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Sediments as a Non-Point Source of Nutrients to Malibu Lagoon, California (USA)

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Los Angeles Regional Water Quality Control Board

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EXECUTIVE SUMMARY

Malibu Lagoon is a 7.5 ha (18.5-acre) brackish water coastal lagoon situated at the base of the Malibu Creek watershed in Los Angeles County, California. Land use changes in the Malibu Creek watershed have lead to increased freshwater and nutrient loads to the Lagoon and have resulted in a decline in the Lagoon's wildlife beneficial uses. In 1996 the Los Angeles Regional Water Quality Control Board (LARWQCB) placed Malibu Lagoon on the federal 303(d) list of impaired water bodies due to the excessive abundance of primary producers (*Rhizoclonium hookeri*, a green, mat-forming alga, and *Ruppia maritima*, a submerged aquatic vascular plant) in the Lagoon and associated dissolved oxygen (DO) problems. To reduce excessive primary producer abundance and DO problems in Malibu Lagoon, the U.S. Environmental Protection Agency (USEPA) promulgated a Total Maximum Daily Load (TMDL) to limit nutrient pollution in the watershed. The LARWQCB is currently refining the numeric water quality objectives (WQOs) set forth in the 2003 TMDL and the new limits will be adopted in order to limit the seasonal and/or annual nutrient inputs from the watershed to the Lagoon. Our study addressed three major questions that are relevant for refining the WQOs:

1) What is the load of N and P associated with the wet season input of sediments into the Lagoon?
2) What is the exchange of N and P between the surface waters from the sediments?
3) What are the other sources of N and P to the Lagoon and how does N and P remobilized from sediments compare with these sources?

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

1) Investigate the seasonal patterns of bulk and pore water sediment N and P concentrations in the Lagoon;
2) Estimate wet season and long-term average annual sediment deposition rates and associated particulate N and P load to the Lagoon and determine, to the extent possible, the major anthropogenic sources associated with this deposition;
3) Estimate ambient benthic nutrient exchange under a variety of environmental conditions observed in the Lagoon over an annual cycle and integrate these rates to evaluate annual net nutrient exchange; and

4) Compare the importance of sediment remobilization and exchange of nutrients with surface waters relative to the magnitude of other nutrient non-point sources to Lagoon.

Specifically we hypothesized that sediments serve as storage for nutrients that enter the Lagoon during wet weather periods and these nutrients are later remobilized to surface waters, providing fuel for primary producer growth during dry weather periods.

A total of 8 sampling events were conducted between February 2002 and September 2003 at a total of 10 sites distributed throughout the Western and Central portions of Malibu Lagoon. The central lagoon (approximately 50,000 m^2 in size) is the main channel of Malibu Creek where it discharges the ocean and is a mixture of intertidal flats, subtidal channels and sand bars. The western lagoon (approximately 25,000 m^2 in size) is primarily the result of a restoration project that created three channels with sloping mudflats subtidal channels, emergent marsh and upland habitat. Sampling occurred over two phases; the former was a limited investigation of primary producers, water column nutrients, and bulk surficial sediment nutrients and grain size in the Lagoon while the latter included all the same parameters plus characterization of sediment pore water profiles and sediment deposition using natural radionuclide tracers.

At each site, water column salinity, temperature, DO, total suspended sediment (TSS), chlorophyll *a*, particulate organic carbon (POC), particulate N (PN), and particulate P (PP), ammonia (NH_4), nitrate and nitrite (NO_3+NO_2), total Kjeldahl N (TKN), soluble reactive P (SRP), dissolved organic carbon (DOC) and total dissolved P (TDP) were measured. Sediment cores were into 1-2 cm intervals to a depth of 10 cm. Sediment pore waters were separated by centrifugation and the filtered for analysis of NH_4^+, NO_3^-, SRP, TKN, TDP, and DOC. The dried solid phase material was analyzed for sediment grain size, sediment total organic carbon (SOC), sediment total N (SN), sediment total P (SP), and beryllium-7 (^{7}Be – a natural radionuclide tracer of short-term sediment deposition). Sediment ^{210}Pb were measured at one site to determine the long-term average annual sedimentation rate. Percent cover of each primary producer species or functional group was also measured at each site.

We found that sediment enriched in particulate N and P was deposited in the Lagoon during the wet season and these particulate nutrients were remobilized as dissolved inorganic nutrients to the surface waters during dry season. Sediment release of nutrients during the dry season provides a major source of nutrients for primary producer growth in the Lagoon – thus linking wet season nutrient loading and summertime hypoxia in the Lagoon. The four major findings of our study provide evidence for this assertion:

1. **Wet season sediment deposition from the Malibu Creek watershed increased in the N and P content of Malibu Lagoon sediments from pre-wet season baseline conditions.**

   We documented an average of 3 ± 1 cm of sediment deposited to the Western Lagoon during the 2002-2003 wet season (October 2002-April 2003). The Western Lagoon increased in sediment nutrient content by 2928 kg N (6456 lb) and 219 kg P (482 lbs) over this period. Diffusion of high NO_3 from surface waters into sediments can only account for a small portion of this increase in sediment inventory (~5%), so particulate N and P deposition from wet weather events is the major process responsible for this net increase. Comparison of the 2002-2003 wet season sedimentation rate (associated with a mild El Niño-influenced rainfall) versus the maximum long-term average annual rate (0.1 cm yr^{-1}) estimated with ^{210}Pb highlights the pulsed nature of sedimentation events in the Lagoon. Net loss of nutrients from sediments during the dry season only depleted about 10% of the amount deposited during the wet season. One implication of this is that, while wet season sedimentation rates and associated N and P load may be an order of magnitude less than estimated for this study during the 2002-2003 wet season, these infrequent El Niño events may be providing particulate N and P loads to the Lagoon that will take a decade or more to metabolize. Attempts to identify the particular anthropogenic source of sediment N based on carbon and nitrogen stable isotopes was inconclusive.

2. Newly deposited particulate N and P in lagoon sediments are remineralized and provide a source of nutrients to surface waters.

Processes of sediment diagenesis (organic matter decomposition, oxidation-reduction reactions, etc.) remineralize this newly deposited particulate N and P, resulting in pore water NH4, dissolved organic N (DON), SRP, and DOP nutrient concentrations that are elevated relative to surface water levels. Estimates of benthic flux show a net release of dissolved inorganic and organic nutrients from the sediments to the surface waters. Sediment N and P inventories in the Western Lagoon decreased over the dry season by 283 kg N (623 lbs) and 130 kg P (286 lbs P), consistent with an estimated net flux of 302 kg (666 lbs) of total dissolved N and 25 kg (55 lb) of total dissolved P from sediments to the surface waters. Our data show the progression of these transformations in Western Lagoon sediments as pore water SRP, DOP, NH_4 and dissolved organic N (DON) concentrations increased markedly over wet season concentrations. NO_3 concentration increased during the wet season as higher concentrations in the surface water cause a net flux of NO_3 into the sediments. As temperatures in the late wet season and dry season increase, pore water NO_3 decreased to non-detectable levels microbially-mediated denitrification converts NO_3 to nitrogen gas.

The build-up of NH_4, DON, SRP and DOP in sediment pore waters after deposition is responsible for a predicted net release of these constituents to the surface waters throughout the year; calculations of potential diffusive flux, which when summed by season, predict a net release of 523 kg (1154 lbs) of TDN and 48.5 kg (107 lbs) of TDP annually to surface waters in for the entire Lagoon. Predicted fluxes from the Central Lagoon represent only 1-2% of this total annual net release of TDP and TDN to the surface waters. The dominance of the Western Lagoon as a source of remineralized nutrients from sediments can be explained by the hydrodynamics of the Lagoon – and the effect that it has on the spatial patterns in deposition of fine- versus coarse-grained sediments. Sediments in the hydrodynamically-active Central Lagoon are predominantly sandy and devoid of nutrients relative to the Western Lagoon. In the Western Lagoon, where circulation is poorer and water velocities during storm events are likely to be much lower, deposition of fine-grained, nutrient-rich sediment dominates.

3. Primary producer community abundance and DO impairment in Malibu Lagoon is linked with dry season sediment nutrient release.

Dense stands of *Ruppia maritima* created hypoxic surface water conditions during the dry season of the first year we sampled. Nutrient enrichment found in surface waters and sediments in the Lagoon drives high SAV biomass. We found that the sediments of Malibu Lagoon (both solid phase and pore waters) were highly enriched with nutrients. Sediment N and P in surficial sediments of the Western region of Malibu Lagoon (0.341 ± 0.228 % N and 0.081 ± 0.032 % P) were equal to or greater than values from several of the most eutrophic systems studied worldwide. The timing of the *R. maritima* growth in the Lagoon coincides with periods of high nutrient release from Lagoon sediments. SAV abundance and the subsequent low DO was also a function of the timing of Lagoon closure, which affects salinity and hydrodynamic regime. In 2002, a year with little rainfall, the mouth of the Lagoon closed in April, tidal exchange ceased, and the water became brackish. A large seasonal community of *R. maritima,* a brackish water species, was established in the Western Lagoon early during the dry season and caused severe hypoxia. In 2003, with significant rainfall occurring as late as May, the mouth of the Lagoon closed in June 2003, so higher salinities (i.e., 8-10 ppt) occurred much later than the previous year. Thus nutrient availability as well as the timing of Lagoon inlet closure (and subsequent impacts on salinity) controlled the degree to which *R. maritima* was established and created hypoxic condition in the Lagoon during the dry season.

4. Nutrient Release from Sediments is a Significant Source to Primary Producers Relative to Other Non-Point Inputs During the Dry Season

The net increase in sediment nutrient inventory over the wet season is a small fraction of the total loading to the Lagoon from point and non-point sources, most of which occur during the wet season. Thus, most of the wet season loads are transported directly into the Pacific Ocean. However, this small fraction retained provides an ecologically significant source of nutrients to the Lagoon during the dry season.

A variety of non-point sources such as groundwater seepage and nuisance flows from the watershed are contributing nutrients that fuel *R. maritima* growth during the dry season. Nutrient release from sediments equals 18% of the TN sources and 5% of the TP from other nonpoint source inputs. These estimates are based on calculations of potential diffusive fluxes, which are likely to be an underestimate of the net release of nutrients into the surface waters. Many studies have found that advective transport of water through the sediments, which includes processes such as groundwater seepage, tidal pumping and bioturbation, increase the exchange between surface waters and sediments; for this reason, it is likely that sediment release of nutrients is larger than what is estimated by this study. Thus, sediment release is a significant source of TN and TP available to fuel dry season primary producer growth – thus strongly linking wet season particulate N and P loading to the Lagoon with high primary producer abundance and low DO events in the dry season.

In conclusion, we found that sediment enriched in particulate N and P was deposited in the Lagoon during the wet season. While the net increase in sediment nutrients over the wet season is a small fraction of the total loading to the Lagoon from point and non-point sources, it provides an ecologically significant source of nutrients to the Lagoon during the dry season when nutrients are remobilized to the surface waters as dissolved inorganic nutrients. Comparison with other dry season non-point sources indicates that sediment release approximately equals 18% of the TN sources and 5% of the TP from other nonpoint source inputs to the Lagoon during the dry season and is a significant source of nutrients to primary producers. Thus wet season particulate N and P loading to the Lagoon is strongly linked with high primary producer abundance and low DO events in the dry season. Major data gaps in understanding of the source, transport and fate of anthropogenic nutrients to Malibu Lagoon include: 1) quantification of the rates of denitrification in groundwater (septic seepage to the lagoon), 2) direct measurements of groundwater seepage into the Lagoon and denitrification rates within Lagoon sediments, 3) direct measurements of nitrogen fixation in the Lagoon, 4) identification of the major anthropogenic sources of sediment N to the Lagoon, and 4) extent to which N and P stored in SAV tissue is recycled back to sediments during the wet season.

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1. INTRODUCTION

Malibu Lagoon is an 7.5 ha (18.5-acre) coastal lagoon situated at the base of the Malibu Creek watershed, which drains directly into Santa Monica Bay and the Pacific Ocean (Figure 1). Malibu Lagoon is utilized by hundreds of different species, many of which are commercially and ecologically important. Federally listed threatened or endangered species such as the tidewater goby (*Eucyclogobius newberri*), steelhead trout (*Oncorhynchus mykiss*), brown pelican (*Pelecanus occidentalis*), California least tern (*Sterna antillarum browni*), light-footed clapper rail (*Rallus longirostris levipes*) and salt marsh bird's-beak (*Cordylanthus maritimus* ssp. *maritimus*) inhabit the Lagoon (Ambrose et al.,. 2000). Many birds also use the Lagoon as an important migratory stopover along the Pacific flyway. Land use changes in the Malibu Creek watershed have lead to increased freshwater and nutrient loads to the Lagoon and have resulted in a decline in its wildlife beneficial uses. In 1996 the Los Angeles Regional Water Quality Control Board (LARWQCB) placed Malibu Lagoon on the federal 303(d) list of impaired water bodies due to the excessive abundance of primary producers in the Lagoon and associated dissolved oxygen (DO) problems.

Several dominant dry-season primary producers in the Lagoon are green, mat-forming algae, such as *Rhizoclonium hookeri*, and submerged aquatic vegetation (SAV), *Ruppia maritima*. 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 oxygen from the water column causing hypoxia (low oxygen) or anoxia (no oxygen) (Valiela et al., 1992), which can be extremely stressful to resident organisms.

Primary producer abundance is often limited by availability of nutrients (Harlin and Thorne-Miller 1981, Delgado and Lapointe 1994, Kamer et al., 2004), such as nitrogen (N) and phosphorus (P), which are present in both the water column and the sediments. Algae generally obtain their nutrients directly from the water column, and *Ruppia maritima* can absorb nutrients through its leaves as well as its roots (Verhoeven 1979). There is also evidence that algae may intercept nutrients fluxing out of sediments (Lavery and McComb 1991, Larned and Stimson 1996, McGlathery et al., 1997) or use nutrients fluxed from sediments once they enter the water column (Kamer et al., 2004). Thus, for both algae and SAV, sediments may be a critical nutrient source.

Availability of nutrients within the Lagoon can vary both temporally and spatially in relation to climate, watershed loading, and hydrodynamics. Rainfall in winter months increases stream flow and the volume and velocity of freshwater inputs keep the mouth of the Lagoon open. During this period, the Lagoon receives most of its nutrient loads; seasonal storm flows from the watershed can contribute a large proportion of the overall annual nutrient load to southern California estuaries and coastal lagoons (Boyle et al., 2004). In addition, during the rainy season, the Tapia Water Reclamation Facility (Tapia) discharges treated wastewater directly to Malibu Creek, which flows into Malibu Lagoon. With the onset of the dry season, longshore transport of sand causes a berm to build up and close off the Lagoon from the Pacific Ocean. Subsequently, salinity in the Lagoon drops as the freshwater inputs from the watershed are impounded. During summer months, Tapia is prohibited from discharging directly to Malibu Creek and creek flows are generally lower; urban runoff and groundwater seepage are the main sources of freshwater inputs to southern California estuaries and nutrient loads are lower than in winter. Spatial variations in nutrient availability in estuaries and lagoons can also be significantOften, water column and sediment N and P concentrations are higher near the head of an estuary where the primary freshwater-nutrient input is and decrease with proximity to the mouth (Rizzo and Christian 1996, Nedwell et al., 2002, Kennison et al., 2003).

When nutrient concentration in the water column is high, nutrients can diffuse into the sediments (Rizzo and Christian 1996, Trimmer et al., 2000, Tyler et al., 2003) where they may be stored and later re-mobilized. Additionally, particulate nutrients associated with sediment can be deposited in an estuary. Over time, the organic matter can be remineralized and the nutrients are released into sediment pore waters, where they can diffuse into the overlying water column (Boynton et al., 1980, Grenz et al., 2000, Hamersley and Howes 2003). Pore water nutrients can also be released from sediments by bioturbation and resuspension. In Upper Newport Bay, sediment N peaked in spring 1997 following nutrient inputs during the winter rainy season. Sediment nitrogen decreased through subsequent seasons but peaked again in spring 1998 (Boyle et al., 2004). Thus, through storage in sediments, wet season nutrient inputs followed by dry season sediment nutrient release served to temporally decouple nutrient inputs and the resulting macroalgal bloom.

To reduce excessive primary producer abundance and DO problems in Malibu Lagoon, the U.S. Environmental Protection Agency (USEPA) promulgated a Total Maximum Daily Load (TMDL) to limit nutrient pollution in the watershed. The LARWQCB is currently refining the numeric water quality objectives (WQOs) set forth in the 2003 TMDL and the new limits will be adopted in order to limit the seasonal and/or annual nutrient inputs from the watershed to the Lagoon.

In particular, our study addressed three major questions that are relevant for refining the WQOs: 1) What is the load of N and P associated with the wet season input of sediments into the Lagoon? 2) What is the exchange of N and P between the surface waters from the sediment? and, 3) what is the importance of sediments as a net source of remobilized nutrients to surface waters relative to other nonpoint inputs to the Lagoon? Currently, one major assumption made about water quality in the Lagoon is that, because the system is intertidal during the wet season, all wet season nutrient loads are transported directly into the Pacific Ocean; thus wet season loads are not linked to water quality impairments during the dry season. Suffet and Sheehan (2000), in their study of major nutrient sources to the Lagoon, recognized that watershed-derived sediments deposited in the Lagoon could be a source of nutrients during the dry season; however, they assumed that the amount of sediment deposited in one storm was scoured out in subsequent storms, and therefore only the sediments deposited during the final storm of the season are a source of nutrients during the following dry season. The relationship between sediment deposition, nutrient cycling, and water quality in the Lagoon needs to be more clearly defined.

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

1. Investigate the seasonal patterns of bulk and pore water sediment N and P concentrations in the Lagoon

2. Estimate wet season and long-term average annual sediment deposition rates and associated particulate N and P load to the Lagoon;
3. Estimate ambient benthic nutrient exchange under a variety of environmental conditions observed in the Lagoon over an annual cycle and integrate these rates to evaluate annual net nutrient exchange; and
4. Compare the magnitude and relative importance of sediment remobilization and exchange of nutrients with surface waters relative to other nutrient nonpoint sources to Lagoon.

Specifically we hypothesized that sediments serve as storage for nutrients that enter the Lagoon during wet weather periods and these nutrients are later remobilized to surface waters, providing fuel for primary producer growth during dry weather periods.

2. METHODS

2.1 Site Description

Malibu Lagoon is an 7.5 ha (18.5-acre) brackish water lagoon situated at the base of the Malibu Creek watershed, the second largest of the watersheds that drain into Santa Monica Bay, California (Figure 1). Malibu Creek watershed encompasses an area of 282 km^2 (109 $mile^2$) with a mix of high intensity land uses primarily in the upper watershed and natural habitat in the narrow lower portion of the watershed where the Creek drains through the Santa Monica Mountains. The Mediterranean climate of southern California leads to unique, seasonal hydrologic patterns in Malibu Lagoon. Precipitation during the rainy season increases stream flow and the volume and velocity of freshwater inputs keep the mouth of the Lagoon open. During the dry season, longshore transport of sand causes a berm to build up and close off the Lagoon from the Pacific Ocean. Subsequently, water levels rise and salinity in the historically hypersaline Lagoon during the dry season drops as the freshwater inputs from urban runoff in the watershed are impounded.

Two distinct areas characterize the Lagoon: the Central Lagoon and the Western Lagoon. The Central Lagoon is the main channel of Malibu Creek where it discharges into the ocean and is a mixture of intertidal flats, subtidal channels and sand bars. This area, which is approximately 50,000 m^2 in size, is more hydrodynamically active and receives more direct tidal exchange then the Western Lagoon when the tidal inlet of the Lagoon is open. The Western Lagoon, 25,000 m^2 in size, is primarily the result of a restoration project in 1983, which involved excavating a section of the lagoon that had been filled in the 1950s. The restoration involved the creation of three channels with sloping mudflats to reintroduce tidal flow, which created a mixture of mudflats, subtidal channels, emergent marsh and upland habitat. It is believed that the excavated channel may contribute to problems with water circulation due to stagnant water occurring at the ends of some channels (Ambrose and Orme 2000).

2.2 Study Design and Field Methods

The study design for this project had four components: 1) characterize the temporal and spatial trends in surface water and sediment nutrient concentrations and percent cover of dominant primary producer communities, 2) measure seasonal and average annual sedimentation rates in the and rate of particulate N and P deposition to the sediments using the radioisotopes beryllium-7 (^{7}Be) and lead-210 (^{210}Pb), 3) identify major sources of nutrients and organic matter using carbon (C) and N stable isotopes, and 4) quantify the exchange of nutrients between the surface waters and sediments and compare these loads with other non-point source nutrient inputs to the lagoon.

To optimize the sample design, the study was conducted in two phases. Phase I, February to July 2002, was a limited investigation of primary producers, water column nutrients, and bulk surficial sediment nutrients and grain size in the Lagoon (Table 1). Preliminary data from Phase I was used to enhance the sampling design Phase II. Phase II included all the same parameters as Phase I plus characterization of sediment pore water profiles and sediment deposition using radioactive isotopes. In addition, a total of 5 sites were added to both the Western Lagoon and the Central Lagoon to increase the spatial resolution of sampling.

A total of 8 sampling events were conducted during Phase I and II (February 2002 and September 2003). The status of the mouth (open or closed) changed during the course of the project (Figure 2) and not all sites were sampled during each event (Table 1 and Figure 1).

Phase I

Upon arrival at each site, water column temperature, salinity, and dissolved oxygen (DO) were measured using hand held probes. In February and April 2002, measurements were only at the surface of the water column. Beginning in July 2002, measurements were made at the surface, middle and bottom of the water column at each site. Duplicate mid-water column 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. 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 25 mm glass fiber filter (0.7 µm pore size), and frozen for analysis of total suspended sediment (TSS), chlorophyll a, particulate organic carbon (POC), particulate N (PN), and particulate P (PP). The filtered water was frozen immediately for later analysis of ammonia (NH4), nitrate and nitrite (NO3+NO2), total Kjeldahl N (TKN), soluble reactive P (SRP), dissolved organic carbon (DOC) and total dissolved P (TDP). In the offshore surf zone and mouth of Malibu Creek, water samples were collected approximately 30 cm below the surface.

Table 1. Sampling Dates and Sites Sampled in the Main and Central Lagoons, Offshore Surf Zone and Mouth of Malibu Creek.

Date	**Main Lagoon**							**Central Lagoon**			**Offshore Surf Zone**[1]	**Malibu Creek**[1]
	1	2	3	4	5	6	7	8	9	10		
Phase I												
February 2002	X	X	X	X							X	X
April 2002	X	X	X	X							X	X
July 2002	X	X	X	X	X	X					X	X
Phase II												
September 2002	X	X	X		X	X	X	X	X	X	X	X
January-February 2003	X	X	X		X	X	X	X	X	X	X	X
April 2003	X	X	X		X	X	X	X	X	X	X	X
July 2003	X	X	X		X	X	X	X	X	X	X	X
September 2003	X	X	X		X	X	X	X	X	X	X	X

Sediment cores were taken with 4-inch inner diameter (ID) polycarbonate tubing at Sites 1-4 in February and April 2002. In July 2002, when sites 5 and 6 were added, duplicate cores were taken at sites 1 and 3; at all other sites single cores were taken. The top 2 cm of the cores were extruded in 1 cm intervals. The wet and dry weights of the sediment intervals were recorded for analysis of percent solids and porosity. The dried material was analyzed for sediment grain size, sediment total organic carbon (SOC), sediment total organic N (SN) and sediment total P (SP).

To estimate percent cover of each primary producer species or functional group, at each site a 30 m transect line was laid down parallel to the water line ~1 m from the edge of the vascular vegetation, which is a good proxy for elevation. At five randomly chosen points along the transect line, primary producer percent cover was measured with a 0.25 m^2 quadrat strung with

[1] Surface water samples only

fishing line to create 36 intercepts. The species or functional group under each intercept was identified and recorded.

Phase II

Phase II marked a transition to intensive sampling of water and sediments at an increased number of sites. Phase I preliminary results demonstrated that sediments of the Western Lagoon had 2-8 times higher concentrations of N and P than those of the Central Lagoon (see Results in Section 3.0). Therefore the decision was made to concentrate efforts in quantifying sediment solid phase and pore water nutrients in the Western Lagoon site and sites 5, 6, and 7 were added to the Western Lagoon to increase spatial coverage (Figure 1). Site 4 was dropped from the sampling design, as it was similar in sediment characteristics to Site 3. Sites 8, 9 and 10 were added to the Central Lagoon, but with more limited biological and water quality observations and sampling of sediments at depth (see paragraph below).

During Phase II, surface water nutrient samples were taken at both the Western and Central Lagoon sites, as was done in Phase I. In addition, surface water DO, temperature, salinity and percent cover of primary producer community were recorded at each of the Western Lagoon sites. The protocol for sediment sampling in the Western Lagoon was altered during Phase II in order to more intensively sample the solid and pore water phases as well as increase the vertical depth of analysis done on each core for the Western Lagoon sites. At each site, a sediment core was taken with 4''-ID polycarbonate tubing. Two duplicate cores were taken at Sites 1 and 3 in September 2002 and Sites 1 and 5 in February 2003 in order to determine the amount of spatial variability within a site. The cores were capped securely on bottom and top, placed in a rubber bin, covered with a towel, and transported with overlying water in an upright position to the laboratory for processing (within 2 hours of collection). At the laboratory, each core was extruded in a glove box under nitrogen gas to prevent oxidation artifacts. The core was sectioned vertically in 1-2 cm intervals down to 10 cm. A portion of the section was taken to determine percent solids and the remainder was centrifuged at 3500 rpm for 20 minutes. The pore water centrate was filtered under nitrogen gas with a 0.7 µm glass fiber filter. Pore waters were immediately frozen for analysis of NH_4, NO_3, SRP, TDN, TDP, and DOC. Sediment solid phase remaining after centrifugation was dried at $50^{O}C$ in an oven for 48 hours. Following homogenization, a portion of the sediment was used to determine grain size and dry density. Another portion was ground to a particle size of <125 µm for analysis of ^{7}Be, SOC, SN, and SP. Surficial sediment samples from selected dates were measured for the stable isotopes ^{15}N and ^{13}C.

For Central Lagoon Sites 8, 9, and 10, the technique for collecting pore water was modified because of the difficulty in centrifuging pore water from sandy sediments. A pore water "sipper" technique was used, where a needle attached to a 60 ml syringe was inserted into sediments to a depth of 6 cm. Approximately 60 ml of pore water was drawn up into the syringe, and filtered immediately in the field with a 0.7 µm glass fiber filter. Thus the volume extracted represents a composite pore water sample. Laboratory experiments showed that a needle depth of 6 cm, 60 mls of porewater could be removed without drawing surface water into the sediments. The filtrate was immediately frozen for analysis of nutrients and organic carbon. Next a core was taken immediately adjacent to the area where pore waters were sampled and the top 3 cm sectioned in 1-cm intervals for analysis of solid phase nutrients. Sediment solid phase samples were processed as was done with the Western Lagoon samples.

In March 2003, one 50 cm core at Site 1 was taken for analysis of average annual sedimentation rate using the radioisotopes ^{210}Pb and ^{137}Cs. The core was sectioned vertically in 2 cm intervals, the wet and dry weights recorded, then ground to a particle size <125 µm for analysis of radioisotopes. During an initial analysis of ^{7}Be and ^{210}Pb inventories in lagoon sediments during Phase I, it was quickly determined that the tidal channels in the Western Lagoon (Sites 2 and 3) as well the Central Lagoon sediments contained radioisotope activities below detectable levels due to the high quartz content. Therefore radioisotope analyses were not performed on these Stations during Phase II of the study and sediment deposition work focused on Stations 1, 5, 6 and 7 in the Western Lagoon.

Throughout Phase I and II, field blanks for all surface water and porewater analyses consisted of Milli-Q deionized water filtered through the same filtering equipment that was used for the field samples.

2.3 Analytical Methods

Surface and porewater samples were assayed for dissolved inorganic nutrients using an Alpkem Autoanalyzer for the analysis of NH_4, SRP and NO_3+NO_2 (APHA 1992). TP was digested by combustion and hydrolysis as in Solorzano and Sharp (1980) then analyzed as SRP by autoanalyzer (APHA 1992). DOC was determined via high temperature catalytic combustion using a Shimadzu 5000 TOC Analyzer (EPA Method #415.1). TKN was analyzed using the micro-kjeldahl method (APHA 1992). DON and DOP were calculated by subtracting the NH4 or SRP concentration from TKN 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 spectrophotomer (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 μm 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 and ^{210}Pb. Natural radionuclides ^{7}Be (half-life of 53 days) and ^{210}Pb (half-life of 22 years) are produced in the atmosphere and have a constant rate of supply to the earth via wet (rainfall) or dry deposition, where they adhere to suspended particles in surface waters. They 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). ^{7}Be and ^{210}Pb 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). Average annual sedimentation rate for Site 1 was determined by alpha particle spectrometric analysis of ^{210}Pb activities (half-life = 22 years). Activity of ^{7}Be (half-life = 53 days), 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. The energy peak at 477.6 was used to determine ^{7}Be activities. 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).

^{15}N and ^{13}C are naturally occurring isotopes that each have one extra proton than their more abundant counterparts, ^{14}N and ^{12}C, respectively. Estuaries generally receive nutrients from either the ocean or the watershed, and the ratios of these isotopes in estuarine materials indicate the source of the N and C (Table 2; Sweeney and Kaplan 1980, Mulholland and Olsen 1992, Middelburg and Nieuwenhiuze 1998). The use of these values in combination can assist in nutrient and organic matter source identification. Natural abundance of stable C and N isotopes was determined by the Stable Isotope Facility of UC Davis using an Anca-GSL autosampler. The ratios of ^{15}N:^{14}N and ^{13}C:^{12}C are reported in per mille (‰) relative to standards, which are atmospheric N and PeeDee Belemnite (PDB).

2.4 Data Analysis

Calculation of Porosity and Wet Bulk Density

Calculation of sediment porosity and wet bulk density was necessary to estimate seasonal and annual sediment deposition rates and to evaluate changes in sediment nutrient inventories. Porosity is essentially a measure of the amount of "empty space" in a material and is 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 (ϕ), a dimensionless unit, is given by Eq. 1:

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

Where X_{SED} is the fraction of solids in the sediment, σ_{H20} is the density of water, and σ_{SED} is the dry grain density of the sample. Wet bulk density (ρ) in g cm^{-3} is given by the Eq. 2:

$$\rho = \phi \sigma_{H20} + (1 - \phi \sigma_{SED}) \qquad \text{Eq.}$$

Average porosity at ML1 was 0.68 and at ML5, 6, and 7 was 0.48 within the upper 10 cm of each core. Average wet bulk density was about 1.5 g cm^{-3} at all lagoon stations.

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

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

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

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); ϕ is the porosity (dimensionless); ρ 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 that the first sampling event sets a baseline of low ^{7}Be activity because of a 4-month dry season. Subsequent sampling trips (during rainy season and throughout dry season) would reveal possible changes occurring at the site in the intervening time period including: (1) an inventory reflecting recent deposition and/or a residual inventory reflecting older deposition events, (2) a small residual inventory associated with decay or partial sediment removal if no recent deposition events have occurred, and (3) and no inventory, indicating complete removal of the uppermost sediment layer or complete decay if the sampling interval is 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: 1) evaluate the short-term sediment deposition rate, 2) discern if a site is a focal point for sediment deposition or a net loss site through time, and 3) observe reworking of sediments that may be 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 sediments. 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 is washed 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 half-life (half-life = 22.6 year). 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 that measured for the modern 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 Seasonal Changes in Sediment Nutrient Inventories

Sediments in coastal lagoon, lakes and estuaries act as an integrator for the sum of nutrient sources, sinks, and the impact of physical and biological processes occurring in the water column and sediments. Therefore, calculation of the net change in the seasonal inventories of N or P in the sediments is a method of tracking the net effect of nutrient sources, sinks and transformations in the Lagoon.

The inventories of SN and SP for each core were calculated using Eq. 4:

$$SI = \Sigma X_i (1 - \phi) * \rho * SNUT_i \qquad \text{Eq. 4}$$

Where SI is the total inventory of the sediment core (g cm^{-2}); X_i is the sediment section interval (i) thickness (cm); ϕ is the porosity (dimensionless); ρ is the wet sediment bulk density (g cm^{-3}); and $SNUT_i$ is the sediment nutrient concentration (either SN or SP) in within a given section interval.

SI values for SN and SP were calculated for each core for the September 2002, April 2003, and September 2003 sampling periods. A mean and standard deviation of SI values for N and P (SI_{MEAN}) were calculated for all Western Lagoon sites (Sites 1, 2, 3, 5, 6 and 7) and Central Lagoon sites (Sites 8, 9, and 10) for each of these three sampling periods.

Mean SI (SI_{MEAN}) for the Western and Central portions of the Lagoon were then multiplied by the respective surface area ($Area_{WL}$ or $Area_{CL}$) in each section (Western Lagoon = 24,928 m^2, Central Lagoon = 50,140 m^2) to yield the total inventory of N and P for each section of the Lagoon for each of the three sampling periods:

$$SI_{WL.} = SI_{MEAN\text{-}WL}\ Area_{WL} \qquad \text{Eq. 5}$$

$$SI_{CL.} = SI_{MEAN\text{-}CL}\ Area_{CL} \qquad \text{Eq. 6}$$

Change of SN and SP inventory for the 2002-2003 wet season was calculated by subtracting the April 2003 SI from the September 2002 SI values for each section of the Lagoon. Likewise, change of SN and SP inventory for the 2003 dry season was calculated by subtracting the April 2003 SI values from the September 2003 values. Annual change in SI was calculated by subtracting September 2002 from September 2003 values.

Separate calculations were made to estimate the load of SN and SP associated with newly deposited sediments during the 2002-2003 wet season for each site. An SI value for SN and SP were calculated for the depth at which 7Be was detected in each core in the April 2003 sampling period. The SI values for SN and SP were averaged over all the Western Lagoon sites to give a mean value for Sites 1, 5, 6 and 7.

Calculation of Potential 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 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 potential diffusive fluxes can give reasonable estimates in terms of the magnitude as well as direction of flux. In this study, instantaneous diffusive flux rates were calculated for each species of nutrient with the use of Ficke's law given in Eq. 7

$$J = -\phi D_{AQ} \theta^{-2} (dC / dz) \qquad \text{Eq. 7}$$

where J is the rate of flux of species (mol m^{-2} s^{-1}), ϕ is the porosity (dimensionless), D_{aq} is the aqueous diffusion coefficient, θ 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). θ^{-2} was estimated from Boudreau's law (Boudreau 1997) given in Eq. 8:

$$\theta^{-2} = 1 / (1- \ln (\phi^2)) \qquad \text{Eq. 8}$$

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

Table 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

Seasonal and annual net exchange of nutrients between sediments and surface waters were calculated from potential diffusive flux rates by making the following assumptions:

- Exchange between the sediments and surface waters occurred at steady state;
- Advective transport processes in Lagoon (groundwater, tidal pumping, and bioturbation) were minor relative to diffusive transport;
- Instantaneous diffusive fluxes calculated based on surface water concentrations at each site were representative of the month and/or season in which sampling occurred; and

- Chemical or biological processes that can modify chemical fluxes at the sediment water interface (oxygen content, benthic diatoms, sediment redox chemistry, etc.) had a negligible impact relative to diffusion on exchange rates.

Seasonal and annual net exchanges of nutrients were calculated by first averaging instantaneous ambient rates (grams m^{-2} s^{-1}) by sampling date for the Western (Site 1, 5, 6, and 7) and Central Lagoon (Sites 8, 9, and 10). These rates were prorated to month (or closest month) then summed to season or year. Total seasonal or annual load was then obtained by multiplying the rate by surface area of Western (24,928 m^2) or Central Lagoon (50,140 m^2).

3. RESULTS

3.1 Temporal Trends in Dominant Primary Producer Communities and Surface Water Quality Within the Lagoon

Relationship Between Meteorological Forcing and Lagoon Mouth Closures, Primary Producers, and Surface Water Quality

Phase I and II sampling captured distinct seasonal patterns in surface water quality associated with meteorological and hydrological forcing in the Lagoon. Figure 2 shows the timing of sampling events relative to the seasonal patterns of rainfall and Lagoon closure. The duration of the 2001-2002 and 2002-2003 wet seasons was the same (approximately 7 months from October - April). However, total rainfall in the 2002-2003 wet season (35 cm or 13.76 inches) was double that of the 2001-2002 season (15 cm or 5.92 inches) due to the influence of a mild El Niño in the second year of sampling. The magnitude of rainfall during the wet season had a direct impact on the length of time the Lagoon mouth was open to tidal influence. The Lagoon mouth was closed approximately 2 months earlier in the 2001-2002 wet season than in 2002-2003.

The timing of Lagoon mouth closure had a direct impact on salinity regime recorded during the eight sampling events of the study. In February 2002 the mouth of the Lagoon was open and tidal exchange influenced Lagoon salinity; the highest value of our study (~15 ppt) was recorded (Figure 3). In March 2002 the Lagoon mouth closed, and April 2002 salinity measurements dropped to the lowest value recorded during our study (~3 ppt) due to the impoundment of freshwater inputs to the Lagoon. Salinity rose over the next two sampling events due to evaporation and seawater seepage through the sand berm. In February 2003 the mouth of the Lagoon was open, but as sampling occurred on an outgoing tide, the salinity showed the influence of freshwater on the Lagoon. In April and July 2003, salinities were higher than in corresponding months in 2002. July 2003 salinity measurements were higher than those of July 2002 due to the recent closure of the Lagoon mouth in June. By September 2003 salinity had dropped to less than 6 ppt because of freshwater impoundment.

The Western Lagoon primary producer community was relatively constant in the wet season but showed strong inter-annual variation in the dominant species or functional group during the late wet and the dry seasons (Figure 3). During the 2002 and 2003 February sampling events when the Lagoon mouth was open to tidal influence, benthic diatoms were abundant; percent cover was ~99%. In both years, a *Ruppia maritima* community began to develop in the early dry season after the mouth of the Lagoon closed, however development was much delayed in 2003 compared with 2002. In 2002 *R. maritima* reached 60 % cover by July and increased to 80 % by September. During this time, the water column was filled with *R. maritima* (Figure 4), which dramatically decreased circulation in the Western Lagoon (K. Kamer, pers. obs.). In July 2003, there was only a small amount of *Enteromorpha* spp. in the Lagoon; small *R. maritima* seedlings were germinating, although our sampling did not capture their presence. By September 2003, *R. maritima* reached 60% cover in the Lagoon but the overall biomass was less than the previous year; the plants were smaller than the previous year and did not fill the water column nor create stagnant conditions as they did in 2002 (K. Kamer, pers. obs.). While we did not quantitatively sample primary producer abundance in the Central Lagoon, R. maritima was not observed. Sediments were either bare or covered with benthic diatoms.

There was a strong inter-annual variation in dry season DO concentrations. Severe hypoxia/anoxia occurred in July and September 2002 (Figure 5), when *R. maritima* was abundant. There were strong vertical gradients in oxygen availability during both sampling events, even though water temperatures were cooler in September relative to July. High biomass of *R. maritima* in the water column during these two sampling periods prevented mixing and shaded the water column at depth, causing bottom waters to be severely depleted of oxygen. During the 2003 dry season sampling events, no hypoxia was recorded, even during relatively warm events. As mentioned, though *R. maritima* percent cover in September 2003 was similar to that in July 2002, the biomass was less, the water column was not filled with these plants and water circulation was not as drastically reduced. Circulation in the Lagoon was adequate to prevent strong vertical stratification and bottom water hypoxia from occurring.

Temporal and Spatial Trends in Surface Water Nutrient and Dissolved Organic Carbon Concentrations

DON was typically the predominant form of total dissolved N (TDN) in the Lagoon during the late wet season and throughout the dry season sampling events, comprising 78.7 ± 11.7% (mean ± SE) of TDN measured in the eight sampling periods (Figure 6a). The highest TDN concentrations were in September 2002 and were almost exclusively DON. DOC concentrations throughout the study ranged from 0.45 ± 0.10 to 12.47 ± 0.64 mg L^{-1} and tracked trends in DON concentration. Particulate N was generally ≤25% of the total N available (Figure 6b). Exceptions were April 2003, when particulate N was greatest, and July 2003, when total N was low.

Surface water nutrient concentrations followed distinct seasonal patterns of higher dissolved inorganic nutrient concentrations during the February sampling events and higher dissolved organic nutrients during the dry season. DIN concentrations were highest in February 2002 and 2003, when stormwater runoff from the watershed likely resulted in elevated NO_3+NO_2 concentrations. DIN concentrations and the relative contribution of DIN to TDN were lower in February 2002 relative to 2003, though it is not clear if the differences were due to higher rainfall in 2003 or because timing of sampling within the tidal cycle for the two sampling events was different. 2002 dry season DIN concentrations were <0.01 mg l^{-1}; concentrations in the 2003 dry season were higher (up to 0.13 ± 0.01 mg l^{-1}), but still low relative to DON. DON also showed some interannual variability with average concentrations of 2.49 ± 0.88 mg l^{-1} in 2002 compared with 0.75 ± 0.30 mg l^{-1} in 2003.

Particulate P was the dominant fraction of TP in surface waters, while SRP made up the largest component of total dissolved P (TDP) in the Lagoon in February of 2002 and 2003 (Figure 7a). The greatest percentage of TP was in the particulate form. There was strong interannual variability in the relative concentrations as well the partitioning of TDP between SRP and DOP between the 2002 versus 2003 sampling periods. SRP measured during 2003 sampling events was approximately four times higher than in 2002 (0.288 ± 0.036 mg L^{-1} versus 0.061 ± 0.017 mg L^{-1}, with the exception of the September 2002 sampling event. Conversely, DOP was higher in 2002 sampling events than in 2003, with the exception of slightly higher DOP in February 2003 than in 2002 (Figure 7a).

Much of the water column total P was often comprised of particulate P (Figure 7 b). Exceptions were February 2002 and 2003 when SRP was relatively high and July 2003 when particulate P was lowest. Total P was greatest in April 2003 due to high particulate P, followed by February 2003 when SRP was highest.

3.2 Seasonal and Annual Sediment Deposition Rates

Vertical profiles of ^{7}Be inventories in the sediments show a distinct pattern related to the wet season input of sediment into the Lagoon (Figure 8). September 2002 inventories showed little detectable ^{7}Be, indicative of a 3.5-month period without rainfall. February 2003 showed approximately 2 cm of sediment deposition at all sites associated with rainfall that occurred primarily during the period of December 2002 through January 2003 time period. Heavy rainfall in the watershed during late February through mid-April accelerated deposition, with total accumulation typically ranging from 3 to 5 cm at most sites within the Western Lagoon. Total seasonal deposition at Site 7 (2 cm or 0.8 in), a tidal channel site, was slightly less than at Sites 1 and 6 (3 cm or 1.2 in) or Site 5 (5cm or 2.0 in) located in the interior of the Western Lagoon. Average 2003 wet season sedimentation rate for the Western Lagoon was 3 ± 1 cm (1.2 ± 0.4 in).

^{7}Be inventories in July and September 2003 sampling periods show vertical profiles indicative of no sediment new sediment deposition (and therefore radioactive decay of remaining ^{7}Be in the first several centimeters). Some sites (Site 1 and 6 in July as well at Sites 1, 6, and 7 in September 2003) show a profile with ^{7}Be present at 1 to 2 cm, but no ^{7}Be activity in the uppermost interval, indicating sediment erosion and reworking by benthic infauna or birds.

^{210}Pb activities at Site 1 were generally well mixed in the upper 10 cm (Table 4). A long-term average sedimentation rate calculated with this site yielded a rate of 0.09 cm (0.035 in) yr^{-1}. Low activities and lack of a clear profile showing radioactive decay at depth made it difficult to have confidence in this number. However, this number represents the upper limit or maximum long-term average sedimentation rate for the interior Lagoon, and as such is useful to put the seasonal rate of 3 cm (1.2 cm) yr^{-1} measured by ^{7}Be into perspective.

Table 3: ^{210}Pb Activities in a 50-cm Sediment Core Collected on 3 April 2003 at Site 1. Excess Pb Was Not Present Below 10 cm. BD = Below Detection.

Mid-depth (cm)	ex Pb-210 (dpm g^{-1})
0.5	0.994
1.5	1.341
2.5	2.427
3.5	1.200
4.5	2.248
5.5	0.250
7	BD
9	0.453
11	bd
13	bd

3.3 Seasonal and Spatial Patterns in Bulk Sediment Characteristics

Spatial Patterns in Bulk Sediment Characteristics

Vertical profiles of sediment bulk characteristics (grain size, SOC, SN and SP) show clear spatial as well as seasonal trends in Malibu Lagoon. One such trend was a consistent decrease in grain size from the Central to the Western Lagoon. Grain size, in turn, exerted a major control on the SOC, SN and SP concentrations.

Grain size at Central Lagoon Sites 8, 9, and 10 was consistently greater than 95% sand through out the study period. Particle size tended to decrease towards the Western Lagoon, with tidal channel Sites 2 and 3 having approximately 80% sand and sites at the confluence of tidal channels but in the interior of the Lagoon (Sites 1 and 6) ranging from 45-85% sand, depending on the sampling period. Site 5 (located in the most interior position of the Western Lagoon) and Site 7 (located within a tidal channel but at the edge of a *Juncus* marsh) both had grain size distributions that varied from 40-75% sand, depending on sampling period. Grain size was highly variable with depth for all Western Lagoon sites, but no clear trends were discernable in from site to site.

Sediment grain size determined nutrient content to a large degree (Figure 9); thus sediment N, P, and organic carbon all decreased as percent sand increased (r^2: 0.55-0.59, p-value$_{\alpha=0.05}$ <0.05) and SOC, SN and SP content in Central Lagoon sediments were typically ~2-4 times lower than interior locations of the Western Lagoon (Sites 1, 5, 6 and 7).

Temporal Trends in Sediment Nutrient Concentrations

Graphs of surficial sediment (0-2 cm) and vertical profiles of SOC, SN and SP by site show consistent seasonal trends in the sediments (Figures 10, 12, and 13). In the Western Lagoon sites, mean SN, SP and SOC content in the top 2 cm of sediment generally increased during the February and April sampling periods during both years, signaling increased sediment nutrient content associated with wet season sediment input (Figure 10). SN, SP and SOC content generally dropped by July 2003; at Sites 1, 5 and 6 this decrease was as much as 50% of peak wet season concentration. At Sites 5 and 6, sediment nutrient and organic carbon content remained low relative to wet season values through the September 2003 sampling. At Site 1, September 2002 and 2003 SOC, SN and SP content increased relative to July values.

Vertical profiles of sediment SN, SP and CN ratio for Sites 1, 5, 6 and 7 show these temporal trends in greater detail, as well as illustrate a consistent pattern of decreasing N and P content with depth (see Figures 12-13).

The sandy tidal channel (Sites 2, 3 and 4) and Central Lagoon sites (Sites 8, 9, and 10) illustrate a distinctly different trends that the interior Western Lagoon sites (Figure 10). At these sites, mean SN, SP and SOC content in the top 2 cm was generally depressed through the wet season, but increased markedly in the dry season, particularly in September sampling periods. Vertical profiles of nutrient and organic carbon content at these sites show that high dry season values were typically concentrated in the upper 1-2 cm of the sediment column and were associated with high concentrations of benthic diatoms observed at these sites (M. Sutula, pers. obs.).

Surficial sediment C:N ratios show peaks in September 2002 and in July 2003 and were lower in February and April 2003 at most sites during the study (Figure 11).

Net Changes in Sediment Nutrient Inventories

Calculation of SN and SP associated with newly deposited sediment during the 2002-2003 wet season in the interior of Western Lagoon yielded 3353±1602 kg TN (7391 ± 3533 lbs) and 834 ± 257 kg TP (1839 ± 566 lbs). This deposition of new nitrogen is comparable in magnitude to the net change in SN inventory calculated from September 2002 through April 2003, which showed a net increase of 2928 kg (6456 lb) TN in the Western Lagoon (Table 4). The value for new deposition of sediment P differs from the net change over the wet season by a factor of 4. This discrepancy is due to a larger loss of P from deeper sediments (3-10 cm in depth) during the wet season relative to an increase in surface P from newly deposited sediments (Table 4).

Change in dry season inventories show a net loss of TN and TP from Western Lagoon sediments, while calculations for Central Lagoon sediments show a net increase in TN (958 kg or 2114 lbs) and a net loss of TP (-83 kg or -184 lbs).

Table 4:. Net Seasonal and Annual Change in Sediment N and P in the Western and Central Lagoon. Positive Number Indicates a Net Storage of N or P in the Designated Portion of the Lagoon.

	Region	Change in SI for SN (lbs)	Change in SI of SP (lbs)
Wet Season (Oct-April)	Western Lagoon	6456	482
	Central Lagoon	-247	-278
	Total	6209	203
Dry Season (May-Sept)	Western Lagoon	-623	-286
	Central Lagoon	2114	-184
	Total	1491	-471
Annual (Oct 02- Sept 03)	Western Lagoon	5833	195
	Central Lagoon	1868	-462
	Total	7700	-267

Trends in Staple Isotope Signatures

Carbon and nitrogen stable isotope signatures and C:N ratios of the western lagoon sediments show a significant amount of variability spatially as well as temporally. $\delta^{13}C$ values ranged from –17 to –26 $^{0}/_{00}$. Sites 2 and 3 had a slightly lighter $\delta^{13}C$ values than the other sites, though these differences were not statistically significant (Figure 14). Sites 1 and 7 and, to a lesser degree, site 6 showed a great degree of temporal variability. $\delta^{15}N$ values ranged from 6.5 to 16 $^{0}/_{00}$ and mirrored similar spatial trends seen in $\delta^{13}C$ data. C:N ratios ranged from 7:1 – 16:1.

3.4 Temporal Trends in Sediment Pore Water Nutrient Profiles

In general, pore water NH_4 and SRP concentrations in the interior sites of the Western Lagoon were lowest in concentration during early to mid wet season, increased dramatically through mid-dry season, then declined again in late dry season to early wet season (Figures 15-16). In all seasons, pore water NH_4 and SRP concentrations were generally higher than those of the overlying water column. Pore water nitrate (NO_3) concentrations generally ranged from <0.01 to 3 μM (0.001 to 0.042 mg L^{-1}) in the mid to late dry season when overlying surface water concentrations ranged from <0.1 to 5 μM (0.001 to 0.07 mg L^{-1}; Figure 17). During the rainy season, when overlying surface water ranged from 15 to 200 μM (0.21 to 2.8 mg L^{-1}), pore water NO_3 concentrations increased to levels of 5-10 μM (0.07 – 0.14 mg L^{-1}).

Pore water DON and DOP concentrations were more highly variably and showed less consistent temporal trends (Figures 18-19). These constituents were generally a minor component (2-20%) of the total dissolved nutrient concentration in pore waters at Site 1 and 7; NH_4 and SRP were dominant forms of N and P at these sites. At Sites 5 and 6, NH_4 and SRP concentrations in pore waters were much less in comparison with Sites 1 and 7, and thus the dissolved organic form represented a larger fraction of the total dissolved nutrient content at these sites (20-50%). The spatial differences in pore water concentrations between Sites 1 and 7 versus 5 and 6 may be related to the hydrology as well as biotic communities present at this site. Sites 1 and 7 were shallower sites that were intertidal during the wet season. Sites 5 and 6 were deeper, subtidal sites, which often supported a greater abundance of *R. maritima.*

3.5. Exchange of Nutrients Between Sediments and Surface Waters

Predictions of potential diffusive flux in the Western Lagoon sites show a positive flux (from the sediments into the surface waters) of NH_4 and SRP regardless of season (Table 5, Figure 20). When rates are averaged over sites, NH_4 and SRP fluxes are highest April and July (27 – 52 g N and 5.5 – 8.0 g P m^2 yr^{-1}) and lowest in September. Rates among sites were highly variable and reflect the differences observed in pore water chemistry between Sites 1 and 7 versus Sites 5 and 6. DON and DOP fluxes were also generally positive but small and highly variably by site and season. NO_3 fluxes were negative in February, April and July, with the peak rate in February (-19 g N m^2yr^{-1}) and positive flux in September 2002 and 2003. TDN and TDP fluxes were dominated by NH_4 and SRP respectively therefore show the same trends as those species in the Western Lagoon.

Like in the Western Lagoon, predictions of potential diffusive flux in the Central Lagoon sites show a positive flux of NH_4 and TDN, but the magnitude of fluxes estimated are 5, Figure 21). NH_4 fluxes rates in the Central Lagoon were highest in April (0.61 g N m^2 yr^{-1}) and lowest in February (0.0073 g N m^2 yr^{-1}). SRP, DON and DOP fluxes were very small and highly variable in direction and magnitude by site and season. As in the Western Lagoon, NO_3 fluxes were negative in February and April, but the peak rate in February (-0.029 g m^2yr^{-1}) was approximately 2 orders of magnitude less than that of the Western Lagoon.

Predicted seasonal and annual diffusive flux estimates for the Lagoon are dominated by the terms from the Western Lagoon, with the Central Lagoon flux comprising only 1-2% of the total annual N and P flux from the Lagoon (Table 6). TDN annual rates in the Western Lagoon show a net flux of 1141 lbs from sediments to surface waters, with 60% of that flux occurring during the dry season (Table 6). A large negative flux of 163 kg (359 lbs) NO_3-N yr^{-1} was counteracted by a large positive flux of 610 kg (1344 lbs) NH_4-N yr^{-1}, which comprised 90% of TDN flux. 98% of the TDP flux in the Western Lagoon was SRP, while 90% of the TDN flux was NH_4.

Table 5. Average Flux rates for Western and Central Lagoon by Sampling Period. All Rates are Given in g m^{-2} yr^{-1}. Negative Numbers Represent a Flux into the Sediments From the Water Column. 95% Confidence Intervals (CI) are Based on a Sample Size of 4 Sites.

	Sampling Date				
NH_4	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	1.4E+01 ± 8.7E+00	1.9E+01 ± 1.7E+01	5.2E+01 ± 5.2E+01	2.7E+01 ± 1.7E+01	3.4E+00 ± 4.0E+00
Central	1.71E-01 ± 8.02E-02	7.30E-03 ± 7.71E-03	6.10E-01± 4.41E-01	6.98E-02 ± 9.64E-02	1.85E-01 ± 2.29E-01
NO_3	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	1.2E-01 ± 1.9E-01	-1.9E+01 ± 3.9E+00	-9.6E-01 ± 1.3E+00	-7.5E-01 ± 3.5E-01	1.1E-01 ± 6.4E-02
Central	6.81E-03 ± 3.82E-03	-2.89E-01 ± 1.91E-01	-2.35E-01 ± 1.88E-01	2.61E-02 ± 3.25E-02	1.26E-03 ± 3.54E-04
DON	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	-5.6E-01 ± 9.4E-01	5.3E+00 ± 1.5E+00	4.8E+00 ± 5.2E+00	7.2E-02 ± 1.5E+00	4.7E+00 ± 6.4E+00
Central	-4.05E-01 ± 6.08E-02	3.90E-01 ± 3.45E-01	1.70E-01 ± 1.54E-01	1.36E-02 ± 6.16E-02	-5.52E-02 ± 6.41E-03
TDN	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	1.4E+01 ± 8.8E+00	5.7E+00 ± 1.8E+01	5.6E+01 ± 5.2E+01	2.6E+01 ± 1.7E+01	8.2E+00 ± 6.7E+00
Central	-2.27E-01 ± 1.07E-01	1.08E-01 ± 3.95E-01	5.45E-01 ± 5.11E-01	1.09E-01 ± 1.24E-01	1.31E-01 ± 2.29E-01
SRP	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	1.8E+00 ± 1.3E+00	3.5E+00 ± 4.4E+00	8.8E+00 ± 5.2E+00	5.0E+00 ± 3.5E+00	2.0E+00 ± 4.8E+00
Central	4.93E-02 ± 3.55E-02	-3.15E-02 ± 1.81E-02	5.29E-02 ± 4.27E-02	1.81E-02 ± 1.55E-02	-4.14E-02 ± 4.07E-02
DOP	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	6.1E-02 ± 6.4E-02	1.1E-01 ± 1.5E-01	8.9E-02 ± 1.4E-01	1.5E+00 ± 2.1E+00	3.2E+00 ± 2.4E+00
Central	2.59E-02 ± 3.15E-02	-9.23E-04 ± 3.70E-04	5.91E-03 ± 1.96E-03	-2.15E-03 ± 1.86E-03	1.75E-02 ± 5.15E-03
TDP	**Sep-02**	**Feb-03**	**Apr-03**	**Jul-03**	**Sep-03**
Western	1.9E+00 ± 1.3E+00	3.6E+00 ± 4.4E+00	8.8E+00 ± 5.2E+00	6.6E+00 ± 4.1E+00	5.2E+00 ± 5.4E+00
Central	7.52E-02 ± 4.75E-02	-3.24E-02 ± 1.81E-02	5.88E-02 ± 4.27E-02	1.60E-02 ± 1.56E-02	-2.39E-02 ± 4.10E-02

Table 6: Seasonal and Annual Integrated Fluxes for NH_4, NO_3, DON, TDN, SRP, DOP and TDP. October 2002 – April 2003 = Wet Season, May – September 2003 = Dry Season. Positive Rates Represent Flux From Sediments to Water Column. All Fluxes are in Pounds (lbs) Except Where Designated.

	NH_4	NO_3	DON	TDN	SRP	DOP	TDP
Western Lagoon							
Oct-April 03	711.7	-344.2	107.4	474.9	47.7	1.5	49.2
May-Sept 03	632.3	-14.4	48.2	666.1	50.6	4.6	55.2
Annual (lbs yr^{-1})	1344.0	-358.6	155.6	1141.0	98.3	6.1	104.4
Central Lagoon							
Oct-April 03	9.0	-12.6	10.5	6.9	0.2	1.3	1.6
May-Sept 03	9.3	-1.5	-1.2	6.7	0.8	0.1	0.9
Annual (lbs yr^{-1})	18.3	-14.0	3.2	13.5	1.0	1.5	2.5

4. DISCUSSION

Eutrophication of estuaries and coastal lagoons has increasingly become a global environmental issue, with clear links between anthropogenic changes in watersheds, nutrient loading to coastal waters, increased primary productivity and decreases in DO availability (Sfriso et al., 1987, Valiela et al., 1992, Kamer and Stein 2004). We found that sediment enriched in particulate N and P was deposited in the Lagoon during the wet season and these particulate nutrients were remobilized as dissolved inorganic nutrients to the surface waters during dry season. Sediment release of nutrients during the dry season provides a major source of nutrients for primary producer growth in the Lagoon – thus linking wet season nutrient loading and summertime hypoxia in the Lagoon. The four major findings of our study provide evidence for this assertion:

1) Wet season sediment deposition from the Malibu Creek watershed increased in the N and P content of Malibu Lagoon sediments from pre-wet season baseline conditions.
2) Processes of sediment diagenesis (organic matter decomposition, oxidation-reduction reactions, etc.) remineralize this newly deposited particulate N and P, resulting in pore water nutrient concentrations that are elevated relative to surface water levels. Estimates of benthic flux show a net release of dissolved inorganic and organic nutrients from the sediments to the surface waters. Sediment N and P inventories decreased over the dry season by 623 lbs N and 286 lbs P, consistent with an estimated net flux of 666 lbs of total dissolved N and 55 lb of total dissolved P from sediments to the surface waters.
3) Dense stands of *R. maritima* create hypoxic surface water conditions during the dry season. Nutrient enrichment found in surface waters and sediments in the Lagoon drives high SAV biomass. SAV abundance and the subsequent low DO is also a function of the timing of Lagoon closure, which affects salinity and hydrodynamic regime. The timing of the *R. maritima* growth in the Lagoon coincides with periods of high nutrient release from Lagoon sediments.
4) While a variety of non-point sources of nutrients are contributing to *R. maritima* growth during the dry season, nutrient release from sediments is a significant source fueling growth of primary producers in the Lagoon (17 % of TN and 5% of TP sources).

These findings are discussed in detail below.

4.1 Wet Season Sediment Deposition From Malibu Creek Watershed Increased the Inventories of N and P in Lagoon Sediments

Sediments are the less mobile or transient component of an estuary and for this reason are good integrators of the net balance of nutrient sources and sinks estuaries and coastal lagoons (Boyton et al., 1995). Sources of particulate and dissolved nutrients to the Lagoon can include creek discharge, local storm drains, fecal input from birds and other animals, tidal inflow, groundwater inflow and direct atmospheric deposition (see Table 8). Seasonal storm flows can contribute a large proportion of the overall annual nutrient load to southern California estuaries (Boyle et al., 2004), and, during winter months, Tapia discharges treated wastewater directly to Malibu Creek, which flows into Malibu Lagoon. During summer months, creek discharge and suspended sediment transport are generally lower and Tapia effluent is not discharged into Malibu creek; urban runoff and groundwater seepage are the main source of freshwater inputs to southern California estuaries and nutrient loads are lower than in winter (Boyle et al., 2004, cite new groundwater report). Nutrient sinks in the Lagoon include tidal scouring and outflow to the ocean, groundwater outflow, and denitrification (conversion of NO_3 to N_2 gas; Boyton et al., 1995). Nutrients can also move into and out of the different components of the Lagoon where they are stored (i.e., sediments, surface waters, plant and animal biomass; Figure 20). However, the change in nutrient storage in surface waters and animal and plant biomass in tidal estuaries and coastal lagoons is highly variable and generally negligible relative to nutrient storage in sediments (Boyton et al., 1995, Sutula et al., 2001).

Because Malibu Lagoon has an inlet to the ocean that is intermittently open during the wet season, it is very difficult to construct a budget to account for the fate of these highly variable nutrient sources and sinks that occur during this time period. However, the net change in the sediment inventory (or storage) of N or P over the wet season represents the net effect of the sources of N or P minus the sinks (Sutula et al., 2001; Eq. 9).

$$\text{Nutrient Sources} - \text{Nutrient Sinks} = \text{Change in Nutrient Storage} \qquad \text{Eq. 9}$$

During the 2002-2003 wet season, we documented a net increase in the sediment nutrient inventory of 2829 kg (6456 lb) N and 219 kg (482 lbs) P in the Western Lagoon (Table 4). Calculations of the N and P content associated with 3 ± 1 cm of sediment deposition in the Western Lagoon (3352 kg (7391 lbs) TN and 834 kg (1839 lbs) TP based on April 2003 sediment nutrient values) exceed the calculated net increase in the sediment nutrient inventory in that region. Diffusion of high NO_3 from surface waters into sediments can only account for a small portion of this increase in sediment inventory (~5%), so particulate N and P deposition from wet weather events is the major process responsible for this net increase. While it may be possible that a storm event may scour out nutrients deposited by previous events in the Central Lagoon (Suffet and Sheehan 2000), ^{7}Be data show that particulate nutrient accumulation in the Western Lagoon throughout the wet season is clearly additive. Significant sediment reworking is only occurring in the Western Lagoon during the dry season, most likely by benthic infauna or birds then by physical scouring of the sediments.

Table 7. Tabulation of Estimated Point and Nonpoint Sources Loads to Malibu Lagoon. Numbers are Derived from Suffet and Sheehan (2000)

Source Category	N Loads (lbs yr^{-1})	% TN Watershed Loading	P Loads (lbs yr^{-1})	% P Watershed Loading
Point				
Tapia Discharge	190,989	0.3	41,760	0.48
Nonpoint				
Watershed Discharge	398,922	0.64	41,721	0.48
Atmospheric Deposition	7,470	0.01	91	0
Lagoon Drains	103	0	2	0
Birds	1,782	0	642	0.01
Tidal Inflow	24,046	0.04	1,578	0.02
Total	623,312	1	85,794	1

Comparison of the 2002-2003 wet season sedimentation rate (associated with a mild El Nino-influenced rainfall) versus the maximum long-term average annual rate (0.1 cm yr^{-1}) estimated with ^{210}Pb highlights the pulsed nature of sedimentation events in the Lagoon. Interestingly, net loss of nutrients from sediments during the dry season only depleted about 10% of the amount deposited during the wet season. One implication of this is that, while wet season sedimentation rates and associated N and P load may be an order of magnitude less than estimated for this study during the 2002-2003 wet season, these infrequent El Nino events may be providing particulate N and P loads to the Lagoon that will take a decade or more to metabolize.

In estuarine or lagoon environments, carbon and nitrogen isotope signatures have been used in combination with C:N ratios to determine particulate organic carbon and nitrogen sources (Fry and Sheer 1984) and relative contributions from terrestrial or marine environments (Struck et al., 2000). Nitrogen isotope signatures have been used with some success to differentiate between various anthropogenic sources of nitrogen (Sweeney and Kaplan 1980, Mulholland and Olsen 1992, Middelburg and Nieuwenhiuze 1998).

In Malibu Lagoon, the combined results of the $\delta^{15}N$ and $\delta^{13}C$ signatures and C:N ratios show a mixture of sources, but results are not conclusive because terrestrial and marine end members as well as in situ sources such as SAV and macroalgae were not sampled.

In general, the ranges of $\delta^{13}C$ and C:N ratios are indicative that sediments are comprised of a mixture of terrestrial (watershed derived), marine (ocean-derived) and autochthonous sources (produced in situ through the production of phytoplankton, macroalgae or SAV). There is some variability within the western lagoon with respect to sediment organic matter source, although when averaged over time these differences are not statistically significant; Site 6 appears to have a slightly more significant terrestrial signature as indicated by a lighter range of $\delta^{13}C$ and higher C:N ratios – both indicative of more terrestrial plant sources of organic matter. Sites 2 and 3, located in tidal channels leading to the western lagoon, are slightly heavier with respect to their carbon isotopic ratio and show lower C:N ratios – indicating the organic matter sampled here is more likely to be produced in situ or transported from the ocean. This is logical, given that these sites have higher quantities of sands relative to finer grain size fractions and were noted to support benthic diatom mats during the late wet season and throughout the dry season (M. Sutula, personal observation).

Results of N stable isotope in Malibu Lagoon do not clearly point to a particular source of anthropogenic N to the Lagoon (Figure 14). This is due in part to a lack of characterization of possible organic N sources (i.e., creek sediment and algae, marine sediment and algae, etc.) but also due to difficulty in resolving source signature with mixtures of these same sources. Heavier $\delta^{15}N$ values of 10-14‰ have been shown to characterize river borne particulates and surface sediments with a heavy fertilizer influence (Voss and Struck 1997). The enrichment in the heavy isotope is the result of fractionation processes, which operate in the soil of arable land: nitrogen uptake during plant growth and denitrification of a large, initially light pool of nitrate from artificial fertilizer creates an isotopically heavy residual. This heavy residue can made heavier still by nitrate uptake during phytoplankton growth in the river and denitrification in the lagoonal water. In situ or marine-derived N signature varies, but generally can be found in ranges of 4 – 8 $^{o}/_{oo}$. In general, marine or in situ produced organic nitrogen is isotopically lighter due to uptake of nitrate by marine algae or production of organic nitrogen via cyanobacteria blooms (Struck et al., 2000). Values ranging from 8-10 $^{o}/_{oo}$ have been found in algal mats found at the outfalls of sewage or municipal effluent (Savage and Elmgren 2004). Notably, the isotopic composition of a sample will depend on the composition of the source material as well as fractionation processes that change the composition from its initial value (Cifuentes et al., 1988, Owens and Law 1989). These processes include uptake and assimilation, microbial activity, decomposition and remineralization (Cifuentes et al., 1988). N stable isotope values in Malibu Lagoon sediments ranged from 6 to 16 $^{o}/_{oo}$, which do not clearly point to any of these sources and are likely a complex mixture of allochthonous and autochthonous sources. Additional work needs to be done to better characterize the isotopic signatures of the various nitrogen sources to the Lagoon, including groundwater.

4.2. Newly Deposited Particulate N and P in Lagoon Sediments are Remineralized and Provide a Source of Nutrients to Surface Waters

After deposition, the sediments of estuaries and coastal lagoons undergo a series of transformations that control the remineralization 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 CO2 (Froelich and Klinhammer 1979). During this process, the decomposition of organic matter will result in the build-up of NH_4, DON, SRP and DOP in pore waters. SRP can also be desorbed and released from iron compounds (Fe(II)-hydroxide-PO_4 complexes and/or Fe(II)-PO_4 minerals) commonly found in clay and silt sediments in anoxic conditions (Roden and Edmonds 1997). Our data show the progression of these transformations in Western Lagoon sediments as pore water SRP, DOP, NH_4 and DON concentrations increased markedly over wet season concentrations. NO_3 concentration increased during the wet season as higher concentrations in the surface water cause a net flux of NO_3 into the sediments. As temperatures in the late wet season and dry season increase, pore water NO_3 decreased to non-detectable levels as microbially-mediated denitrification converts NO_3 to nitrogen gas (Seitzinger 1988).

When overlying surface water nutrient concentrations are less than pore water concentrations, a net release of the constituent will likely occur, as predicted by Ficke's law of diffusive transport (Berner 1980). The build-up of NH_4, DON, SRP and DOP in sediment pore waters is responsible for a predicted net release of these constituents to the surface waters throughout the year; calculations of potential diffusive flux, which when summed by season, predict a net release of 1254 lbs of TDN and 107 lbs of TDP annually to surface waters in for the entire Lagoon.

Predicted fluxes from the Central Lagoon represent only 1-2% of this total annual net release of TDP and TDN to the surface waters. The dominance of the Western Lagoon as a source of remineralized nutrients from sediments can be explained by the hydrodynamics of the Lagoon – and the effect that it has on the spatial patterns in deposition of fine- versus coarse-grained sediments. Sediments in the hydrodynamically-active Central Lagoon are predominantly sandy and devoid of nutrients relative to the Western Lagoon. In the Western Lagoon, where circulation is poorer and water velocities during storm events are likely to be much lower, deposition of fine-grained, nutrient-rich sediment dominates (Wolanski and Ridd 1986). A number of studies have found that sandy sediments generally have lower pore water dissolved nutrient and organic carbon concentrations and thus will have lower benthic flux rates relative to fine-grained clays and silts (Berner 1980; Klump and Martens 1983; Sutula et al., 2004).

Our confidence is low that the potential diffusive flux rates, when integrated into seasonal or annual rates, represents robust estimates because many of the assumptions that we made in order to derive these estimates are not likely to hold for Malibu Lagoon. Particularly suspect are the estimates of SRP fluxes, which can be modified by surficial sediment chemistry when oxygen content of the sediments is high (McManus et al., 1997, Klump and Martens 1987). Nevertheless, calculated potential diffusive fluxes are likely to be an underestimate of the net release of nutrients into the surface waters. 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). ^{7}Be data show that bioturbation (possibly by burrowing worms) is intensively reworking the first 0-2 cm, particularly during the dry season. This bioturbation may be greater at shallower, intertidal sites such has Site 1, where ^{210}Pb indicate that the sediment column is fairly well mixed over decadal timeframes down to depths of 10 cm. Both groundwater seepage and bioturbation would result in greater release of dissolved organic and inorganic nutrients to the surface waters than was predicted in this study by potential diffusive flux.

It is surprising to note that the dry season loss of sediment N was equal in magnitude to the predicted flux of TDN in the Western Lagoon. Sediment nutrient uptake by SAV, sediment nutrient release to surface waters, and denitrification are all pathways by which sediment N inventory may decrease over dry season. One explanation is the magnitude of dry season TN sources such as groundwater seepage and dry weather nuisance flows into the Lagoon may be equal in magnitude to loss of TN via such processes as denitrification. Little is known about the rates of denitrification in coastal lagoons in southern California, though the published rates for eutrophic estuaries range from 50-250 μmol N m^{-2} h^{-1} (Seitzinger 1988). These numbers when integrated over the dry season would represent a loss of 64 – 318 kg (140-700 lbs) N in the Western Lagoon – numbers that are comparable to some nonpoint source inputs to the Lagoon during the dry season. To better understand the N budget of Malibu Lagoon, denitrification should be quantified. It is also important to better understand the quantity of nutrients stored in SAV biomass during the dry season, and the fate of these nutrients as SAV dies off at the beginning of the wet season. It is possible that a portion of TN and TP tied up in SAV biomass is returned to the sediments at the beginning of each wet season (Tyler et al.,, 2001). The resolution of our temporal sampling did not allow us to discern whether this was the case. A better understanding of these data gaps would help refine estimates of nutrient sources and sinks in the Lagoon and their net impact on primary producer growth.

Also interesting to note is the large increase in sediment N in Central Lagoon sediments during the dry season (959 kg or 2114 lbs TN) relative to a loss in sediment P during this period (83 kg or 184 lb TP. Note that there is some uncertainty in the magnitude of these estimates due to the limited sampling of the Central Lagoon. The increase in the TN content of sediments during the dry season may be related to the growth of benthic algal mats in Central Lagoon sediments. It is likely that some of the nitrogen used by the algal mat for growth is derived from the Western Lagoon, although some cyanobacteria mats are known for their ability to fix atmospheric nitrogen.

4.3. Primary Producer Community Abundance and DO Impairment in Malibu Lagoon is Linked with Dry Season Sediment Nutrient Release

Dry season DO impairment in Malibu Lagoon was driven by the presence of dense stands of *R. maritima*. The abundance of the SAV and subsequent DO impairment were ultimately a function of the high degree of nutrient enrichment in sediments and surface waters as well timing of Lagoon closure, which affected the salinity regime that control *R. maritima* growth. The timing of the *R. maritima* growth in the Lagoon was coincident with periods of high nutrient release from sediments.

High nutrient availability was responsible for the dense biomass of SAV observed in the Western Lagoon during the 2002 dry season. *R. maritima* can take up nutrients via the roots or leaves. The sediments of Malibu Lagoon (both solid phase and pore waters) were highly enriched with nutrients. Sediment N in the top 2 cm in the Western region of Malibu Lagoon 0.341 ± 0.228 % was equal to or greater than values from several of the most eutrophic systems studied worldwide (Venice Lagoon, Italy- 0.27-0.53% (Marcomini et al., 1995, Sfriso et al., 1995); and the Peel-Harvey Inlet, Australia- 0.45% dry wt (McComb et al., 1998)) as well as the maximum values found in local estuaries (0.166 ± 0.01% dry wt TKN in Upper Newport Bay; Boyle et al., 2004) and <0.3% dry wt TN in Carpinteria Salt Marsh Reserve and Mugu Lagoon; Kennison et al., 2003). The same is true for sediment P; in Malibu Lagoon, average sediment P in the top 2 cm (0.081 ± 0.032 % was equal to or greater than maximum concentrations found in Upper Newport Bay (0.072% dry wt, Boyle et al., 2004), Mugu Lagoon (0.13% dry wt, Kennison et al., 2003), Venice Lagoon and Peel-Harvey Inlet (0.07% dry wt for each, Marcomini et al., 1995, McComb et al., 1998). *R. maritima* roots, which have a higher affinity for NH_4 than NO_3 (Thursby 1984b), have access to high concentrations of NH_4 in pore waters. *R. maritima* uptake of pore water NH_4 could have accounted for the lower pore water NH_4 at Sites 5 and 6 relative to Sites 1 and 7, which had less SAV.

Surface water nutrients also provided a source to *R. maritima* via uptake at its leaves (Verhoeven 1979, Thursby and Harlin 1986). Thursby (1984a) showed that *R. maritima* grown in culture without sediments was limited by N at concentrations of NO_3 <110 μM (1.54 mg l^{-1}) and by P at concentrations of PO_4 <2.3 μM (0.0713 mg l^{-1}). Concentrations of N and P in Malibu Lagoon were higher than those cited by Thursby (1984a) and could have supported a high degree of productivity.

The abundance of the SAV and subsequent DO impairment were also a function of the timing of the closure of the Lagoon, which affected the salinity and hydrodynamic regimes. In 2002, a year with little rainfall, the mouth of the Lagoon closed in April, tidal exchange ceased, and the water became brackish. A large seasonal *Ruppia maritima* community was established in the Western Lagoon early during the dry season and caused severe hypoxia. In 2003, with significant rainfall occurring as late as May, the mouth of the Lagoon closed in June 2003, so higher salinities (i.e., 8-10 ppt) occurred much later than the previous year. *R. maritima* can tolerate a broad range of salinity (Lazar and Dawes 1991) but its natural distribution is generally limited to areas with salinity < 20 ppt (Mayer 1967, Verhoeven 1979, Koch and Seeliger 1988). Several studies have shown that seed germination (Koch and Seeliger 1988, Koch and Dawes 1991) and rhizome and root production (Bird et al., 1993) increase as salinity decreases to <15 ppt. Another study (Mayer 1967) found that *R. maritima* seed germination and growth were greatest in freshwater and that reproduction was greatest at <12 ppt. *R. maritima* can reproduce asexually through fragmentation or rhizome propagation but reproduction through seeds is probably the most important mechanism for *R. maritima* (Verhoeven 1979). Therefore, it is likely that higher salinity later in 2003 inhibited *R. maritima* seed germination resulting in a less developed community that year. Additionally, the root systems of *R. maritima* do not extend deeply into the sediments and plants can be easily plants can be easily dislodged by turbulence, which would be greater when the mouth of the Lagoon is open.

4.4 Nutrient Release from Sediments is a Significant Source to Primary Producers Relative to Other Non-Point Inputs During the Dry Season

The net increase in sediment nutrient inventory over the wet season is a small fraction of the total loading to the Lagoon from point and non-point sources, most of which occur during the wet season (Table 7). Thus, most of the wet season loads are transported directly into the Pacific Ocean. However, this small fraction retained provides an ecologically significant source of nutrients to the Lagoon during the dry season.

The timing of the *R. maritima* growth in the Lagoon is coincident with periods of high nutrient release from sediments. Comparison with other dry season non-point sources indicates that sediment release represents 18% of the TN sources and 5% of the TP from other nonpoint source inputs to the Lagoon during the dry season (Table 8). A recent study of groundwater seepage into the Lagoon estimates that TN loading from this sources ranges between 4- 13 kg (8 – 28 lb) day^{-1} (Douglas et al., 2004), comparable in magnitude to the original estimate by Ambrose and Orem (2000). Seepage thus represents the largest input of TN to the lagoon during the dry season (52%). Douglas et al., 2004 note that the upper range of this estimate represents groundwater N transport into the Lagoon without attenuation or losses via denitrification. Groundwater monitoring data show that TN is being attenuated and that denitrification is the most probable explanation. Another significant source is urban runoff and septic seepage from the watershed, which represents 25% of N and 96% of TP sources to the Lagoon. . Although sediment release is less than these two major sources, it nevertheless represents a significant fraction of the TN input into the Lagoon and is available to fuel primary producer growth. . Thus wet season particulate N and P loading is strongly linked to the Lagoon with high primary producer abundance and low DO events in the dry season.

Table 8: Comparison of Sediment N and P Release to Surface Waters With Other Dry Season Non-Point Sources to Lagoon. Total Dry Season Loads are Based on a Period of 153 Days.

Dry Season Source	N (lbs d^{-1})	% of N Loading	Dry Season N Load (lbs)	P (lbs d^{-1})	% of P Loading	Dry Season P Load (lbs)
Storm Drains to Lagoon[a]	1.3	5.2%	201.2	7.2E-03	0.1%	1.1
Septic Seepage to Lagoon[a]	13.1	52.2%	2005.0	--	--	--
Watershed Septic Seepage & Urban Runoff[a]	6.3	25.1%	962.9	6.6	94.7%	1012.8
Sediment Release (This Study)	4.4	17.5%	672.8	0.4	5.2%	56
Total	25.1	100%	3841.9	7.0	100%	1070.0

[a] Ambrose & Orme 2000

5. CONCLUSIONS

In conclusion, we found that sediment enriched in particulate N and P was deposited in the Lagoon during the wet season. While the net increase in sediment nutrients over the wet season is a small fraction of the total loading to the Lagoon from point and non-point sources, it provides an ecologically significant source of nutrients to the Lagoon during the dry season when nutrients are remobilized to the surface waters as dissolved inorganic nutrients. Comparison with other dry season non-point sources indicates that sediment release equals 18% of the TN sources and 5% of the TP from other nonpoint source inputs to the Lagoon during the dry season and is a significant source of nutrients to primary producers. Thus wet season particulate N and P loading to the Lagoon is strongly linked with high primary producer abundance and low DO events in the dry season.

Despite our findings, several major data gaps exist that limit understanding of the source, transport and fate of anthropogenic nutrients to Malibu Lagoon. These include: 1) quantification of the rates of denitrification in groundwater (septic seepage to the lagoon), 2) direct measurements of groundwater seepage into the Lagoon and denitrification rates within Lagoon sediments, 3) direct measurements of nitrogen fixation in the Lagoon (a natural source of N to Lagoon), 4) identification of the major anthropogenic sources of sediment N to the Lagoon from the watershed, and 4) the extent to which N and P stored in SAV tissue during the is recycled back to sediments during the wet season.

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7. FIGURES

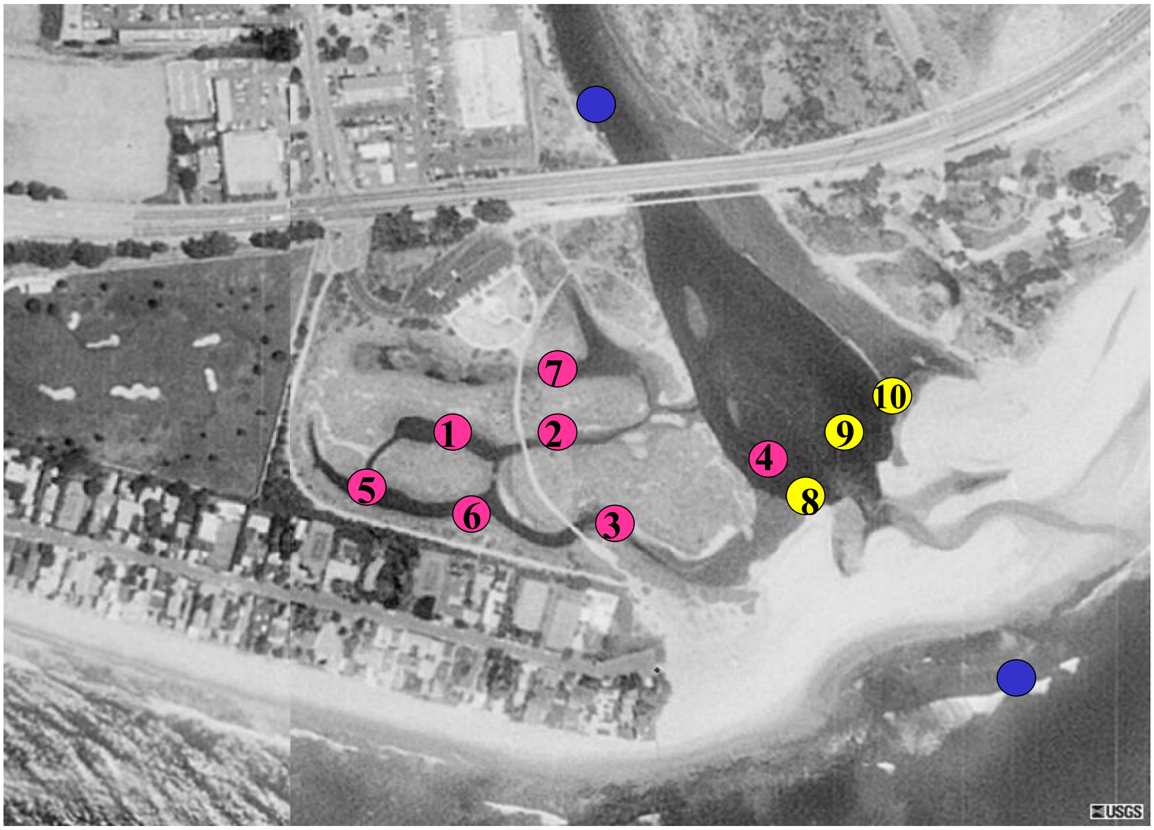

Figure 1: Map of study area showing sampling locations.

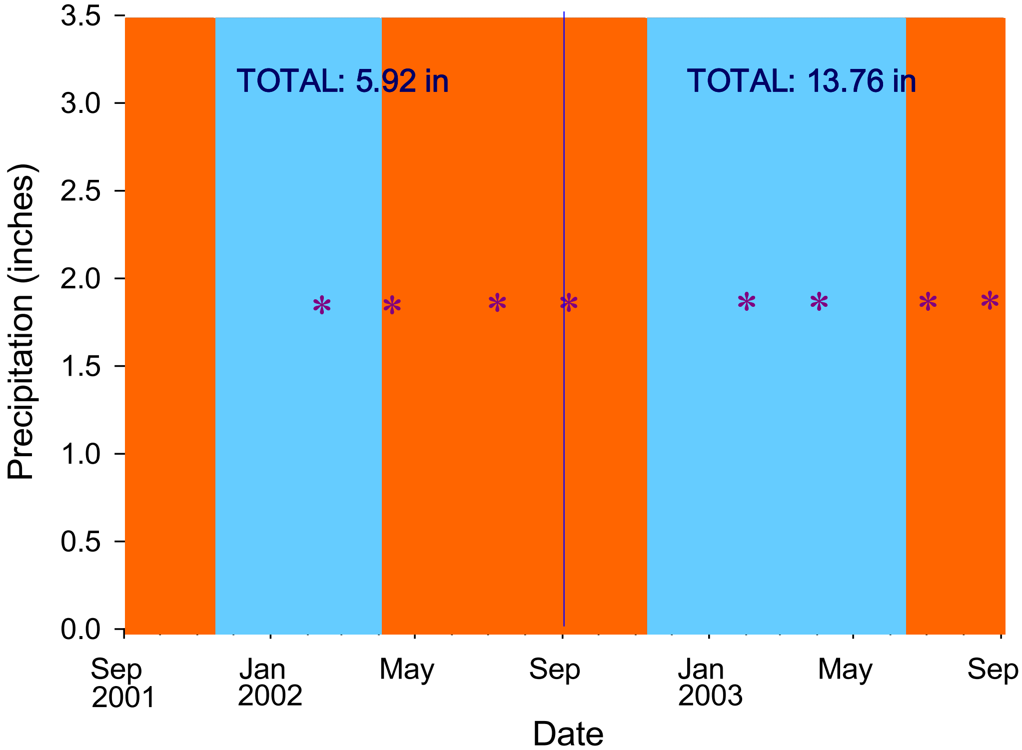

Figure 2: Graph of rainfall during the study period. Rainy season and lagoon inlet opening designated in blue. Dry season and lagoon mouth closures are shown in red. Asterisks designate sampling periods.

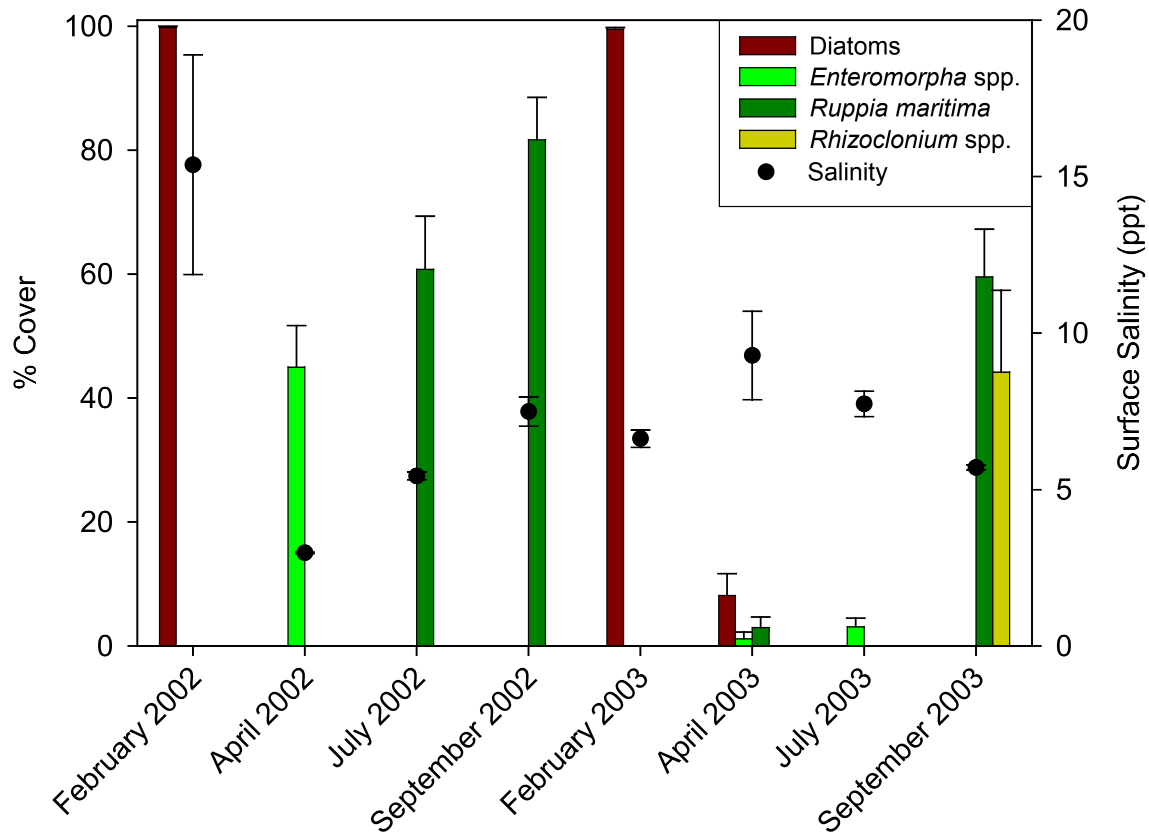

Figure 3: Percent cover of dominant primary producers and salinity in Malibu Lagoon from February 2002 through September 2003. Bars represent ± 1 SE.

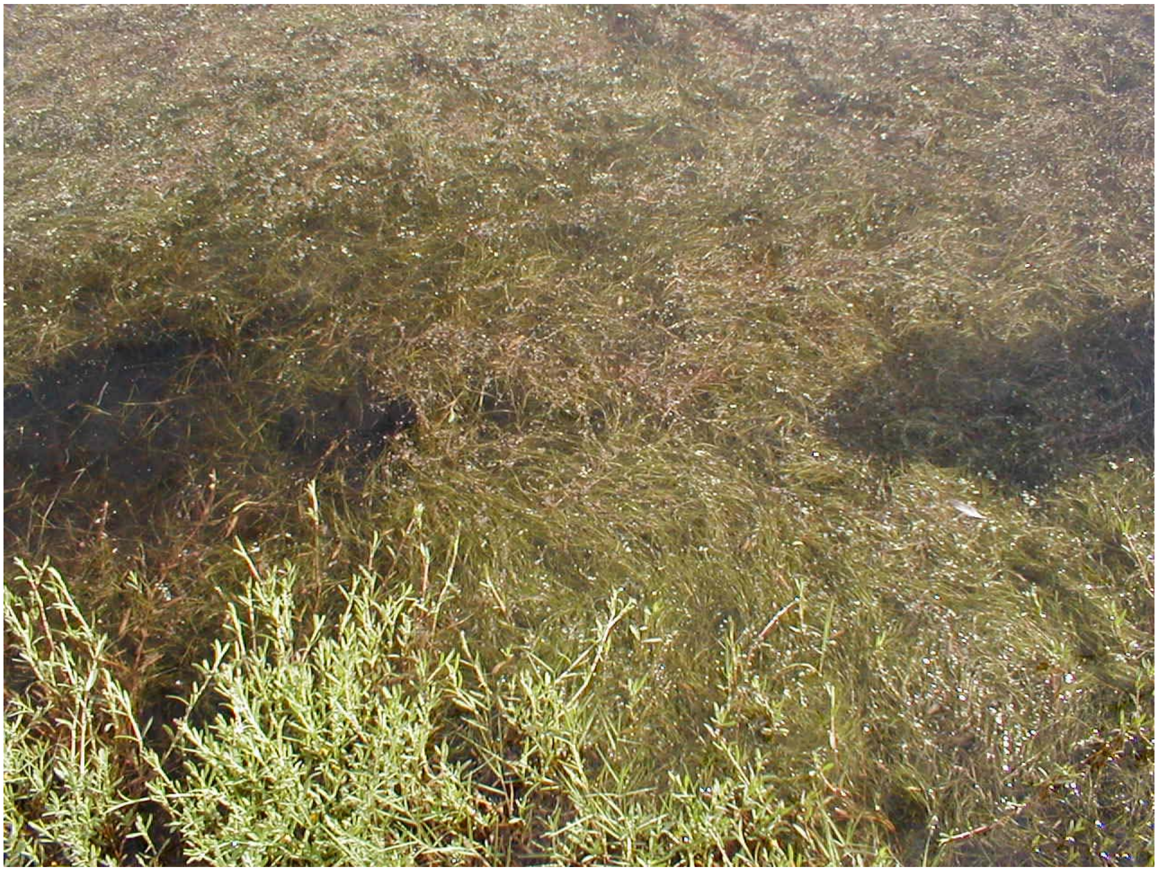

Figure 4: *Ruppia maritima* in Malibu Lagoon July 2002.

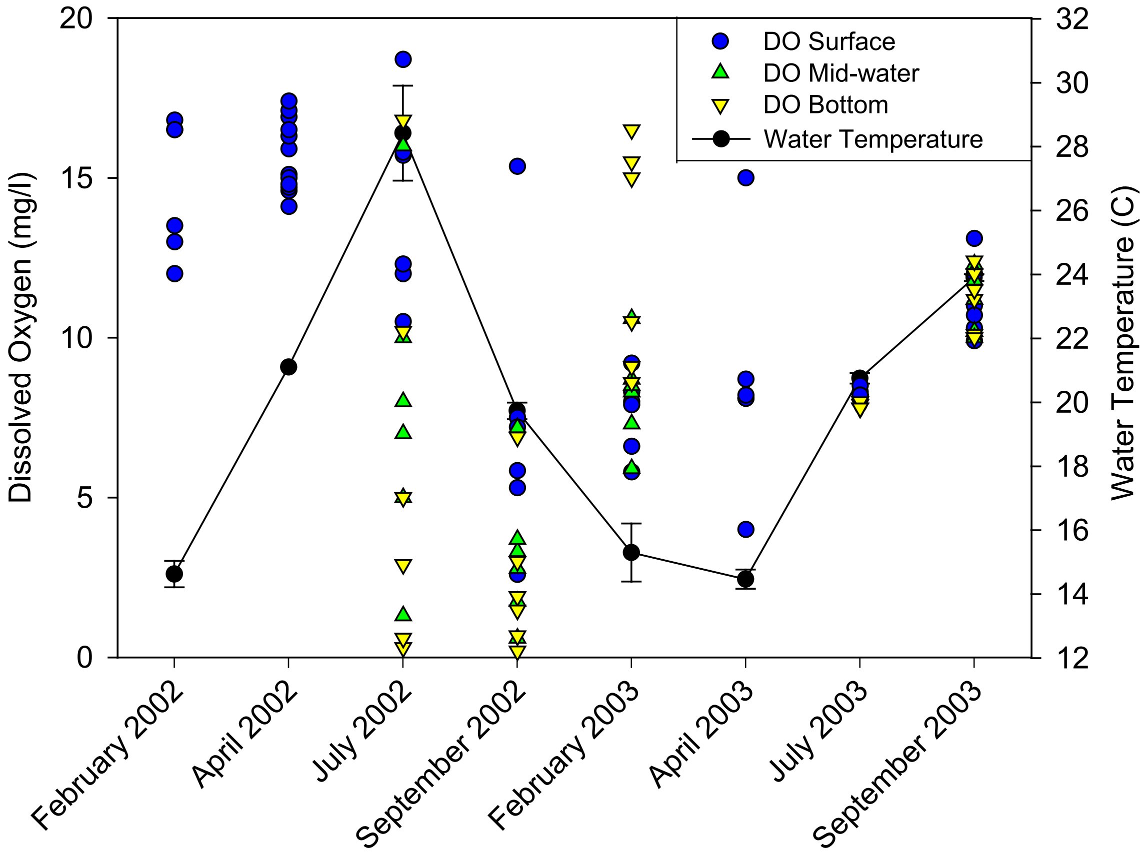

Figure 5: Water column dissolved oxygen and temperature in Malibu Lagoon from February 2002 through September 2003. Bars represent ± 1 SE.

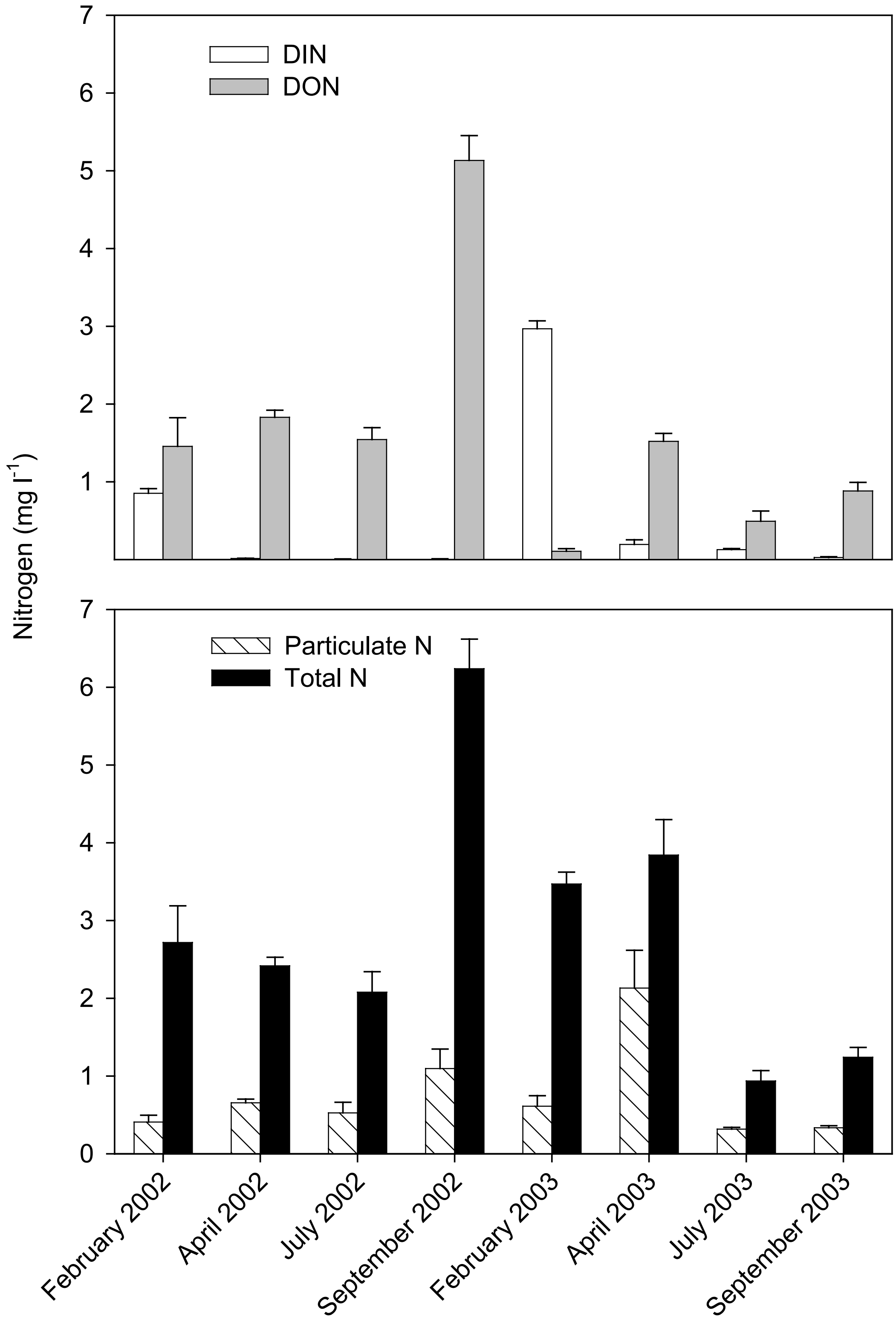

Figure 6: Mean concentrations of a) dissolved inorganic N (DIN) and dissolved organic N (DON) and b) particulate and total N in Malibu Lagoon. Bars represent ± 1 SE.

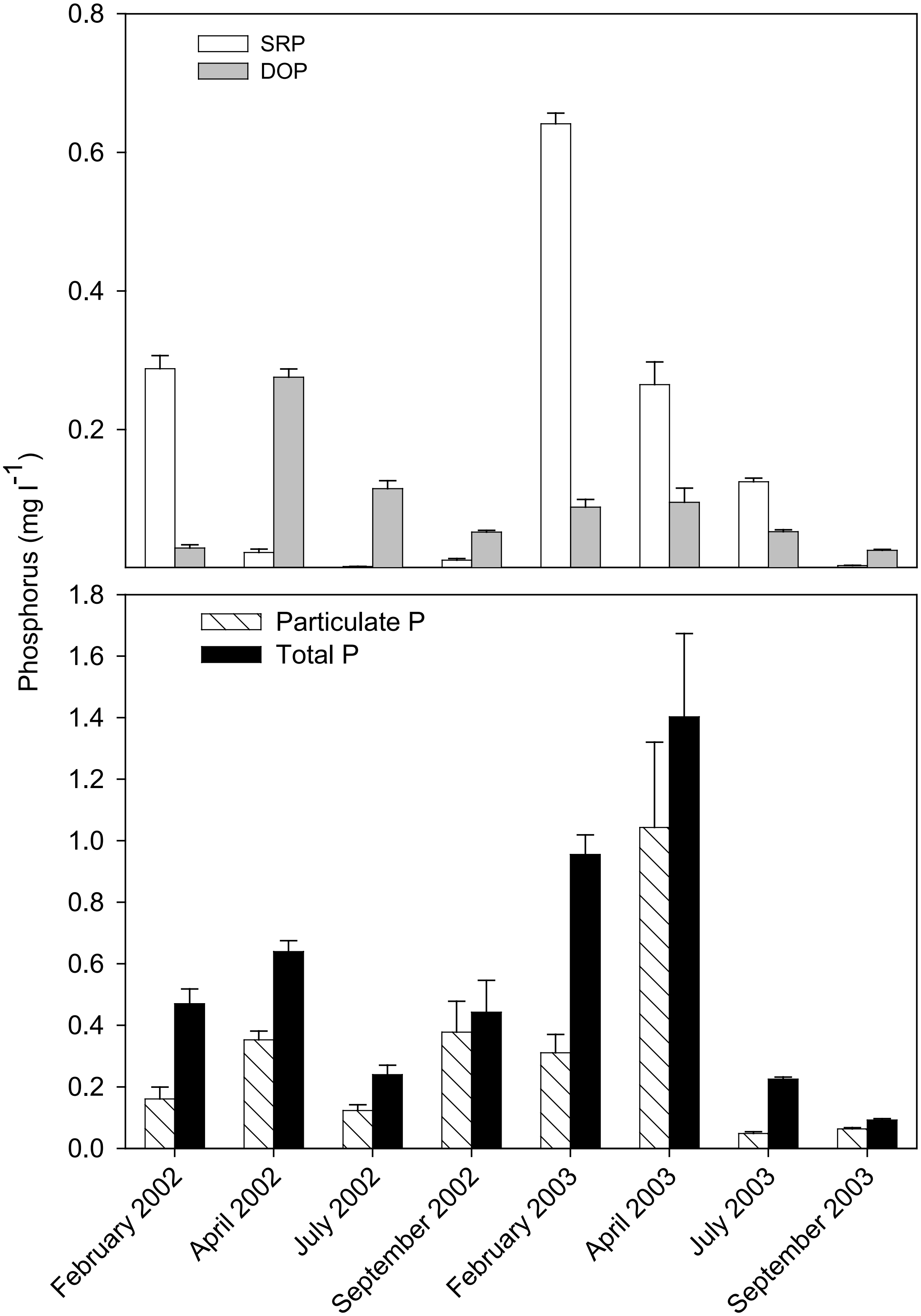

Figure 7: Mean concentrations of a) soluble reactive P (SRP) and dissolved organic P (DOP) and b) particulate and total P in Malibu Lagoon. Bars represent ± 1 SE.

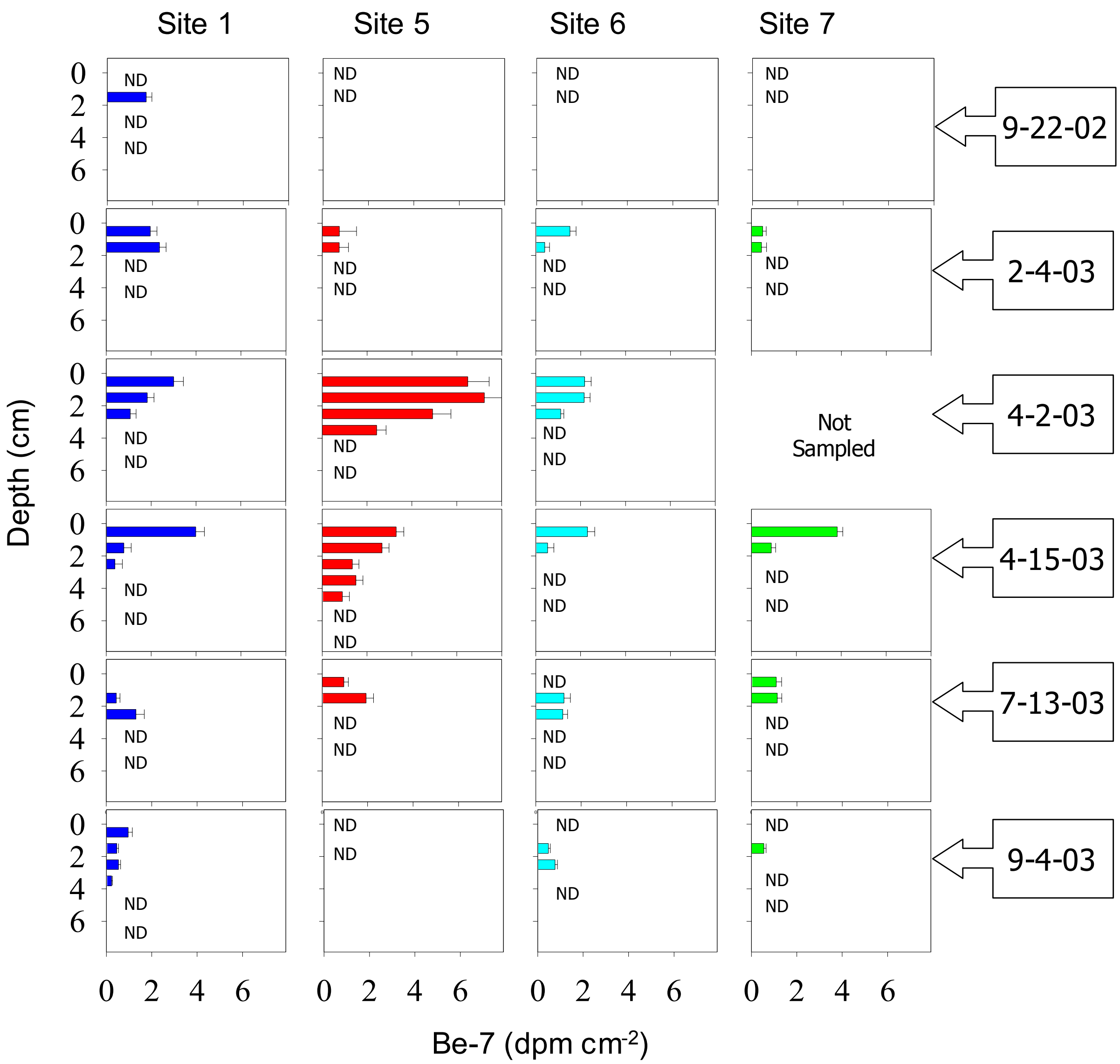

Figure 8: ^{7}Be inventories with depth by site and sampling period. Bars represent ± 1 SE. N.D. represents a non-detectable ^{7}Be activity.

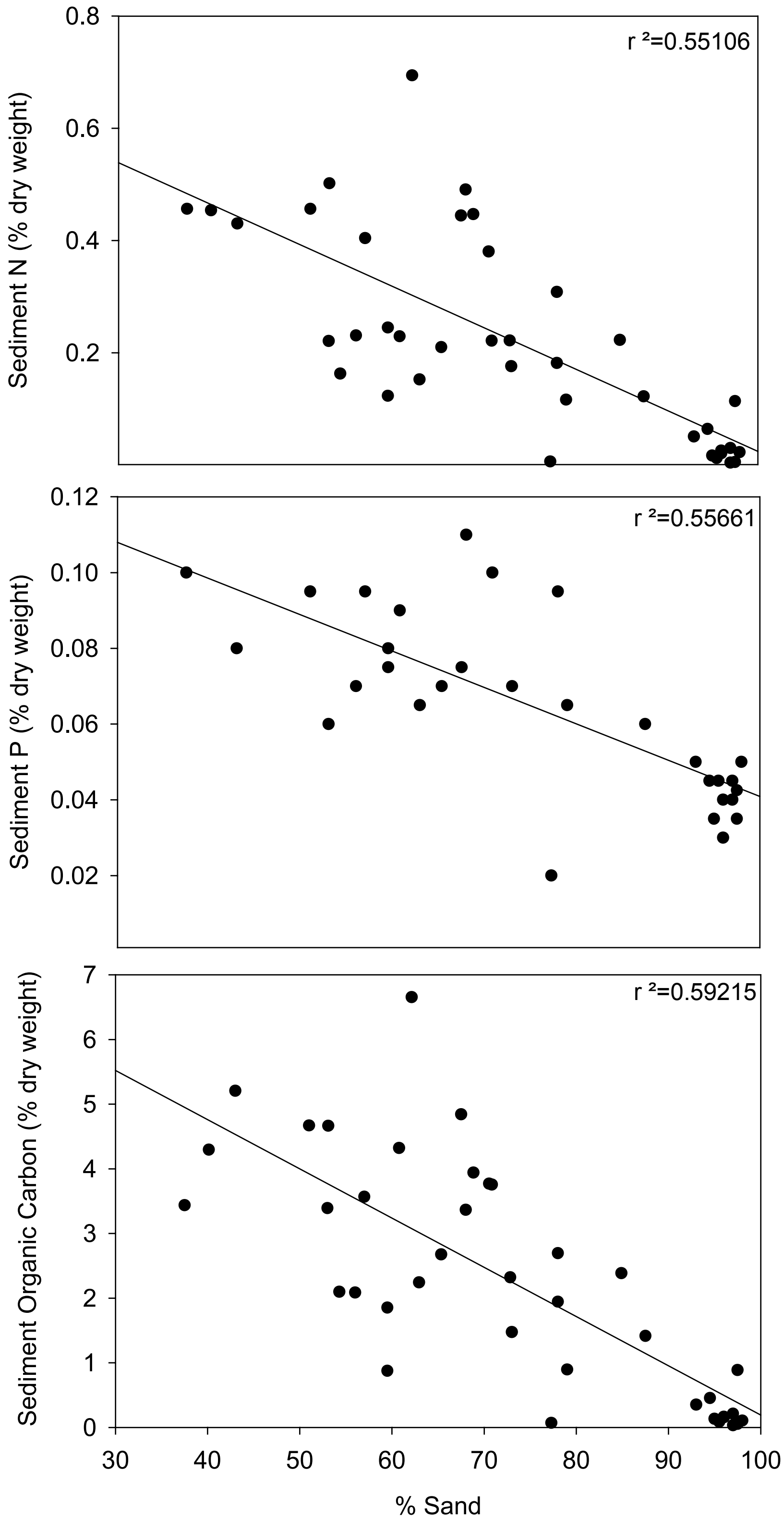

Figure 9: Regressions of sediment a) N, b) P, and c) organic carbon versus percent sand in Malibu Lagoon.

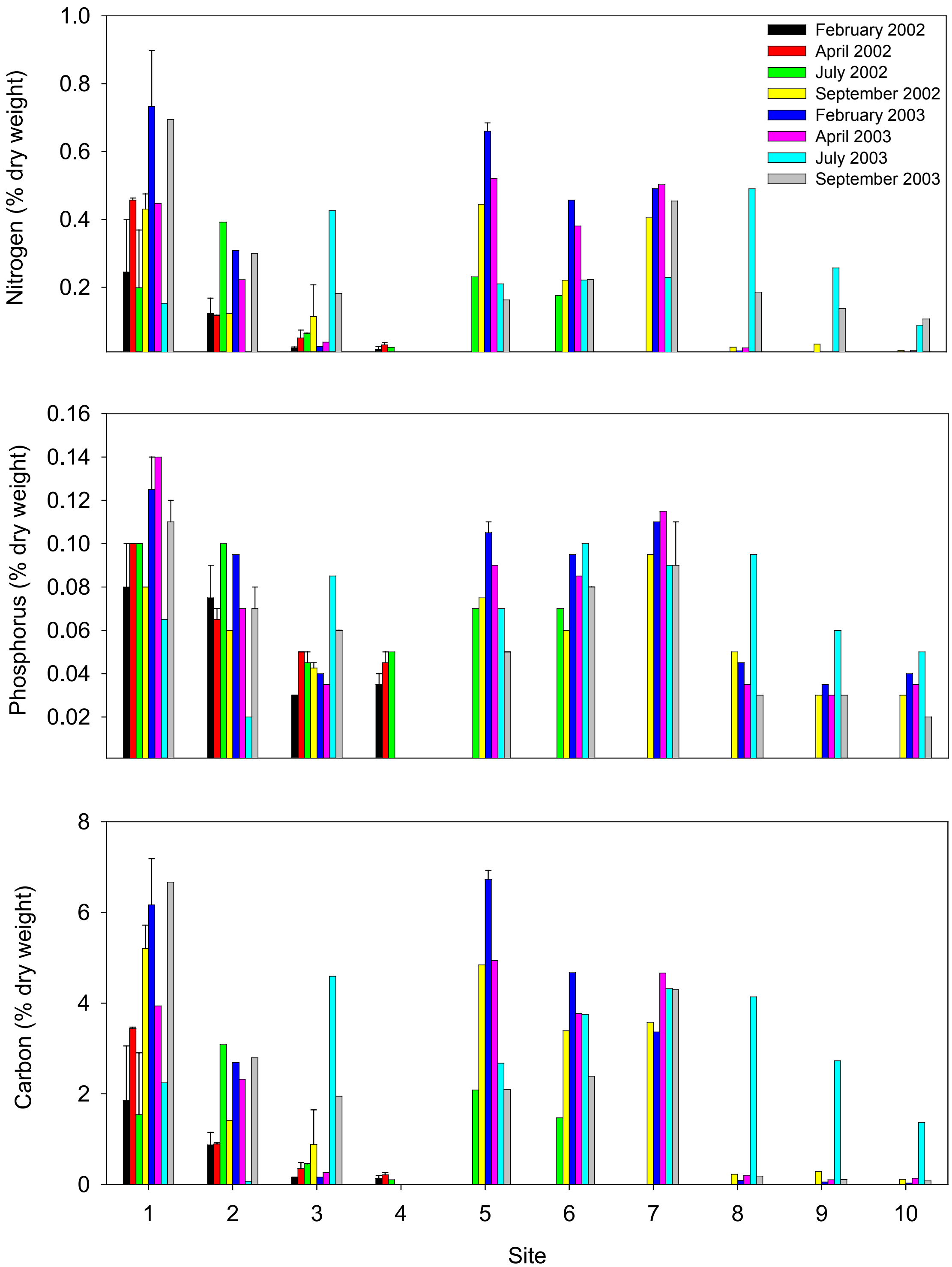

Figure 10: Sediment a) N, b) P, and c) carbon content in the Main and Central portions of Malibu Lagoon from February 2002 through September 2003. Bars represent ± 1SE.

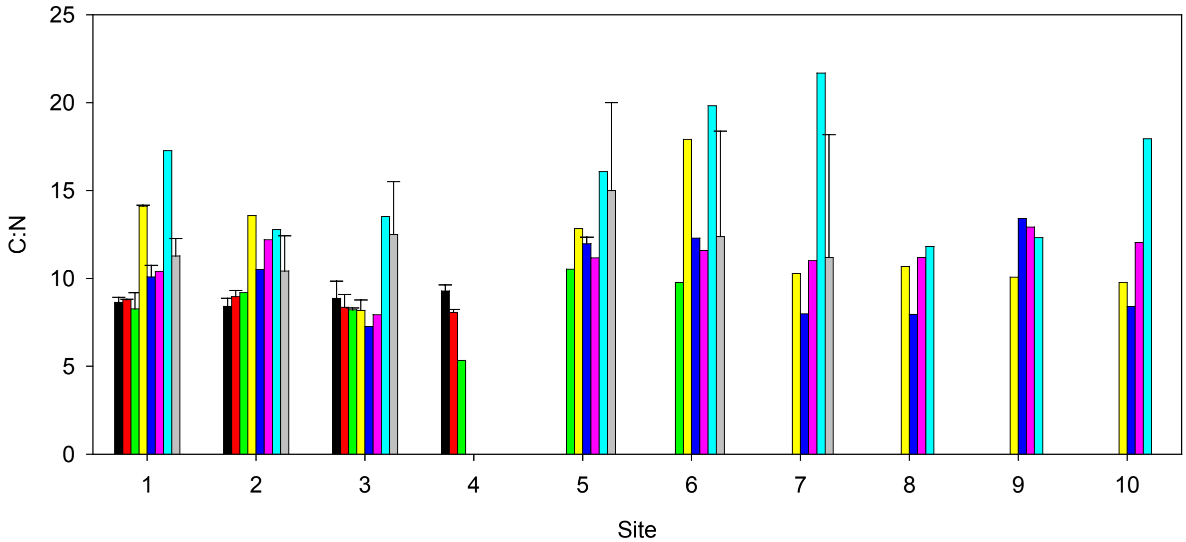

Figure 11: Sediment a) N:P and b) C:N ratios in the Main and Central portions of Malibu Lagoon from February 2002 through September 2003. Bars represent ± 1 SE.

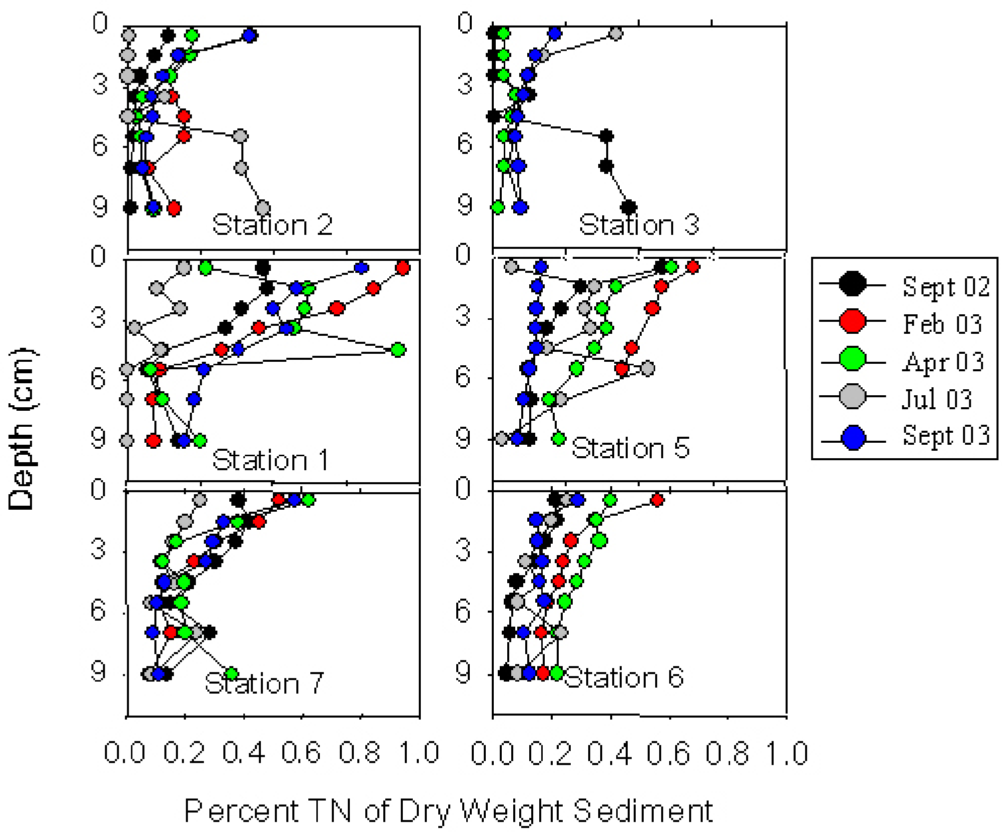

Figure 12: Vertical profile of sediment N by site and sampling period.

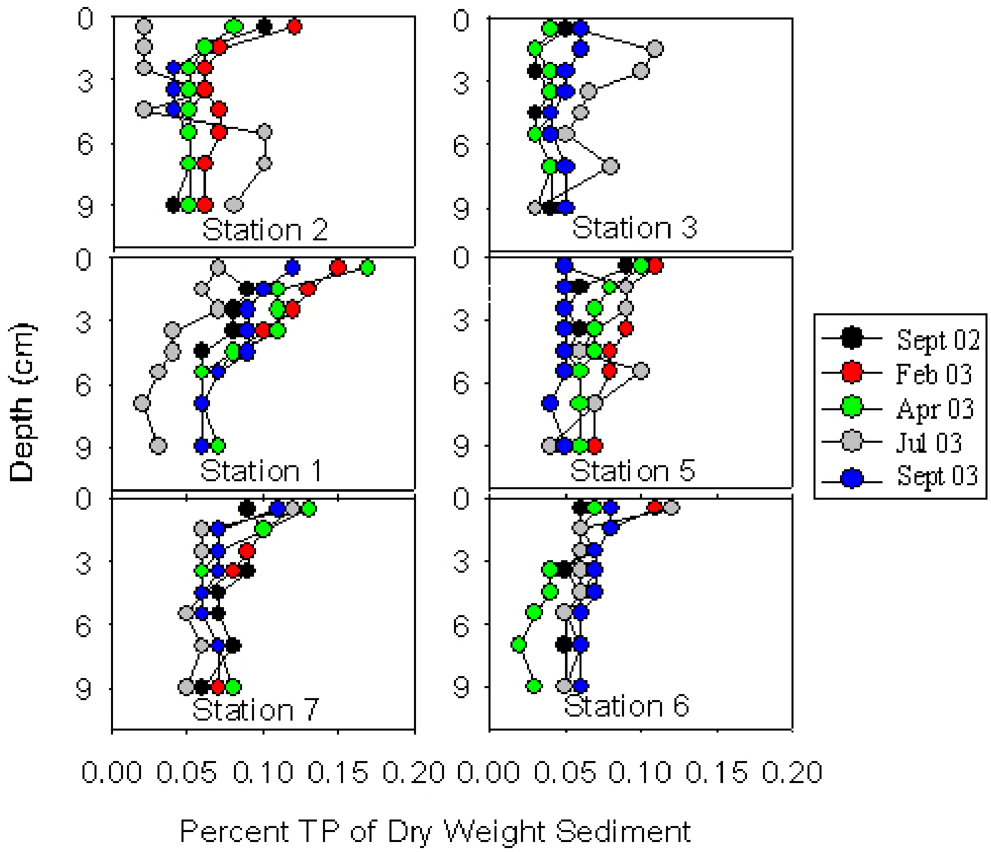

Figure 13: Vertical profile of sediment P by site and sampling period.

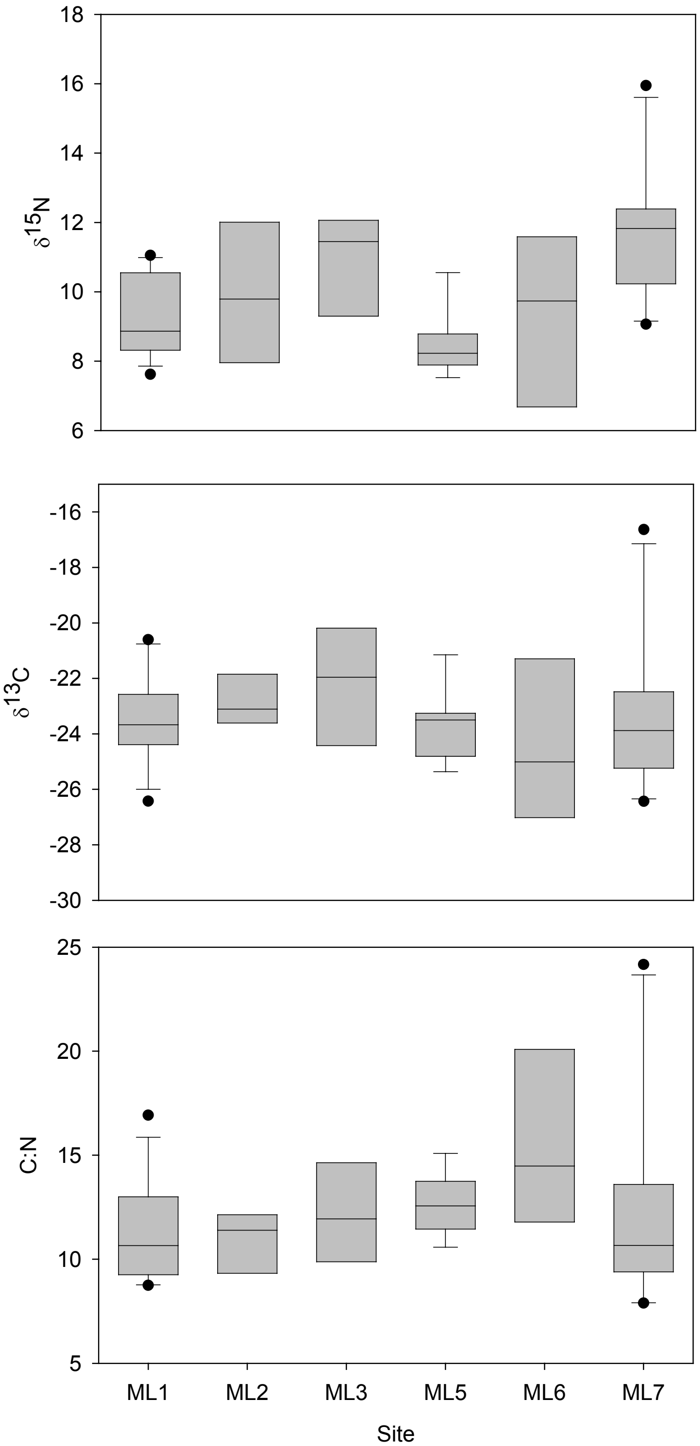

Figure 14: Sediment N and C stable isotope and C:N ratios by site. The line within each box represents the median, the boundary of each box closest to zero indicates the 25th percentile, and the boundary of each box farthest from zero indicates the 75th percentile. Whiskers above and below each box indicate the 90th and 10th percentiles, and any outlying points are graphed.

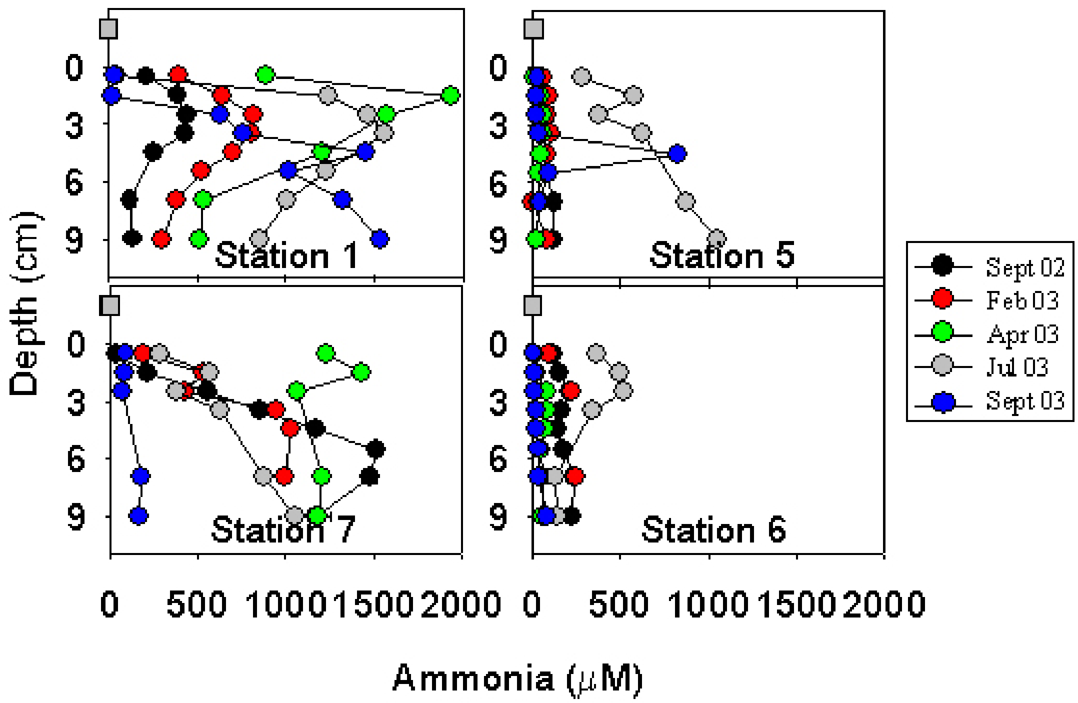

Figure 15: Vertical profile of pore water NH_4 concentration by site and season.

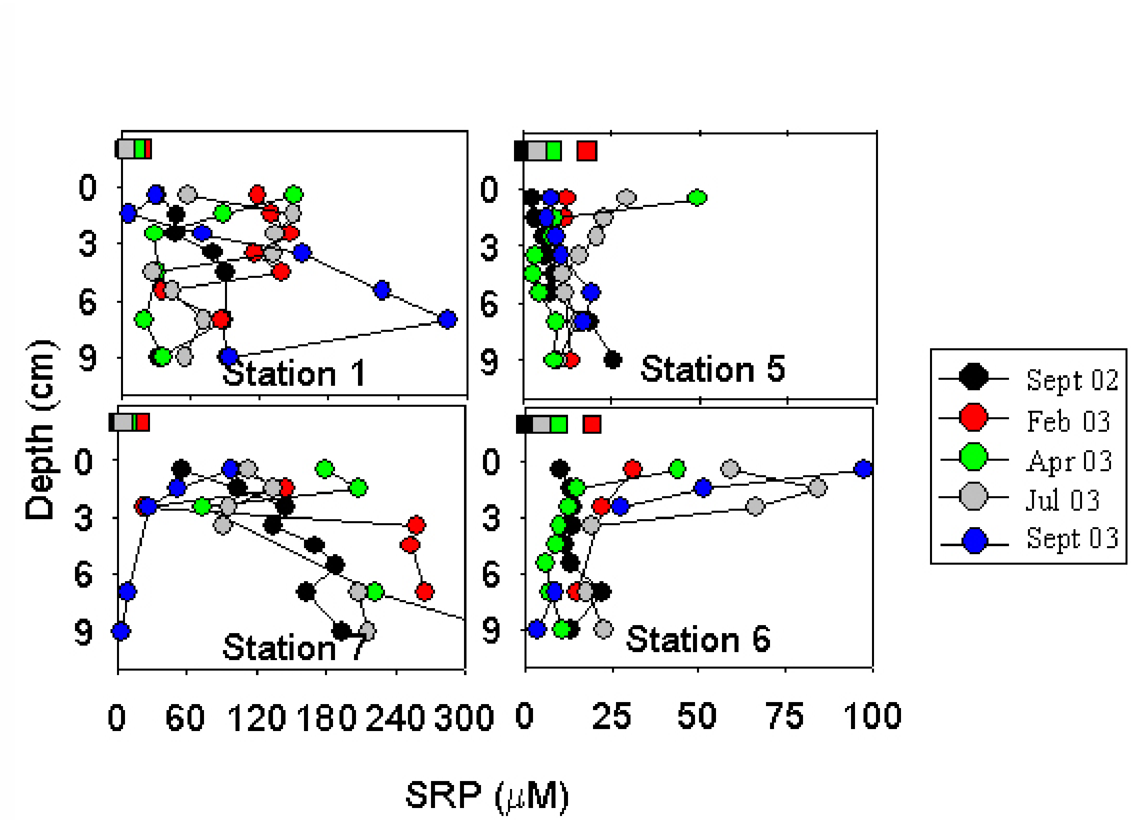

Figure 16: Vertical profile of pore water SRP concentration by site and season.

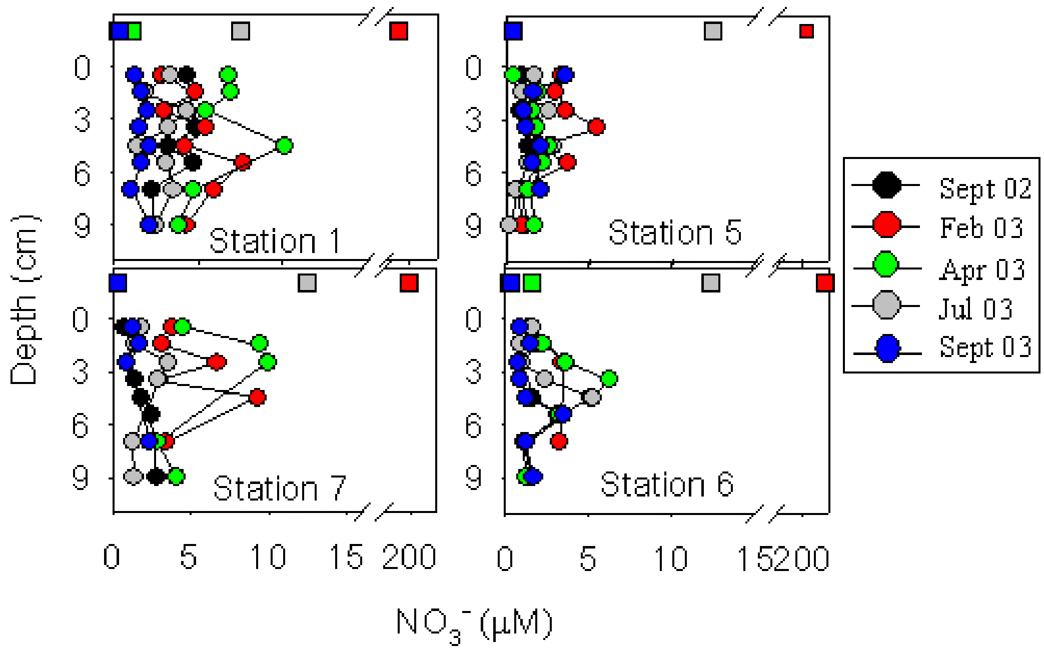

Figure 17: Vertical profile of pore water NO_3 concentration by site and season

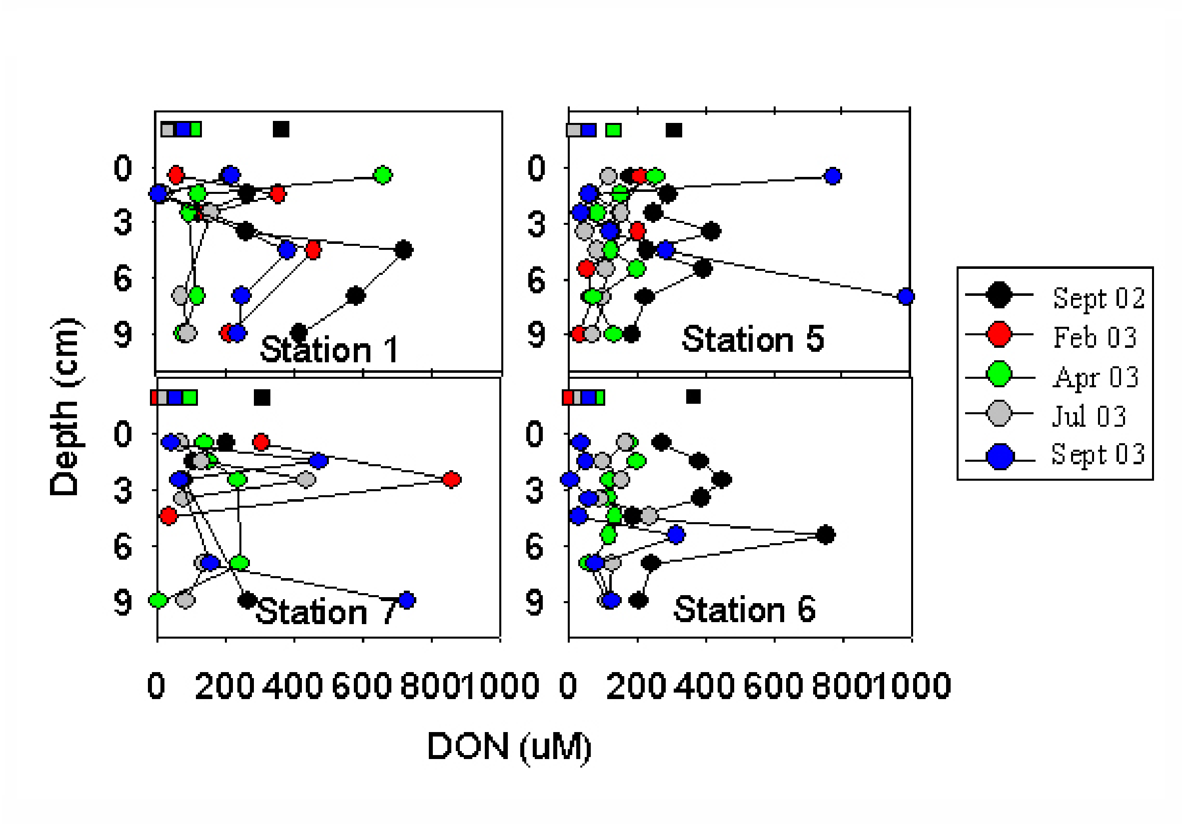

Figure 18: Vertical profile of porewater DON concentration by site and season.

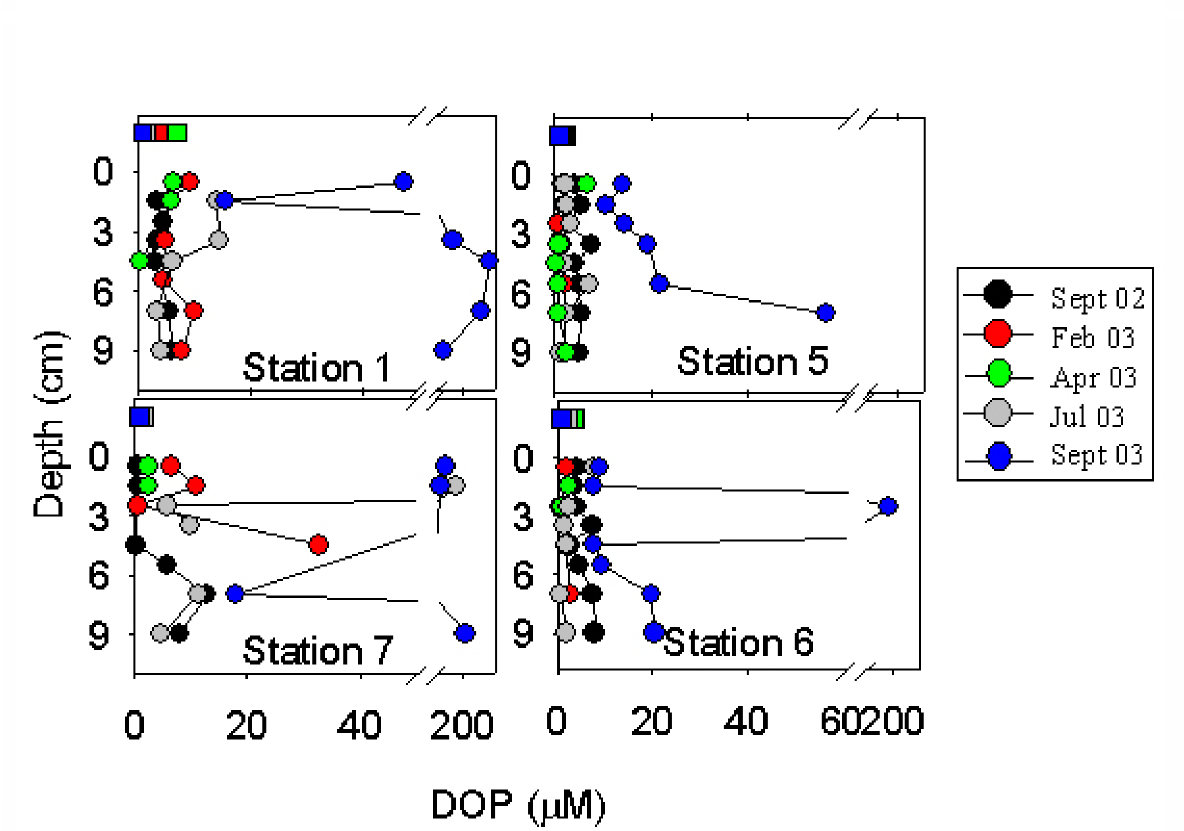

Figure 19: Vertical profile of DOP concentration in pore waters by site and season.

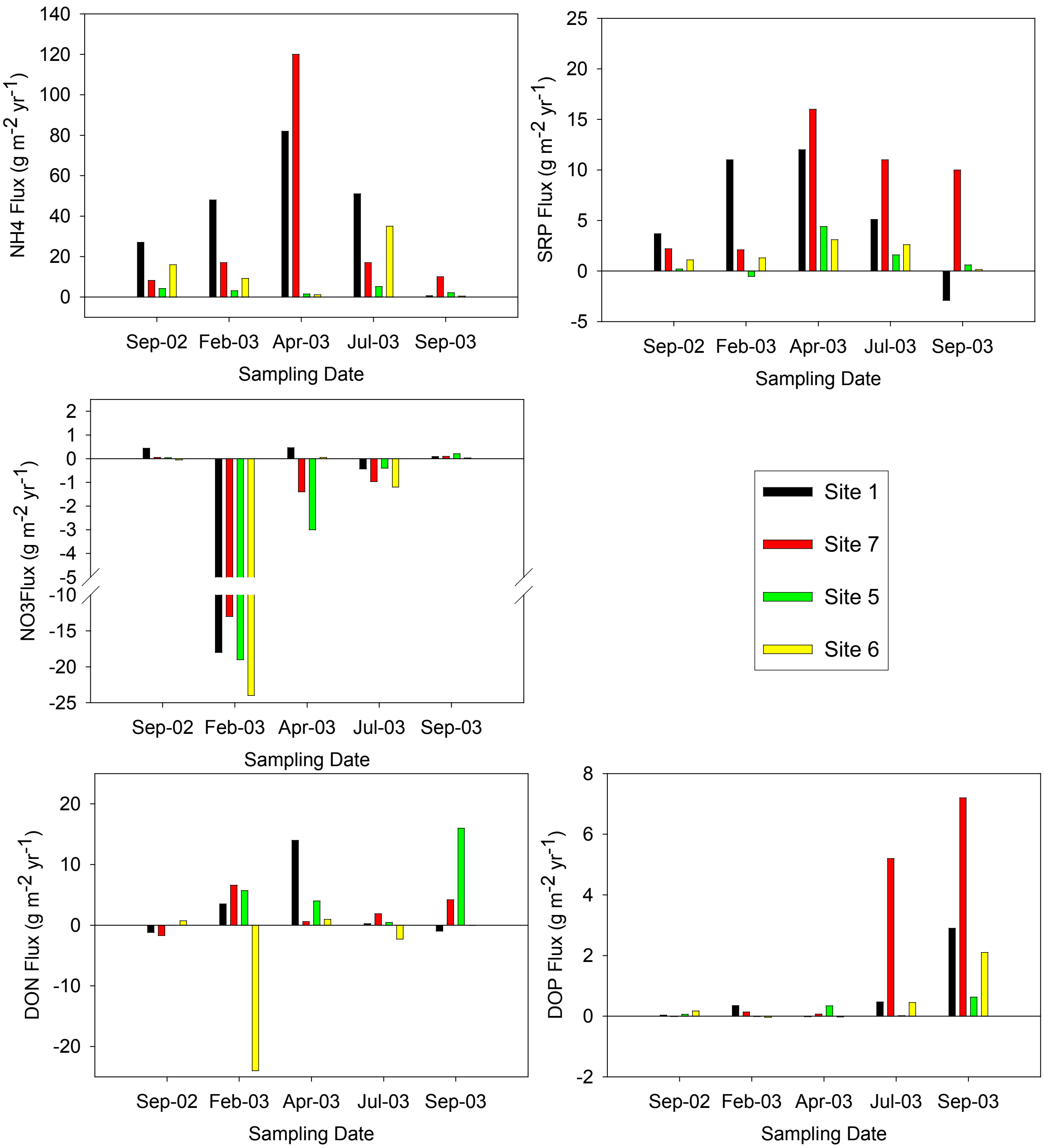

Figure 20: Instantaneous flux rates for Western Lagoon by site and sampling period. All rates are given in g m^{-2} yr^{-1}. Negative numbers represent a flux into the sediments from the water column.

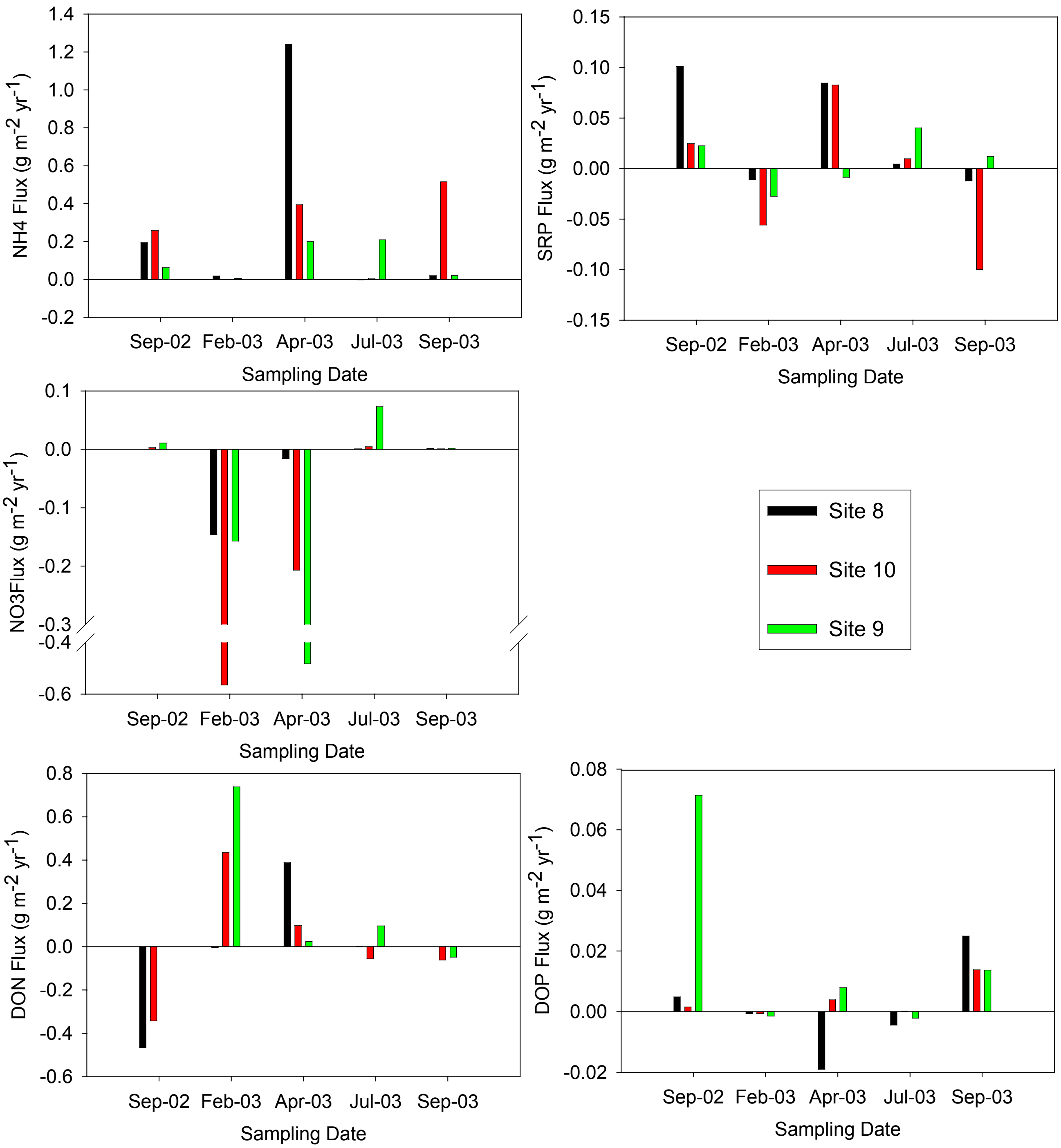

Figure 21: Instantaneous flux rates for Central Lagoon by site and sampling period. All rates are given in g m^{-2} yr^{-1}. Negative numbers represent a flux into the sediments from the water column.

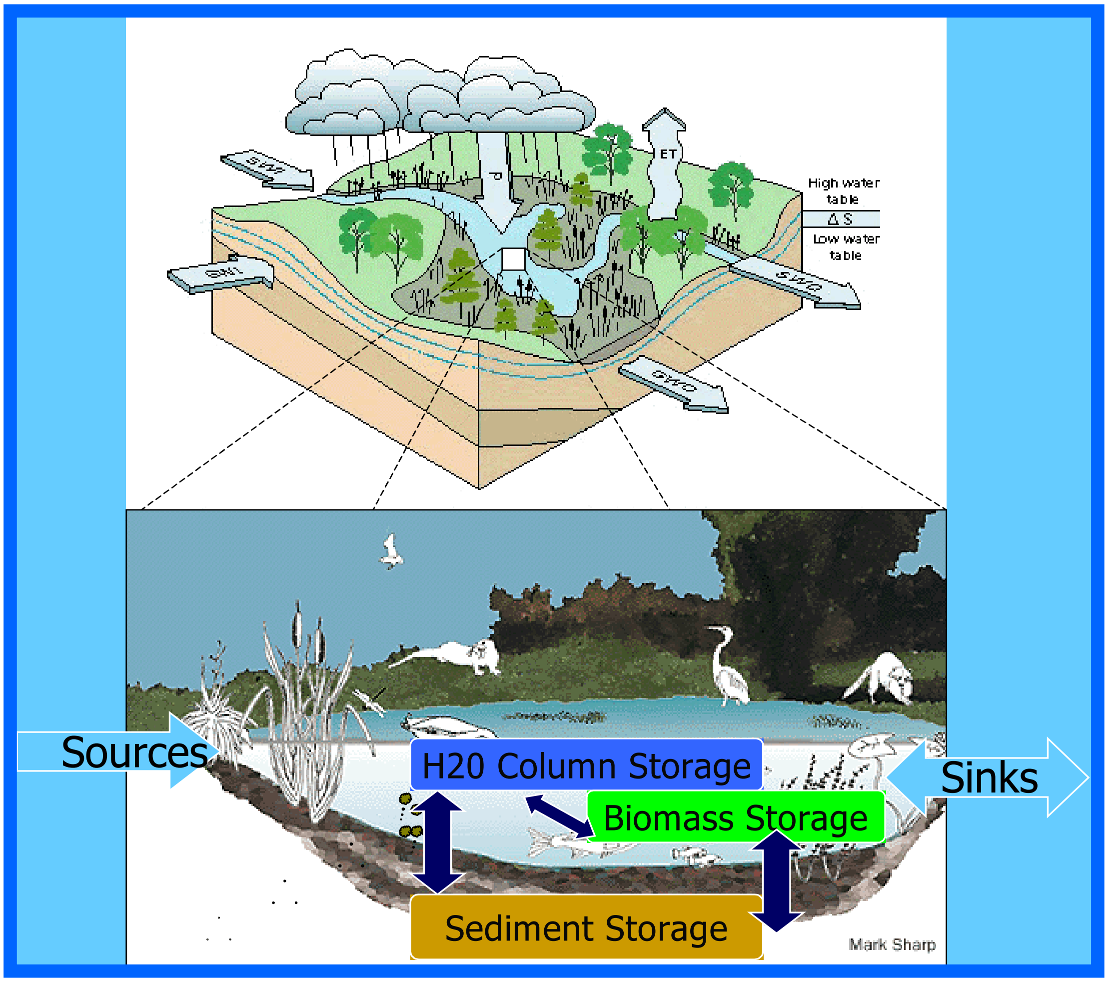

Figure 22: Schematic of nutrient mass balance model showing sources, sinks, and storage compartments. Top graphic modified from figure on EPA Office of Water Website.

8. Appendix

8.1 Study Data