, DOP, $NO_3^+$, $NH_4^+$, and DON. Regression line and upper and lower 95% confidence intervals are depicted. Regression equations and statistical information are given in Table 5-4.**

As with the *in situ* fluxes, diffusive fluxes also performed well in predicting the direction of fluxes measured by incubating sediment cores, but not the magnitude (Table 5-5). The slopes for the

linear regression equations ranged from 31 to 176, indicating that the diffusive fluxes were underpredicting measured fluxes by approximately 1-2 orders of magnitude.

### *5.4.2 Estimates of Seasonal and Annual Internal Loading of Nutrients*

Tables 5-6 and 5-7 present estimated seasonal and annual TP and TN loading estimates from benthic exchange from UNB. Annual TN and TP loading estimated based on corrected fluxes (102,685 lbs and 18,302 lbs) were 21 and 6 times (respectively) those based on uncorrected flux estimates.

**Table 5-6. Estimated seasonal and annual loading of N from benthic exchange based on uncorrected diffusive and corrected flux estimate. All units are in pounds (lbs).**

| Estimate Type | Nutrient Species | Wet Season (October 2003–March 2004 | | | Dry Season (April – September 2004) | | | Annual (October 2003 – September 2004) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Subtidal | Intertidal | Total | Subtidal | Intertidal | Total | Subtidal | Intertidal | Total |
| Uncorrected | NH4 | 1,753 | 18 | 1,771 | 1,740 | 339 | 2,079 | 3,493 | 357 | 3,850 |
| | $NO_3^-$ | -1,389 | -781 | -2,170 | -305 | -157 | -462 | -1,693 | -938 | -2,632 |
| | DON | 1,348 | 1,076 | 2,424 | 687 | 369 | 1,055 | 2,034 | 1,445 | 3,479 |
| | **TN** | **1,712** | **313** | **2,025** | **2,122** | **550** | **2,672** | **3,834** | **863** | **4,697** |
| Corrected | $NH_4^+$ | 40,509 | -10,672 | 29,838 | 49,458 | 956 | 50,413 | 89,967 | -9,716 | 80,251 |
| | $NO_3^-$ | -9,167 | -10,224 | -19,392 | 2,091 | 1,470 | 3,561 | -7,077 | -8,754 | -15,831 |
| | DON | 15,315 | 36,624 | 51,939 | -5,628 | -8,046 | -13,674 | 9,687 | 28,578 | 38,265 |
| | **TN** | **46,657** | **15,728** | **62,385** | **45,920** | **-5,620** | **40,300** | **92,577** | **10,108** | **102,685** |

Of the corrected loading estimates, NH4 flux represented approximately 68% of annual DON and NH4 load to surface waters; N03 loss to the sediments represents approximately 13% of the magnitude of DON + NH4 annual load (Table 5-6). The wet season TN load (62,385 lbs) was slightly higher than the dry season load (40,300 lb), in part because of the contribution of DON to surface waters. N03 and DON exchange during the dry season was negligible. The intertidal zone represented approximately 30% of the TN load to surface waters during the wet season and a negligible portion during the dry season.

Of the corrected loading estimates, SRP flux represented approximately 57% of annual TP load to surface waters (Table 5-7). The wet season TP load (8,972 lbs) was slightly lower than the dry season load (9,331 lb), in part because of the negligible contribution of intertidal zone to TP

flux during the wet season. The magnitude of SRP and DOP load during the dry season were roughly equivalent. The intertidal zone represented a negligible portion of TP flux during the wet season and approximately 60% of the TP load to surface waters during the dry season.

**Table 5-7. Estimated seasonal and annual loading of N from benthic exchange based on uncorrected diffusive and corrected flux estiamtes. All units are in pounds (lbs).**

| Estimate Type | Nutrient Species | Wet Season (October 2003–March 2004) | | | Dry Season (April 2004–September 2004) | | | Annual (October 2003–September 2004) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Subtidal | Intertidal | Total | Subtidal | Intertidal | Total | Subtidal | Intertidal | Total |
| Uncorrected | SRP | 1,654 | 95 | 1,749 | 915 | 173 | 1,089 | 2,569 | 268 | 2,837 |
| | DOP | 37 | 10 | 48 | 11 | 54 | 65 | 49 | 64 | 113 |
| | **TP** | **1,691** | **105** | **1,796** | **927** | **227** | **1,154** | **2,618** | **332** | **2,950** |
| Corrected | SRP | 7,976 | -1,005 | 6,971 | 3,574 | -81 | 3,494 | 11,550 | -1,086 | 10,464 |
| | DOP | 1,584 | 417 | 2,001 | -81 | 5,918 | 5,837 | 1,503 | 6,335 | 7,838 |
| | **TP** | **9,560** | **-589** | **8,972** | **3,494** | **5,837** | **9,331** | **13,054** | **5,249** | **18,302** |

## 5.5 Discussion

### *5.5.1 Comparison of Predicted Diffusive Versus Measured Benthic Exchange Rates and Loading Estimates*

Comparison of predicted diffusive fluxes with fluxes measured *in situ* and from incubating sediment cores showed that diffusive fluxes underpredicted measured fluxes by roughly 1-2 orders of magnitude. Several researchers have found similar results (Callender and Hammond 1982, Gomez-Parra and Forja 1993, Devol 1987, Hopkinson 1987, Fisher and Reddy 2001, McCaffrey et al. 1980). Callender and Hammond (1982) found that nutrient fluxes measured *in situ* with benthic chambers may be 1 to 10 times higher than diffusive and that the difference could be attributed to irrigation of sediments by macrofauna. Gomez-Parra and Forja (1993) compared flux based on sediment porewater concentrations gradients to benthic chamber P flux in the coastal waters of the southwest of Cadiz, Spain and found that in all cases the *in situ* measured flux exceeded the diffusive flux, sometimes by as much as 29 times. Many of these cited authors found that field locations that had the lowest concentrations of macrofauna were the least hydrodynamically active had the best agreement between calculated and measured flux. Benthic exchange in UNB, a fully-tidal estuary with abundant benthic infauna community, has been shown to be driven by advective transport – perhaps by a factor of 3-5 times the amount contributed by diffusion alone may be contributing (Worshnapp et al. 2004; Chapter 3). Thus, if used to estimate annual internal loading of nutrients from the sediments, uncorrected diffusive fluxes greatly underestimate the magnitude of this source of nutrients to UNB.

For this reason, seasonal and annual loads presented in this study were estimated from corrected fluxes. This correction was based on a linear regression between benthic exchange rates measured *in situ* in April and October 2004 and diffusive fluxes predicted from pore water profiles during those time periods. These loading estimates are considered reasonable in terms of predicting the order of magnitude and direction of benthic nutrient exchange, and can be used to interpret the relative importance of benthic exchange of nutrients relative to other nutrient sources to UNB.

Less confidence is attributed to the precise accuracy of these estimates, for the following reasons. First, the calculations are based on the assumptions that the derived rates are constant for the time period during which the load is being estimated. The results of the laboratory batch incubation experiment illustrated the degree to which benthic flux rates may change as concentrations of nutrients in the overlying water column change (Chapter 4). Water

column concentration of nutrients can change dramatically on time scales of hours to season, so static rates applied to an entire month introduce a great deal of uncertainty into the loading estimate. These loading rates can be refined by developing a benthic nutrient exchange component of the UNB water quality model. If the model correctly simulates surface water nutrient concentrations, then a more accurate prediction of diffusive flux may be derived and employed for each model time step. This diffusive rate can then be adjusted with an empirical correction for advective transport, as was done here. This approach will also yield more accurate estimates of loading from the intertidal zone. Correspondingly, a simplifying assumption has been made that surface water covers the intertidal mudflat area approximately one-half the time; consequently, loads calculated from the intertidal zone were reduced by 50% to take into account the approximate amount of time the sediment surface was wetted. A dynamic simulation model would allow an improved integrated estimate of intertidal mudflat loading of nutrients, based on an integration of available surface area over a tidal cycle.

Another uncertainty is the correction of diffusive fluxes, based on a linear regression between *in situ* measured and predicted diffusive fluxes. While it is believed that the approach is valid, the number of chamber deployments upon which the statistical relationship is based was limited – particularly for NH4 and DON (four deployments for Sites 1 and 2 in month of October only). Regression statistics show that predicted diffusive flux explain only approximately 40-50% of the variation in measured flux. Because the October 2004 chamber deployment took place shortly after a storm when the sediment column was likely disturbed, and because NH4 flux represents 68% of annual TN loads, uncertainty in the TN and TP loading estimates could be reduced with additional deployments throughout the year, coupled with pore water profiles. In addition, because no measured fluxes were made of the intertidal mudflat zone, loading estimates from this habitat type could be improved through either incubation of sediment cores or chamber deployments of short duration.

### *5.5.2 Comparison of Estimated Benthic Nutrient Loading to UNB with Other Sources*

This study found that internal loading of nutrients from the sediments to the surface waters represents a significant proportion of total annual and dry season loading to UNB. Total annual load of TN from the sediments (102,685 lbs), estimated for the period of October 2003 – September 2004, represents approximately 10% of estimated average annual load from the San Diego Creek watershed during years 1990-1997 (1,087,000 lb; SARWQCB 1998). Not included in this term are other potential important sources of nutrients, including atmospheric deposition.

It is also not clear the extent to which this average annual load includes particulate N from suspended sediment load, which in this study was estimated at 122,000 lbs during the 2003-2004 wet season. TP loads from the watershed have not been assessed for this watershed, in part because of the recognition that particulate loads, not addressed by currently monitoring, would likely bear the majority of P loads coming from the watershed. In this study, it was estimated that approximately 48,000 lbs of particulate P were deposited in UNB during the 2003-2004 wet season. Annual benthic release of TP to surface waters represents approximately 40% of this total wet season load.

It can be argued that benthic release of nutrients have their most significant biological effect during the dry season, when other factors such as light availability and temperature enhance the growth of macroalgal blooms (Kamer et al. 2001, Sutula et al. 2004). During this period, benthic release of TN and TP is a significant portion of summertime watershed nutrient loads. In their monitoring of the UNB watershed nutrient loads, Orange County reported a summertime load of approximately 42,500 lbs of TN for the period of April–September 2003 for the San Diego Creek site at Campus Drive (abstracted from Figure 10, OC 2004). Estimated benthic TN nutrient loading to surface waters for the same period in 2004 was 40,300 lbs. This number, normalized to a daily rate (220.2 lb $d^{-1}$), is equivalent to the estimated daily dry season TN loading for July 2003–June 2004 from all Nutrient TMDL Regional Monitoring Program channels (217.2 lbs $d^{-1}$; OC 2004). This is approximately 20% of the allocated summertime TMDL for UNB for 2002 and 26% of the allocated TMDL for 2007 (Table 5-8, SARWCB 1998). While loads for TP are not reported, annual benthic release of TP from UNB is equivalent to 20% of the annual TMDL allocated for TP in 2002 and 30% of the allocation projected for 2007 (Table 5-8, SARWQCB).

**Table 5-8. Projected TMDL allocations for TN and TP (lbs) from the UNB watershed (From SARWQCB 1998).**

| Allocation Type | 12/31/2002 | 12/31/2007 | 12/31/2012 |
|---|---|---|---|
| UNB Watershed TN Summer Load | 200,097 | 153,861 | |
| UNB Watershed TN Winter Load | | | 144,364 |
| UNB Watershed TP Annual Load | 86,912 | 62,080 | |

## 5.6 References

ACOE 2000. Upper Newport Bay Ecosystem Feasibility Restoration Study Final Report. U.S. Army Corps of Engineers, Los Angeles District. September 2000.

Callender, E. and D. Hammond (1982) Nutrient exchange across the sediment-water interface in the Potamac River Estuary. Esturarine, Coastal and Shelf Science, 15, 395-413.

Devol, A.H. 1987. Verification of flux measurements made with in situ benthic chambers. Deep Sea Res. 34:1007–1026.

Fisher M.M. and K.R. Reddy. 2001 Phosphorus Flux from Wetland Soils Affected by Long-Term Nutrient Loading. Journal of Environmental Quality 30:261-271

Gomez-Parra, A., and J.M. Forja. 1993. Benthic nutrient fluxes in Cadiz Bay. Hydobiologia 252:23–34.

Kamer, K., K. A. Boyle, and P. Fong. 2001. Macroalgal bloom dynamics in a highly eutrophic southern California estuary. Estuaries 24(4): 623-635.

Hopkinson, C.S. 1987. Nutrient regeneration in shallow water sediments of the estuarine plume region of the nearshore Georgia Bight, USA. Marine Biol. 94:127–142.

McCaffrey, R.J., A.C. Myers, E. Davey, G. Morrison, M. Bender, N. Luedtke, D. Cullen, P. Froelich, and G. Klinkhammer. 1980. The relation between porewater chemistry and benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island. Limnol. Oceanogr. 25:31–44.

Orange County 2004. Report of the Regional Monitoring Program for the Newport Bay/San Diego Creek Watershed Nutrient TMDL (Resolution 98-9, as Amended by 98-100). November 2004.

SARWQCB 1998. Resolution 98-100 Ammending Water Quality Control Plan for Santa Ana River Basin to Incorporate Nutrient TMDL for Newport Bay/San Diego Creek Watershed.

Sutula, Martha, K.Kamer and J.Cable. 2004. Sediments as a non-point source of nutrients to Malibu Lagoon, California (USA). Southern California Coastal Water Research Project, Westminster, CA. Technical Report #441.

Worsnopp, M.B., Hammond, D.E., and Cable, J.E. (2004) Radium and radon as tracers of ground water flow into Upper Newport Bay, CA, EOS Transactions, American Geophysical Union, 85 (47), Fall Meet. Suppl., Abstract H21B-1013, San Francisco, CA, 13-17 December 2004.

# 6 CONCLUSIONS

The findings of this study have shown that particulate N and P, associated with sediment, was deposited in UNB during the wet season and that these particulate nutrients were remobilized as dissolved inorganic nutrients to the surface waters during dry season. The direction of sediment-surface water exchange of nutrients was driven by the concentration gradient between pore waters and surface waters (diffusive transport). However, the magnitude of this exchange was driven to a greater extent by advective transport processes, including bioirrigation by benthic infauna and tidal pumping of water through sediments. When water column nutrient concentrations decrease, often occuring during the summer when nutrient inputs are low and primary productivity is high, flux from sediments may be promoted by macroalgae. Sediment release of nutrients during the dry season provides a major source of nutrients for primary producer uptake in UNB – a number equal in magnitude to dry season watershed runoff of N. These estimates also represent approximately 20% of the 2002 TMDL load allocation for N and P to UNB during the dry season. N uptake by macroalgae provides a mechanism for N retention in the estuary and decreases the importance of denitrification as a pathway of permanent N removal from the estuary. This may explain why eutrophic conditions in an estuary often persist, even after anthropogenic nutrients loads have been curtailed.