The importance of benthic nutrient flux in supporting eutrophication in an intermittently tidal coastal lagoon

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Abstract

Coastal lagoons are unique coastal environments, occupying about 13% of coastal areas world-wide. Coastal lagoons are often poorly flushed and, as a consequence, sensitive to eutrophication. This sensitivity is heightened in lagoons that are intermittently closed to oceanic exchange. We investigated the seasonal patterns of sediment nitrogen (N) and phosphorus (P) biogeochemistry in Malibu Lagoon, an intermittently tidal coastal lagoon in Los Angeles County, California, USA. Wet season sediment deposition to the lagoon was hypothesized to provide a dry season source of nutrients through the remobilization of pore water nutrients to surface waters, thus fueling blooms of aquatic plants. The objectives of the study were to: 1) characterize seasonal patterns of bulk sediment and pore water N and P and relative cover of primary producer communities, 2) estimate wet season and average annual sediment deposition rates and associated particulate N and P load to the Lagoon using radioisotopes beryllium-7 (^{7}Be) and lead-210 (^{210}Pb), and 3) estimate the benthic flux of nutrients to surface waters during five sampling periods over an annual cycle. Malibu Lagoon sediment nutrient content was within the range of several of the most eutrophic systems worldwide. During the wet season, the lagoon inlet was open, the system well flushed, and primary producer cover low. During the dry season, flows diminished and the inlet closed, causing a decrease in salinities, an increase in water level, and the growth of dense beds of *Ruppia maritima*. During the wet season, an estimated 3 ± 1 cm of sediment was deposited in the Western Lagoon, bringing an associated 3300 kg of total nitrogen (TN) and 830 kg of total phosphorus (TP). Estimates of pore water diffusive fluxes predicted a net dry season release of 673 lbs of TN and 52 lbs of TP. Comparison with other dry season nonpoint sources indicates that sediment release represented 22% of the TN sources and 7% of the TP from nonpoint source inputs to the Lagoon during the dry season. Thus, remobilization of nutrients from sediment helped to support dry season eutrophication and hypoxia in this intermittently tidal coastal lagoon.

Introduction

Eutrophication is a global cause of impairment of biological resources in estuaries, with demonstrated links between anthropogenic changes in watersheds, increased nutrient loading to coastal waters, elevated estuarine primary production, harmful algal blooms, hypoxia, and impacts on aquatic food webs (Valiela *et al*. 1992, Burkholder *et al*. 1992, Paerl 1999, McGlathery 2001). Understanding the factors controlling estuarine biogeochemical response to nutrient loads is critical to successfully mitigating the effects of eutrophication. The biological response of estuaries to nutrient loading is complex, varying greatly as a function of physiographic setting, tidal regime, timing and magnitude of freshwater inputs, etc. (NAS 2000). To date, the majority of research on eutrophication in estuaries has been concentrated in deepwater estuaries and embayments, where aquatic primary production is typically dominated by phytoplankton. Less data are available for shallow, coastal lagoons, which are connected to the ocean at least intermittently by a restricted inlet or barrier island (Kjerfve 1994) and where most of the primary production is carried out by angiosperms

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such as *R. maritima*, epiphytic algae, drift and attached macroalgae, and microphytobenthos, (Nixon and Buckley 2001). Biogeochemical controls on nutrient cycling in these systems are complicated by the extreme variability in lagoon hydrodynamics, particularly with respect to the timing and duration of inlet closures relative to freshwater flows, sediment and nutrient loads. Among coastal lagoons with intermittent inlet closures, salinity regime and dominant primary producer communities are highly variable, both seasonally and interannually, and in turn significantly influence the cycling and ultimate fate of N and P within the lagoon (e.g., Flores-Verdugo *et al*. 1988).

In southern California, which has a Mediterranean climate with distinct wet and dry seasons, peak freshwater flows during the wet season often cause the sand bars at the tidal inlets of intermittently tidal coastal lagoons to breach, thus allowing full tidal exchange for a period typically from November to April (Elwany *et al*. 1998). During the dry season, freshwater flows decline and the inlets close for lengths of time varying from two to six months. In systems that were historically hypersaline during the dry season, urban nuisance flows assure that the lagoons remain brackish to fresh during inlet closure. It is during the time period of inlet closure that indicators and effects of eutrophication are most visible. The effects include overgrowth of brackish water submerged aquatic vegetation (SAV) such as *R. maritima*, blooms of green, mat-forming algae, such as *Rhizoclonium hookeri*, dense benthic diatom and cyanobacterial mats, low dissolved oxygen (DO), and fish kills (Rizzo and Christian 1996). It is commonly assumed that wet season nutrient inputs are flushed into the coastal ocean, rather than retained within the lagoon, and common management strategies to control eutrophication in these lagoons have focused on identifying nutrient sources to the lagoon during the dry season. Such calculations typically ignore sediments deposited during the wet season as a potential source of nutrient loads to these lagoons.

Sediments have the potential to be a significant source of nutrients to primary producers. Through the process of sediment diagenesis, particulate nutrients in watershed-borne sediments are remineralized to more biologically-active dissolved inorganic forms in sediment pore waters (Boynton *et al*. 1980, Grenz *et al*. 2000, Hamersley and Howes 2003). As advective mixing and diffusive transport occur between sediment pore waters and surface waters, these nutrients become available for primary production. However, few studies have described the relationship between wet season sediment deposition, benthic nutrient flux, and the primary producers in intermittently tidal lagoons.

The purpose of this study was to investigate the seasonal patterns of N and P biogeochemistry in sediments of intermittently tidal lagoons, specifically with three principal objectives: 1) characterize the seasonal patterns of bulk and pore water sediment N and P concentrations and relative cover of primary producer communities in the Lagoon, 2) estimate wet season and long-term average annual sediment deposition rates and associated particulate N and P loads, and 3) estimate benthic nutrient fluxes under a variety of environmental conditions observed over an annual cycle.

Methods

Study Locations

Malibu Lagoon is a 7.5-ha brackish water lagoon situated at the base of the 282-km^2 Malibu Creek watershed, the second largest watershed that drains into Santa Monica Bay, California (Figure 1). Malibu Creek watershed encompasses 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 (November - April) increases stream flow and the volume and flow 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 drops as the freshwater inputs from urban runoff in the watershed are impounded.

Seasonal storm flows can contribute a large proportion of the overall annual nutrient load to southern California estuaries and coastal ocean (Ackerman and Schiff 2003) and, during winter months, an inland publically owned treatment works (POTW) discharges treated wastewater directly to Malibu Creek, that flows into Malibu Lagoon. During summer months, creek discharge and suspended sediment transport are generally lower and POTW efflu-

Figure 1. Map of study area showing Lagoon sampling locations. Offshore sampling occurred within shallow subtidal zone of the western lagoon. Sampling of Malibu Creek occurred just upstream of the Pacific Coast Highway (PCH) Bridge, shown in the photo above.

ent is not discharged into Malibu creek; urban runoff and groundwater seepage are the main source of freshwater inputs to the lagoon and nutrient loads are lower than in winter (Boyle *et al*. 2004, Douglas *et al*. 2004).

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. The central lagoon, which is approximately 5 ha in size, is more hydrodynamically active and receives more direct tidal exchange then the Western Lagoon when the tidal inlet is open. The Western Lagoon, 2.5 ha in size, is primarily the result of a restoration project in 1983, that involved excavating a section of the Lagoon that had been filled in the 1950s. It is believed that the restoration may have contributed to problems with water circulation due to stagnant water occurring at the ends of the three excavated channels (Ambrose and Orme 2000).

Field Methods

Eight sampling events were conducted between February 2002 and September 2003 at a total of nine sites distributed throughout the Western and Central portions of Malibu Lagoon. Four sites were sampled initially (Western Lagoon Sites 1 - 3, Central Lagoon Site 4; Figure 1) to document baseline surface water physiochemical characteristics, nutrients, and sediment bulk nutrients and grain size. Additional sites were added to the Western Lagoon (Sites 5 - 7) and Central Lagoon (Sites 8 and 9) beginning in September 2002 using the full complement of methods to sample surface water, sediment bulk and pore water nutrients, primary producer percent cover, and radioisotopes (Table 1).

Sampling of surface water physiochemical characteristics consisted of water column salinity, temperature, and DO measured with a hand-held YSI meter, typically between the hours of 8 and 10 a.m. Duplicate mid-water column samples were taken at each site in 1-L precleaned high-density polyethyl-

Table 1. Sampling dates and sites sampled in the Western and Central Lagoons.

Date	Western Lagoon						Central Lagoon		
	Interior				Channel				
	1	5	6	7	2	3	4	8	9
Feb-02	X				X	X	X		
Apr-02	X				X	X	X		
Jul-02	X			X	X	X	X		
Sep-02	X	X	X	X	X	X	X	X	X
Jan- to Feb-03	X	X	X	X	X	X	X	X	X
Apr-03	X	X	X	X	X	X	X	X	X
Jul-03	X	X	X	X	X	X	X	X	X
Sep-03	X	X	X	X	X	X	X	X	X

ene (HDPE) bottles that were triple-rinsed in the field with sample water. Samples were placed on ice in a cooler for 1 to 4 hours until 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 (chl a), particulate N (PN), and particulate P (PP). The filtered water was frozen immediately for later analysis of ammonia (NH_4), nitrate and nitrite (NO_3+NO_2), total Kjeldahl N (TKN), soluble reactive P (SRP), and total dissolved P (TDP).

Sediment cores were taken at each of the sites with four-inch inner diameter polycarbonate tubing. The cores with overlying water were transported in an upright position to the laboratory for processing (within two hours of collection). At the laboratory, each core was extruded in a glove box under N gas to prevent oxidation artifacts; sediment cores were sectioned into 1- to 2-cm intervals to a depth of 10 cm. A portion of each section was taken to determine percent solids and the remainder was centrifuged at 3500 rpm for 20 minutes. The pore water concentrate was filtered under nitrogen gas with a 0.7-µm glass fiber filter and immediately frozen for analysis of NH_4, NO_3, SRP, TKN, and TDP. Sediment solid phase remaining after centrifugation was dried, then used to determine grain size distribution and dry grain density, sediment total organic carbon (SOC), sediment total N (SN), sediment total P (SP), and ^{7}Be. In March 2003, one 50-cm core at Site 1, sectioned vertically in 2-cm intervals, was taken for analysis of average annual sedimentation rate using the radioisotope ^{210}Pb.

For Central Lagoon Sites 4, 8, and 9, 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. Field experiments showed that a needle depth of 6 cm, 60 ml of pore water could be removed without drawing surface water into the sediments. The filtrate was immediately frozen for analysis of nutrients and organic carbon.

To estimate percent cover of each primary producer species or functional group, a 30-m transect line was laid down parallel to the water line at each site ~1 m toward the water from the edge of the vascular vegetation, which was a good proxy for elevation. At five randomly chosen points along the transect line, the percent cover of each primary producer species or functional group was measured using the point intercept method with a 0.25-m^2 quadrant and 36 intercept points.

Analytical Methods

Surface and porewater samples were analyzed for dissolved inorganic nutrients using an Alpkem Autoanalyzer for the analysis of NH_4, SRP and NO_3+NO_2 (APHA 1992). Total P was digested by combustion and hydrolysis as in Solorzano and Sharp (1980) then analyzed as SRP by autoanalyzer (APHA 1992). Total KN was analyzed using the micro-kjeldahl method (APHA 1992). Dissolved organic N (DON) and dissolved organic P (DOP) were calculated by subtracting the NH_4 or SRP concentration from TKN or TDP respectively. Chlorophyll a was measured with a spectrophotomer (APHA 1992). Suspended particulate matter and sediment samples were acidified and analyzed for SOC and SN using a CHNS-O Elemental Analyzer. Sediment TP was analyzed by microwave acid digestion followed by inductively coupled atomic emission spectroscopy (Sah and Miller 1992). Sediment dry grain density was determined by volumetric displacement. Grain size distribution was determined by wet sieving coarse 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 (half-life of 53 days) and ^{210}Pb (half-life of 22 years; Nittrouer *et al*. 1979, McKee *et al*. 1983, DeMaster *et al*. 1985, Giffin and Corbett 2003, Sutula *et al*. 2004). Activity of ^{210}Pb was determined by alpha particle spectrometric analysis. 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.

Data Analysis

Use of ^{7}Be and ^{210}Pb to calculate seasonal and annual sediment deposition rates

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 low sedimentation rates during the four-month dry season. Subsequent sampling trips capture changes occurring at the site 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) no inventory, indicating complete removal of the uppermost sediment layer or complete decay if the sampling interval is sufficiently long (Giffin and Corbett 2003). 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 through time, and 3) observe reworking of sediments that may be caused by bioturbation (birds, burrowing organisms, etc.). 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, porosity and wet bulk density following Canuel *et al*. (1990). Average values of porosity and wet bulk density were 0.58 and 1.5 g cm^{-3} in Western Lagoon sites, respectively.

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 (e.g., groundwater flow, bioirrigation) also contribute to exchange across the sediment-water interface, calculation of potential diffusive fluxes have been widely used to provide estimates of the magnitude and direction of flux (Burdige and Zheng 1998), particularly for sites that are intermittently intertidal and therefore difficult to measure with *in situ* benthic flux chambers. In this study, instantaneous diffusive flux rates were calculated for each species of nutrient with the use of Ficke's law given in Equation 1,

$$J = -\phi D_{AQ} \theta^{-2} (dC/dz) \qquad (1)$$

where: J is the rate of flux of species (M 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).

Inverse squared tortuosity (θ^{-2}) was estimated from Boudreau's law (Boudreau 1996) given in Equation 2.

$$\theta^{-2} = 1 \;\; (1- \ln (\phi^2))^{-1} \qquad (2)$$

The D_{AQ} for each nutrient species were obtained from Boudreau (1996) and are given in Table 2. 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. Lactate was used as a proxy for DON and DOP (Boudreau 1996).**

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	6.44E-10	7.54E-10	8.64E-10	9.72E-10

Results

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

Sampling captured distinct seasonal patterns in salinity, DO, nutrient concentrations and primary producer cover 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 seven months from October to April). However, total rainfall in the 2002-2003 wet season (35 cm) was double that of the 2001-2002 season (15 cm) 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 two months earlier in the 2001-2002 wet season (April) than in 2002-2003 (June).

The timing of Lagoon mouth closure had a direct impact on salinity regime recorded during the eight sampling events of the study (Figure 2). Salinity was typically highest during the wet season when the lagoon was open to tidal exchange, with values ranging from 7 to 15 ppt. Lagoon salinities were lowest when the mouth was closed (as low as to 3 ppt), particularly if the lagoon closure occurred in late the wet season when the baseflow from Malibu Creek was still significant.

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, the percent cover of benthic diatoms was near 99%. Surface water chl a was relatively low in spring 2002 (9 - 20 µg L^{-1}), high beginning in the summer 2002 and extending through the spring of 2003 (50 - 72 µg L^{-1}), then low in the summer and fall of 2003 (7 - 12 µg L^{-1}). In both years, a *R. maritima* community began to devel-

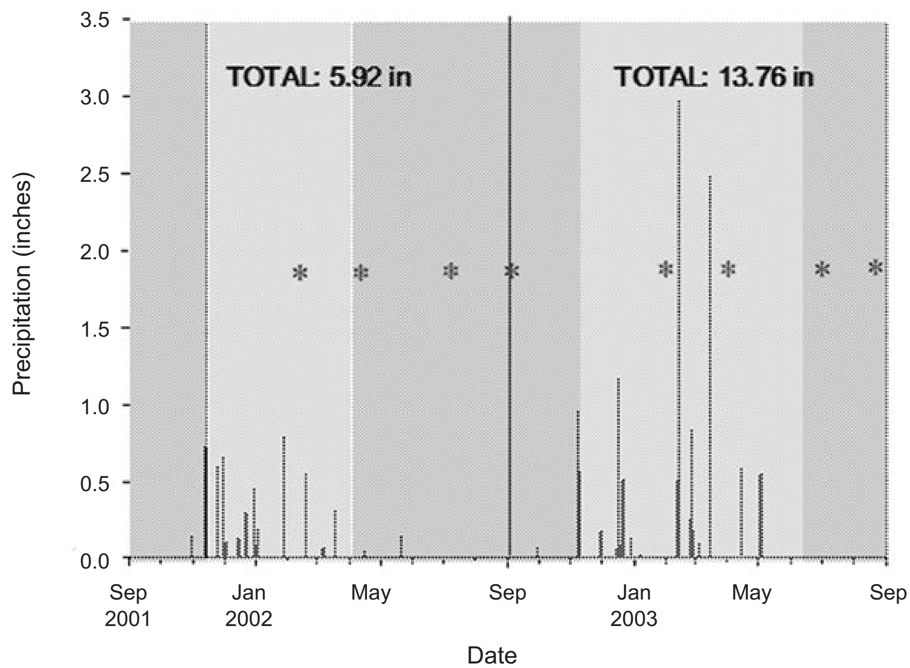

Figure 2. Graph of rainfall during the study period. Rainy season and lagoon inlet opening occurred during Nov 2001 through April 2002 and Nov 2002 through June 2003. Asterisks designate sampling periods.

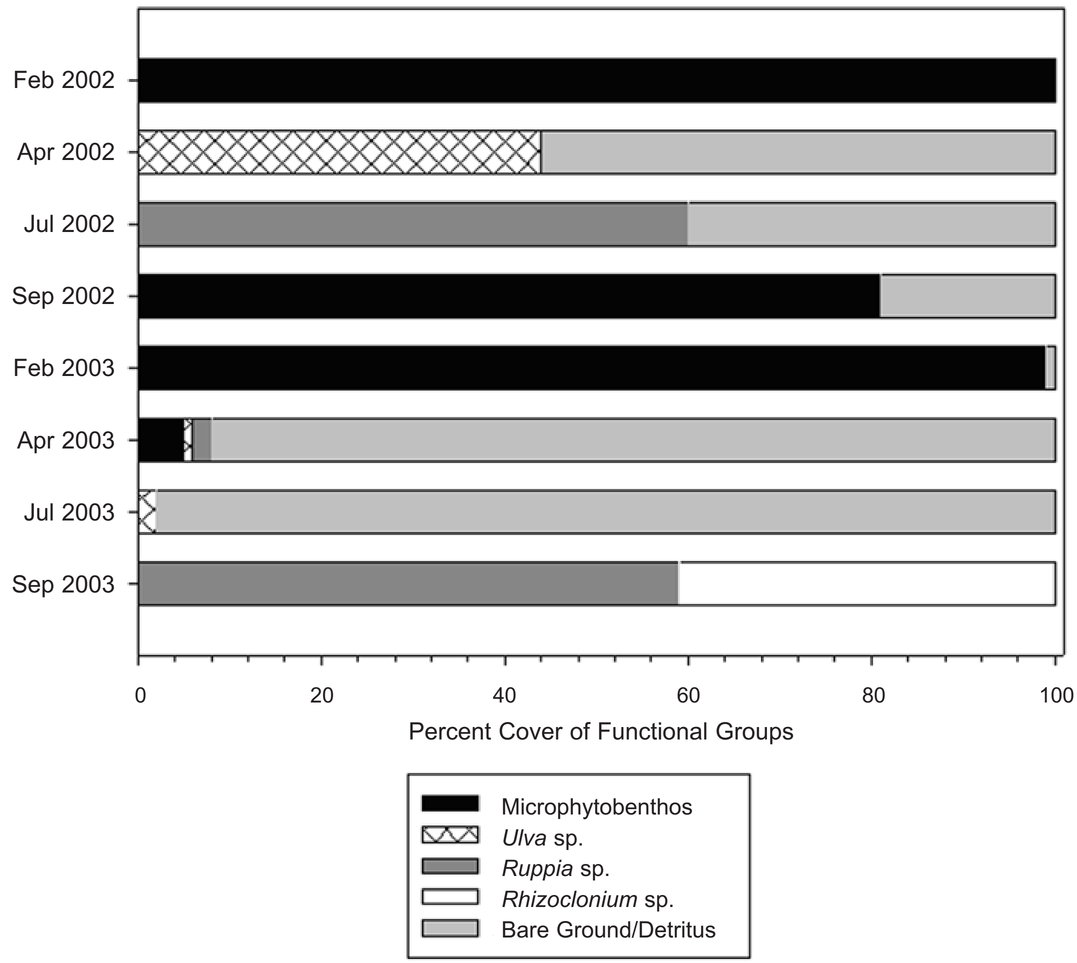

Figure 3. Mean percent cover of dominant primary producer functional groups in the western portion of Malibu Lagoon from February 2002 through September 2003. Standard error (SE) of the mean was less than 6% in all cases except for *Ruppia sp*. in September 2003, where SE was 10%. Wet season = February and April 2002 and 2003; Dry season = July and September 2002 and 2003.

op in the early dry season after the mouth of the Lagoon closed. However, *R. maritima* development was much delayed in 2003 compared with 2002. In 2002, *R. maritima* reached 60% cover by July and 80% by September, dramatically decreasing circulation in the Western Lagoon. In July 2003, there was only a small amount of *Ulva* spp. in the Lagoon and 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. Plant height was shorter than the previous year and did not create stagnant conditions as they did in 2002. 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 microalgal mats.

There was a strong inter-annual variation in dry season DO concentrations. Severe hypoxia (DO <1 mg L^{-1}) was observed during sampling events in July and September 2002, when *R. maritima* was abundant (Table 3). There were strong vertical gradients in oxygen availability during both sampling events, with values ranging from 15 mg L^{-1} at the surface to <1 mg L^{-1} in the bottom waters (1.5 m in depth). During the 2003 dry season sampling events, no hypoxia was recorded, even during relatively warm events. At this time, *R. maritima* biomass was visually less than in July 2002, even though percent cover was comparable between the two periods.

Overall, surface water nutrient concentrations varied widely as a function of wet season inputs, degree of tidal exchange, growth, senescence, die off of primary producer communities, and when in the

Table 3. Range of surface water salinity, surface, and bottom water dissolved oxygen (DO), and mean ± standard error of TSS, nutrients, and chl a by sampling period. All nutrient concentrations are expressed in µM. February, April, and July 2002 sampling periods do not include sites 5, 6, 7, 8, and 9.

Sampling Event	Season	Salinity Range (ppt)	DO Range ($mg\ L^{-1}$)	TSS ($mg\ L^{-1}$)	TN	DON	NH4	NO_3+NO_2	TP	DOP	SRP	Surface Water Chl a ($\mu g\ L^{-1}$)
Feb-02	Mid-Wet	14-18	12-20	77±47	201±74	104±70	0.5±0.2	60±11	16±4	0.9±0.3	9.1±2.2	9±6
Apr-02	Late-Wet	3-4	14-17	23±6	182±22	130±17	0.5±0.2	0.4±0.5	22±2	8±1	0.7±0.4	20±6
Jul-02	Mid-Dry	6-7	0.3 -19	32±4	148±48	110±36	0.4±0.1	0.2±0	8±2	3.7±1.3	0.7±0.3	24±19
Sep-02	Late- Dry	7-8	0.2-15	64±33	445±130	377±86	0.4±0.2	0.2±0.1	15±11	1.6±0.3	0.3±0.3	61±40
Feb-03	Mid-Wet	6-7	6-16	33±12	269±52	8±16	1.9 ±1.7	231±42	28±8	2.4±1.3	17.9±4.1	50±48
Apr-03	Late-Wet	9-10	4-9	103±59	223±125	94±29	5.0±3.4	57±34	30±26	2.0±22.1	7.4±4.3	72±85
Jul-03	Mid-Dry	7-8	7-9	68±32	63±29	34±29	0.7±0.4	5.9±1.2	7±1	1.7±0.3	3.2 ±1.2	7±2
Sep-03	Late-Dry	4-8	11-16	45±18	70±25	61±24	1.7±1.3	0.3±0.1	2±0.1	0.8±0.1	0.2±0.1	12±1

tidal cycle sampling occurred (Table 3). Total N remained high for most of the year (182 - 445 µMol), with the exception of the July and September 2003 sampling periods. Peak TN in September 2002 coincided with the dieoff of dense stands of *R. maritima*. Higher dissolved inorganic nutrient concentrations were observed during the wet season sampling events, particularly with respect with NO_3+NO_2 (maximum of 231 ± 42 µM during Feb 2003). Dissolved organic nutrients were highly variable, but generally much higher than the dissolved inorganic fraction. Particulate N, estimated as the difference between TKN and total dissolved KN (TDKN), was generally ≤25% of the TN available. Exceptions occurred in April 2003, when PN was greatest, and July 2003, when TN was low. Particulate P was the dominant fraction of TP in surface waters. The SRP was generally low, with the exception of February of 2002 and 2003, when SRP made up the largest component of TDP in the Lagoon.

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 4). September 2002 inventories showed little detectable ^{7}Be, indicative of a period of three and one-half months 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

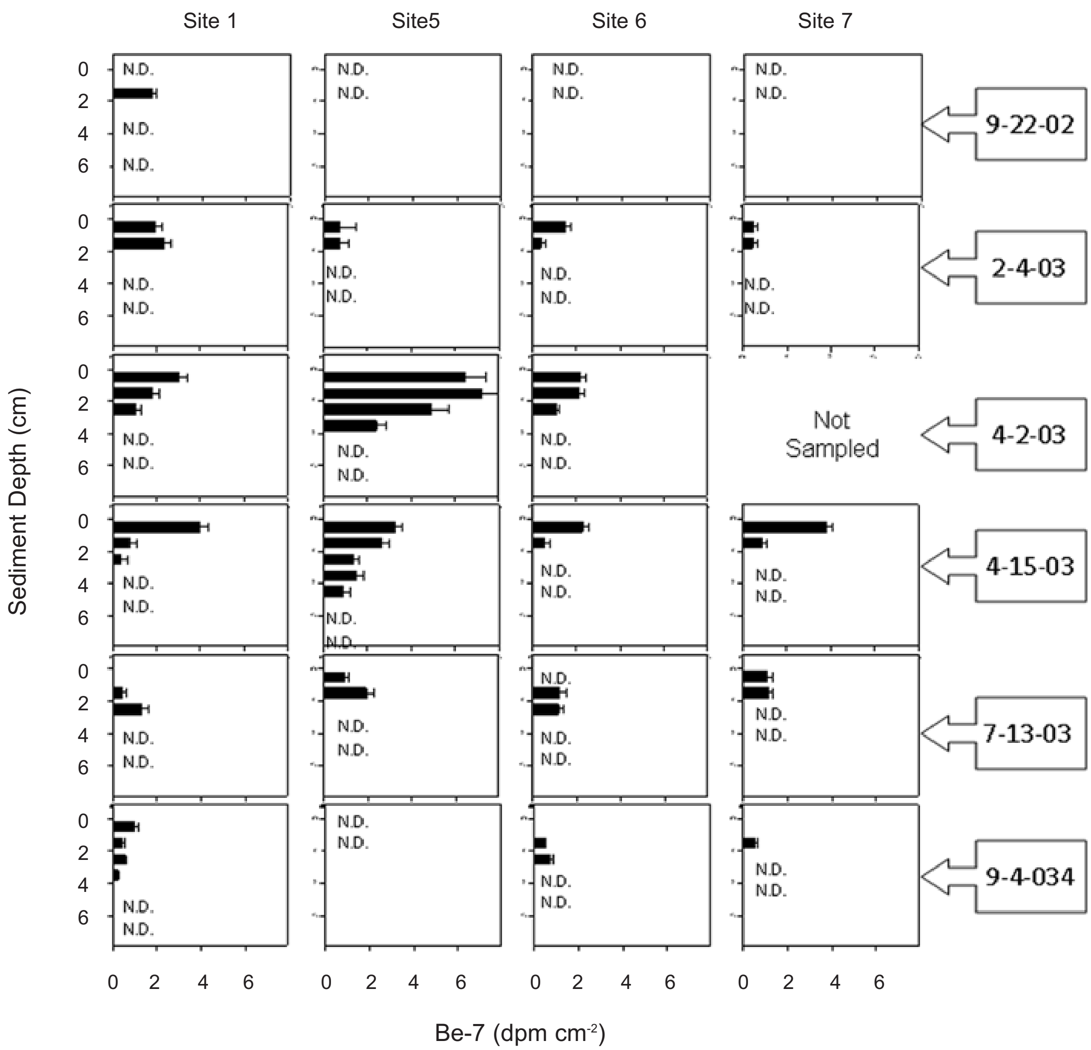

Figure 4: ^{7}Be inventories with depth by site and sampling period. Bars represent ± 1 SE. N.D. represents a non-detectable ^{7}Be activity. Wet season = February and April 2002 and 2003; Dry season = July and September 2002 and 2003.

from 3 to 5 cm at most sites within the Western Lagoon. Average 2003 wet season sedimentation rate for the Western Lagoon was 3 ± 1 cm. Inventories of ^{7}Be in July and September 2003 sampling periods show vertical profiles indicative of no new sediment deposition (and therefore radioactive decay of remaining ^{7}Be in the first several centimeters). Some sites (Sites 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. Activities of ^{210}Pb at Site 1 were generally well mixed in the upper 10 cm (Table 4). A long-term average sedimentation rate calculated at this site yielded a rate of 0.09 cm yr^{-1}. Short-term (^{7}Be) versus long-term (^{210}Pb) sedimentation rates would be expected to differ as the latter is a reflection of sediment compaction and dewatering as well as variable deposition and scour events.

Spatial and Temporal 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. Grain size decreased from the Central to the Western Lagoon. Grain size at Central Lagoon Sites 4, 8, and 9 was consistently greater than 95% sand through out the study period. Grain 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 located in the interior of the Lagoon (Sites 1, 5, 6, and 7) ranging from 40 to 85% sand, depending on the sampling period. Grain size was highly variable with depth for all internal sites within the Western Lagoon, but no clear trends were discernable from site to site. Sediment grain size determined nutrient content to a large degree. 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). SOC, SN and SP content in Central Lagoon sediments were typically two to four times lower than interior locations of the Western Lagoon (Sites 1, 5, 6, and 7; Figure 5).

SN and SP content in surficial sediments of the Western and Central Lagoon (0 - 2 cm) showed distinct seasonal trends (Figure 5). In the interior sites of the Western Lagoon, SN and SP content increased during the wet season (corresponding to the February and April sampling periods), then decreased by as much as 50% during the dry season (July and

Table 4. ^{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	1.2
4.5	2.248
5.5	0.25
7	BD
9	0.453
11	bd
13	bd

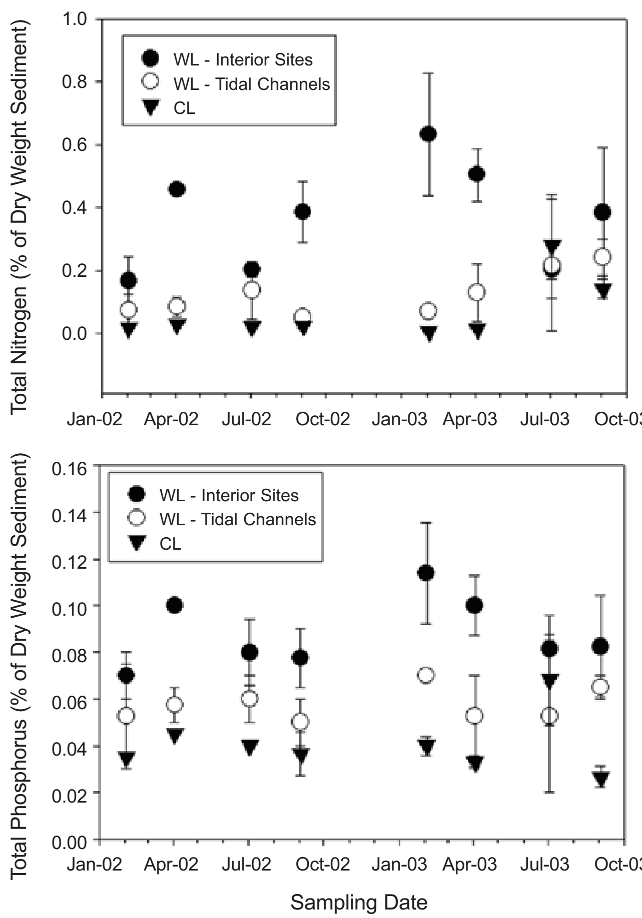

Figure 5. Mean and standard error of SN and SP content for surficial sediments (0 - 2 cm) in the Western Lagoon (interior sites versus tidal channels) and Central Lagoon sites by sampling period. Wet season = February and April 2002 and 2003; Dry season = July and September 2002 and 2003.

September sampling periods). In the Central Lagoon sites and Western Lagoon tidal channel sites, SN generally was lowest during the wet season, but then increased during the dry season. Sediment total P content in these sites did not show a consistent pattern. Vertical profiles of sediment SN and SP for Western Lagoon interior and tidal channel sites show these temporal trends in greater detail as well as illustrate a consistent pattern of decreasing N and P content with depth (Figure 6). Vertical profiles of nutrient and organic carbon content at these sites show that high dry season SOC values were typically concentrated in the upper 0 to 2 cm of the sediment column that decreased markedly with depth (data not shown).

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 (Figure 6). In all seasons, pore water NH_4 and SRP concentrations were generally higher than those of the overlying water column.

Pore water NO_3 concentrations showed a different pattern than NH_4 and SRP. Generally, NO_3 ranged from <0.01 to 3 µM in the mid to late dry season when overlying surface water concentrations ranged from <0.1 to 5 µM (Figure 6). During the rainy season, when overlying surface water ranged from 15 to 200 µM, pore water NO_3 concentrations increased to levels of 5 to 10 µM.

Pore water DON and DOP concentrations were more variable and showed less consistent spatial and temporal trends than NH_4 and SRP. These constituents were generally a minor component (2 - 20%) of the total dissolved nutrient concentration in pore waters at Sites 1 and 7, where 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 lower compared to Sites 1 and 7, and the dissolved organic forms each 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 Sites 5 and 6 may be related to the hydrology as well as biotic communities present at these sites. Sites 1 and 7 were shallower sites that were intertidal during the wet season. Sites 5 and 6 were deeper, subtidal sites, and often supported a greater abundance of *R. maritima*.

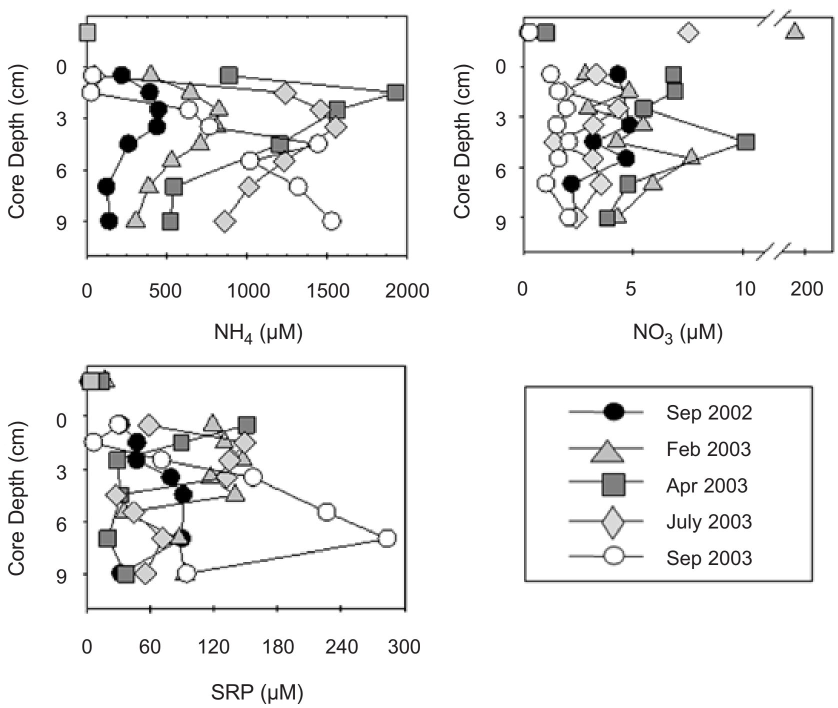

Figure 6. Vertical profile of pore water NH_4, NO_3, and SRP concentration by site and season. Wet season = February and April 2003; Dry season = September 2002 and July and September 2003.

Exchange of Nutrients between Sediments and Surface Waters

Predictions of potential diffusive flux in the Western Lagoon sites showed a positive flux (from the sediments into the surface waters) of NH_4 and SRP regardless of season (Table 5; Figure 7). When rates are averaged over all sites, NH_4 and SRP fluxes were highest April and July (27 - 52 g N and 5.5 - 8.0 g P m^2 yr^{-1}) and lowest in September. Flux rates between sites in these species were highly variable and reflected the differences observed in pore water chemistry at Sites 1 and 7 versus Sites 5 and 6. Generally, DON and DOP fluxes were also positive, but small and highly variable by site and season. The NO_3 fluxes were negative in February, April, and July, with the peak rate in February (-19 g N m^2 yr^{-1}) and positive flux in September 2002 and 2003. TDN and TDP fluxes were dominated by NH_4 and SRP, respectively. Therefore, TDN and TDP 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 estimated fluxes were several orders of magnitude less (Figure 8). The NH_4 flux 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}). The 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 N m^2 yr^{-1}) was approximately two orders of magnitude less than that of the Western Lagoon.

Predicted seasonal and annual diffusive flux estimates for the Lagoon were dominated by the terms from the Western Lagoon, with the Central Lagoon flux comprising only 1 to 2% of the total annual N and P flux from the Lagoon (Table 6). Total annual DN flux rates in the Western Lagoon show a net flux of 517 kg yr^{-1} from sediments to surface waters, with 60% of that flux occurring during the dry season (Table 6). A large negative flux of 163 kg NO_3-N yr^{-1} was counteracted by a large positive flux of 610 kg NH_4-N yr^{-1}, which comprised 90% of TDN flux. An estimated 98% of the TDP flux in the Western Lagoon was SRP, while 90% of the TDN flux was NH_4.

Discussion

Coastal lagoons are unique coastal environments, occupying about 13% of coastal areas world-wide (Kjerfve 1994). Even in their natural state, many coastal lagoons are poorly flushed. As a consequence, lagoons have a tendency towards high productivity and are sensitive to eutrophication (Kennish *et al*. 2007). This sensitivity would be expected to be heightened in lagoons that are intermittently closed to oceanic exchange, particularly during the growing season.

Overall, Malibu Lagoon appears to be in a hypereutrophic state. Total nutrient content in surficial sediments of the Western Lagoon (0.341% TN and 0.081% TP) was equal to or greater than values from several of the most eutrophic systems studied

Table 5. Seasonal and annual integrated fluxes for NH_4, NO_3, DON, TDN, SRP, DOP, and TDP. October 2002 to April 2003 = Wet Season; May to September 2003 = Dry Season. Positive rates represent flux from sediments to water column. All fluxes are in kilograms (kg) except where designated.

	NH_4	NO_3	DON	TDN	SRP	DOP	TDP
				Western Lagoon			
Oct-Apr 03	322.8	-156.1	48.7	215.4	21.6	0.7	22.3
May-Sep 03	286.8	-6.5	21.9	302.1	23	2.1	25
Annual (kg yr^{-1})	609.6	-162.7	70.6	517.5	44.6	2.8	47.4
				Central Lagoon			
Oct-Apr 03	4.1	-5.7	4.8	3.1	0.1	0.6	0.7
May-Sep 03	4.2	-0.7	-0.5	3	0.4	0	0.4
Annual (kg yr^{-1})	8.3	-6.4	1.5	6.1	0.5	0.7	1.1

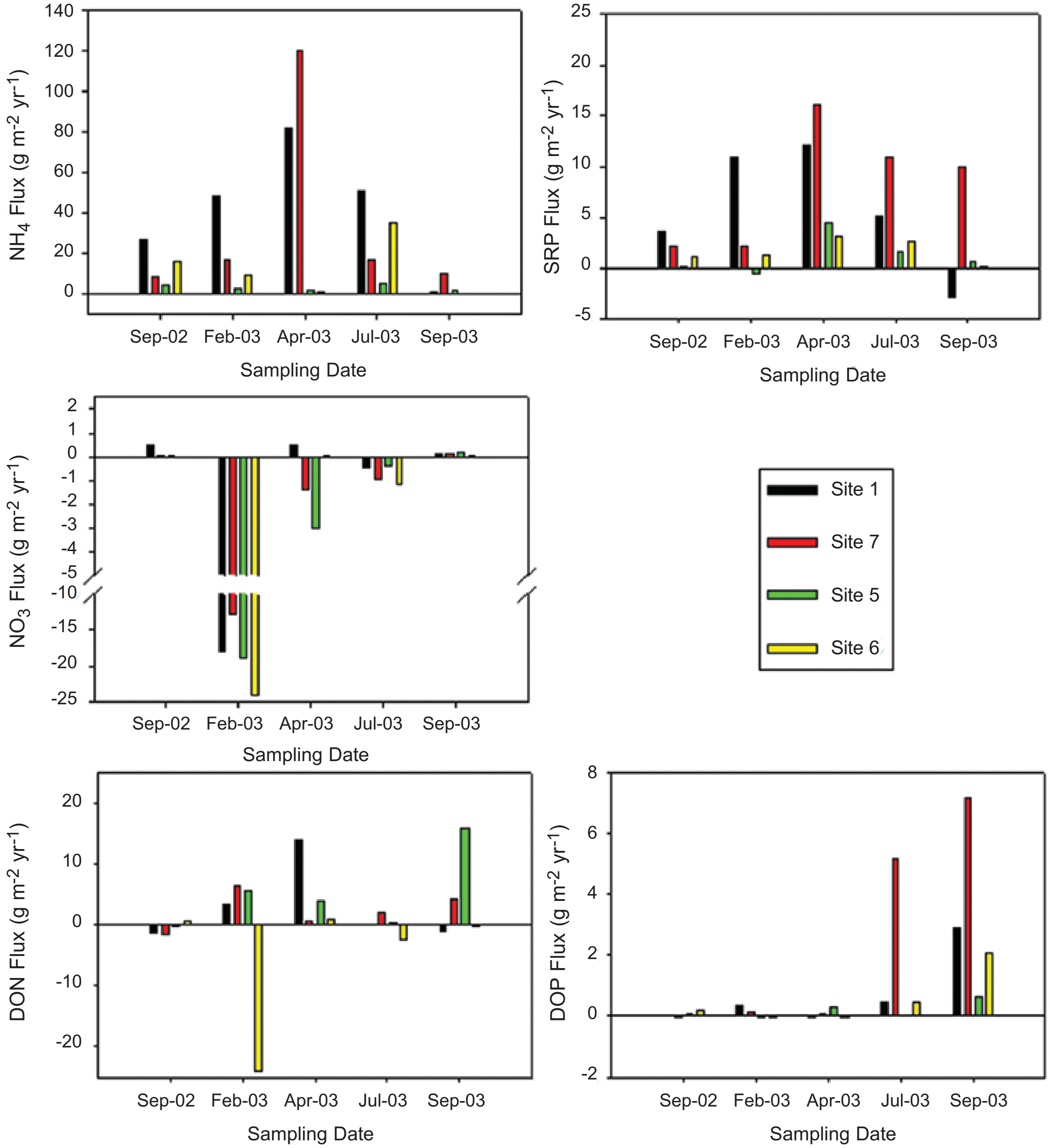

Figure 7. Instantaneous flux rates for Western Lagoon by site and sampling period. Negative numbers represent a flux into the sediments from the water column. Wet season = February and April 2003; Dry season = September 2002 and July and September 2003.

worldwide (0.27 - 0.53% TN and 0.7%TP in Venice Lagoon and Peel-Harvey Inlet; Marcomini *et al*. 1995, Sfriso *et al*. 1995, McComb *et al*. 1998). Mean surface water chl a was 31 ± 23 µg L^{-1} and the 90th percentile was 111 µg L^{-1}, values that would be considered as highly eutrophic or hypereutrophic by the NOAA Assessment of Estuarine Trophic Status framework (ASSETS; Bricker *et al*. 1999, 2003, 2007). Likewise, mean TN and TP concentrations in Malibu Lagoon would be considered by the ASSETS framework to be high (>1 mg L^{-1} TN and >0.1 mg L^{-1} TP; Bricker *et al*. 2003). Total annual N loads to the Lagoon (376 g N m^{-2} yr^{-1}) exceed those published for highly eutrophic coastal Maryland and Delaware Bays, ranging from 2.4 g N m^{-2} yr^{-1} to 106 g N m^{-2} yr^{-1} (Boyton *et al*. 1996, Kennish *et al*. 2007). The timing of lagoon closure and the inherent controls on lagoon residence time appear to control the degree to which symptoms of eutrophication were expressed in Malibu Lagoon. Episodes of bottom hypoxia were evident during the 2002 summer sampling event, when dense stands of *R. maritima* were present, but

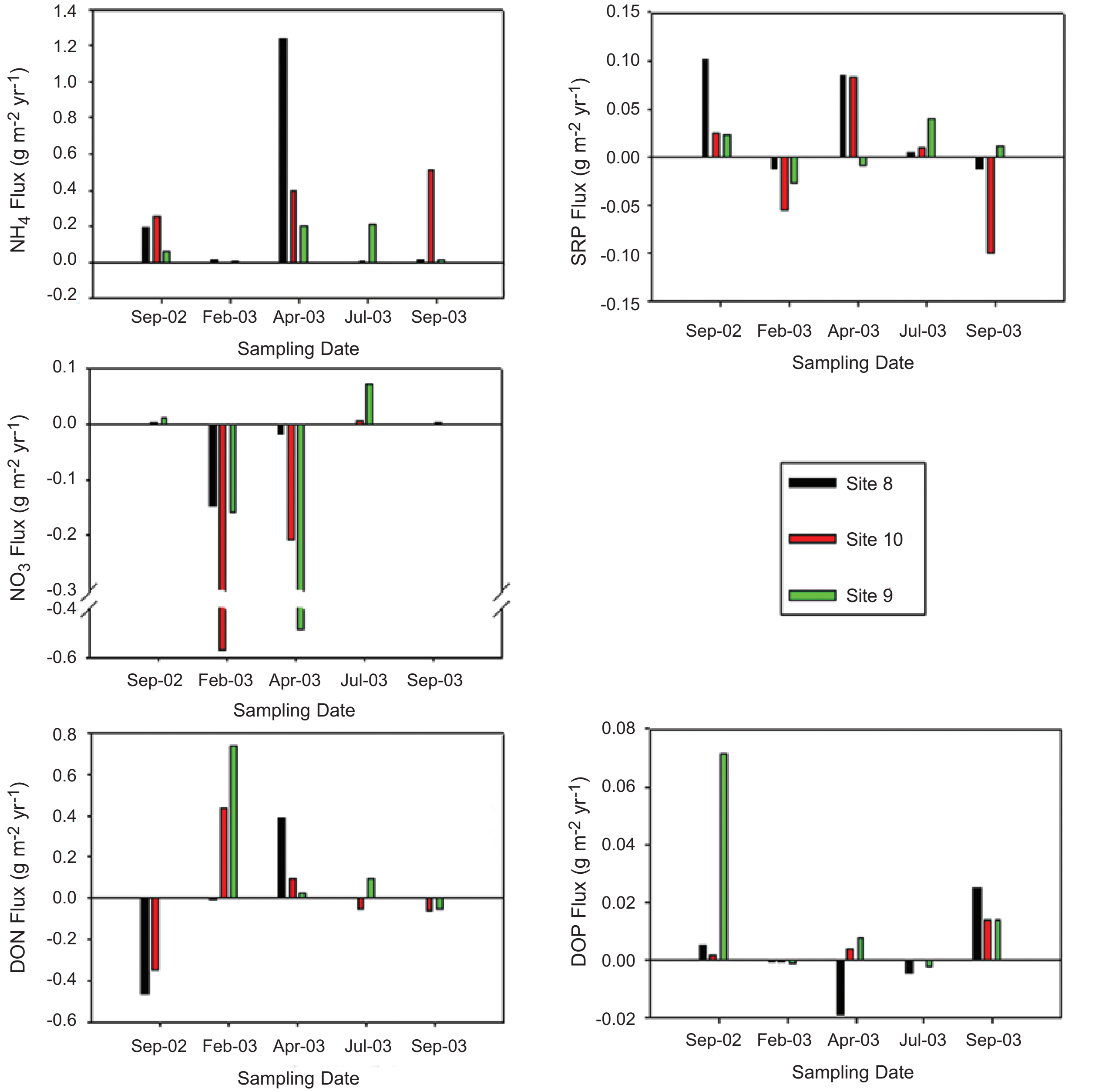

Figure 8. Instantaneous flux rates for Central Lagoon by site and sampling period. Negative numbers represent a flux into the sediments from the water column. Wet season = February and April 2003; Dry season = September 2002 and July and September 2003.

hypoxia was not observed the following year, when the timing of lagoon closure resulted in the delay in peak *R. maritima* biomass (Thursby 1984b).

Malibu Lagoon exhibited distinct seasonal patterns of primary producer abundance relative to wet season freshwater runoff and dry season inlet closure typical of intermittently closed coastal lagoons (e.g., Flores-Verdugo *et al*. 1988). Because the lagoon is mostly intertidal when open and approximately 2 to 3 m in depth when closed, benthic species tended to dominate aquatic primary productivity. During the wet season when the ocean inlet was open and the lagoon was completely intertidal, primary producer cover was low and dominated by macroalgae and benthic diatoms. As the lagoon closed and wet season flows diminished, the water levels increased and salinities dropped to an oligohaline range under the influence of urban nuisance freshwater flows. During these periods, dense stands of seasonal *R. maritima* were established in the Western Lagoon, while the Central Lagoon was dominated by phytoplankton and, in the shallower areas, dense mats of microphytobenthos.

Table 6. 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 (kg d^{-1})	N Loading (%)	Dry Season N Load (kg)	P (kg d^{-1})	P Loading (%)	Dry Season P Load (kg)
Storm Drains to Lagoon[a]	0.6	5.20%	91	0.003	0.10%	0.5
Septic Seepage to Lagoon[a]	5.9	52.20%	909	--	--	--
Watershed Septic Seepage & Urban Runoff[a]	2.9	25.10%	437	3	99.90%	459.4
Total	9.4	100%	1437	3.003	100%	459.9
Sediment Release (This Study)	2	21.28%	305	0.2	7%	25.4

[a] Ambrose and Orme 2000

The timing and relative cover of *R. maritima* cover in the lagoon appeared to be related to the salinity regime in the lagoon. 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. Studies have found that *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, Koch and Dawes 1991). Additionally, the root systems of *R. maritima* do not extend deeply into the sediments and plants can be easily dislodged by turbulence, which would be greater when the mouth of the Lagoon is open. This would explain the dominance of *R. maritima* in the quiescent Western Lagoon, where sediment particle sizes were relatively fine, versus the dominance of benthic diatoms in the sandy Central Lagoon. With the advent of the first rain event in the fall, the lagoon mouth open, intertidal conditions resumed and all *R. maritima* died off. Thus salinity and flow provide major control on the relative dominance of primary producers in intermittently tidal coastal lagoons (Flores-Verdugo *et al*. 1988).

The linkage between wet season deposition of particulate nutrients and dry season remobilization of these nutrients from the sediments to the surface waters was found to be an important factor driving eutrophication in Malibu Lagoon. During the 2002-2003 wet season, an estimated 3 ± 1 cm of sediment was deposited in the Western Lagoon. We estimate that this sediment brought an associated 3,352 kg of TN (8.8 g N m^{-2} yr^{-1}) and 834 kg of TP (2.2 g P m^{-2} yr^{-1}), based on April 2003 sediment nutrient values. While the magnitude of this nutrient deposition is minor to total wet season loads to the estuary (estimated at 282,000 kg TN (376 g m^{-2} yr^{-1}) and 39,000 kg of TP (52 g m^{-2} yr^{-1}; Suffet and Sheehan 2000), the deposition of particulate N and P effectively represents the net wet season contribution to the dry season nutrient budget of the lagoon as water column nutrients and loosely attached biomass or other organic matter are flushed directly to the Pacific Ocean.

Particulate nutrients associated with estuarine sediments are remobilized to become a source of nutrients to surface waters. Organic matter decomposes, proceeding through a well-established sequence of terminal electron acceptors: O_2, NO_3-, MnO_2, FeOOH, SO_4^{2-}, and CO_2 (Froelich *et al*. 1979). During this process, the decomposition of organic matter will result in the increase of pore water NH_4, DON, SRP and DOP concentrations. The 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. Pore water NO_3 concentration increased during the wet season. This may be due to a variety of factors such as increased nitrification in surficial sediments (Joye and Anderson 2008) and increased influx of NO_3 into the sediments due to high water column concentrations. As temperatures in the late wet season and dry season increased, pore water NO_3 decreased to non-detectable levels. Dissimilatory nitrate reduction (microbially mediated conversion of nitrate to ammonia) may be contributing to the depletion of pore water NO_3 and the extremely high levels of pore water NH_4 found in this study, as this process is favored over denitrification in hypereutrophic systems (Joye and Anderson 2008). Denitrification may be further minimized by competition from *R. maritima* uptake of nitrate; Bartoli *et al*. (2008) found denitrification rates within *Ruppia cirrhosa* beds 50% less than at nearby bare sediments.

When overlying surface water 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 was predicted to result in the net release of these constituents to the surface water throughout the year. Calculations of potential diffusive flux, which when summed by season, predict a net dry season release of 302 kg TN and 25 kg TP. Comparison with other non-point sources indicated that sediment release represents approximately 21% of the TN sources and 7% of the TP inputs to the Lagoon during the dry season. Seepage represents the largest input of TN to the lagoon during the dry season (52%), though this estimate does not account for attenuation via denitrification. Direct urban runoff accounts for approximately 25%. Nitrogen fixation can also supply a source of nitrogen to lagoon sediments, but no published studies have documented nitrogen fixation rates in intermittently tidal lagoons in southern California. 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*. 1996).

Although sediment release is less than estimated seepage and groundwater runoff, it nevertheless represents an ecologically significant fraction of the TN source to surface waters into the Lagoon and is available in a form easily assimilated by *R. maritima* and other primary producers (Lavery and McComb 1991). *R. maritima* can take up nutrients via the roots or leaves. *R. maritima* roots, which have a higher affinity for NH_4 than NO_3 (Thursby 1984a; Thursby and Harlin 1984), have access to high concentrations of NH_4 in pore waters. The timing of the *R. maritima* growth in the Lagoon was coincident with periods of high predicted nutrient release from sediments. High nutrient availability was responsible for the dense biomass of *R. maritima* observed in the Western Lagoon during the 2002 dry season.

Relative to Western Malibu Lagoon, fluxes from Central Malibu Lagoon were two to three orders of magnitude lower. Predicted fluxes from the Central Lagoon represented only 1 to 2% of this total 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 1987, Sutula *et al*. 2004).

Estimated benthic flux of nutrients from Western Malibu Lagoon, predicted from pore and surface water concentration gradients, was equal or greater in magnitude those measured in many eutrophic estuaries (Table 7). Our confidence is low, however, that the potential diffusive flux rates accurately capture the order of magnitude of flux. Benthic primary producers are known to tightly regulate the fluxes of dissolved inorganic nutrients across the sediment water interface (Sundback and McGlathery 2005). SRP fluxes can be modified by surficial sediment chemistry when oxygen content of the sediments is high (McManus *et al*. 1997, Klump and Martens 1987). Calculated potential diffusive fluxes are likely to be an underestimate of the net release of nutrients into the surface waters and/or uptake and storage by primary producers. Qu *et al*. (2005) found an order of magnitude greater difference in fluxes measured *in situ* versus via diffusive fluxes estimated from pore water profiles (Qu *et al*. 2005). Many

Table 7. Comparison of estimated benthic flux rates of nitrogen and phosphorus in Malibu Lagoon with published rates in other systems. All rates given in mMol m^{-2} d^{-1}.

Source	SRP	NH4	N03
Malibu Lagoon (this study)			
Western Lagoon	0.4 ± 0.2	5.4 ± 3.2	-3.0 ± 5.3
Central Lagoon	0.001 ± 0.003	0.04 ± 0.02	-0.03 ± 0.02
Newport Bay, California (Sutula *et al.* 2006)	0.36 ± 0.52	5.7 ± 2.7	-3.0 ± 5.3
Shallow NE Australian Lagoons (Ferguson *et al.* 2004)		-0.2±0.3	-0.4 ± 0.3
Valli di Comacchio Lagoon (northern Adriatic coast, Italy; Bartoli *et al.* 2008)		-4 to 8	-6 to 1
San Francisco Bay (Hammond *et al.* 1985)	0.10 ± 0.50	1.1 ± 0.1	-0.5 ± 0.6
Chesapeake Bay (Callender and Hammond 1982; Cowan and Boynton 1996)	0.8	10.2	-2.9 – 0.2
Tomales Bay (Dollar *et al.* 1991)	0.24 ± 0.40	1.96 ± 2.39	-0.01 ± 0.17
Plum Island Sound (Hopkinson *et al.* 1999)	-0.25 – 1.5	4.8 – 21.2	

studies have found that advective transport of water through the sediments (e.g., processes such as groundwater seepage, tidal pumping, and bioturbation) are dominant factors relative to diffusive transport in controlling benthic flux (Watson and Frickers 1995, Giffin and Corbett 2003). The ^{7}Be data show that bioturbation (possibly by burrowing worms) is intensively reworking the first 0 to 2 cm, particularly during the dry season. This bioturbation may be greater at shallower, intertidal sites such as 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.

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. Interestingly, the estimated efflux 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 although long-term annual sedimentation rates and associated N and P load may be an order of magnitude less than estimated for this study, these infrequent El Niño events may be providing particulate N and P loads to the Lagoon that will take years to assimilate.

In order to better constrain the nutrient budget of Malibu Lagoon, the relative rates of N fixation, denitrification and dissimilatory nitrate reduction, and plant uptake of N must be quantified. Little is known about the rates of denitrification in coastal lagoons in southern California. Published rates within *R. cirrhosa* beds in an eutrophic lagoon in Italy were 92 mMol m^{-2} yr^{-1} (Bartoli *et al*. 2008). Using Bartoli estimates when integrating over the dry season would represent a loss of 13 kg N in the Western Lagoon: numbers far less than the estimated nonpoint source inputs to the Lagoon during the dry season. 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, 2003). 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.

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