EUTROPHICATION AND NUTRIENT CYCLING IN SANTA MARGARITA RIVER ESTUARY: A SUMMARY OF BASELINE STUDIES FOR MONITORING ORDER R9-2006-0076

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Executive Summary

The purpose of this report is to summarize the findings of the Southern California Coastal Water Research Project (SCCWRP) study conducted in the Santa Margarita River Estuary (SMRE) in support of the San Diego Regional Water Quality Control Board (SDRWQCB) Monitoring Order (R9-2006-0076), which requires stakeholders to collect data necessary to develop models to establish total maximum daily loads (TMDLs) for nutrients and other contaminants (e.g. bacteria). SCCWRP, Louisiana State University (LSU) and University of California Los Angeles (UCLA), supported by a Proposition 50 grant from the State Water Resources Control Board (SWRCB), conducted studies in support of model development including monitoring of primary producer biomass, measurement of sediment and particulate nitrogen (N) and phosphorus (P) deposition, measurement of benthic dissolved oxygen (DO) and N and P fluxes, and sediment bulk and porewater N and P.

The purpose of this report is two-fold:

- Provide a summary of SCCWRP study data that will be used to develop and calibrate the water quality model for the SMRE.
- Synthesize study data to inform management actions to address eutrophication and improve the efficiency of nutrient cycling in the SMRE.

Following are the major findings of this study:

1. The SMRE is exhibiting symptoms of eutrophication, as documented by high biomass and percent cover of macroalgae, as well as episodes of low DO.

    a. Biomass and percent cover of macroalgae were high with a mean averages of 1465 to 1714 g wet wt m^{-2} over the fall 2008 and 2009 TMDL and Bight '08 field studies, and cover up to 100%. No established framework exists to assess adverse effects from by macroalgae, though a recent review (Fong *et al.* 2011) found studies documenting adverse effects of macroalgae on benthic infauna as low as 700 g wet wt m^{-2} and with cover greater than 30 to 70%.

    b. Dissolved oxygen concentrations measured at Segment 1 showed surface waters to be below 5 mg L^{-1} approximately 19% of the wintertime and 23% of the summertime.

2. High dry season concentrations of dissolved inorganic nutrients indicate anthropogenically-enriched nutrient sources. Four types of data provide evidence for this finding:

    a. During the summer and fall, little freshwater was delivered to the estuary, yet estuarine ambient dry season soluble reactive phosphorus (SRP) and ammonium (NH_4) were especially high in Segment 2 (16.1 ±10.1 µM SRP and 29.8 ±19.3 µM NH_4) and nitrate (NO_3) was high in Segment 1 (69.4 ±29.2) relative to the other San Diego Lagoons in this study.

    b. Mixing diagrams (plots of salinity relative to nutrient concentrations) of transect data indicate dry season sources of NO_3, phosphate (PO_4) and NH_4, not associated with direct freshwater input. Lateral inputs of groundwater or, at Segment 2, runoff from holding ponds, may be contributing an unquantified source of nutrients to the estuary.

c. Comparison of mass emission sources of NO_3 versus benthic influxes of NO_3during the summer and fall show that SMRE surface waters has more NO_3 than can be predicted by inputs from the Mass Emission site (ME). These data indicate that there are additional sources, such as lateral groundwater inputs of NO_3. This is a reasonable assumption, given the proximity of intensive, irrigated agriculture that was occurring at the time of sampling and permeable, sandy substrates which dominate the estuary.

d. The quantities of N and P required to grow macroalgae during the fall sampling period is not met by measured sources of terrestrial loads nor benthic flux. These data indicate that there are additional sources, such as lateral groundwater inputs of PO_4 that are occurring.

3. During the wet season (Nov- Apr), terrestrial total nitrogen (TN) and total phosphorus (TP) loads were the dominant source of nutrients to surface waters, but during the dry season benthic $NH_4$and SRP flux dominated measured sources to surface waters and provide nutrients in excess of that required to grow the abundance of macroalgae measured in the estuary. Three types of data are used to support this finding:

   a. Terrestrial wet and dry weather TN loads were generally balanced, while wet weather dominated annual TP loads (65%). Winter dry weather runoff (Nov-Jan, 41,627 kg TN) represents 36% of the total annual export and 65% of the total dry weather runoff. With respect to TP, 88% of the total annual dry weather runoff (2,882 kg) occurred over the winter and spring index periods. Terrestrial runoff of N and P were during summer and fall were low (535 to 0 kg TN and 328 to 0 kg TP respectively).

   b. With respect to relative sources, terrestrial TN and TP input overwhelmed all other sources[1] during the wet season (Nov-Apr), but during the summer and fall estimated terrestrial input only represented 0 to 25% of TN and TP loads to the surface waters and direct atmospheric deposition is a negligible source. In contrast, benthic flux ranged acted as a sink for about 10% of the terrestrial N and P during the winter index period but then became a dominant source during the summer and fall (>75%), the periods of peak primary producer biomass.

   c. During peak periods of macroalgal blooms, benthic fluxes of NH_4 and SRP are 1.5 to 19X the N and 0.2 to 4X the P required to grow the abundance of macroalgae observed. Macroalgae is an efficient trap for dissolved inorganic nitrogen (DIN) and has been shown to intercept benthic nutrient effluxes and can even increase the net flux by increasing the concentration gradient between sediments and surface. The storage of large quantities of N and P as algal biomass thus diverts loss from denitrification and burial and providing a mechanism for nutirent retention and recycling within the estuary.

4. The patterns of NH_4 and NO_3 fluxes suggest that denitrification (loss of NO_3 to N gas) may be playing a large role during the winter and spring time when sediments are better flushed and oxygenated but that dissimilatory nitrate reduction (DNR), the conversion of NO_3 to NH_4 under anoxic sediment conditions, is clearly a dominant pathway during the summer time and is likely

[1] The net exchange of groundwater is unknown.

responsible for the large fluxes of NH_4 observed during these periods. Thus in the winter and spring, the SMRE is better able to assimilate external DIN inputs through denitrification, but will be more likely to retain N inputs during the summer and fall as DNR-derived NH_4 is incorporated into algal biomass and to some degree retained within the estuary.

5. As a fluvially-dominanted river mouth estuary, the SMRE has an inherent capacity to scour fine-grained sediments, thus making it less susceptible to eutrophication because particulate sources of nutrients such as watershed sediments and decaying organic matter tend to be more quickly exported. Two types of data support this finding:

    a. Meaurement of benthic oxygen (O_2)fluxes indicated that, on average, estuary net positive flux of O_2 to surface waters in spring to net uptake of $O_2$by sediments in the fall. These rates of O_2 uptake were moderate relative to other eutrophic estuaries. High net total carbon dioxide (TCO_2) effluxes are typically driven by respiration of accumulated dead or decaying biomass (organic matter accumulation) in the sediments rather than respiration of live biomass.

    b. While the SMRE had among the highest peak biomass of macroalgae documented, this biomass does not appear to accumulate in SMRE sediments from season to season. Surficial sediments were primary sandy, had surface C:N values <10, indicative of algal carbon sources, but these values increased dramatically with depth and with often non-detect with respect to N, indicating that organic matter is not accumulating with depth. In fluvially-dominated river mouth estuaries such as the SMRE, this lack of interannual organic matter accumulation would make them less susceptible to eutrophication and is a factor responsible for the lower sediment O_2 demand, given the high abundances of algal biomass.

Management Options to Reduce Eutrophication

The SMRE has the advantage, as a river mouth estuary, that sediments do not appear to have accumulated excessive organic matter with depth. Hypoxia was present in the estuary, but not chronic. Interestingly, both N and P appear to be seasonally limiting in the SMRE. Therefore, options for management of eutrophication in the SMRE are aimed at reducing the availability of nutrients for primary production during the growing season and increasing tidal exchange in order to increase availability of DO and enhance denitrfication. Surface water nutrients were P limited during the winter, and N limited during the summer and fall. Thus management of both N and P sources and the ratios available for primary productivity is critical for managing eutrophication.

Three types of options could be considered:

1) Reduce terrestrial loads in order to limit primary productivity. Emphasis should be placed on reducing both P as well as N from the watershed and lateral inputs. **Because sources during the growing season appear to be lateral inputs rather than those estimated by the ME site, minimizing these loads will be a critical and effective management strategy.**

2) Increase flushing during peak periods of primary productivity, particularly when SMRE has reduced tidal exchange to surface water exchange with ocean during summer. Clearly this is a

trade off with the need preserve available tidewater goby habitat during summer. Improved circulation during closed condition could help to limit stratification and therefore ameliorate, to a minor extent, problems with hypoxia.

3) Restoration to improve exchange with expansive area of wetland habitat west of Interstate Highway 5 (I-5). Denitrification rates are typically highest in wetland habitats (Day *et al.* 1989). Restoration to increase connectivity and exchange of surface waters with the large expanse of intertidal habitat south of the main channel would help to divert excessive NO_3 available during dry season from DNR towards denitrification and permanent loss. This could be accomplished through grading of portions of the natural levee with separates this the central channel from the wetland area.

Future Studies

Quantification of additional sources of nutrients such as groundwater to the estuary during dry season is a critical research need, as it will effect TMDL allocations.

Disclosure

Funding for this project has been provided in full or in part through an agreement with the State Water Resources Control Board. The contents of this document do not necessarily reflect the views and policies of the State Water Resources Control Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use (Gov. Code 7550, 40 CFR 31.20).

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1 Introduction

1.1 Background and Purpose of Report

The Santa Margarita River Estuary (SMRE) is a 192 acre estuary located one mile north of the City of Oceanside, in the southwest corner of the Camp Pendleton Marine Corps base. The lower river and estuary have largely escaped the development typical of other regions of coastal Southern California, and are therefore able to support a relative abundance of functional habitats and wildlife, including populations of federally- or state-listed endangered species such as the Least Tern, Western Snowy Plover, Tidewater Goby and Belding's Savannah Sparrow.

The estuary drains the Santa Margarita River watershed, which encompasses approximately 750 square miles in northern San Diego and southwestern Riverside counties. The Santa Margarita River is formed near the City of Temecula in Riverside County at the confluence of the Temecula and Murrieta Creek systems, one of the fasted growing areas in California. Once formed, the majority of the Santa Margarita River main stem flows within San Diego County through unincorporated areas, the community of Fallbrook, and the Marine Corps Base Camp Pendleton. These urban and agricultural land uses in the watershed resulted in hydrological modifications to the SMRE and have led to increased nutrient loading to the Estuary.

Increased nutrient loads are known to fuel the productivity of primary producers such as macroalgae or phytoplankton in the SMRE, in a process known as eutrophication. Eutrophication is defined as the increase in the rate of supply and/or in situ production of organic matter (from aquatic plants) in a water body. While these primary producers are important in estuarine nutrient cycling and food web dynamics (Mayer 1967, Pregnall and Rudy 1985, Kwak and Zedler 1997, McGlathery 2001, Boyer *et al.* 2004), their excessive abundance can reduce the habitat quality of a system. Increased primary production can lead to depletion of dissolved oxygen (DO) from the water column causing hypoxia (low O_2) or anoxia (no O_2; Valiela *et al.* 2002, Camargo and Alonso 2006, Diaz and Rosenberg 2008), which can be extremely stressful to resident organisms. An overabundance of macroalgae or phytoplankton can also shade out or smother other primary producers and reduce benthic habitat quality through the stimulation of sulfide and ammonium (NH_4) production (Diaz 2001).

As a result of excessive algal abundance and low DO, the SMRE was placed on the State Water Resources Control Board's (SWRCB) 303(d) list of impaired waterbodies. In order to establish Total Maximum Daily Loads (TMDLs) of nutrients to the estuary, the San Diego Regional Water Quality Control Board (SDRWQCB) issued a Monitoring Order (R9-2006-0076) requiring stakeholders to collect data necessary to develop watershed loading and estuarine water quality models. SMRE stakeholders contracted with CDM, Inc. to collect data on nutrient loading, estuarine hydrology, and ambient sediment and water quality to address the requirements of Investigation Order R9-2006-0076. The Southern California Coastal Water Research Project (SCCWRP), Louisiana State University (LSU) and University of California Los Angeles (UCLA), supported by a Proposition 50 grant from the State Water Resources Control Board (SWRCB), conducted studies to aid model development including monitoring of primary producer biomass, measurement of sediment and particulate nitrogen (N) and phosphorus (P) deposition, measurement of benthic DO and nutrient fluxes, and sediment bulk and porewater

nutrients. During October 2007 through October 2008, SCCWRP and CDM conducted field studies to collect the necessary data.

The purpose of this report is two-fold:

- Provide a summary of SCCWRP study data that will be used to develop and calibrate the water quality model for the SMRE.
- Synthesize study data to inform management actions to address the causes of eutrophication and maximize natural nutrient sinks in the SMRE.

Studies were conducted in order to address the following research objectives:

- Characterize the seasonal trends in surface water ambient nutrient concentrations, sediment solid phase and porewater nutrients, and primary producer communities.
- Estimate the seasonal and long-term annual deposition of sediments and particulate nutrients to the SMRE
- Characterize the seasonal trends in N and P exchange between the Estuary sediments and surface waters (benthic nutrient flux).
- Assess the efficiency of nutrient cycling in the SMRE by estimating, to the extent possible, N and P budgets.

1.2 Report Organization

This report is organized into an executive summary and four Sections:

Executive Summary
Section 1: Introduction, purpose, and organization of report, site description, and general study design
Section 2: Seasonal trends in SMRE surface water and sediment nutrients and primary producer communities
Section 3: Seasonal trends in exchange of nutrients between surface waters and sediments
Section 4: SMRE N and P budgets

Appendix 1 provides a summary of quality assurance documentation. Appendix 2 provides data tables summarizing SCCWRP study data (as a complement to graphs used in Sections 2 through 4) to facilitate use of data for modeling.

1.3 Site Description

The SMRE is located within the Ysidora Hydrologic Basin of the 750 square mile Santa Margarita Watershed just north of Oceanside California. The Estuary is a 192 acre estuary located in the southwest corner of the Camp Pendleton Marine Corps base. Sixty-seven percent of the estuarine habitat is dominated by mudflats, salt panes and salt marsh habitat, with the remaining 33% as subtidal habitat. The primary source of freshwater input into the estuary is surface flow from the Santa

Margarita River, though ancillary freshwater input for the estuary comes from runoff and ground seepage. The estuary is open to the ocean; however flow is constricted by rock jetties from Interstate 5 and railroad crossings. During periods of higher freshwater flow, the ocean inlet is completely open and the main channel of the estuary is intertidal. During periods of lower freshwater flow, the ocean inlet can become partially restricted by sand bars at the mouth, restricting exchange with the ocean reducing tidal flushing.

Prior to 1942, the Santa Margarita floodplain was cultivated for agricultural purposes and until the 1970's the SMRE was used for military tank training and as a site for the discharge of secondarily treated sewage. Currently this area is designated as a special management zone by the Marine Corps, with no allowances for development. Nutrient sources appear to be predominantly from the watershed and include agriculture, nursery operations, municipal wastewater discharges, urban runoff, septic systems, and golf course operations. Camp Pendleton leases land for agriculture on the headlands north of the estuary, so additional nutrient loading from infiltration and groundwater discharge into the estuary are also possible.

1.4 General Study Design

The general study design for all monitoring conducted to support TMDL modeling is based on a basic conceptual model developed to describe the sources, losses, and transformations of targeted constituents within the SMRE (Figure 1.1; McLaughlin *et al.* 2007). The three principal types of monitoring were conducted:

1. Continuous monitoring of hydrodynamic and core water quality parameters (salinity, temperature, etc.);
2. Wet weather monitoring, which was conducted during and immediately following a specified number of storm events at the mass emission (ME) site in the main tributary, targeted locations in the lagoon, and at the ocean inlet; and
3. Dry weather monitoring, which was conducted during four "index" periods that were meant to capture representative seasonal cycles of physical forcing and biological activity in the estuary. During each index period, sampling was conducted at the ME site and the ocean inlet site, as well as two segment sites within the Estuary. In the SMRE, the Ocean Inlet site represents exchange between the ocean and the lower portion of the Estuary, while the Segment 1 and 2 sites provide information on the mid and upper estuarine reaches.

In general, stakeholder monitoring was intended to cover: 1) continuous monitoring of hydrodynamic and core water quality parameters, 2) all wet weather monitoring, 3) dry weather ambient monitoring of surface water nutrient concentrations within the lagoon and at points of exchange between the lagoon and the ocean inlet and watershed freshwater flows (ME site), and 4) longitudinal transect studies (Figure 1.2).

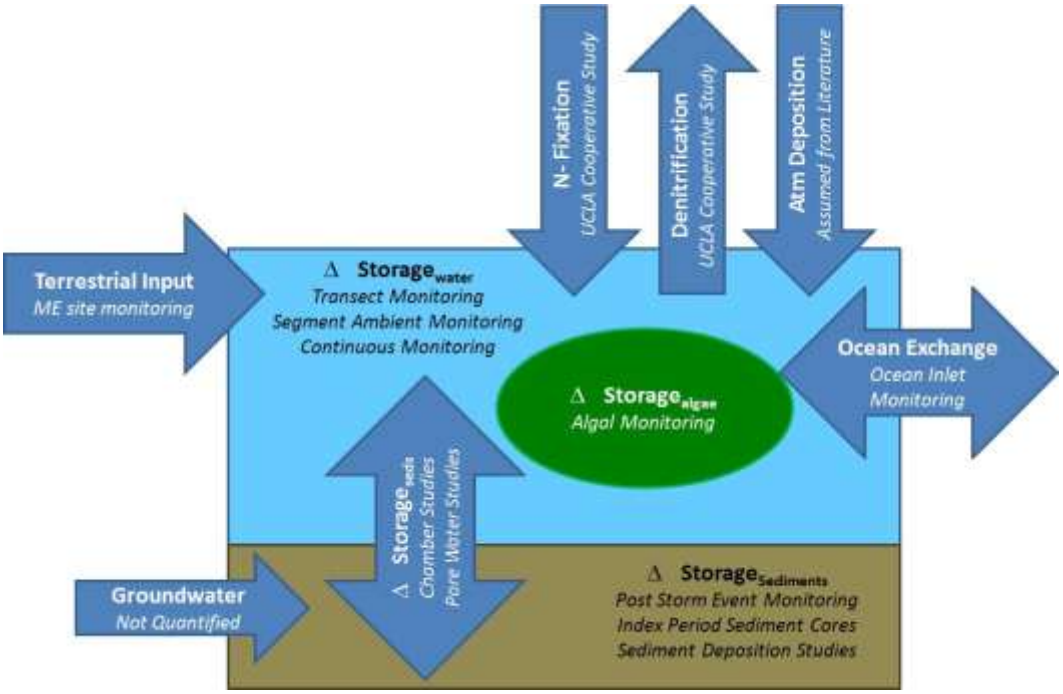


Figure 1.1. Conceptual model of sources, sinks and transformations of nutrients into Santa Margarita River Estuary. Italics indicate data source used to characterize inputs, outputs and fluxes. Sampling events when these data are collected are given in Table 1.1.

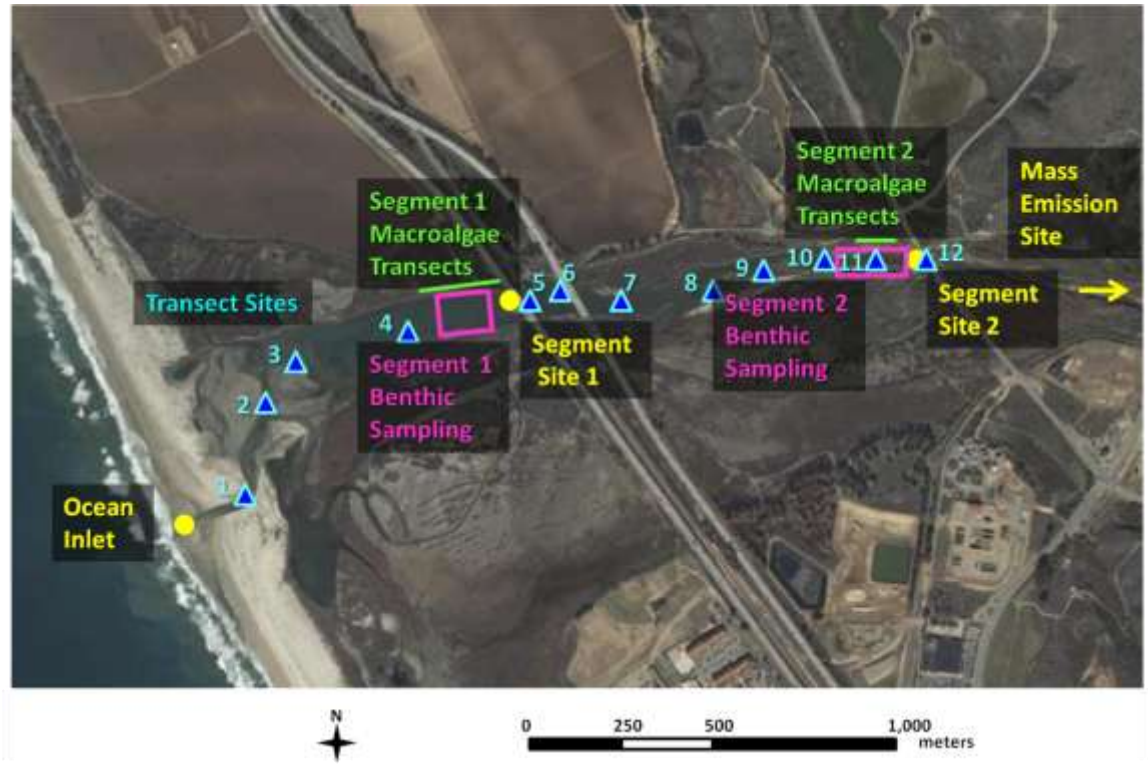


Figure 1.2. Location of sampling activities in Santa Margarita River Estuary.

SCCWRP studies collected three types of data: 1) estimates of nutrients associated with sediments and primary producer biomass to complement stakeholder sampling during dry weather index periods, 2) measurements of key rates of exchange or transformation within or among sediments and surface waters, and 3) rates of net sediment and particulate N and P deposition to support sediment transport and estuary water quality modeling. In addition SCCWRP conducted continuous monitoring of water quality parameters and primary producer surveys for a second year following the initial TMDL sampling.

Sampling to develop the dataset occurred during four index periods in one year (October 2007 to September 2008; Table 1.1). Each index period represents seasonal variations in the estuary: Storm season (January 2008), post-storm/pre-algal bloom (March 2008), high algal bloom (July 2008), and post-algal bloom/pre-storm (September 2008). This sampling design aimed to provide a means to examine seasonal variability in estuary processes affecting nutrient availability and cycling. SCCWRP sampling was coordinated to coincide with stakeholder monitoring of dry weather ambient water quality (WestonSolutions 2009).

To supplement the TMDL field studies, data collected in the SMRE under SCCWRP's 2008 Southern California Bight Regional Monitoring Survey (Bight '08) Coastal Wetland and Estuary Eutrophication Assessment (October 2008-2009) are also summarized in this report. Specifically this includes:

- Continuous DO, conductivity, pH, temperature, chlorophyll a (chl a) fluorescence, and turbdity conducted at the Segment 1 site (Interstate Highway 5 (I-5) bridge) at bottom waters
- Bimonthly primary producer biomass and percent cover for the following primary producers: microphytobenthos (as benthic chl a), macroalgal biomass and cover, phytoplankton biomass (as water column chl a).
- Bimonthly sediment %OC, %N and %P in surface sediments
- Bimonthly dry weather nutrient water samples in the estuary and at the ME site

Methods used to collect these data are given in the Bight '08 Eutrophication Assessment Quality Assurance Project Plan. The data are summarized in this report for the Santa Margarita River estuary when appropriate.

Table 1.1. Summary of the different sampling activities in the SMRE by time period, types of sampling event, organization and actual dates sampling occurred.

Sampling	Period	Event	Organization	Date
TMDL Monitoring	Wet Weather Monitoring	Storm Sampling (3 storm events)	CDM	1/5/08, 1/27/08, 11/26/08
	Wet Weather Monitoring	Post Storm Sediment Sampling	CDM	12/4/08
	Continuous Monitoring	Water Quality Monitoring	CDM	10/4/07-9/30/08
	Interim Period	Sediment Deposition	LSU	11/15/07
	Interim Period	Sediment Deposition	LSU	12/13/07
	Index Period 1	Ambient Sampling	CDM	1/30-2/8/08
		Transect Sampling	CDM	2/7/08
		Benthic Chamber Study- SEG 1	SCCWRP	1/14/08
		Benthic Chamber Study- SEG 2	SCCWRP	1/15/08
		Porewater Peeper Deployment	SCCWRP	1/7-1/21/08
		Sediment Core	SCCWRP	1/21/08
		Macroalgae Monitoring	UCLA	1/21/08
		Sediment Deposition	LSU	1/21/08
	Interim Period	Sediment Deposition	LSU	2/28/08
	Index Period 2	Ambient Sampling	CDM	3/24-4/2/08
		Transect Sampling	CDM	3/27/08
		Benthic Chamber Study- SEG 1	SCCWRP	3/26/08
		Benthic Chamber Study- SEG 2	SCCWRP	3/27/08
		Porewater Peeper Deployment	SCCWRP	3/18-4/3/08
		Sediment Core	SCCWRP	4/3/08
		Macroalgae Monitoring	UCLA	4/11/08
		Sediment Deposition	LSU	4/3/08
	Interim Period	Sediment Deposition	LSU	5/14/08
	Index Period 3	Ambient Sampling	CDM	7/21-7/30/08
		Transect Sampling	CDM	7/24/08
		Benthic Chamber Study- SEG 1	SCCWRP	7/8/08
		Benthic Chamber Study- SEG 2	SCCWRP	7/9/08
		Porewater Peeper Deployment	SCCWRP	7/3-7/24/08
		Sediment Core	SCCWRP	7/24/08
		Macroalgae Monitoring	UCLA	7/21/08
		Sediment Deposition	LSU	7/24/08
	Interim Period	Sediment Deposition	LSU	8/20/08
	Index Period 4	Ambient Sampling	CDM	9/23-10/1/08
		Transect Sampling	CDM	9/25/08
		Benthic Chamber Study- SEG 1	SCCWRP	9/24/08
		Benthic Chamber Study- SEG 2	SCCWRP	9/25/08
		Porewater Peeper Deployment	SCCWRP	9/12-9/30/08
		Sediment Core	SCCWRP	9/30/08
		Macroalgae Monitoring	UCLA	9/29/08
		Sediment Deposition	LSU	9/30/08
Bight '08 Eutrophication Assessment	Continuous Monitoring	Water Quality Monitoring	SCCWRP	12/18/08-11/13/09
	Bight Sampling 1	Primary Producer Monitoring	SCCWRP	11/24/08
	Bight Sampling 2	Primary Producer Monitoring	SCCWRP	1/20/09
	Bight Sampling 3	Primary Producer Monitoring	SCCWRP	3/23/09
	Bight Sampling 4	Primary Producer Monitoring	SCCWRP	5/18/09
	Bight Sampling 5	Primary Producer Monitoring	SCCWRP	6/26/09
	Bight Sampling 6	Primary Producer Monitoring	SCCWRP	9/18/09

2 Patterns in Surface Water and Sediment Nutrients and Primary Producer Communities in the Santa Margarita River Estuary

2.1 Introduction

All estuaries exhibit distinct temporal and spatial patterns in hydrology, water quality and biology that are integral to the ecological services and beneficial uses they provide (Day *et al.* 1989, Loneragan and Bunn 1999, Caffrey 2004, Rountree and Able 2007, Shervette and Gelwick 2008, Granek *et al.* 2010). Characterization of seasonal and spatial patterns in surface water and sediment nutrient concentrations and aquatic primary producer communities provides valuable information about the sources, dominant transport mechanisms, and fate of nutrients in the SMRE and helps to generate hypotheses regarding the controls on biological response to nutrients.

The purpose of this Section is to present a baseline characterization of the patterns in surface water and sediment nutrients and aquatic primary producers in the SMRE. This work forms the foundation for interpretation of sediment porewaters and benthic fluxes (Section 3) and characterizing nutrient cycling through N and P budgets for the SMRE (Section 4).

2.2 Methods

The following types of field data were collected and methods are explained in detail in this section:

- Longitudinal and seasonal trends in surface water ambient nutrient concentrations, conducted in conjunction with CDM
- Seasonal trends in aquatic primary producer biomass and/or percent cover and tissue nutrient content
- Seasonal variation in sediment bulk characteristics (grain size, solid phase N and P content)

A detailed presentation of the intent and field, analytical, and data analysis methods associated with each of these data types follows below.

When appropriate, ambient water quality data collected and analyzed by CDM are incorporated into the results and discussion. These data are cited when used and for a detailed explanation of methods, see CDM (2009).

2.2.1 Field Methods

2.2.1.1 Surface Water Nitrogen and Phosphorus Along a Longitudinal Gradient

Longitudinal transects of surface water nutrient concentrations provide valuable spatial information about how concentrations vary along a gradient from the freshwater source to the ocean (or in this case river) end-member.

Surface water samples were collected by CDM at 12 sites along a longitudinal transcect of the SMRE (Figure 1.1; CDM 2009). Longitudinal transect sampling occurred on the fourth day of the first week of each index period. Transect sampling was performed using kayaks and grab-sampling techniques.

Sampling occurred in the main channel and samples were collected once at ebb tide and once at flood tide.

The sample bottle was triple rinsed with lagoon water before filling completely with surface water. Sample bottles were open and closed under water to avoid contamination with surface films or stratified water masses. One liter sample bottles were returned to the shore for immediate filtering where appropriate. Ambient water samples were subsampled for a suite of analytes (total nitrogen (TN), total phosphorus (TP), total dissolved nitrogen (TDN), total dissolved phosphorus(TDP), nitrate (NO_3), nitrite (NO_2), NH_4, soluble reactive phosphorus (SRP), dissolved organic carbon (DOC), iron (Fe) and manganese (Mn)) using a clean, 60 ml syringe. Each syringe was triple rinsed with sample water. Mixed cellulose ester (MCE) filters were used for nutrient analysis and polyethersulfone (PES) filters were used for DOC and metals analysis. Each filter was rinsed with ~20 ml of sample water (discarded) before collection into vials.

2.2.1.2 Inventory of Aquatic Primary Producer Cover and Tissue Content

Aquatic primary producer communities include macroalgal and cyanobacteria mats, benthic algal mats, suspended phytoplankton, and submerged aquatic vegetation (SAV). The purpose of this study element was to characterize seasonal variation in the standing biomass, cover, and the tissue nutrient content of these communities. This information will be used to calibrate the component of the eutrophication water quality model that accounts for the storage and transformation of nutrients in primary producer community biomass.

Aquatic primary producer biomass was measured during the four index periods at the two segment sites at low tide. At these sites, intertidal macroalgae were sampled along a 30-m transect parallel to the waterline and one meter down-slope from the vascular vegetation. Macroalgal abundance was determined by measuring percent cover and algal biomass; including both attached and detached mats. At 5 randomly chosen points along each transect, a 0.25-m^2 quadrat with 36 evenly spaced intercepts (forming a 6X6 grid) was placed on the benthos. The presence or absence of each macroalgal species in the top layer under each intercept was recorded. Percent cover was calculated from the number of points where algae was covered, divided by the total number of points possible. When present, algae were collected from a 530.9 cm^2 area circumscribed by a plastic cylinder placed on the benthos in the center of each quadrat. Each sample was placed in an individual ziploc bag in a cooler, transported to the laboratory and refrigerated.

In the laboratory, algal samples were transferred to low nutrient seawater where they were cleaned of macroscopic debris, mud and animals. For each sample, algae were placed in a nylon mesh bag, spun in a salad spinner for one minute, wet weighed, rinsed briefly in deinonized water to remove salts, and dried at 60°C to a constant weight. Macroalgal biomass was normalized to area (g wet wt m^{-2}). Fine macroalgal filaments that grow within the sediment may be visible but biomass cannot be collected quantitatively at this early growth stage, making percent cover in this case a more sensitive measurement. In addition, when there is 100% cover, and mats are different thicknesses, biomass will be a more useful measure to make distinctions between sites (Sfriso *et al.* 1987). Thus it is important to use both methods to estimate abundance. Samples were cleaned and weighed to determine wet and

dry weights. Dried samples were analyzed for percent organic carbon (%OC), percent organic N and percent P.

2.2.1.3 Sediment Bulk Characteristics and Solid Phase Nutrients

All sediments carry nutrients, either as organic matter or, in the case of P, associated with particles. When deposited in the estuary, these particulate nutrients may break down to biologically available forms and may build up in high concentrations in sediment porewaters. Sediment bulk characteristics control nutrient content; finer particle size fractions are associated with higher organic carbon (OC), N and P content (Sutula *et al.* 2006).

The purpose of this study element was to characterize the inventories of nutrients associated with sediments. Specifically, this involved measurement of the sediment solid phase bulk characteristics (grain size, porosity, etc.) and sediment OC, N and P concentrations.

Sediment bulk characteristics and solid phase nutrient concentrations were estimated for a vertical profile in one sediment core taken from each segment site per index period. For each sampling period, one sediment core was taken and vertically sectioned on site into 1 cm intervals from the sediment water interface until 6 cm depth and then sectioned every 2 cm down to 12 cm. Sediments were placed in plastic storage bags and stored on ice in the dark until they reached the laboratory. In the lab, sections were wet weighed, dried at 50°C to a constant weight, and reweighed to determine percent solids and wet bulk density. A subsample of each section (~10 grams dry weight) was removed and ground to a fine powder for %OC, percent total nitrogen (%TN) and percent total phosphorus (%TP) analysis. The remainder of the section was utilized for grain size analysis (percent fines).

2.2.2 Analytical Methods

All water samples were assayed by flow injection analysis for dissolved inorganic nutrients using a Lachat Instruments QuikChem 8000 autoanalyzer for the analysis of NH_4, NO_3, NO_2, and SRP. Dissolved Fe and Mn were measured by atomic adsorption spectrophotometry on a Varian Instruments AA400. Water samples were assessed for TDN, TDP, TN and TP via two step process: first water samples undergo a persulfate digest to convert all N from all N compartments into NO_3 and the P from all P compartments into orthophosphate; then the resulting digests are analyzed by automated colorimetry (Alpkem or Technicon) for nitrate-N and orthophosphate-P (Koroleff 1985). Water DOC was analyzed on a Shimadzu TOC-5000A Total Organic Carbon Analyzer with ASI-5000A Auto Sampler. Water total carbon dioxide (TCO_2) was analyzed on a UIC instruments carbon dioxide coulometer. Inorganic nutrients analyses were conducted by the Marine Science Institute at the University of California, Santa Barbara; TDN, TDP, TN, and TP analyses were run at the University of Georgia Analytical Chemistry Laboratory.

Dried sediment samples were subsampled and ground for analysis of %OC, %TN, and %TP. Samples for %OC were acidified to remove carbonates; %OC and %TN were measured by high temperature combustion on a Control Equipment Corp CEC 440HA elemental analyzer at the Marine Science Institute, Santa Barbara. Sediment %TP were prepared using and acid persulfate digest to convert all P to

orthophosphate, which was then analyzed by automated colorimetry (Technicon) at the University of Georgia Analytical Chemistry Laboratory.

To determine percent fines, a portion of sediment from each interval was weighed dry (total dry weight), then wet sieved through a 63 µm sieve, dried at 50 °C to a constant weight, and reweighed as sand dry weight. Percent sand was calculated as a function of the sand dry weight divided by the total dry weight of the sample. Percent fines were calculated as the total weight minus the percent sand.

2.2.3 Data Analysis

Analysis of variance (ANOVA) tests were used to test for differences in concentration by index period and, where relevant, by ebb and flood tide (SAS Proc GLM, 2008). Data were transformed to correct for unequal variance and mean and standard errors were generated from Tukey's pairwise comparisons.

Standing biomass of aquatic primary producers groups (phytoplankton, macroalgae, microphytobenthos (MPB), and cyanobacteria mats) were converted to carbon per meter squared in order to make comparisons among the groups. The following assumptions were used in this conversion:

- Phytoplankton- Average 1.5 m depth of water, chl a: C ratio of 30 (Cloern *et al.* 1995)
- MPB – chl a: C ratio of 30:1 (Sundbäck and McGlathery 2005)
- Cyanobacteria: 50% C by dry wt (study data)
- Macroalgae: 22% C by dry wt (study data)

Porosity, fractions of water and sediment, and wet bulk density were used to estimate seasonal and annual sediment deposition rates and to evaluate changes in sediment nutrient and radioisotope inventories. These values are calculated from parameters measured in the laboratory.

The difference between wet and dry weights was used to calculate the fraction water (f_{wet}) and fraction sediment (f_{dry}):

$$f_{wet} = \frac{W_{wet} - W_{dry}}{W_{wet}}$$

Eq. 2.1, 2.2

$$f_{dry} = 1 - f_{wet}$$

where W_{wet} and W_{dry} are the wet and dry sediment weights, respectively. Subsequently, when enough sample was present, a small known fraction of the initial dried sample was weighed, and dry grain density was determined gravimetrically using Archimedes principle, i.e. by volume displacement. The weighed sediment divided by the displaced volume yielded the dry grain density of each sediment core sample section. The dry grain density and fractions wet and dry were used in turn to calculate the porosity and bulk density. Often the shallowest sections of the cores did not contain enough material for a complete sediment physical properties analysis. We took extra cores near the end of the project to complete any missing sediment physical property data needed for future calculations. Porosity is a

measure of the amount of "empty space" in the sediment, defined by the ratio of the volume of voids to the total volume of a rock or unconsolidated material. Porosity was calculated using the following equation:

$$\phi = \frac{\frac{f_{wet}}{\rho_{water}}}{\frac{f_{wet}}{\rho_{water}} - \frac{f_{dry}}{\rho_{drygrain}}} \qquad \textbf{Eq. 2.3}$$

where ϕ is the porosity; ρ_{water} and $\rho_{drygrain}$ are the density of ambient water and dry sediment grains, respectively. Bulk density, $\rho_{wetbulk}$ or $\rho_{drybulk}$, was calculated based on the total mass of each core section divided by the core section interval volume. Thus both a wet and a dry bulk sediment density could be determined on deeper samples more often when a larger mass of sample was available for the different analyses. Wet bulk density (ρ in g cm^{-3}) is given by the Equation 2.4.:

$$\rho = \frac{W_{SEDwet\,(i)}}{V_i} \qquad \textbf{Eq. 2.4}$$

Where $W_{SEDwet\,(i)}$ is the wet weight of each sediment core section interval and V is the volume of the sediment core section interval.

2.3 Results

2.3.1 Seasonal and Spatial Trends in Physiochemical Parameters and Nutrients

Continuous data from Segment 2 (upstream) and Segment 1 (downstream) during the 2007-2008 sampling season had quality assurance problems (see Figures A3.1 and A3.2 in Appendix 3), and thus are not utilized in the data analysis. Data from the Bight '08 Eutrophication Assessment collected during 2008-2009 are presented in order to describe general patterns of hydrology.

Water quality and primary producer biomass would be expected to change as a function of estuary hydrology, salinity, pH and temperature. Figure 2.1 shows SMRE water level, salinity and DO as a function of freshwater flow into the estuary during Bight '08 at Segment 1 (at I-5 Bridge). During the wet season (December 2008-April 2009), freshwater base flow at the Ysidora USGS station averaged 10 cfs, with two large storms (peaks of 500 to 1000 cfs) occurring in mid-december 2008 and February 2009. Tidal range during this time period is 1.4 m, and salinity fluctuates from 0 to 32 ppt, indicating that the estuary mouth is open and fully tidal. Temperatures range 10 to 20 ^{o}C, with mean monthly temperatures increasing from 14 to 16 ^{o}C over this period. With the onset of the dry season (May-October 2009), freshwater base flow gradually reduces to zero. Minimum water levels increase by 0.5 m but retain a strong tidal signal, indicating the restriction, but not closure, of the estuary mouth. Salinities show a decreased influence of freshwater as difference between the daily minima and maxima range from 20 ppt in May to 2 ppt in August. Water temperatures during this period range from 15 to 25^{o}C, with peak temperatures in July and August.

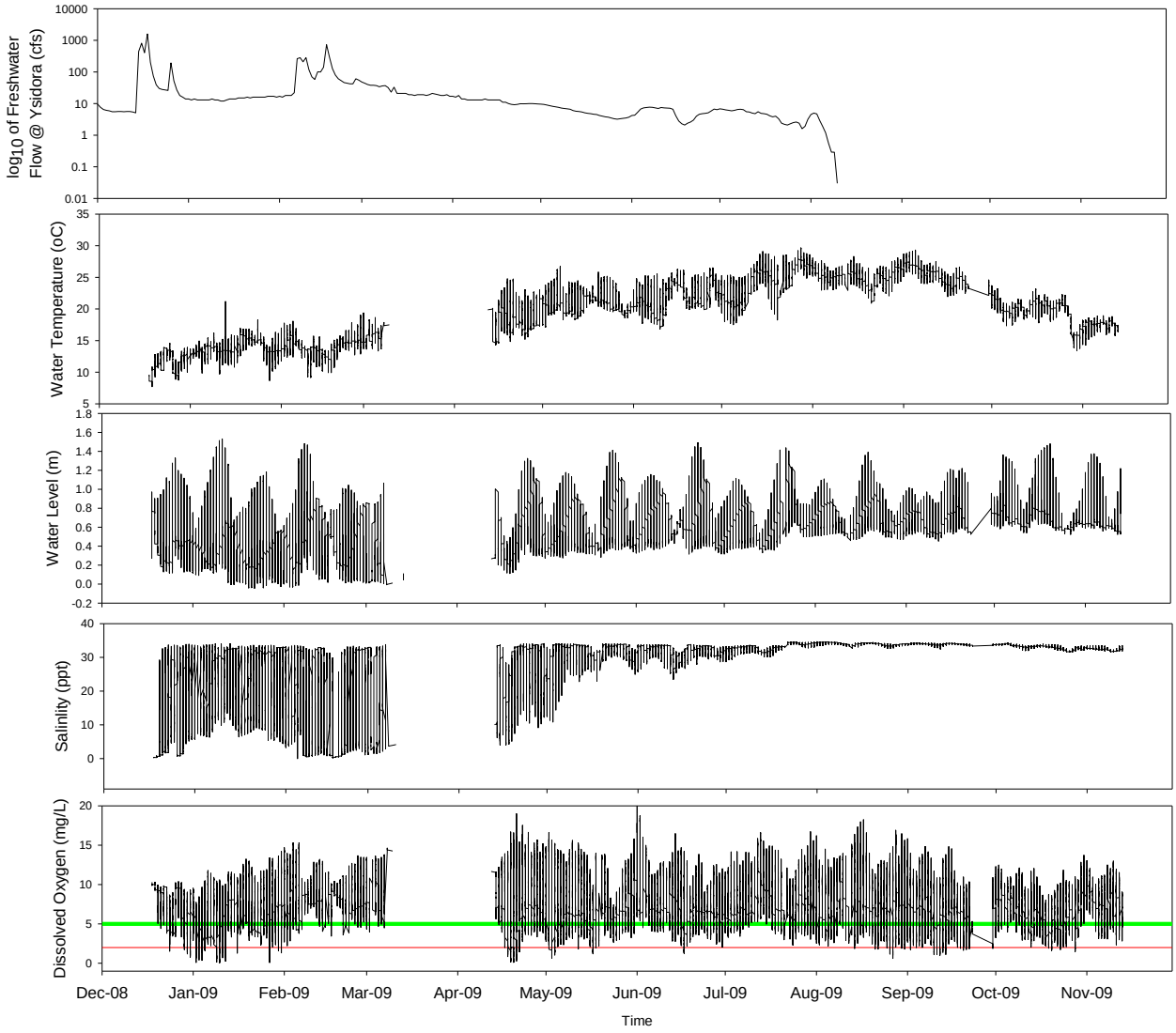


Figure 2.1. Continuous freshwater flow (cfs, log_{10} scale at Ysidora USGS Station) and Segment 1 water temperature, water level (m), salinity (ppt), and dissolved oxygen (mg L^{-1}) during the Bight '08 Eutrophication Study (McLaughlin 2012). Green and red lines in dissolved oxygen graph show the SDREWQCB 5 mg L^{-1} basin plan objective and the 2 mg L^{-1} definition of hypoxia (Diaz 2001), respectively.

Between study years, total freshwater flow was 60% higher and median dry season air temperatures (as a proxy for insolation) was 2°F higher in 2007-2008 then in 2008-2009 (Table 2.1).

Table 2.1. Annual (Dec-Nov), wet season (Dec-Apr), and dry season (May-Nov) total freshwater discharge at Ysidora USGS Gauge and median air temperature at Oceanside California. Air temperature is a proxy for insolation.

Period	2007-2008		2008-2009	
	Dicharge (cf)	Median Air Temp. (°F)	Discharge (cf)	Median Air Temp. (°F)
Annual	1.32E+09	61	8.27E+08	62
Wet Season	1.26E+09	54	7.84E+08	55
Dry Season	6.78E+07	69	4.27E+07	67

Dissolved oxygen concentrations averaged 7 mg L^{-1} during the Bight '08 field study, with instantaneous concentrations below 5 mg L^{-1} , a level considered biologically stressful, approximately 23% of the time during the period of record (December 2008-November 2009; Figure 2.2). The percentage of time below 5 mg L^{-1} was slightly higher during the summer (25%) versus winter (19%), coincident with higher water temperatures, reduced tidal exchange and decreased freshwater flow (Figure 2.1). Concentrations of < 5 mg L^{-1} typically occurred in pre-dawn hours and coincided with periods of low tidal flushing during neap tidal cycles (Figure 2.3).

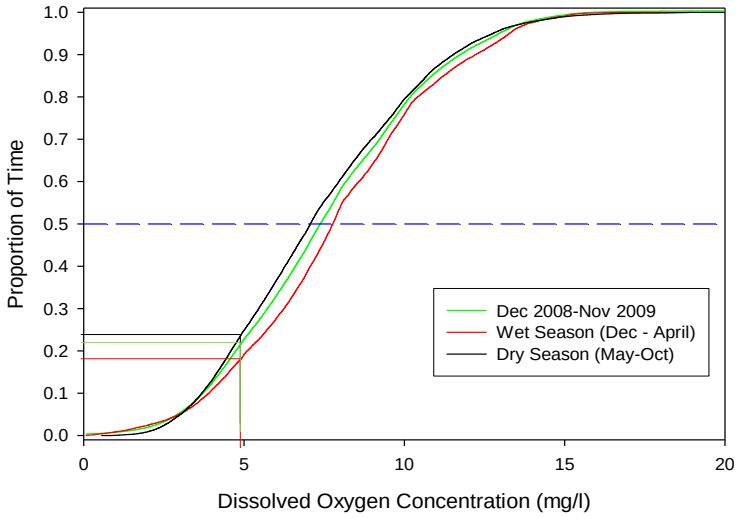


Figure 2.2. Cumulative frequency distribution of dissolved oxygen concentration annually (black line), during wet season (Dec-Apr) and during dry season (May-Oct) at Segment 1 during the Bight '08 study (2008-2009).

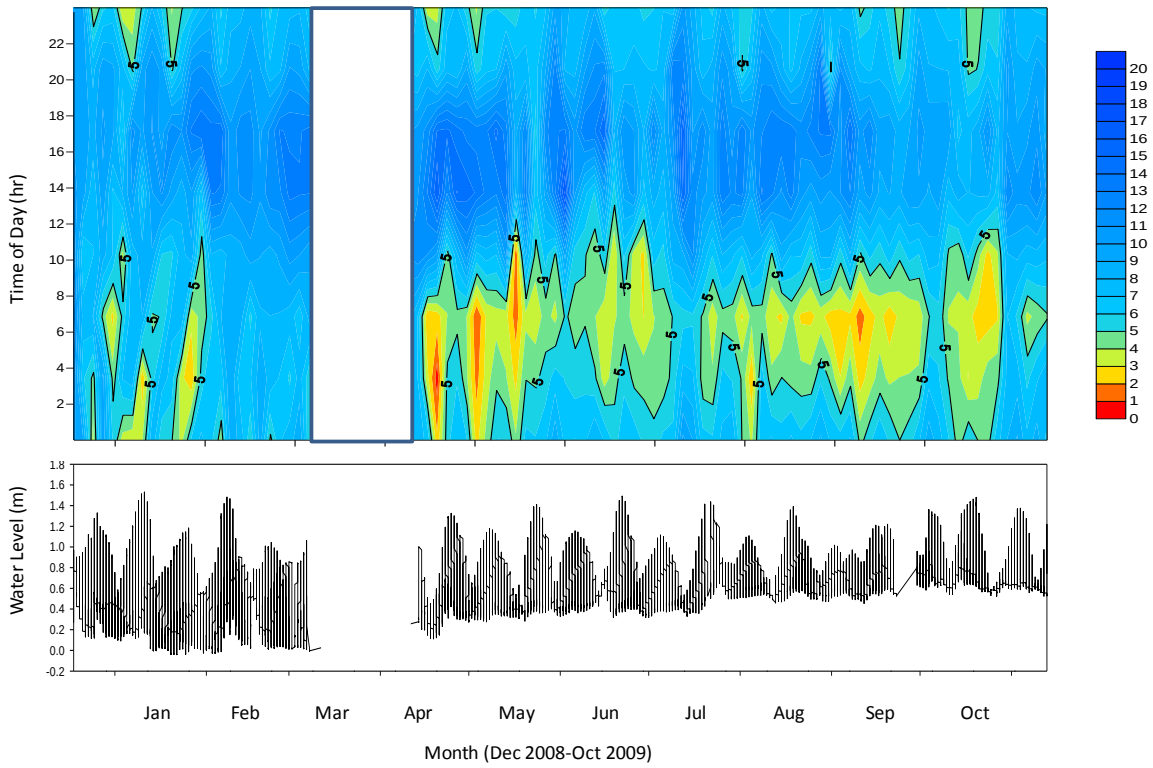


Figure 2.3. Contour plot (top panel) of Segment 1 DO by month (x axis) and time of day (y axis) relative to water level (bottom) during the Bight '08 study. Legend on right shows color key for DO concentration. Contour line represents concentrations <5 mg L^{-1}.

During the 2007-2008 field study, several consistent patterns emerged with respect to ambient wet and dry weather N concentrations (Table 2.2; Figure 2.4). First of all, average wet weather TN concentrations (151±41 µM or 2.1±0.5 mg L^{-1} TN) were almost always lower than dry weather concentrations (234 ±273 µM or 3.3±3.6 mg L^{-1} TN). During wet weather, TN concentration ranged from 152 to 159 µM (2.1 to 2.2 mg L^{-1}) at the ME site, and 97 to 231 µM (1.4 to 3.2 mg L^{-1}) at the estuary segment sites. These values are significantly above basin plan objectives for TN (1 mg L^{-1}). During this time, the ME site generally had higher NH_4 content (16%) than the Segment sites (2 to 6%), while Nitrate+Nitrite (NO_3+NO_2) concentrations generally ranged from 48 to 77% of TN among ME and Segment sites.

During dry weather during the 2008-2009 study, TN had similar average values to the 2007-2008 study but wider ranges. Total nitrogen at the ME station ranged 23 to 223 µM (0.32 to 3.1 mg L^{-1}) TN, while within the estuary, the range was greater, 57 to 971 µM (0.8 to 13.6 mg L^{-1}) TN. During this time, ME station TN was always lower than Segment 1 concentrations (downstream) by roughly a factor of 5, and roughly equal to Segment 2 concentrations. This pattern was also typical of NH_4 and NO_3+NO_2. Dry weather ME and estuary Segment 1 stations generally had lower NH_4 content (3 to 6% TN) relative to Segment 2 (23% TN), while NO_3+NO_2concentrations ranged from 33 to 65% of TN among ME and estuary sites. In general, the higher NH_4 (23 µM) and low NO_3+NO_2 (16 µM) were observed at estuary Segment 2 (upstream of I-5 bridge) during the end of the dry season (July and September 2008;) while Segment 1 (downstream of I-5 bridge) had opposite trends (5 µM NH_4 and 67 µM NO_3+NO_2).

Table 2.2. Mean and standard deviation of Total Nitrogen (TN), Ammonium (NH_4), and Nitrate+Nitrite (NO_3+NO_2) concentrations in wet (storm) and dry (index) weather periods for ME, Segment 1 (Upstream), and Segment 2 (Downstream). All concentrations in µM.

Event	Site	Date	TN	NH_4	NO_3+NO_2
Storm 1	ME	1/5/2008	152.0±123.2	0.9±0.6	84.1±93.7
	Seg 2	1/5/2008	142.8±62.6	11.5±4.8	67.5±56.5
	Seg 1	1/5/2008	122.9±68.3	1.7±1.4	90.0±56.6
Storm 2	ME	1/27/2008	159.7±28.0	48.7±45.3	90.4±23.8
	Seg 2	1/27/2008	97.3±17.2	2.9±0.0	47.9±0.0
	Seg 1	1/27/2008	231.8±11.0	6.3±0.0	189.1±0.0
Index 1	ME	1/31/2008	223.8±40.2	2.2±1.9	194.3±43.4
	Seg 2	1/31/2008	205.4±11.7	15.1±16.1	166.6±27.6
	Seg 1	1/31/2008	971.1±1246.4	20.3±12.8	831.5±845.4
Index 2	ME	3/24/2008	80.1±10.5	10.3±12.5	52.7±3.0
	Seg 2	3/24/2008	60.5±9.4	8.0±5.7	26.9±12.2
	Seg 1	3/24/2008	566.0±906.4	12.5±11.0	518.6±909.8
Index 3	ME	7/21/2008	23.2±3.6	0.6±0.3	0.6±0.0
	Seg 2	7/21/2008	61.3±9.3	12.9±19.2	1.5±0.8
	Seg 1	7/21/2008	164.0±60.3	5.0±2.8	95.5±37.3
Index 4	ME	9/23/2008	No data		
	Seg 2	9/23/2008	57.1±9.6	29.8±19.3	1.6±0.7
	Seg 1	9/23/2008	164.9±147.8	5.6±6.6	37.5±48.5

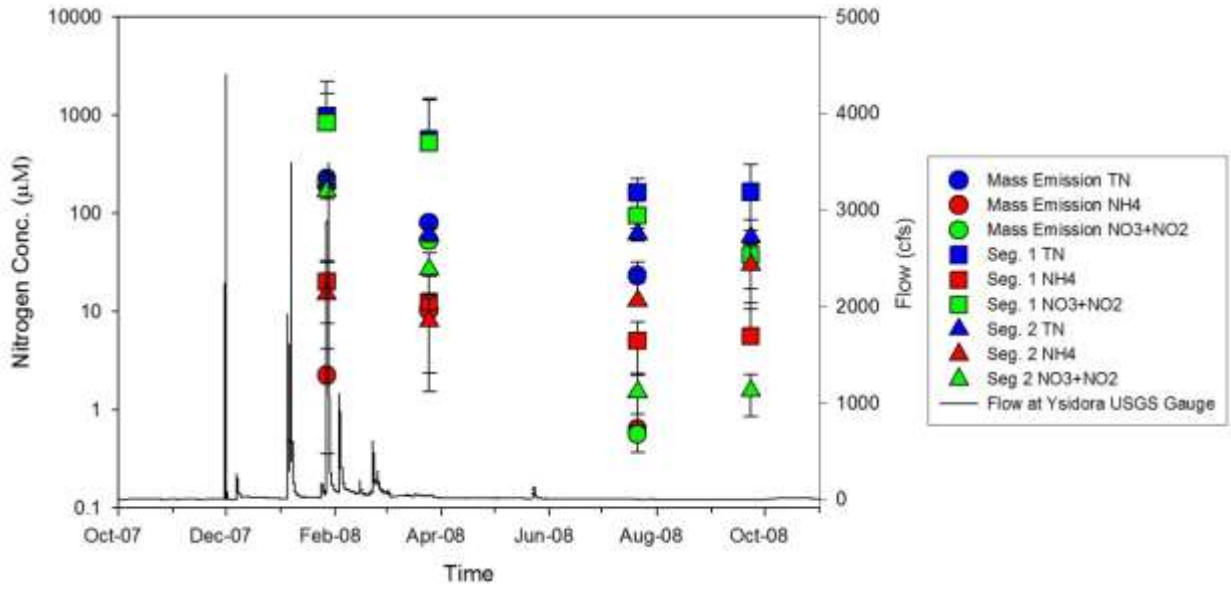


Figure 2.4. Mean and standard deviations of concentrations of TN (blue), NH_4 (red) and NO_3+NO_2 (green) at ME (circle), Segment 1 (upstream, square), and Segment 2 (downstream, triangle) as a function of freshwater flow at Ysidora USGS Station (black line)during dry weather index periods. No data were available for ME during Index period 4 (September 2008). Data from CDM (2009).

Several consistent patterns also emerged with respect to ambient wet and dry weather P concentrations during the 2007-2008 field study (Table 2.3; Figure 2.5). First of all, wet weather average TP

concentrations (8.0±2.3 µM or 0.25±0.1 mg L^{-1} TP) were generally equivalent to dry weather concentrations (7.3 ±4.3 µM or 0.23±0.1 mg L^{-} TP). During wet weather, TP ranged from 6 to 10 µM (0.2 to 0.3 mg L^{-1}) at the Mass Emission site, and 5 to 11 µM (0.2 to 0.3 mg L^{-1}) at the Segment sites. Similar to TN, these values are significantly greater than the Basin Plan objective of 0.1 mg L^{-1} TP. During this time, the ME site generally had a lower SRP content (44% of TP) than the estuary segment sites (60 to 80% of TP), indicating that the particulate fraction was higher at the ME site.

During 2008-2009 dry weather index periods, ME station TP ranged 4 to 6 µM (0.1 to 0.2 mg L^{-1}), while within the estuary, the range was greater (4 to 19 µM or 0.1 to 0.6 mg L^{-1}TP). During the winter and spring index periods, ME station TP was half of that of Segment 1 concentrations (downstream of I-5 bridge) and roughly equal to Segment 2 concentrations (upstream of I-5 bridge). This pattern was also typical for SRP. During the summer and fall index periods, Segment 2 had the highest concentration of TP and SRP, with concentrations two to five times higher than the ME site. During dry weather, the ME and Segment sites generally had SRP concentrations as a percent of TP within the same range (58 to 60% of TP).

Table 2.3. Mean and standard deviation of TP and SRP concentrations in wet (storm) and dry (index) weather periods at ME, Segment 1 (Upstream) and Segment 2 (Downstream). All concentrations in µM.

Event	Station	Date	TP	SRP
Storm 1	ME	1/5/2008	6.3±4.1	3.0±1.5
	Seg 1	1/5/2008	5.4±2.4	4.1±1.9
	Seg 2	1/5/2008	8.7±0.6	6.1±0.3
Storm 2	ME	1/27/2008	10.3±4.4	4.2±2.1
	Seg 1	1/27/2008	10.5±11.7	4.8±0.0
	Seg 2	1/27/2008	6.8±4.8	7.2±0.0
Index 1	ME	1/27/2008	4.3±1.1	3.5±1.0
	Seg 1	1/27/2008	9.2±6.2	6.5±1.2
	Seg 2	1/27/2008	4.5±0.9	3.1±0.9
Index 2	ME	3/24/2008	4.3±0.5	1.9±0.7
	Seg 1	3/24/2008	9.4±7.5	6.7±5.8
	Seg 2	3/24/2008	4.3±0.7	1.7±0.6
Index 3	ME	7/21/2008	6.4±0.9	3.0±0.4
	Seg 1	7/21/2008	5.4±0.5	2.7±0.9
	Seg 2	7/21/2008	9.3±2.0	4.7±2.0
Index 4	ME	No data		
	Seg 1	9/23/2008	4.3±0.7	1.8±1.0
	Seg 2	9/23/2008	19.3±7.2	16.1±10.2

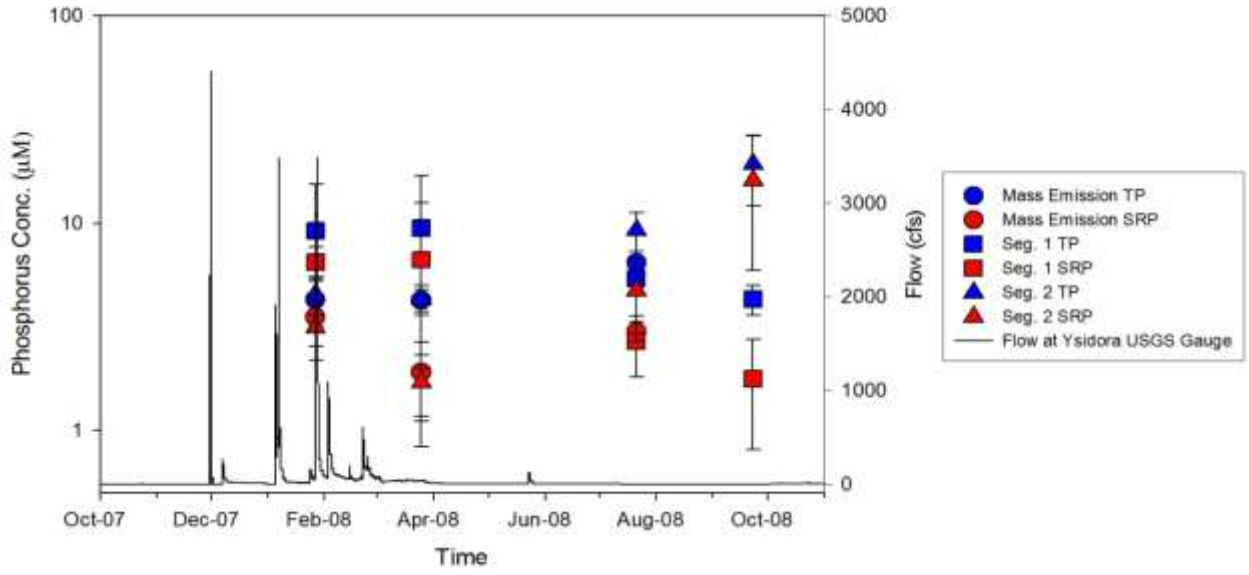


Figure 2.5. Mean and standard deviations of concentrations of TP (blue) and SRP (red) at ME (circle), Segment 1 (upstream, square), and Segment 2 (downstream, triangle) as a function of freshwater flow at Ysidora USGS Station (black line) during dry weather index periods. Data from CDM (2009).

Spatially, trends were visible along a longitudinal gradient in the SMRE (Figures 2.6 and 2.7) and were consistent with trends observed during daily index period samples (Table 2.3 and 2.4). During flood tides, concentrations of TP and SRP increase from near the mouth upstream for most index periods (Figure 2.7). These patterns are less clear, but still visible during ebb tides (Figure 2.6). Slight increases in upstream are visible with TN and dissolved inorganic nitrogen (DIN = NH_4 and NO_3+NO_2) for the spring index period and for TN during the fall index period.

Mixing diagrams (plots of salinity relative to nutrient concentrations) are helpful in interpreting the extent to which freshwater versus marine endmembers are the primary source of nutrient and to what extent within estuary sources (e.g. storm drains, groundwater, benthic flux, biological release) or sinks (benthic flux, denitrification, biological uptake) are visible. Figures 2.8 and 2.9 show that for January 2008 index period, NO_3+$NO_2$and SRP drive the overall patterns in TN and TP respectively, and that in both cases there appears to be a source of these NO_3+$NO_2$and SRP in the 0 to 5 ppt region, while NH_4 appears to have a source in the 10 to 20 ppt region of the estuary.

During the March index period, NO_3+NO_2drives trends in TN, which increases towards the freshwater endmember. Nitrate+nitrite appears to be fairly conservative over the salinity gradient. However, production of NH_4 appears to be occurring over the 0 to 30 ppt range. SRP and TP likewise show an increase towards the freshwater endmember, with a slight convex shape indicating production in the zone 0 to 15 ppt.

During both the July and September 2008 index period, the salinity range was limited because of little to no freshwater input. Total Nitrogen decreased slightly with increasing salinity, with mmonia appeared to drive TN concentrations, with a zone of production in 32 to 36 ppt. In contrast, NO_3+NO_2 concentrations were generally flat, indicating a sink, with the exception of production around 32 to 36 ppt. SRP and TP showed similar trends to TN, with a zone of production likewise around 32 to 36 ppt.

Table 2.4. Analyte data for the estuary site and ME site collected during the Bight '08 study.

Sample Date	Site	Analyte (uM)							
		SRP	NO_2	NO_2+ NO_3	NH_4	TN	TP	TDN	TDP
11/24/08	Estuary	5.2	0.1	1.4	3.4	53.7	8.2	38.5	6.2
2/3/09		2.6	ND	0.9	1.5	17.0	4.3	15.7	3.7
3/23/09		3.1	0.1	0.3	0.6	39.9	4.7	24.1	5.1
5/18/09		0.4	ND	0.4	0.2	90.0	11.3	21.4	3.6
6/26/09		4.5	ND	0.6	0.5	33.2	13.4	25.1	10.0
9/18/09		0.4	ND	2.5	0.6	21.7	11.1	15.6	10.3
11/24/08	ME					70.9	8.2		
2/3/09						22.0	4.1		
3/23/09						21.7	2.4		
5/18/09						144.3	2.9		
6/26/09						29.8	10.2		
9/18/09		10.1	ND	ND	0.9	35.4	15.0	13.7	10.6

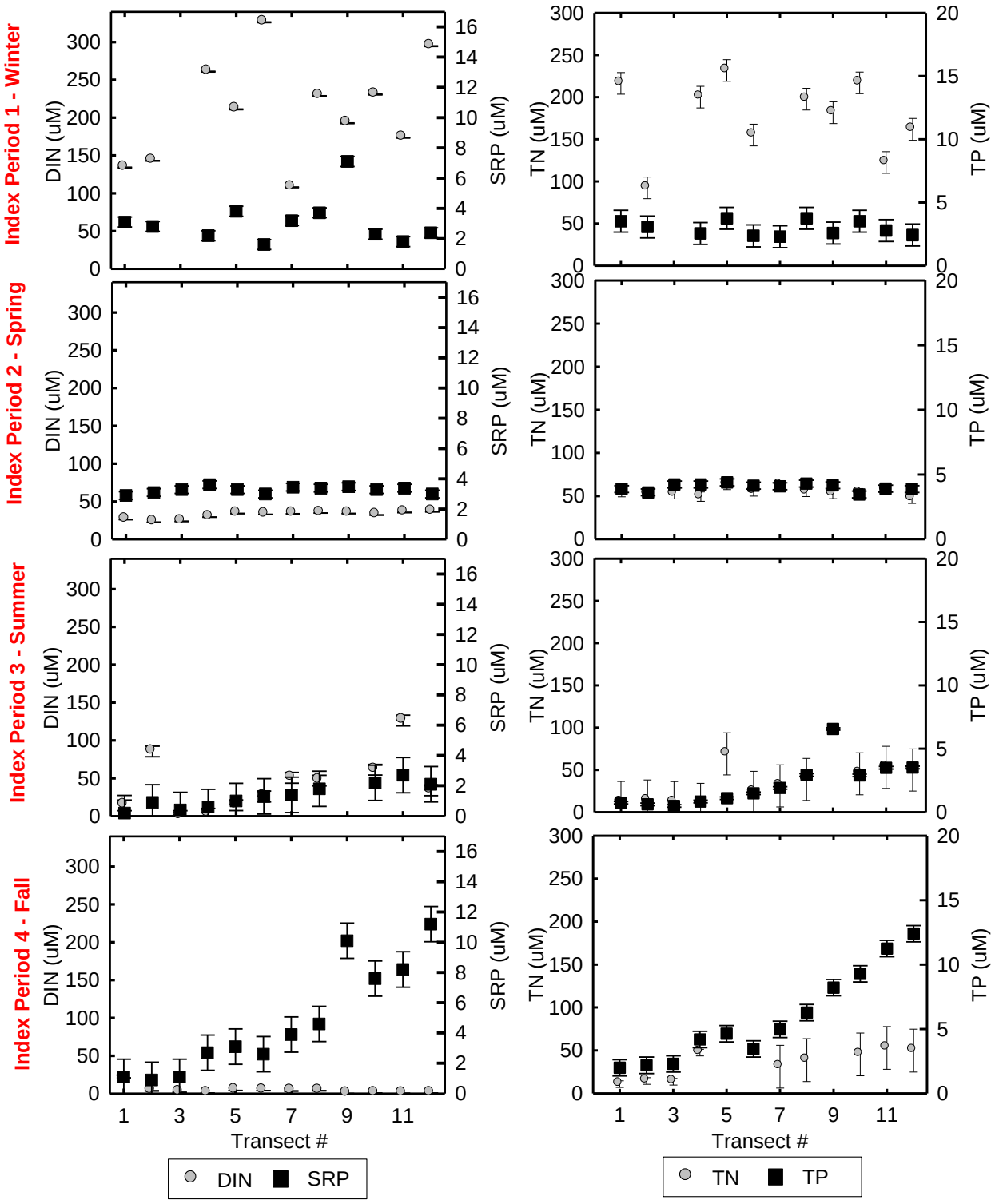


Figure 2.6. Ebb-tide concentrations of N and P along longitudinal transect during dry weather index period. Station numbers are begin at station 1 (proximal to ocean mouth) and terminate at Segment 2 site (Station 12; see Figure 1.1).

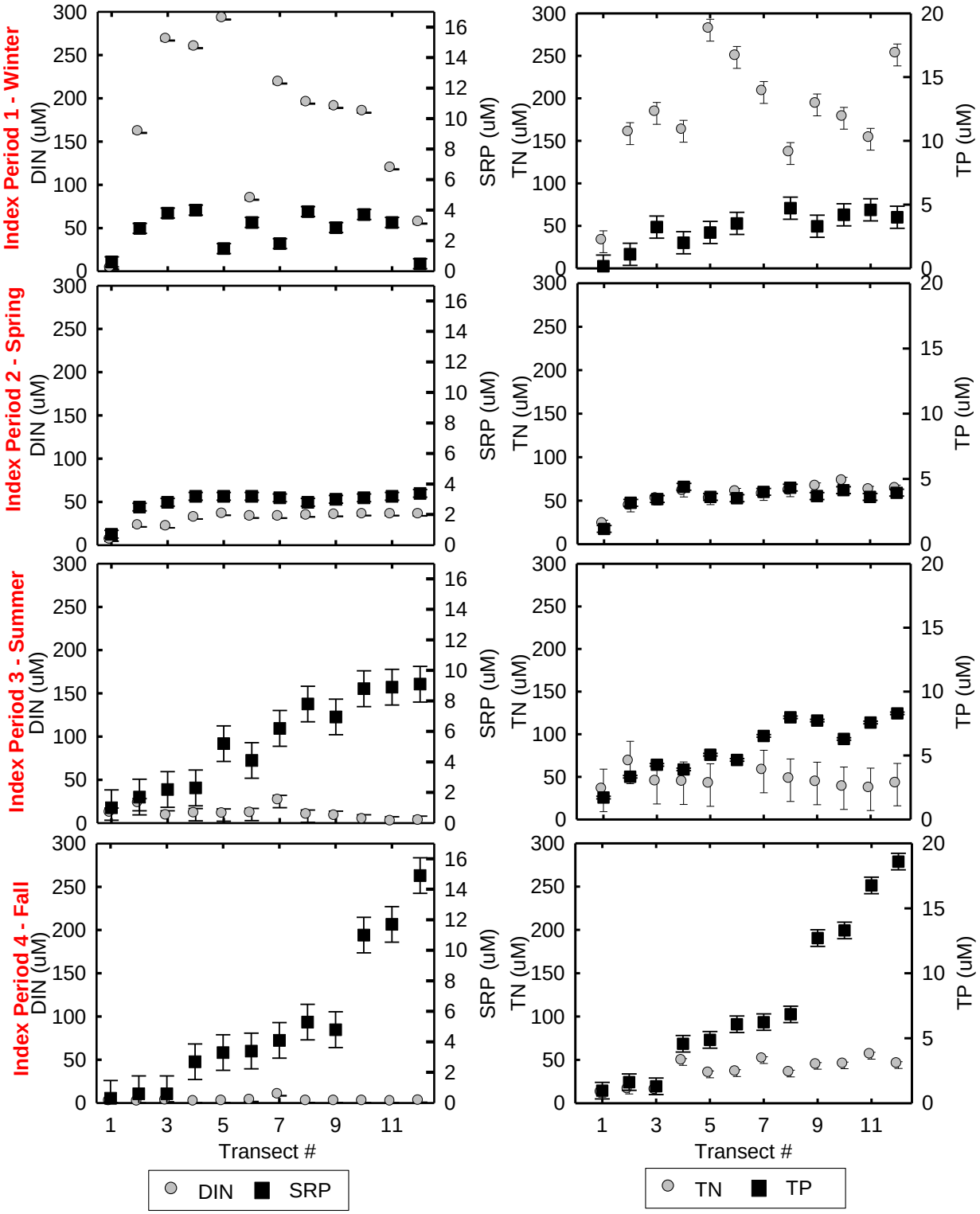


Figure 2.7. Flood-tide concentrations of N and P along longitudinal transect during dry weather index period. Station numbers are begin at station 1 (proximal to ocean mouth) and terminate at Station 12 (Segment 2; see Figure 1.1).

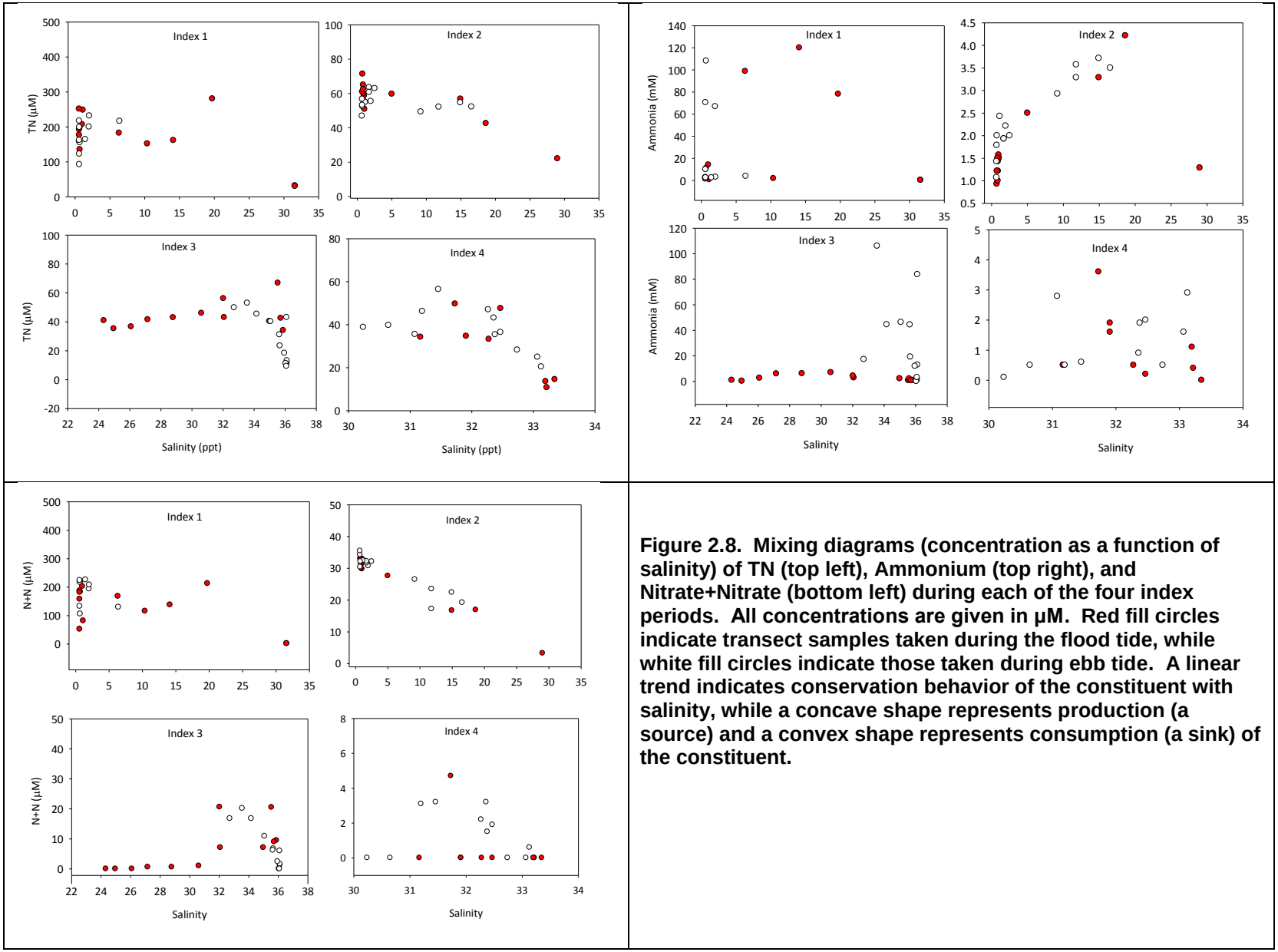


Figure 2.8. Mixing diagrams (concentration as a function of salinity) of TN (top left), Ammonium (top right), and Nitrate+Nitrate (bottom left) during each of the four index periods. All concentrations are given in µM. Red fill circles indicate transect samples taken during the flood tide, while white fill circles indicate those taken during ebb tide. A linear trend indicates conservation behavior of the constituent with salinity, while a concave shape represents production (a source) and a convex shape represents consumption (a sink) of the constituent.

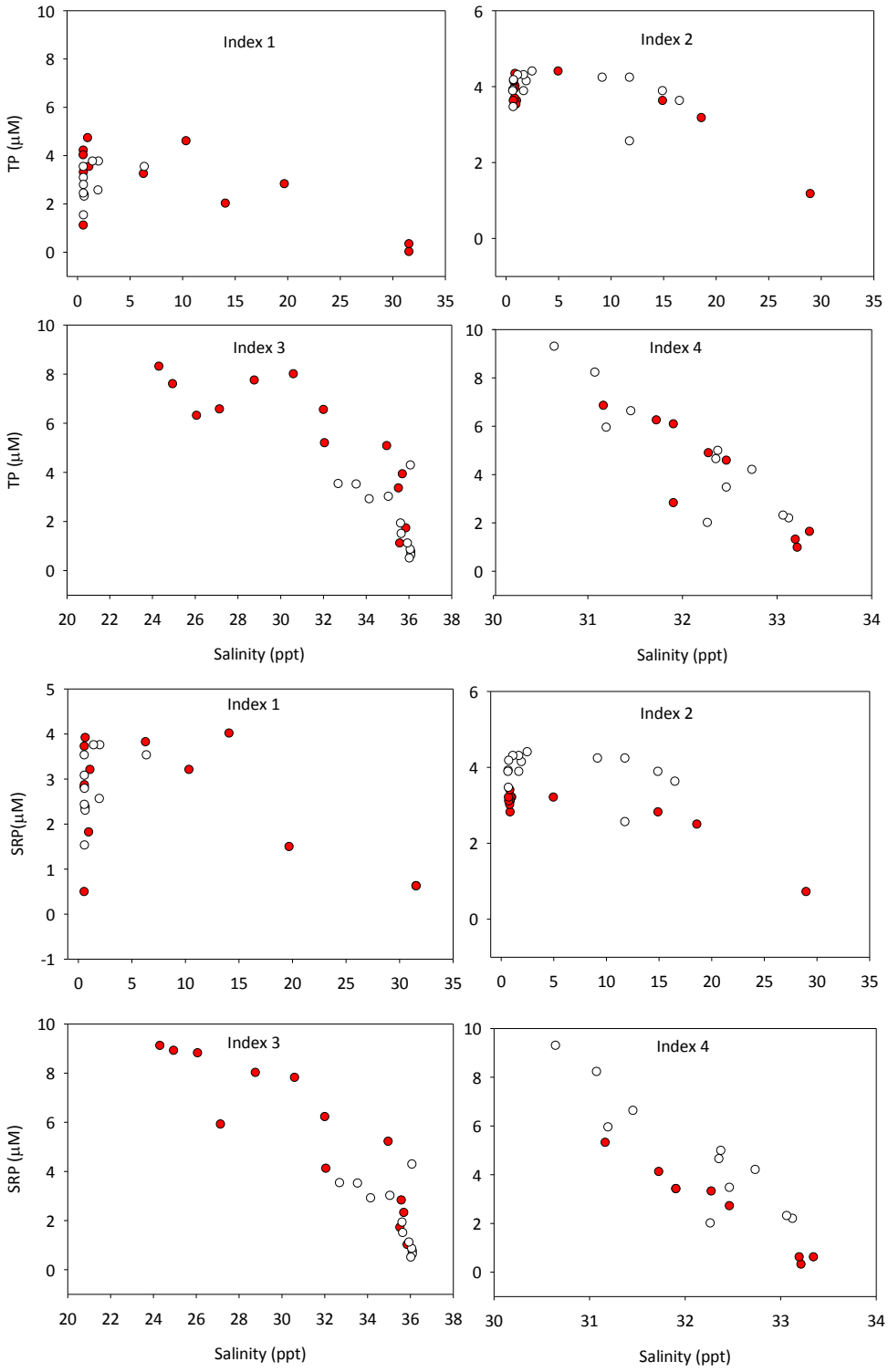


Figure 2.9. Mixing diagrams of TP (top) and SRP (bottom) concentration (µM) during each of the four index periods. Red fill circles indicate transect samples taken during the flood tide, while white fill circles indicate those taken during ebb tide. A linear trend indicates conservative mxing of the constituent with salinity, while a concave shape represents production (a source) and a convex shape represents consumption (a sink).

2.3.2 Seasonal Trends in Primary Producers

This study assessed seasonal trends in biomass and or percent cover of three aquatic primary communities:

- phytoplankton (measured as suspended chl a)
- macroalgae and cyanobacterial mats (biomass and percent *c*over)
- microphytobenthos (MPB; measured as benthic chl a)

A fourth community, SAV, was not observed in the SMRE.

Figure 2.10 shows the comparative biomass of phytoplankton, macroalgae and MPB, standardized to mass of carbon (C) per unit area by 2008 sampling period for Segments 1 and 2; Figure 2.11 shows interannual variation in carbon biomass between TMDL and Bight '08 studies. Biomass and cover between the two sampling years was similar (Table 2.5). Overall, carbon attributable to phytoplankton biomass was insignificant relative to macroalgal and MPB biomass. During the winter index period, no biomass or cover of macroalgae was observed. By the spring index period, MPB dominated the aquatic primary producers. A shift towards dominance by macroalgae and cyanobacterial mats occurred during summer and fall, with peak macroalgal biomass (238±88 g dry wt m^{-2} or 1465 ±548 g wet wt m^{-2}) and percent cover (100%) at Segment 1 during the September 2008 index period and peak biomass (44 g dry wt m^{-2}) at Segment 2 during July 2008 (Figure 2.12). This pattern was generally repeated during the 2008-2009 Bight '08 field survey (Figure 2.11, albeit with lower peak concentrations of macroalgae during the summer 2009 (94 g dry wt m^{-2}).

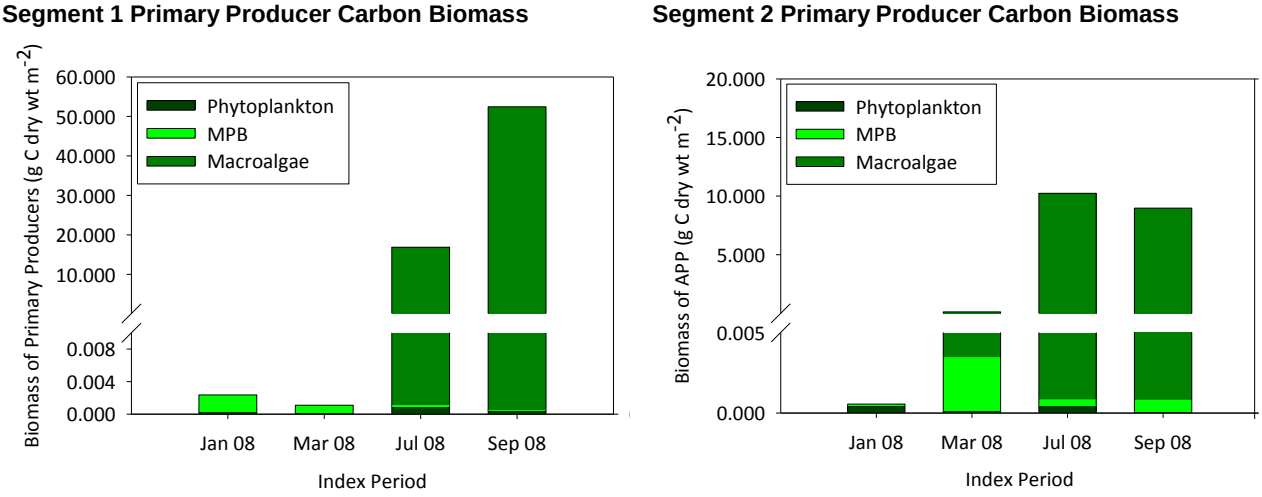


Figure 2.10. Areal mass of carbon associated with three types of aquatic primary producers (APP) observed Segment 1 in SMRE: phytoplankton, microphytobentos (MPB), and macroalgae.

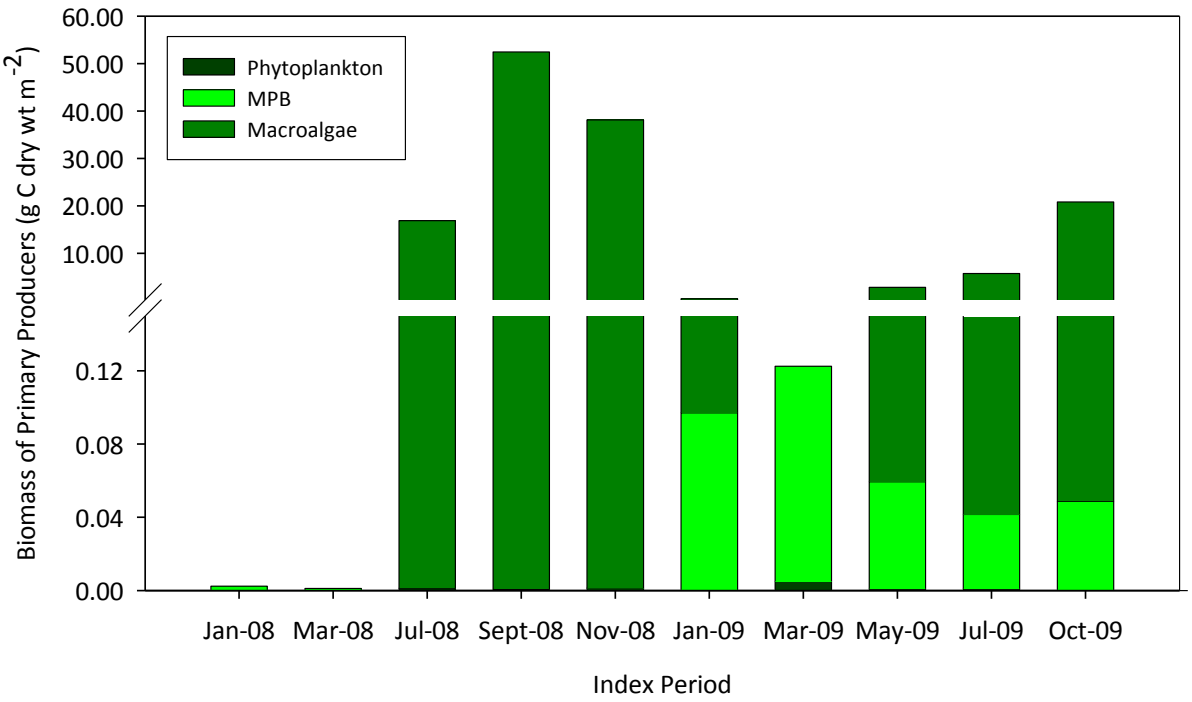


Figure 2.11. Comparison of areal mass of carbon associated with three types of primary producers observed at Segment 1 during TMDL and Bight '08 field studies (Jan 2008-October 2009). Note that microphytobenthos (MPB) were sampled at different elevations during the TMDL field studies (100 cm below MLLW) and Bight '08 study (30 cm above MLLW). Macroalgal biomass and phytoplankton biomass were sampled in using comparable methods.

Table 2.5. Comparison of wet macroalgal biomass and percent cover at Segment 1 during TMDL and Bight '08 studies.

Study	Time Period	Wet Macroalgal Biomass (Mean ± SD) g m^{-2}	% Cover (Mean ± SD)
TMDL Field Study	**Jan-08**	0	0
	Mar-08	0	0
	Jul-08	196±181	82±17
	Sept-08	1465±548	100±0
Bight 08 Study	**Nov-08**	1310±1498	93±14
	Jan-09	10±9	1±3
	Mar-09	30±23	3±4
	May-09	90±128	4±10
	Jul-09	218±24	22±30
	Oct-09	1714±118	33±23

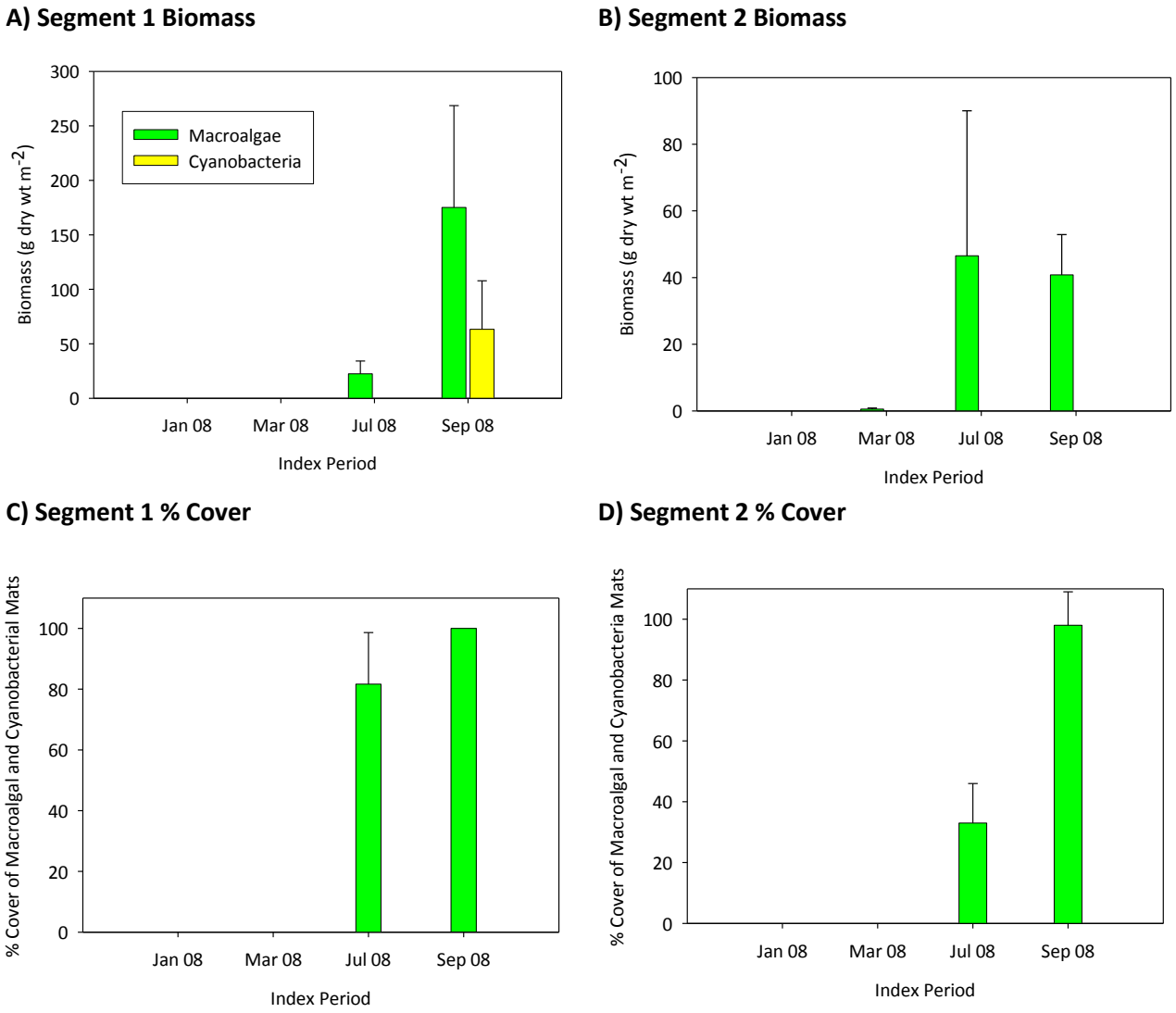


Figure 2.12. 2008 macroalgal and cyanobacterial mat biomass (top panels) and % cover (bottom panels) on intertidal flats for Segment 1 (A and C) and Segment 2 (B and D) by index period.

Microphytobenthos biomass appeared to be higher during the Bight '08 study (peak biomass of 3500 mg chl a m^{-2}) than during the TMDL field study (peak biomass of 62 mg chl a m^{-2}) , though sampling methods among the two studies were conducted at different water depths, making a true comparison difficult (Figure 2.13).

During the 2008 TMDL studies, phytoplankton biomass was highest during summer 2008, with mean values of 11.0 mg m^{-3} and 5.6 mg m^{-3} (Figure 2.14). During the Bight '08 study, phytoplankton biomass peaked in early spring (60 mg m^{-3}), but remained fairly constant throughout the rest of the year. On average, Segment 1 showed slightly higher concentrations of chl a than Segment 2.

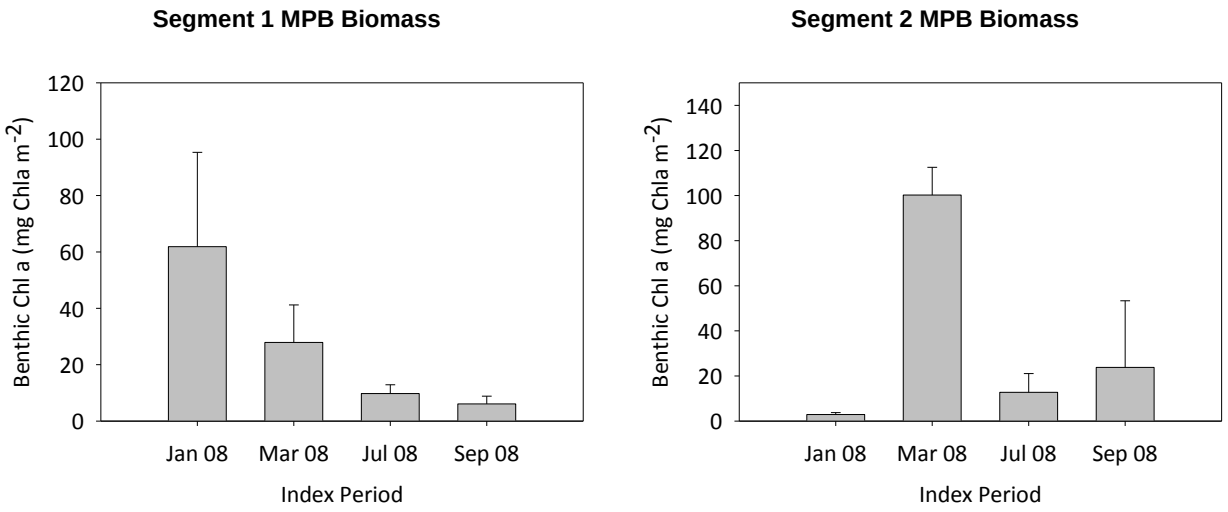


Figure 2.13. Segments 1 and 2 microphytobenthos (MPB; chl abiomass) by index period.

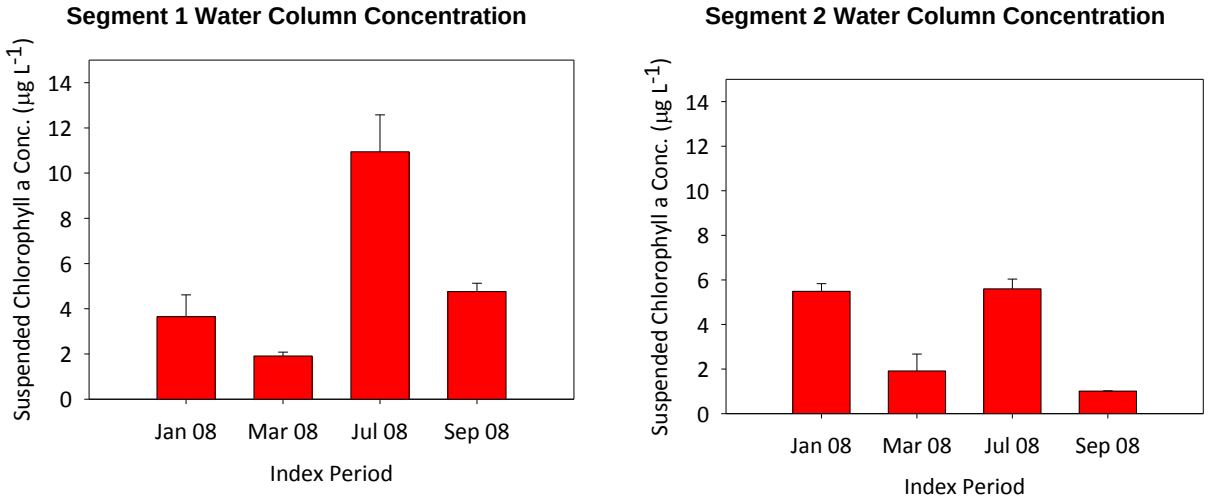


Figure 2.14. Segments 1 and 2 water column chlorophyll a concentrations by index period.

2.3.3 Seasonal Variation in Sediment Grain Size and Total Organic Carbon, Nitrogen and Phosphorus Characteristics by Index Period

Large differences were observed in sediment grain size, total OC, and total nutrient between Segment 1 and 2 (Figure 2.15 and 2.16). Segment 1 generally had higher fractions of fine-grained sediments (mean of 43±22 with ranges of 20 to 55% fines at surface; 5 to 80% fines at depths from 4 to 10 cm). In contrast, Segment 2 sediments were coarse, with mean % fines of 5±8 with ranges of 1 to 30% fines at surface; 0.5 to 3% fines at depths from 4 to 10 cm). As a result, sediment %OC and sediment total nutrients also followed this general trend; Segment 1 sediment %OC, %TN, and %TP (means of 0.8 ±0.5, 0.10 ±0.07, and 0.05 ±0.07% respectively) was higher than that of Segment 2 (0.2 ±0.3, 0.007 ±0.03, and 0.02 ±0.01% respectively), particularly with respect to N content. Ninety-two percent of Segment 2

samples were non-detect for sediment N. Sedment %TP content was unusually high for some samples in Segment 2 (0.04 to 0.09 %TP, given the near zero sediment OC content and percent fines.

Vertically sediment TP content decreased consistently with depth for both Segment 1 and Segment 2 during all index periods, but this was not the case with % OC or %TN. From sampling period to sampling period, sediments at Segment 1 were much more variable in bulk characteristics than Segment 2 sediment. There were no consistent seasonal trends in bulk sediment characteristics over time in either Segment 1 or Segment 2.

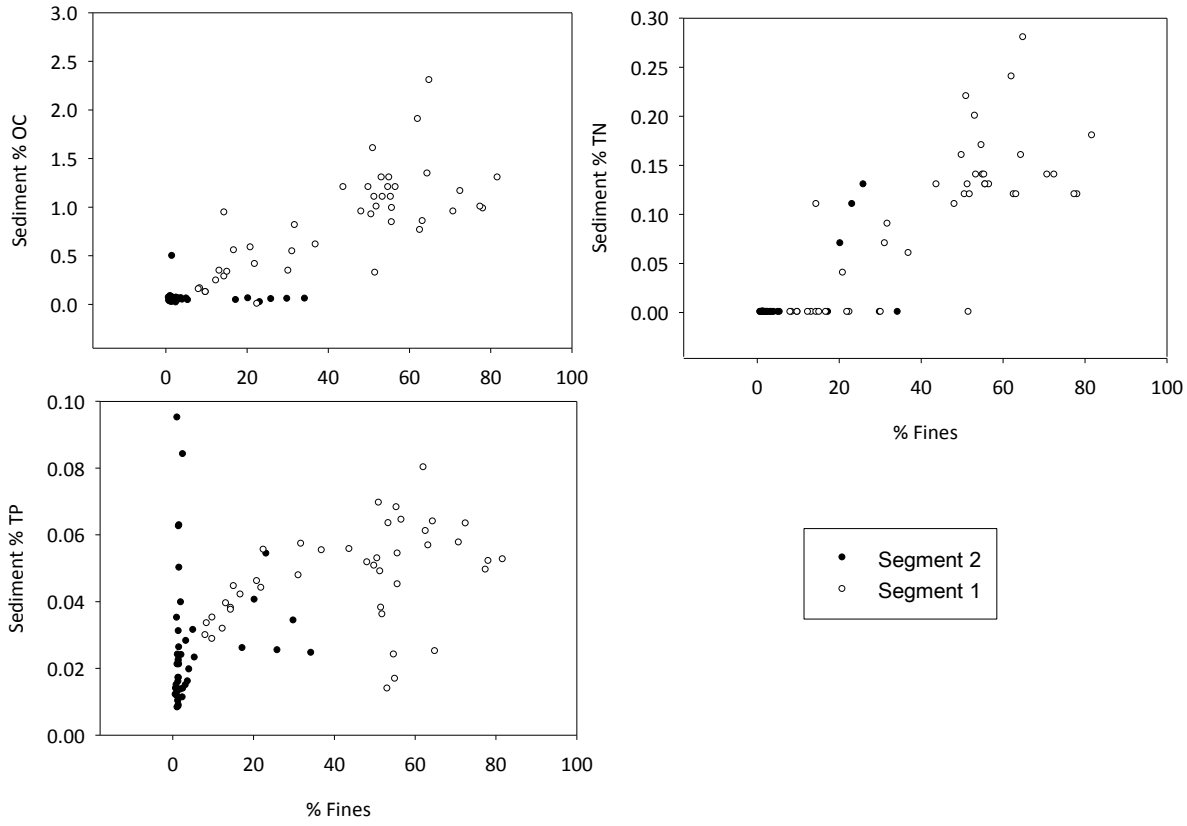


Figure 2.15. Relationship between Sediment %OC, %TP and %TN as a function of grain size at Segment 1 (open circles) and Segment 2 (closed circles).

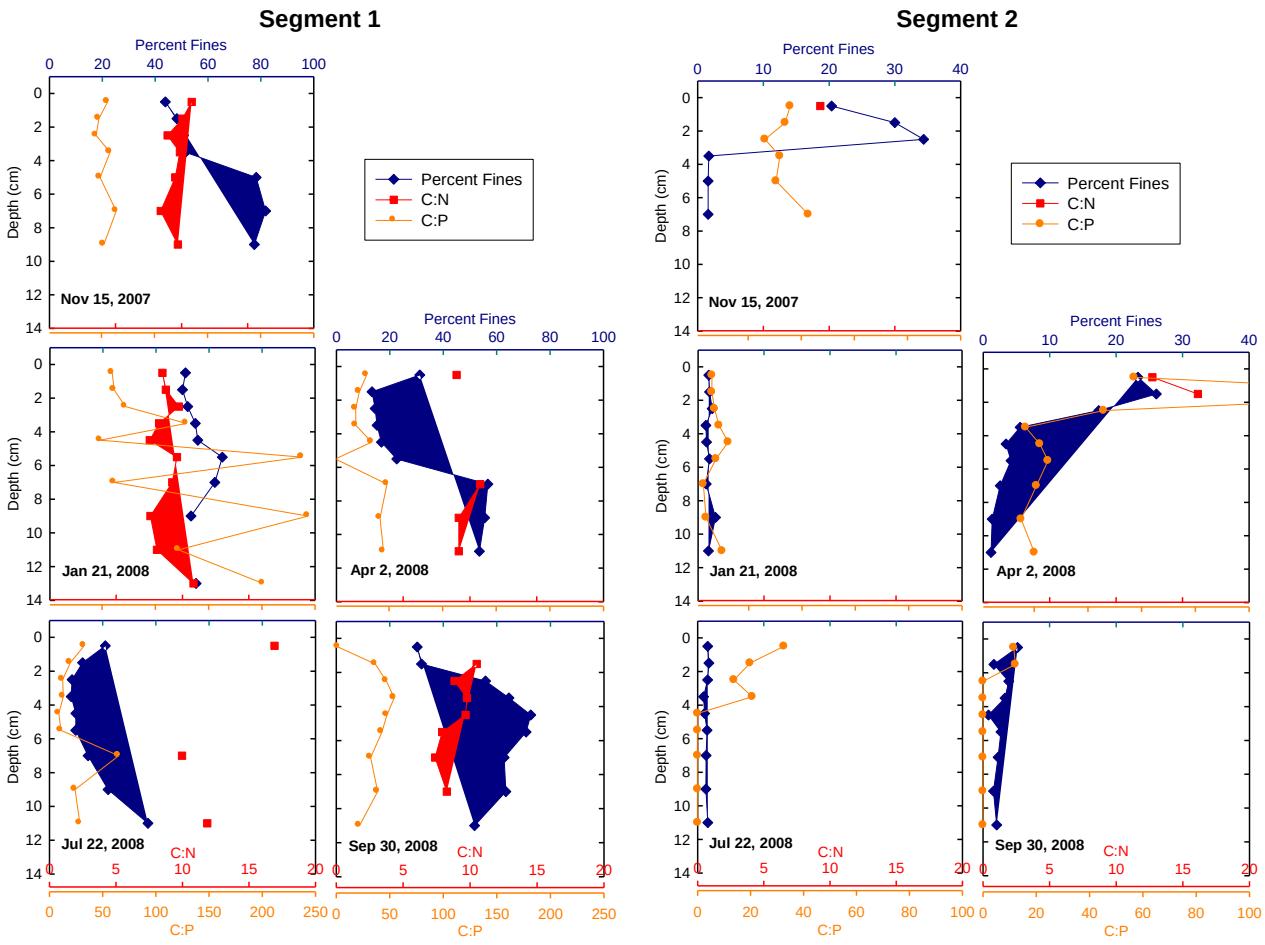


Figure 2.16. Segment 1 and Segment 2 sediment grain size (as percent fines, ♦), carbon:nitrogen (C:N, ■), and carbon:phosphorus (C:P, ●) core ratios for November 16, 2007, and core ratiosfor each 2008 index period. Note difference in X- axis scale for Segment 1 and Segment 2 C:P and C:N core ratio by index period plots.

2.3.4 Seasonal Trends in Sediment Deposition

Sediment deposition and removal events were measured using the particle tracer, ^{7}Be. This cosmogenic radionuclide is produced in the upper atmosphere by spallation of O_2 and N atoms. Because ^{7}Be is particle reactive, it will adsorb to any aerosols or dust present in the atmosphere at the time of formation. These particles are scrubbed from the atmosphere during rain events or fall out slowly as dry deposition. The ^{7}Be particles can then act as particle tracer proxies for all internal sediment movement, and track the downstream flow of sediment in streams (Collis *et al.* 2006).

Total and residual inventories (top panels, Figure 2.17) and new inventories (bottom panels, Figure 2.17) are shown for both stations in the SMRE. Segment 2 was a sandy streambed and retained less ^{7}Be signal, while the muds at Segment 1 show strong deposition and resuspension processes throughout the year. Despite the high sand content at Segment 2, deposition and resuspension were observed for most of the year.

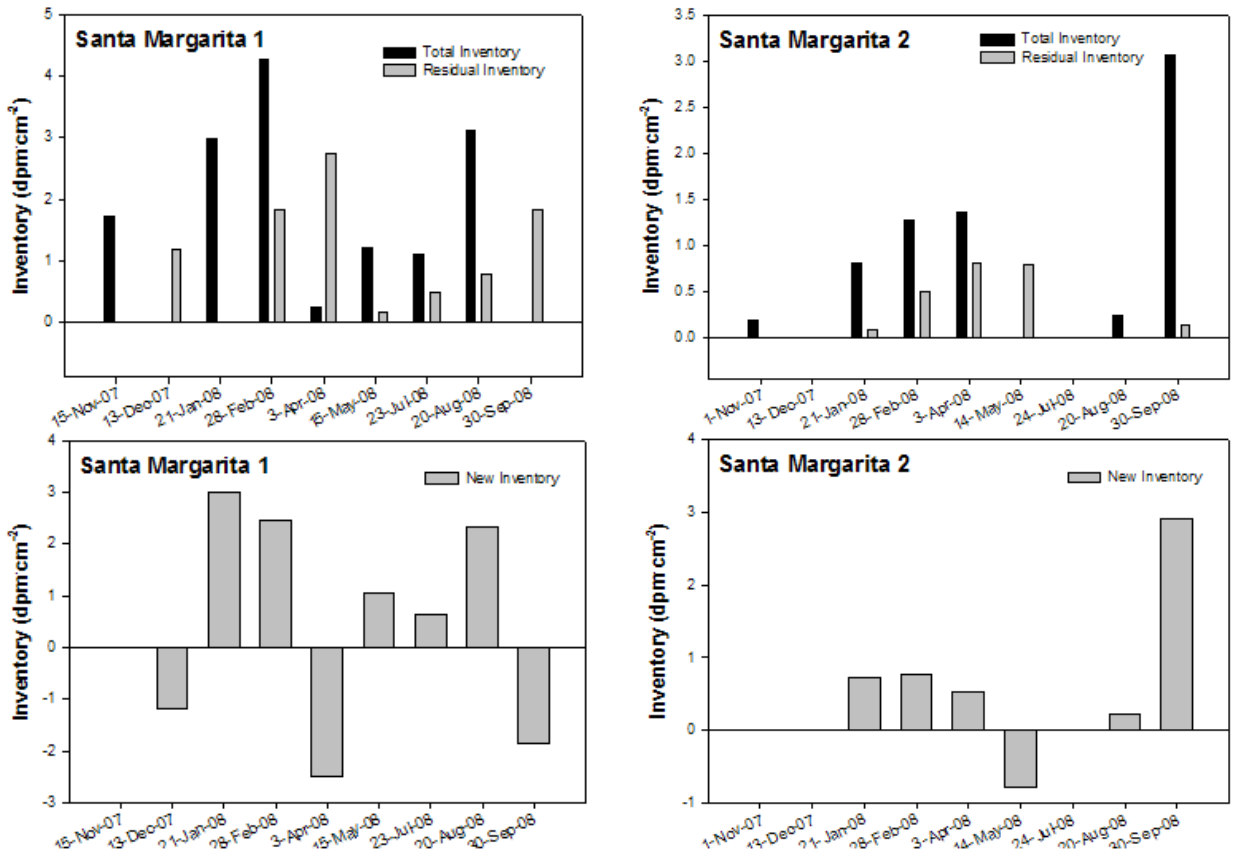


Figure 2.17. Total and residual inventories of ^{7}Be (top panels) and new ^{7}Be inventories (bottom panels) are shown versus time from November 2007 thru September 2008 for Segments 1 and 2.

Benthic sediment transport (mass flux) was quantified as the total mass of sediment deposited or resuspended for a sampling period (top panels, Figure 2.18) and a daily deposition or resuspension rate (bottom panels, Figure 2.18) for both Segment 1 and 2. The mass flux total (top) represents the amount of sediment deposited or removed between sampling trips and indicates that Santa Margarita is primarily a depositional/resuspension environment for the entire monitoring period with little erosion of the sediment bed occuring. Though because mass fluxes are not correlated with any precipitation events, it is likely that the mass fluxes primarily represent resuspension of the sandy sediment bed. The daily mass flux is the total divided by the number of days between sampling trips and is essentially as average rate. It does not account for rapid event sediment deposition or resuspension.

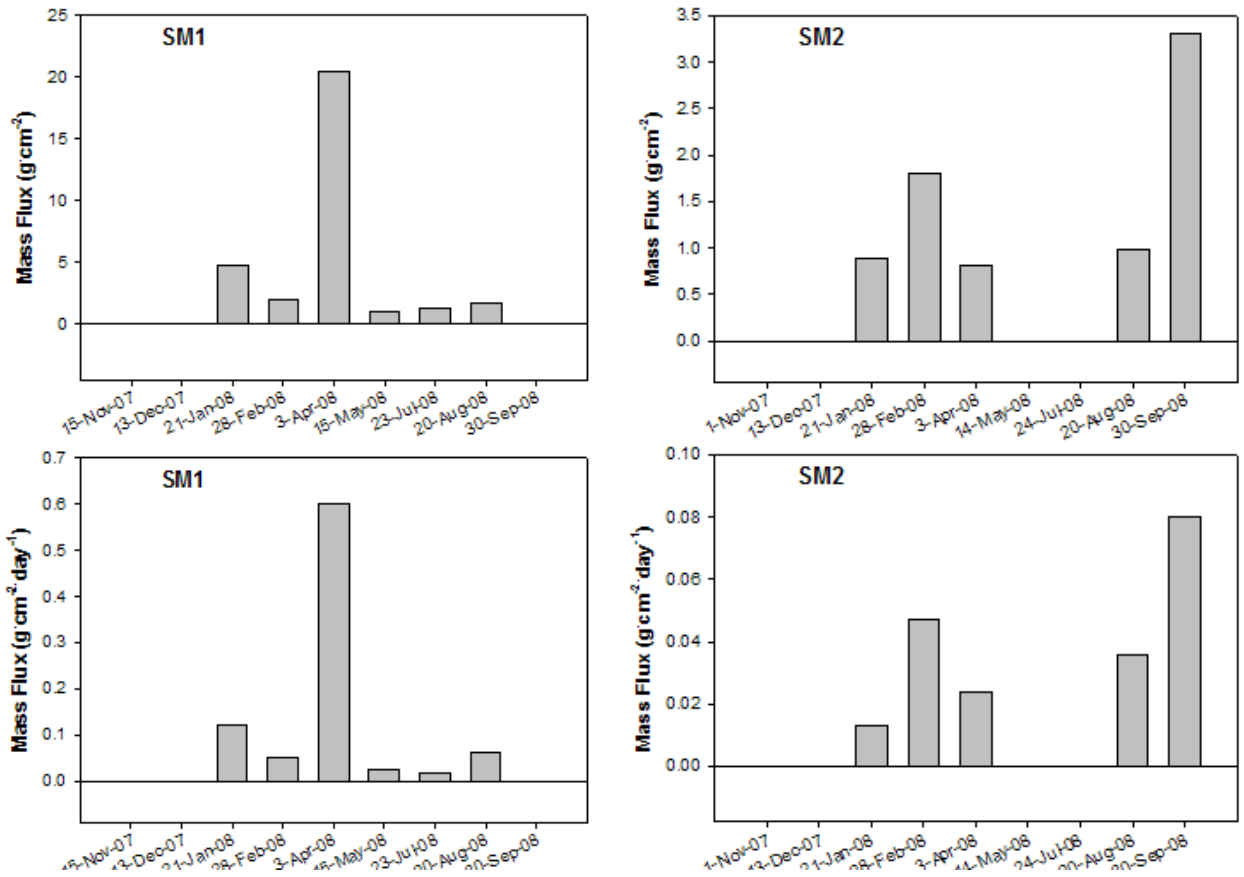


Figure 2.18. Mass flux for Segments 1 and 2 in the Santa Margarita River Estuary.

2.4 Discussion

2.4.1 Summary of Findings

This component of the study documented three major findings:

1. The SMRE seems to be exhibiting symptoms of eutrophication, as documented by high biomass and cover of macroalgae and episodes of low DO (indicators being considered by the State of California for eutrophication in estuaries), and high estuarine TN and TP concentrations.

    a. Biomass and percent cover of macroalgae were high with a mean averages of 1465 to 1714 g wet wt m^{-2} over the fall 2008 and 2009 TMDL and Bight '08 field studies and cover up to 100%. No established framework exists to assess adverse effects from by macroalgae, though a recent review (Fong *et al.* 2011) found studies documenting adverse effects of macroalgae on benthic infauna as low as 700 g wet wt m^{-2} and with cover greater than 30 to 70% and application of a European macroalgae assessment framework indicates biomass and cover in SMRE is sufficient to be considered impacted by algal overgrowth (McLaughlin *et al.* 2012).

b. Dissolved oxygen concentrations were found to be below 5 mg L^{-1} about 19% of the wintertime and 23% of the summertime.

c. Total nitrogen and total phosphorus concentrations are at or above Basin Plan objectives of TN and TP (1 mg L^{-1} and 0.1 mg L^{-1} respectively) for most sampling periods.

2. High dry season concentrations of dissolved inorganic nutrients indicate anthropogenically-enriched nutrient sources. During the summer and fall, little freshwater was delivered to the estuary, yet estuarine ambient dry season SRP and NH_4 were especially high in Segment 2 (16.1 ±10.1 µM SRP and 29.8 ±19.3 µM NH_4) and NO_3 in Segment 1 (69.4 ±29.2). Mixing diagrams (plots of salinity relative to nutrient concentrations) of transect data indicate dry season sources of NO_3, phosphate (PO_4) and NH_4, not associated with direct freshwater input. Lateral inputs of groundwater or, at Segment 2, runoff from holding ponds, may be contributing a source of nutrients to the estuary that has not been quantified.

3. Sediments in the SMRE in general were dominated by sands, with extremely low content of OC and N. Segment 1 generally had higher fractions of fine-grained sediments while Segment 2 sediments were mostly sand with very low %OC and often or non-detectable %N. Fluvially-dominanted river mouth estuaries such as SMRE have an inherent capacity to scour fine-grained sediments, thus making them less susceptible to eutrophication because particulate sources of nutrients such as watershed sediments and decaying organic matter tend to be more quickly removed.

2.4.2 Significance of Macroalgae in the SMRE

Opportunistic macroalgae are highly successful in nutrient–rich freshwater and estuarine systems. These algae typically have filamentous or sheet-like growth forms (e.g., Cladophora or *Ulva* spp.) that can accumulate in extensive, thick mats over the seagrass or sediment surface. Although macroalgae are a natural component of these systems, their proliferation due to nutrient enrichment reduces habitat quality in four ways: 1) increased respiration at night and large O_2 demand from decomposing organic matter, 2) shading and out-competing SAV and MPB (Fong *et al.* 2011), 3) impacts on the density of benthic infauna, which are a principle food source for birds and fish, and 4) development of poor aesthetics and/or odor (Fong *et al.* 1998, Kamer *et al.* 2001, Kennison *et al.* 2003).

As nutrient availability increases, it has been well-documented in many parts of the world that blooms of green or red macroalgae become dominant in shallow subtidal and intertidal estuaries and lagoons, replacing seagrass or MPB (e.g., Sfriso *et al.* 1987, 1992; Raffaelli *et al.* 1989; Valiela *et al.* 1992, 1997; Geertz-Hansen *et al.* 1993; Peckol *et al.* 1994; Marcomini *et al.* 1995; Page *et al.* 1995; Hernández *et al.* 1997; Hauxwell *et al.* 1998; Kamer *et al.* 2001). Figure 2.19 shows that as N availability increases, macroalgae become increasing dominant, eventually outcompeting MPB. Under extreme nutrient availability and in particular with higher P availability, cynanobacterial mats appear (Fong *et al.* 2011).

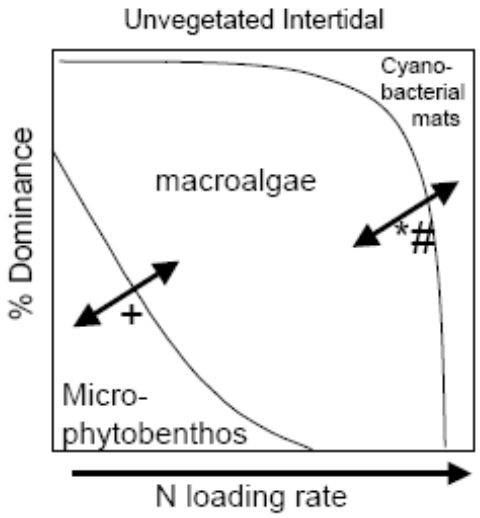


Figure 2.19. Conceptual model of the relationships between N loading rate and the community composition of primary producers in unvegetated shallow subtidal and intertidal habitat in California estuaries.

In the SMRE, the relative biomass of benthic primary producers followed a seasonal trend typical of eutrophic-hypereutrophic coastal lagoons (Fong *et al.* 1993, 1998; Kamer *et al.* 2001). During the winter index period (January 2008), flushing and scouring during storm events act together with low temperatures and light levels to inhibit growth of macroalgae. Microphytobenthos biomass peaked during the winter and spring index periods, but were relatively low in biomass (70 to100 mg chl a m^{-2}. By the summer index period, however, MPB appear to be out-competed by macroalgae *Ulva for both Segment 1 and 2,* and cyanobacteria mats appeared in Segment 1 in the fall. Biomass and percent cover of macroalgae were high with a mean averages of 1465 to 1714 g wet wt m^{-2} over the fall 2008 and 2009 TMDL and Bight '08 field studies and cover up to 100% (September–November 2008). This dominance and high standing biomass macroalgae and cyanobacteria during the summer and fall suggest that the SMRE is moderately disturbed with respect to nutrient over-enrichment (Fong *et al.* 1993).

While primary producer biomass and percent cover are useful for understanding the extent of eutrophication in estuaries, there is currently no established assessment framework to determine whether an estuary has become "adversely effected" by macroalgae. A recent review (Fong *et al.* 2011) found studies documenting adverse effects of macroalgae on benthic infauna found thresholds as low as 700 g wet wt m^{-2} (Bona 2006) and adverse effects with cover greater than 30 to 70% (Jones and Pinn 2006, Pihl *et al.* 1995). Ongoing studies being conducted by SCCWRP and UCLA will help to provide additional data which which to select macroalgal management endpoints for the estuary, if desired.

Macroalgal mats can rapidly deplete dissolved inorganic nutrients from the water column (Pedersen and Borum 1997, McGlathery *et al.* 2007). This depletion of nutrients increases the rate of benthic flux of nutrients from the sediments by creating a concentration gradient, thus diverting N loss from denitrification and providing a mechanism for N retention and recycling within the estuary (Krause-Jensen *et al.* 1999, Fong and Zedler 2000). In the SMRE, the peak in macroalgae productivity coincided

with the reduced freshwater flow and tidal exchange from a narrow ocean inlet. Increased residence time of water during this time period would result in greater residence time, enhancing availability of nutrients that can promote the productivity of macroalgal blooms.

The presence of macroalgae in estuarine environments can alter DO concentrations significantly on a diurnal scale. High rates of respiration from elevated biomass may reduce DO content of estuarine waters at night (e.g., Peckol and Rivers (1995)), while decomposition of accumulated organic matter may cause a large microbial O_2 demand both day and night (Sfriso *et al.* 1987). Dissolved oxygen concentrations found to be below 5 mg for approximately 19% of the wintertime and 23% of the summertime, indicating that macroalgal biomass per se was not the driving factor in depressed DO concentrations; sediment O_2 demand as well as flux of degraded organic matter may also play a role; observations of tidal height relative to DO show low O_2events were associated with neap tide cycles, indicating that water residence time is likely a controlling factor. During neap tides, exchange with oxygen-rich ocean waters is at a minimum and sediment O_2 demand and autotrophic and heterotrophic respiration will act to deplete surface waters of oxygen. Factors affecting DO flux are explored further in Section3.

2.4.3 Patterns in SMRE Surface Water and Porewater Nutrient Concentrations and Sediment Bulk Characteristics

Ambient nutrient concentrations within an estuary are the integration of various pathways of sources, sinks and transformations, including both uptake and release (Valiela *et al.* 1992, 1997; Dalsgaard 2003; Bergamasco *et al.* 2003; Paerl 2009). The relative ratios of the different species can provide some insight into the dominant processes controlling nutrient availability within the estuary.

Surface water nutrient concentrations measured at the ME site and within the estuary show the surface waters to be enriched, with dry weather TN (57 to 971 µM) greater then wet weather concentrations (97 to 231 µM) and wet weather TP approximately equal to dry weather (4 to 11 µM). During winter index and wet weather periods, NO_3+$NO_2$and SRP comprised the largest fractions of TN and TP respectively, typical of surface waters enriched with anthropogenic sources of nutrients. During the summer and fall, little freshwater was delivered to the estuary, and NH_4 and SRP dominated estuarine TN and TP respectively. In particular, estuarine ambient dry season SRP and NH_4 were especially high in Segment 2 (16.1 ±10.1 µM SRP and 29.8 ±19.3 µM NH_4) relative to the other San Diego Lagoons in this study (McLaughlin *et al.* 2010a,b, 2011).

Mixing diagrams (plots of salinity relative to nutrient concentrations) of surface water transect data were particularly instructive as to whether freshwater versus marine endmembers are the primary source of nutrients and to what extent within estuary sources (e.g. storm drains, groundwater, benthic flux, biological release) or sinks (benthic flux, denitrification, biological uptake) are visible (Day *et al.* 1989, Boyton *et al.* 2006, Sutula *et al.* 2006, REFS). Mixing diagrams show that for the SMRE, sources or production of NO_3+NO_2 and SRP appears in the 0 to5 ppt zone of the estuary during the winter and spring index periods, consistent with the concept that additional sources of these constituents may be entering the estuary near Segment 2, either as surface or groundwater inputs.

Nitrate+nitrite was consistently lower throughout the summer and fall index periods then in the winter and spring, with very low concentrations in the upper estuary and higher concentrations in near Segment 1 (mean concentrations ranging from 37.5 to 95.5 µM). Since freshwater input is low during this period, other sources of NO_3 must be entering the estuary near Segment 2 (e.g. groundwater or storm drains). Other internal sources such as nitrification (Seitzinger 1988), which converts NH_4 into NO_3, are possible, but estimates of nitrification are not available for southern California estuaries.

In contrast to NO_3, dry season ambient NH_4 concentration were higher near Segment 2 then 1. Mixing diagrams show a consistent non-freshwater source of NH_4 to the estuary throughout all index periods. Typical sources of NH_4 sources could include, benthic flux or non-point source inputs such as agricultural runoff, groundwater, or storm drains (Valiela *et al.* 2006). In Famosa Slough, Loma Alta Slough, and San Elijo Lagoon, dry season concentrations of dissolved inorganic nutrients were typically non-detect, because external inputs were low and macroalgae were able to deplete sediment sources of nutrients (McLaughlin *et al.* 2010a,b, McLaughlin *et al.* 2011). In the SMRE, summer and fall water column NH_4 and NO_3 were still relatively high, indicating that additional sources of dissolved organic nutrients to the estuary are present.

Sediment organic matter can be decomposed by microorganisms via a series of biogeochemical reactions which result in the release of mineral forms of nutrients to sediment porewaters (Berner 1966). The grain size and organic matter content of the sediment set the capacity of the sediment to produce porewaters of various concentrations, since low organic matter content, associated with sands and coarse substrates, generally have low %OC, %N and %P content (Sutula *et al.* 2002). Segment 1 generally had higher fractions of fine-grained sediments (20 to 80% fines) and higher %OC, %N and %P, while Segment 2 sediments were >90% sand with very low %OC and often or non-detectable %N. Fluvially-dominanted river mouth estuaries such as SMRE have an inherent capacity to scour fine-grained sediments, thus making them less susceptible to eutrophication because particulate sources of nutrients such as watershed sediments and decaying organic matter tend to be more quickly removed.

Sedment %TP content was unusually enriched for some samples in Segment 2 (0.04 to 0.09 %TP, given the near zero sediment OC content and percent fines. This suggests an anthrogenic source of P (Ruttenberg 2001, Sutula *et al.* 2002). Vertically sediment TP content decreased consistently with depth at both Segment 1 and 2 during all index periods, but this was not the case with % OC or %TN. As a result, porewater nutrients, DOC and TCO_2 were 2 to 10 times higher in Segment 1 than in Segment 2 (see Section 3).

2.4.4 Significance Sediment Characteristics and Transport in the SMRE

As noted above, sedimentary organic matter can serve as a source of remineralized N and P to porewaters and surface waters as the organic matter is decomposed. Sediment grain size typically decreased downcore associated with a decrease in N and P relative to organic C and an increase in porewater NH_4 and PO_4. However, the sediments were unlikely to provide a consistent source of remineralized nutrients to the porewaters and surface waters due to the constant resuspension of the sediment bed and large grainsize (Figures 2.16 and 2.18).

3 Estimates and Factors Influencing Benthic Oxygen, Carbon Dioxide and Nutrient Fluxes

3.1 Introduction

Sediments are a potentially significant internal source of N and P to surface waters in estuarine systems. Watershed-derived sediments, deposited in estuaries during the wet season, carry an associated particulate N and P load (Sutula *et al.* 2004, 2006). When deposited in the estuary, particulate nutrients can be mineralized to biologically-available forms and may build up in high concentrations in sediment porewaters. These porewaters can diffuse into the overlying water column or be released through advective processes such as bioturbation by benthic infauna, forced flow of water through sediments by bioirrigation or tidal pumping, or physical resuspension of sediments through scouring or resuspension during strong tidal currents or storm flows (Boynton *et al.* 1980, Grenz *et al.* 2000, Jahnke *et al.* 2003). Once released to the water column, these particulate-derived nutrients are available for uptake by primary producers, including macroalgae, MPB, and SAV.

Primary producer abundance is often limited by availability of nutrients (Howarth 1988, Valiela *et al.* 1997, Kamer *et al.* 2004, Paerl 2009). Macroalgae generally obtain nutrients directly from the water column, though studies have shown that algae may intercept nutrients fluxing out of sediments (Lavery and McComb 1991, McGlathery *et al.* 2007). In Southern California, wet-season particulate-nutrient loads deposited in lagoons where shown to provide a significant source of nutrients that fueled excessive growth of SAV and macroalgae during the dry season (Boyle *et al.* 2004, Sutula *et al.* 2004, Sutula *et al.* 2006). Thus, sediment-derived nutrients may cause algal blooms to persist even when nutrient loading from the watershed is reduced to levels calculated to limit macroalgal biomass (Sutula *et al.* 2004, Neto *et al.* 2008).

The principal methods of estimating sediment contribution of nutrients (benthic flux) include benthic chambers (Hammond *et al.* 1985, Clavero *et al.* 2000, Berelson *et al.* 2003), sediment-core incubations (Risgaard-Petersen and Ottosen 2000, Welsh *et al.* 2000) and porewater profiles (Hammond *et al.* 1999, Qu *et al.* 2005). Vertical fluxes of solutes diffusing between the sediment and overlying waters can be calculated from Fick's law of diffusion (i.e., porewater diffusive fluxes). The major physical controls on diffusive fluxes are sediment porosity and the diffusive boundary layer (DBL). However, diffusive fluxes generally underpredict true fluxes. Benthic chambers and sediment-core incubations are direct measurements and may integrate diffusive and advective transport of porewater by means of bioturbation/or bioirrigation processes (Berelson *et al.* 1999).

In addition to nutrients, the fluxes of O_2,TCO_2, and trace metals provide valuable information on the biogeochemical functioning of the sediments. In particular, O_2 and TCO_2 fluxes provide insight on the rates and dominant pathways of organic matter mineralization and benthic community metabolism, which are of primary interest in understanding ecosystem functioning and disturbances caused by eutrophication (Ferguson *et al.* 2003, Ferguson *et al.* 2004, Qu *et al.* 2005). The production of total inorganic C, measured as the release of TCO_2 from the sediment to the overlying water, has been used to interpret the balance between aerobic and anaerobic mineralization since both yield carbon dioxide

(CO_2) as the ultimate oxidation product of carbon (Berelson *et al.* 1998, Hammond *et al.* 1999). Measurement of dissolved Fe and Mn pore concentrations and fluxes provide valuable information about the redox chemistry of the benthic boundary layer, since these constituents are only released if the environment has a sufficiently low redox potential (hypoxic).

This component of SCCWRP studies had two objectives:

1) Measurement of porewater N, P, TCO_2, sulfide, Fe and Mn concentrations to provide information about the sediment biogeochemistry and redox status of SMRE sediments.

2) Estimation of *in situ* flux of nutrients, DO, and TCO_2 fluxes between sediments and surface waters. Benthic fluxes were estimated via direct *in situ* measurements of nutrient flux and sediment O_2 demand using benthic flux chambers. These data are compared to key factors (sediment characteristics and nutrient content, primary producer biomass as described in Section 2) known to control fluxes in order to understand key drivers on the magnitude and direction of flux.

3.2 Methods

3.2.1 Field Methods

3.2.1.1 Porewater Concentrations

Sediment porewaters were sampled within Segment 1 and 2 using porewater equilibrators (peepers: (Hesslein 1976)) during each index period (Figure 3.1). When the peepers are placed into the sediment, solutes from the porewaters come into contact with the filter and a concentration gradient is established between the cell water (no solute) and the porewaters. This causes solutes to diffuse into the cells and, over time, equilibrium is established between the peeper cells and the porewaters whereby the concentrations on both sides of the filter paper are equal. Each peeper was constructed from a 50 x 18 cm solid plexiglass frame into which cells (0.5 x 3.0 x 13 cm) were milled in at a spacing of approximately 1 cm, which are used to sample a depth profile of the sediment porewaters. Each cell is filled with distilled, deionized water that had been bubbled with N gas for 24 hours to remove the O_2 and covered with a 0.45 µm polycarbonate filter paper. The filter is held in place by an outer plexiglass frame secured with Teflon screws. Peepers are kept under a N atmosphere until deployment. Peepers were pushed by hand into the subtidal sediment, making sure that the peeper is vertical and the top of the sediment surface was flush with the top well of the peeper. Peepers were secured with a 30 m cable attached to a stake driven into the upper intertidal zone to facilitate recovery and the location was recorded using GPS coordinates. After a two-week equilibration period (Hesslein 1976, Brandl and Hanselmann 1991), the peepers were retrieved. Peeper recovery was coordinated with the collection of the sediment core and a collection of ambient bottom water (Section 2). Sediment cores for bulk characteristics and nutrients, described above, were collected within 2 feet of the peeper location.

Immediately following retrieval, the peepers are placed inside large format ziploc bags that were purged with N gas to minimize artifacts from oxidation of porewater fluids. Porewater samples were extracted from each well using a repeater pipette, dispensed into vials and immediately frozen for analysis. Wells sampled represent porewater depths of: 0-1, 1-2, 2-3, 3-4, 4-5, 5-6, 7-8, 10-11, 13-14 cm. Each peeper

is processed within 15 minutes of recovery. Following sub-sampling of the peeper, ambient bottom water samples were also filtered, collected into vials and frozen for analysis. All water samples were analyzed for the following: sulfide, NH_4, NO_3, NO_2, SRP, TDN, TDP, dissolved Fe, dissolved Mn, total carbon dioxide, and DOC. Before freezing sulfide samples were preserved with zinc acetate. One field blank was collected for each porewater analyte and a field blank and duplicate were collected for each ambient sample. Surface water samples were collected at the time of peeper retrieval.

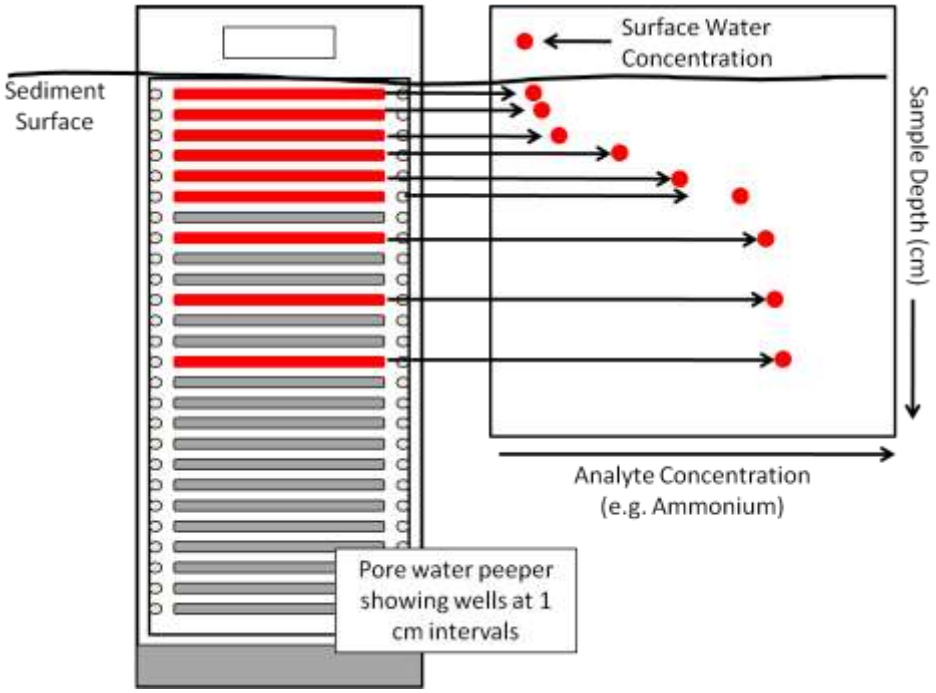


Figure 3.1. Graphic depicting how porewater profiles are generated from porewater peepers.

3.2.1.2 Measurement of In Situ Benthic Fluxes

In situ sediment nutrient, trace metal, and DOC fluxes and sediment O_2 demand were measured using benthic flux chambers (Burdige *et al.* 1999, Berelson *et al.* 2003, Elrod *et al.* 2004). A minimum of two replicate chamber deployments were conducted in each segment during each index period; each replicate was incubated for three to five hours. Water samples were periodically drawn from the chamber as O_2 levels within the chamber decline, with time periods between chamber sampling events based on the rate of O_2 decline in the chamber (Figure 3.2). These samples, when analyzed, yield the change in concentration of the targeted analyte over time. The surface area of the chamber is known and the volume of water contained with the chamber can be calculated, therefore, a flux rate can be derived.

Four identical benthic flux chambers were built based on a modified design from Webb and Eyre (Webb and Eyre 2004). The chamber is made of clear acrylic measuring 25 cm x 25 cm x 26 cm (l x w x h) mounted to an aluminum frame and is designed such that 10 cm of the chamber height is submerged in the sediment (leaving a height of 16 cm above the sediments) (Figures 3.3 and 3.4). The chamber frame is placed on top of an acrylic "skirt", a thin sheet of acrylic measuring 24" x 36" with a hole cut in the center. This "skirt" allowed for the acrylic chamber to sink into the sediments but prevented the frame from also sinking into the sediments and thus changing the chamber height over the deployment time. When properly deployed the total chamber volume is 10 liters. Two of the chambers were left clear and open to variations in ambient light throughout the deployment (light chambers, Figure 3.5); the other two chambers were covered in aluminum foil to prevent ambient light from penetrating the chambers (dark chambers).

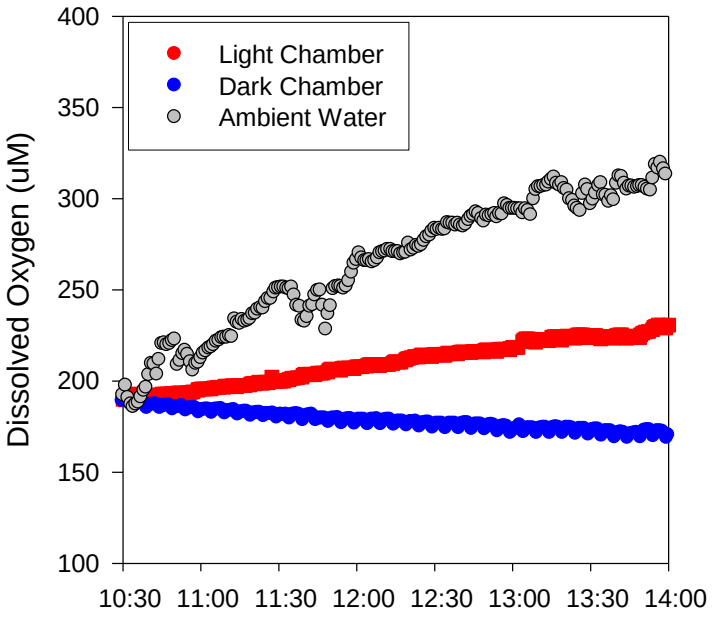


Figure 3.2. Typical chamber time series of dissolved oxygen concentration within the light and dark chambers relative to ambient surface water (Segment 2, July 2008). Oxygen concentrations in both the light and dark chambers steadily decreased over the incubation. Flux calculations were made during the most linear part of the curve.

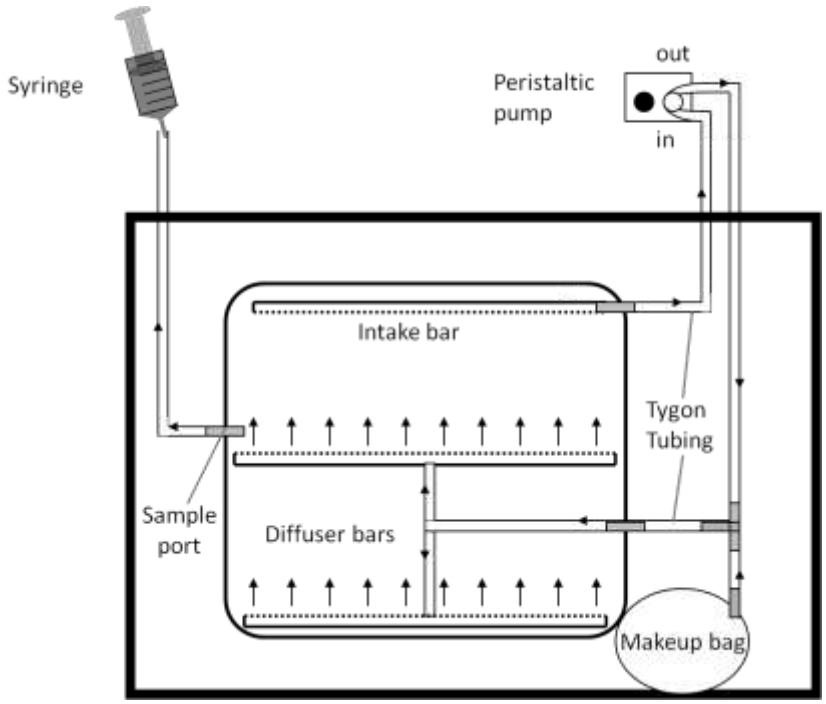


Figure 3.3. Schematic of benthic chamber design as viewed from above.

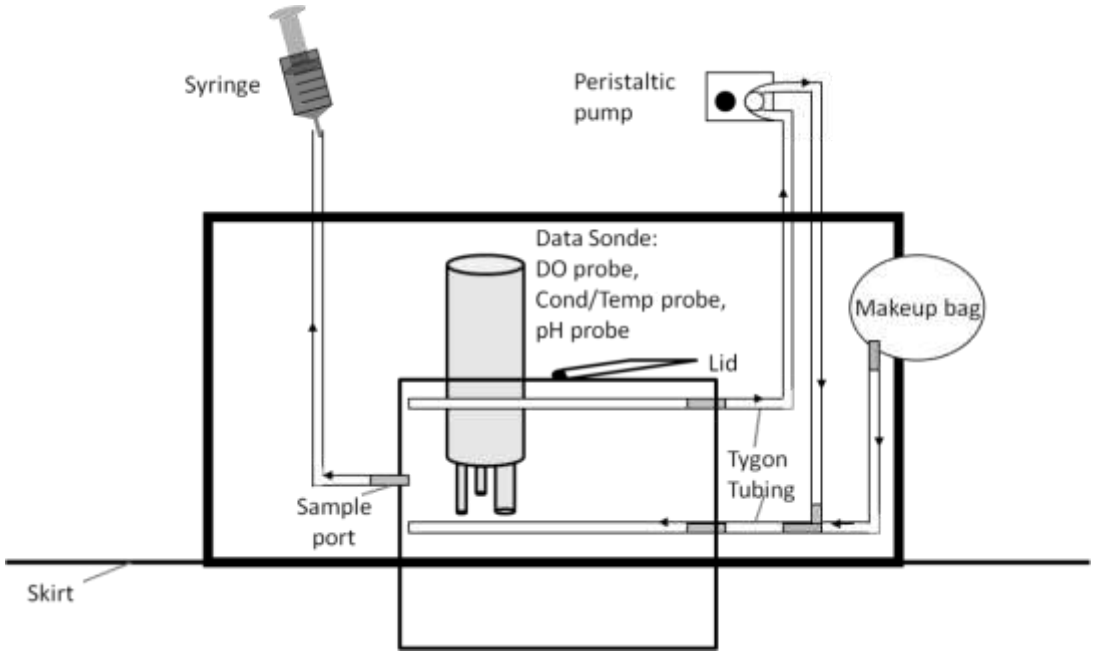


Figure 3.4. Schematic of benthic chamber design as viewed from side.

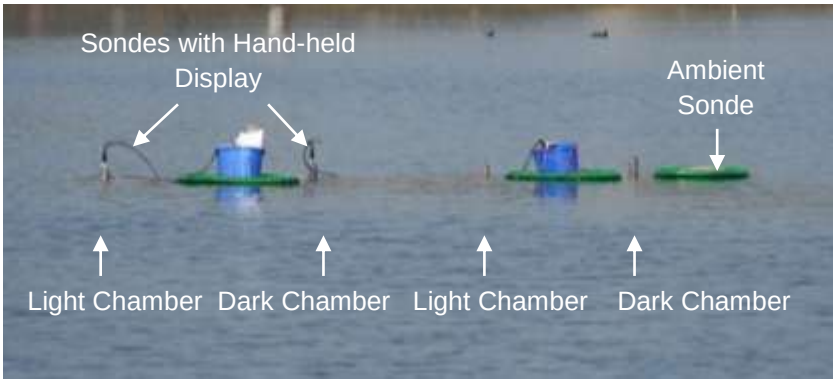


Figure 3.5. Flux chambers during deployment.

Each chamber is equipped with a YSI 6920 data sonde containing a temperature/conductivity probe, optical DO probe, and pH probe allowing for continuous measurements within each chamber and of ambient water every minute. All probes were calibrated in the laboratory before deployment. Two of the chamber probes were connected to a YSI 650 hand-held data display unit allowing for real-time monitoring of DO levels within each chamber. Such a set up allowed the field team to set the timing of chamber samplings to insure that all five samplings were evenly spaced in time and that no sampling would occur after the chamber DO levels fell below 2 mg L^{-1}.

The chamber is "plumbed" with tubing from the chamber to a peristaltic pump which keeps water circulating through the chamber, preventing the development of a benthic boundary layer which would alter the benthic-flux rate (Webb and Eyre 2004). An additional tube is connected to a clean 60 ml syringe which is used to pull water samples from the chamber at the designated intervals. There were five sample draws from each chamber and each sample draw removed approximately 130 ml of water from the chamber (two syringes plus 10 ml of rinse). In order to maintain consistent chamber volume, water from a "make-up" bag is drawn into the chamber as the sample water is withdrawn. The two syringes used to draw chamber water at each sampling port are immediately taken to the shoreline for processing.

Sediments were mildly disturbed during deployment, so chambers were allowed to equilibrate with their surroundings before the tops were closed. Chambers were closed when the turbidity measurement in chamber 1 returned to baseline. Dissolved oxygen, temperature, salinity, turbidity, and pH were measured continuously in each chamber and the surface water directly adjacent to the chambers with data sondes. Dissolved oxygen concentrations in the chambers were monitored during the incubation and observed to steadily decline in both the light and dark chambers over the course of the experiment relative the ambient DO concentration (Figure 3.2). Samples were pulled from the chamber at evenly spaced intervals to measure the change in concentration within the chambers as a function of time; these data were used to calculate the flux from the sediments. The interval between samplings was determined based on the rate at which the real-time measurements of DO decreased; the aim of the experiments was to collect five distinct samplings before the DO levels fell below 2 mg L^{-1} (62 µM).

Chamber water and ambient surface water samples were analyzed for TDN, TDP, NH_4, SRP, NO_3, NO_2, DOC, Fe, Mn and TCO_2. One unfiltered split was collected for TN and TP, and then the syringe was fitted with an MCE filter, which was rinsed with 10 ml of sample water, and splits were collected for dissolved nutrients (NO_2, NO_3, NH_4, and SRP), and total dissolved nitrogen and phosphorus (TDN/TDP). The second syringe was fitted with a PES filter, which was rinsed with 10 ml of sample water, and splits collected for DOC, dissolved metals (Fe and Mn), and TCO_2. All samples were placed in the dark on ice while in the field. Total carbon dioxide samples were analyzed in the laboratory within six hours of collection. The remaining samples were frozen upon return to the laboratory until analysis within their respective holding times.

After the deployment was completed, surface sediment samples were collected and analyzed for grain size, OC, organic N, and TP content, and sediment chl a. Algal biomass and SAV biomass were comprehensively harvested from the chamber whenever applicable, sorted, cleaned and weighed.

Ambient water samples were collected during both the benthic chamber deployment (surface waters) and the porewater peeper extraction (bottom waters). The protocol for sampling and processing was the same as given above for the transect sampling (Section 2.3.1).

3.2.1.3 Benthic Infauna

Benthic infauna cores (5 cm diameter, 10 cm deep) were collected from each benthic flux chamber following deployment in each index period. Individuals were identified and counted by genus and extrapolated to estimate the number of infauna of each genus in the top 10 cm of each square meter of subtidal sediment.

3.2.2 Analytical Methods

All water samples were assayed by flow injection analysis for dissolved inorganic nutrients using a Lachat Instruments QuikChem 8000 autoanalyzer for the analysis of NH_4, NO_3, NO_2, and SRP. Dissolved Fe and Mn were measured by atomic adsorption spectrophotometry on a Varian Instruments AA400. Water samples were assessed for TDN, TDP, TN and TP via two step process: first water samples undergo a persulfate digest to convert all N from all N compartments into NO_3 and the P from all P compartments into orthophosphate; then the resulting digests are analyzed by automated colorimetry (Alpkem or Technicon) for nitrate-N and orthophosphate-P (Koroleff 1985). Water DOC was analyzed on a Shimadzu TOC-5000A Total Organic Carbon Analyzer with ASI-5000A Auto Sampler. Water TCO_2 was analyzed on a UIC instruments carbon dioxide coulometer. Sulfide samples were allowed to react with N,N-dimethyl-p-phenylenediamine and ferric chloride under acidic conditions to yield the product methylene blue, and the concentration of methylene blue was determined spectrophotometrically at 668 nm. Concentration of sulfide in the sample was calculated by reference to a standard curve (absorbance vs. sulfide concentration). Inorganic nutrients and trace metals analyses were conducted by the Marine Science Institute at the University of California, Santa Barbara; TDN, TDP, TN, TP, and DOC were run at the University of Georgia Analytical Chemistry Laboratory. Sulfide and TCO_2 were measured by SCCWRP.

3.2.3 Data Analysis

Flux rates (F) for each constituent (dissolved nutrients, metals, TCO_2, and O_2) are calculated from the chamber height (h) and the change in constituent concentration within the chamber over time (dC/dt):

$$\mathbf{F} = \mathbf{h} * \left(\frac{\mathbf{dC}}{\mathbf{dt}}\right) \qquad \textbf{Eq. 3.1}$$

Concentration versus time was plotted as a linear gradient using all data that passed a quality assurance check. Use of the linear portion of the incubation curve assumes that the flux of a constituent is constant during the incubation interval (Figure 3.1).

Productivity at the sediment/water interface can be estimated from the fluxes of TCO_2 and O_2 as carbon fixation and gross primary productivity (GPP) respectively. Carbon fixation is a measure of the amount of inorganic carbon (carbon dioxide) converted to autotrophic biomass and is calculated from the difference between light (with photosynthesis) and dark (without photosynthesis) TCO_2 fluxes:

$$\text{Carbon Fixation} = \text{Flux } TCO2_{light} - \text{Flux } TCO2_{dark} \qquad \textbf{Eq. 3.2}$$

Gross Primary Productivity is the rate at which primary producers capture and store chemical energy as biomass and can be calculated from the difference between light (with photosynthesis) and dark (without photosynthesis) O_2 fluxes:

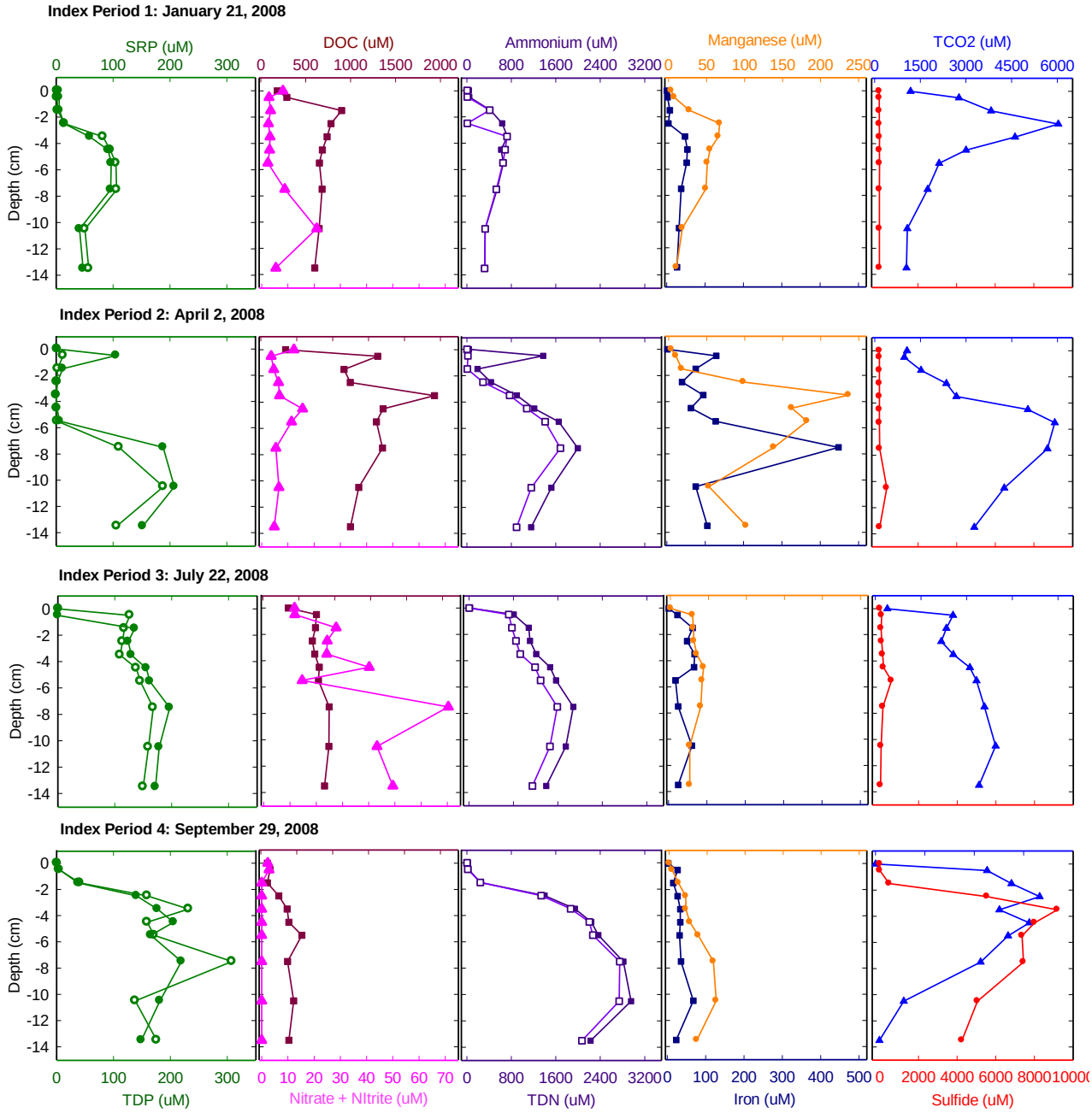
$$GPP = \text{Flux } O2_{light} - \text{Flux } O2_{dark} \qquad \textbf{Eq. 3.2}$$

3.3 Results

3.3.1 Sediment Porewater Concentrations

Differences were observed in porewater N and P concentrations among index periods and sites, as well as vertically (Figure 3.6). With respect to N, Segment 1 TDN mean concentration were roughly an order of magnitude higher than Segment 2. The mean TDN concentrations of the top 6 cm in Segment 1 ranged from 413 ±279 µM TDN during January 2008 to 1168 ±918 µM TDN in September 2008, while that of Segment 2 ranged from 49 ±8 µM TDN during March 2008 to 114 ±46 µM TDN in July 2008. The relative compositions of N forms (NH_4, NO_3+NO_2, and dissolved organic nitrogen (DON)) likewise varied enormously between the two sites. In Segment 1 sediments, DON typically comprised 80% within the first 1-2 cm, then dropped off to <10%, while NH_4 comprised >85% of TDN at depths >2 cm. Nitrate+nitrite typically had concentrations of 10 to 30 µM in the top 1. In Segment 2 sediments during the first two index periods, DON and NO_3+NO_2comprised approximately 40% each of TDN, while NH_4 was <10%. During the summer and fall index periods, TDN increased and NH_4 comprised 65 to 80%, with DON responsible for the remainder and nitrate+nitrate < 2%.

A) Segment 1


Index Period 1: January 21, 2008
SRP (uM)
DOC (uM)
Ammonium (uM)
Manganese (uM)
TCO2 (uM)
Depth (cm)
Index Period 2: April 2, 2008
Index Period 3: July 22, 2008
Index Period 4: September 29, 2008
TDP (uM)
Nitrate + NItrite (uM)
TDN (uM)
Iron (uM)
Sulfide (uM)

B) Segment 2

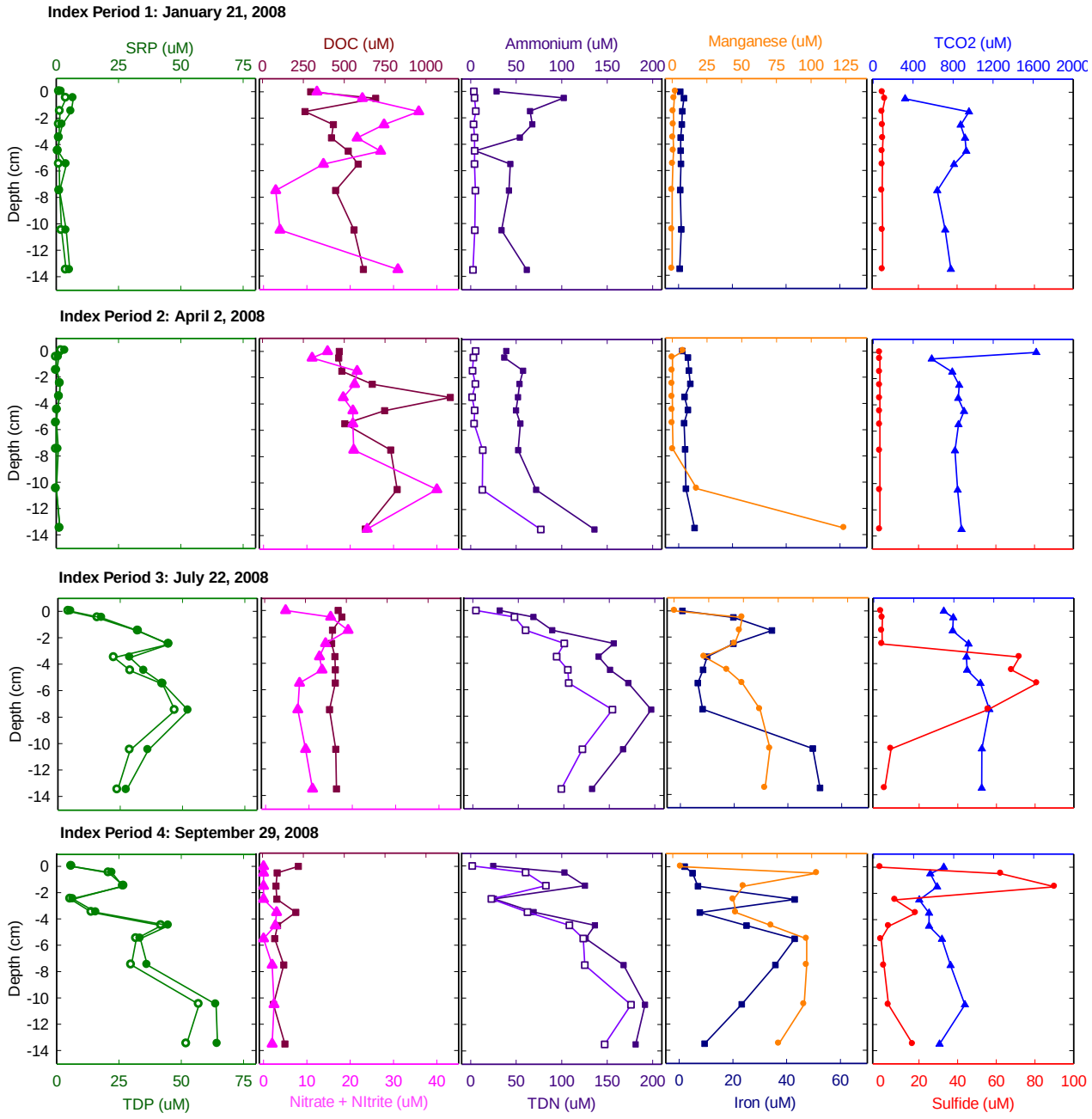


Figure 3.6. Results of sediment porewater sampling in the Santa Margarita River Estuary Segment 1 (A) and Segment 2 (B) during seasonal index periods; each row represents an index period, first column is total dissolved phosphorus (●) and soluble reactive phosphate (○), second column is nitrate+nitrite (▲) and dissolved organic carbon (■), third column is total dissolved nitrogen (■) and ammonium (□), fourth column is iron (■) and manganese (●), fifth column is sulfide (▲) and total carbon dioxide (●). The same scale applies to each column.

As with N, mean porewater TDP concentrations at Segment 1 were an order of magnitude higher during the winter and spring index periods and a factor of 5 higher than that of Segment 2 during summer and fall index periods. The mean TDP concentrations of the top 6 cm in Segment 1 ranged from 30 ±33 µM TDP during January 2008 to 95 ±82 TDN in the September 2008 index period, while that of Segment 2 ranged from 1 ±1 µM TDP during March 2008 to 27 ±12 µM TDP in July 2008. The relative compositions of P forms (SRP versus dissolved organic phosphorus (DOP) were consistent between the two sites. SRP generally comprised 70 to 90% of TDP at Segments 1 and 2 throughout all index periods.

Segment 1 and Segment 2 mean DOC concentrations generally were of the same order of magnitude and followed the same seasonal trend. Peak mean concentration occurred during the Spring index period, and were slightly higher at Segment 1 (1133 ±503 µM DOC) than at Segment 2 (665 ±241 µM DOC). During other time periods, mean concentrations were fairly comparable, with intermediate concentrations of 435 to 556 µM DOC during the January and July 2008 index periods and the lowest concentrations (129 to 176 µM DOC) during the September 2008 index period.

Mean TCO_2 concentrations were higher three times higher in Segment 1 (2185 to 3571 µM) than in Segment 2 (578 to 937 µM TCO_2), with no strong seasonal trend. Segment 2 TCO_2 concentrations tended to be uniform with depth, while Segment 1 TCO_2 typically peaked at mid-core, then declined.

At both Segment 1 and Segment 2, mean sulfide concentrations were near non-detect during the winter and spring index periods <2 µM. During the summer and fall, concentrations at Segment 1 were substantially greater during the July and September index periods (92 ±56 µM to 3870 ±3862 µM) than at Segment 2 (24 ±33 µM to 33 ±33 µM).

At both Segment 1 and Segment 2, vertical profiles of SRP, NH_4, and TCO_2 concentrations tended to covary, showing peaks at mid-depths of the core and declines further down core. Dissolved Organic Carbon and to a lesser extent NO_3+NO_2 tend to covary with reduced Mn and Fe.

3.3.2 Dissolved Oxygen and Carbon Dioxide Fluxes

The sediments in Segment 1 showed a small net uptake of O_2 (-93 mmol m^{-2} d^{-1}) and release of TCO_2 during the winter (19 mmol m^{-2} d^{-1}), indicating that during this time period the sediments were heterotrophic (respiration exceeds primary production; Figure 3.7). From spring through fall, however, light and dark chamber fluxes were fairly well balanced or a net release of O_2 (0 to +125 mmol O_2 m^{-2} d^{-1}) and uptake of TCO_2 (-4 to -20 mmol TCO_2 m^{-2} d^{-1}) was observed, indicating that the sediments in the latter portion of the year were autotrophic (primary production exceeds respiration). There was good correspondence bewteeen the DO and TCO_2 data, showing similar trends between both data types (Tables 3.1 and 3.2).

In contrast, sediments of Segment 2 showed almost opposite trends. Net O_2 fluxes were positive (indicating autotrophy) during the winter and spring index periods (+21 to +23 ±26 mmol m^{-2} d^{-1} respectively; Figure 3.8). During summer and fall, net O_2 fluxes were into the sediment, indicating net heterotrophy (-1 to 61 mmol m^{-2} d^{-1}). Ratios of TCO_2:O_2 were 0.7 to 0.8 during the winter and spring index period increasing to 1.3 to 1.8 during the summer and fall. Ratios greater than 1.3:1 indicate that more CO_2 is being produced than can be respired by aerobic decomposition (net heterotrophic) while the rest of the year is autotrophic (Eyre and Ferguson 2002b, Eyre and McKee 2002).

The mean of DO fluxes from Segment 1 and Segment 2 shows a seasonal trend, with a tendency towards autotrophy in the first three index periods, and net heterotrophy in the September index period (Table 3.1). Unfortunately, the data quality of continuous DO measured via sonde in the water column during the 2008 TMDL studies were poor. However, data from Bight '08 continuous data (presented in Section 2) taken during the subsequent year show no strong trends in seasonal trends in DO and no prolonged periods of hypoxia, consistent with these sediment DO flux results.

Among all chamber incubations at Segments 1 and 2, DO flux was positively correlated with TCO_2 flux (-0.76, $p<0.001$; Table 3.2). Of co-factors measured in benthic chambers, such as sediment C:N, C:P, grain size, benthic chl a, benthic infauna, only DO flux was negatively correlated with salinity and TCO_2 flux was negatively correlated with pH (Table 3.2).

Table 3.1. Mean and standard deviation of Segment 1 and Segment 2 DO fluxes by index period.

Index Period	Mean	Std. Dev.
Jan 2008	25.2	53.4
Mar 2008	25.6	59.4
July 2008	13.7	64.2
Sept 2008	-16.6	69.8

Table 3.2. Spearman's Rank Correlation among DO, TC02, nutrient fluxes and factors known to influence flux (Temperature – Temp, sediment C:N Ratio (CN), sediment C:P (CP), total infaunal abundance (Infauna), sediment % fines, benthic chl a within chambers (chl a)). No macroalgal biomass was present in chambers. Table gives correlation (r) and p-value for α=0.05). Bolded values are significant at p-value<0.05.

Metric	Statistics	Infauna	Chl a	%Fine	C P	C:N	pH	Salinity	Temp	TCO2	DO	NH4	TDN	TDP	NO3	SRP
Total infauna	Corr.	1	0.05	-0.12	0.01	0.14	**-0.51**	-0.09	**0.54**	0.14	-0.20	**0.48**	0.20	**0.49**	-0.24	**0.42**
	p-value		0.79	0.52	0.94	0.43	**0.01**	0.66	**0.00**	0.46	0.30	**0.01**	0.26	**0.00**	0.19	**0.02**
Benthic Chla	Corr.		1.00	0.09	0.02	**-0.47**	**-0.36**	-0.17	-0.15	-0.05	0.04	**-0.40**	-0.04	**-0.36**	0.05	-0.01
	p-value			0.61	0.89	**0.01**	**0.06**	0.40	0.46	0.77	0.86	**0.02**	0.83	**0.04**	0.78	0.96
% Fines	Corr.			1.00	**0.63**	**0.32**	0.16	**0.80**	0.29	0.05	-0.31	0.19	-0.01	0.13	0.00	-0.04
	p-value				**0.00**	**0.07**	0.41	**<.0001**	0.13	0.80	0.11	0.30	0.95	0.47	0.99	0.84
C:P Ratio	Corr.				1.00	**0.43**	0.08	**0.71**	0.21	-0.23	-0.08	0.32	0.07	**0.37**	-0.18	0.08
	p-value					**0.01**	0.68	**<.0001**	0.28	0.21	0.68	0.07	0.71	**0.04**	0.33	0.68
C:N Ratio	Corr.					1.00	**0.21**	**0.48**	**0.45**	-0.17	0.06	**0.39**	0.06	**0.40**	0.00	0.28
	p-value						0.28	**0.01**	**0.02**	0.34	0.75	**0.03**	0.74	**0.03**	0.99	0.12
pH	Corr.						1.00	0.14	-0.03	**-0.36**	0.28	0.01	0.10	-0.05	-0.10	-0.26
	p-value							0.48	0.88	**0.06**	0.15	0.95	0.60	0.82	0.62	0.18
Salinity	Corr.							1.00	**0.49**	0.08	**-0.35**	**0.57**	-0.02	0.31	0.14	0.07
	p-value								**0.01**	0.69	**0.07**	**0.00**	0.91	0.11	0.49	0.73
Temp	Corr.								1.00	-0.02	-0.08	**0.52**	-0.13	**0.37**	0.04	**0.38**
	p-value									0.92	0.67	**0.00**	0.51	**0.05**	0.85	**0.04**
TCO2	Corr.									1.00	**-0.76**	0.25	0.17	0.05	0.04	-0.01
	p-value										**<.0001**	0.17	0.35	0.80	0.81	0.94
DO	Corr.										1.00	**-0.40**	0.03	-0.02	0.12	0.16
	p-value											**0.03**	0.86	0.90	0.55	0.43
NH4	Corr.											1.00	**0.49**	**0.76**	-0.22	**0.42**
	p-value												**0.00**	**<.0001**	0.22	**0.02**
TDN	Corr.												1.00	**0.46**	0.11	**0.33**
	p-value													**0.01**	0.56	**0.06**
TDP	Corr.													1.00	**-0.37**	**0.60**
	p-value														**0.04**	**0.00**
NO3	Corr.														1.00	0.05
	p-value															0.77

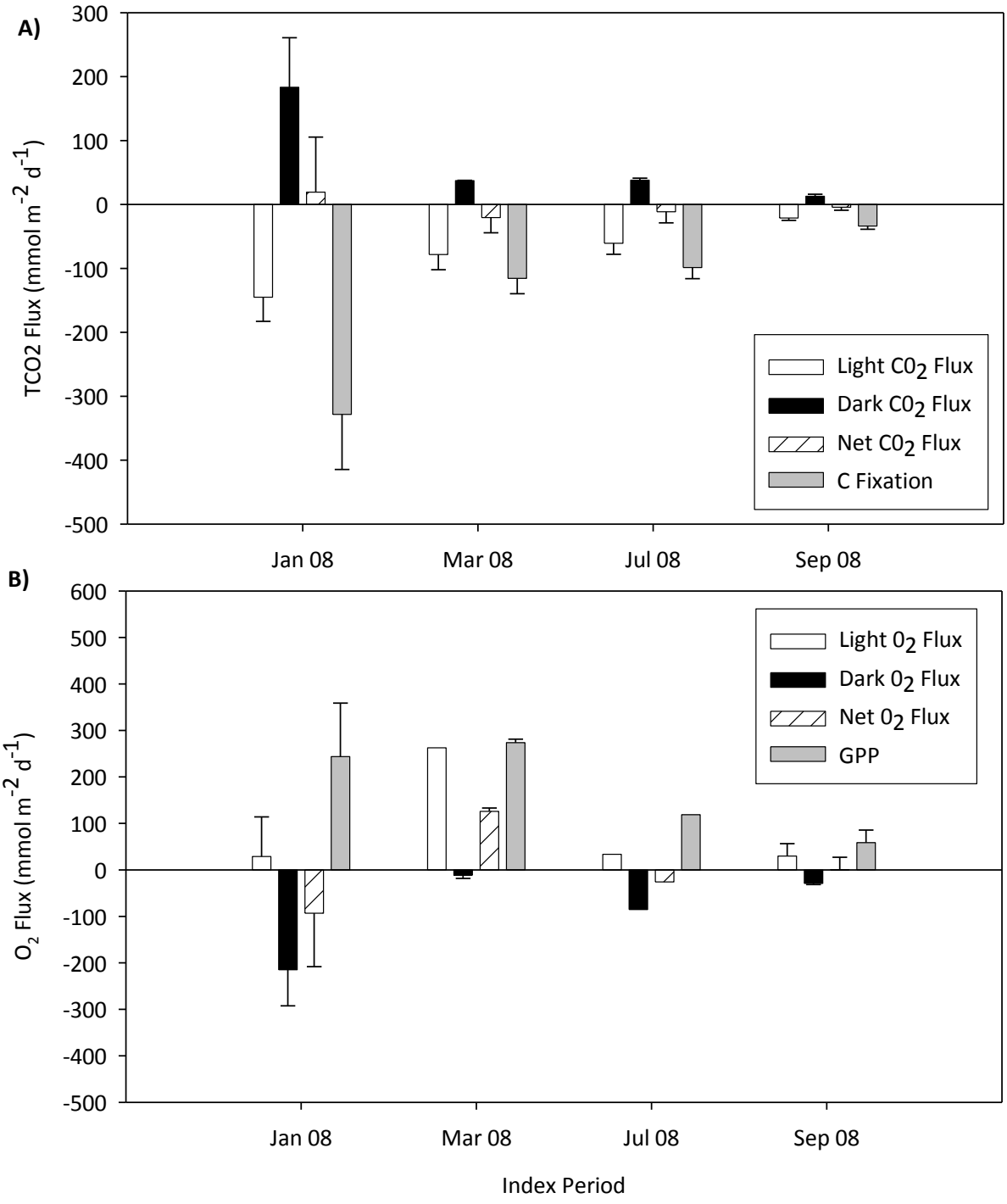


Figure 3.7. Segment 1 light, dark, and net (24-hr average of light and dark) TCO_2 fluxes, and estimated C fixation by index period (A); andlight, dark, and net O_2 fluxes, and Gross Primary Productivity (GPP) by index period (B). Error bars represent the standard deviation between replicates.

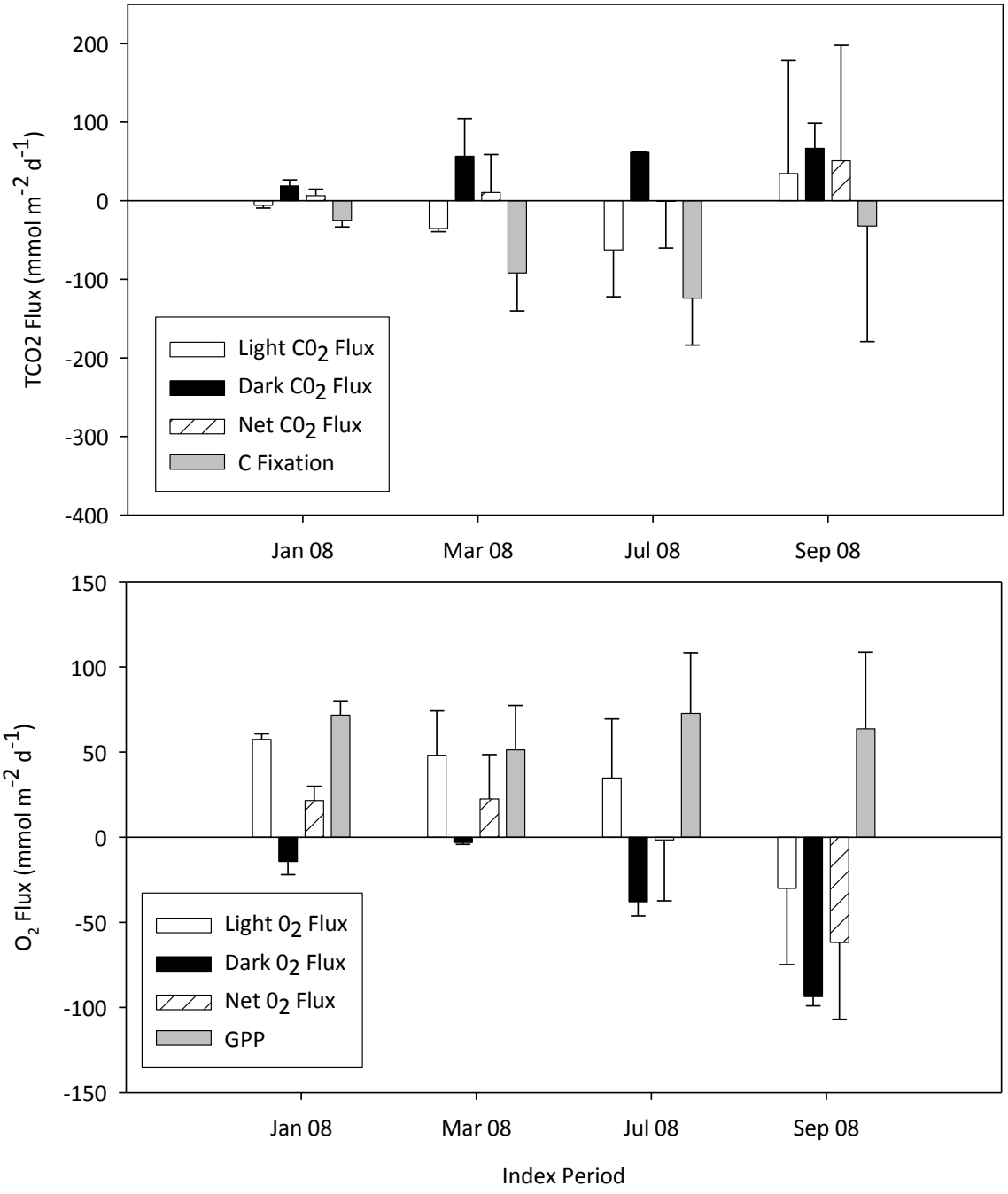


Figure 3.8. Segment 2 light, dark, and net (24-hr average of light and dark) TCO_2 fluxes, and estimated C fixation by index period (A); and light, dark, and net O_2 fluxes, and Gross Primary Productivity (GPP) by index period (B). Error bars represent the standard deviation between replicates.

3.3.3 Nitrogen Fluxes

Net fluxes (mean of light and dark incubations) of N (NH_4, NO_3, and TDN) exhibited some clear patterns with respect to season and segment (Table 3.3, Figure 3.9). Net fluxes across light and dark chambers show Segment 1 was a consistent source of TDN and NH_4 during the summer and fall index periods and a sink for N03 during all index periods. With the exception of the March 2008 sampling period, the magnitude of NH_4 flux out (5.2-28.2 mmol m^{-2} d^{-1}) was slightly higher but within the same order of magnitude as N03 flux in -2.3 to -26.3 mmol m^{-2} d^{-1}). At Segment 2, some of the same general patterns in TDN and NH_4 can be found in the summer and fall, but with much smaller mean fluxes (e.g. -0.2 to 0.9 mmol NH_4 m^{-2} d^{-1} and -0.2 to -1.0 mmol $N0_3$ m^{-2} d^{-1}) and higher variability among light and dark chambers. As with Segment 1, NO_3 flux was negative (into the sediments) for all periods. No significant differences existed between light and dark incubations for TDN, NH_4, or NO_3 fluxes (p-value>0.04; Figure 3.9).

Table 3.3. Nitrogen net fluxes and standard deviations from light and dark chamber fluxes (n=4) by index period. All fluxes are in mmol m^{-2} d^{-1}.

Index Period	Segment	TDN	NH_4	NO_3
Jan-08	2	-0.9±0.4	-0.03±0.1	-0.6±0.4
Mar-08		0.2±1.0	0.01±0.001	-1.0±2.3
Jul-08		2.5±1.4	0.9±0.01	-0.2±0.01
Sep-08		0.5±1.3	-0.2±1.9	-0.3±0.2
Jan-08	1	-12.9±8.0	12.5±3.3	-26.3±6.2
Mar-08		-14.8±2.0	-0.3±0.04	-7.5±8.4
Jul-08		5.3±2.3	28.0±4.2	-25.7±9.1
Sep-08		2.3±0.7	5.2±1.6	-2.3±1.9

Of the co-factors measured in benthic chamber incubations, NH_4 flux had significant positive correlations with total benthic infaunal abundance (0.48), sediment C:N ratio (0.39), salinity (0.57), temperature (0.52), and significant negatively correlation with benthic chl a (Table 3.2). Nitrate fluxes had no significant correlations.

3.3.4 Phosphorus Fluxes

Net fluxes (mean of light and dark incubations) of TDP and SRP exhibited some clear patterns with respect to season and segment (Table 3.4, Figure 3.9). As with N, net fluxes across light and dark chambers show Segments 1 and 2 were a consistent source of SRP during the summer and fall index periods (0.4 to 1.5 mmol m^{-2} d^{-1}) and a sink for SRP in March 2008 (-0.08 to -0.3 mmol m^{-2} d^{-1}). TDP fluxes were net positive at both Segments 1 and 2 for the September and January index period and at during the July period for Segment 1 (0.4 to 4.0 mmol TDP m^{-2} d^{-1}). No significant differences existed between light and dark incubations for TDP and SRP fluxes (p-value>0.05; Figure 3.9) and DOP fluxes were highly variable in direction and magnitude (+2.5 to -0.6 mmol m^{-2} d^{-1}).

Table 3.4. Phosphorus net fluxes and standard deviations from light and dark chamber fluxes (n=4) by index period. All fluxes are in mmol m^{-2} d^{-1}.

Index Period	Segment	TDP	SRP
Jan-08	2	1.1±0.2	-0.2±0.06
Mar-08		0.1±0.01	-0.08±0.05
Jul-08		-0.3±0.05	0.4±0.2
Sep-08		0.4±0.2	0.4±0.4
Jan-08	1	0.6±0.1	0.6±0.4
Mar-08		-0.8±0.5	-0.3±0.2
Jul-08		4.0±0.3	1.5±1.4
Sep-08		0.4±0.2	0.7±0.3

Of the co-factors measured in benthic chamber incubations, SRP flux had significant positive correlations with total benthic infaunal abundance (0.42) and temperature (0.38); Table 3.2). TDP fluxes were significantly correlated with these same parameters, but also positively correlated with sediment C:P and C:N ratio (0.37 to 0.40) and negatively correlated with benthic chl a (-0.36).

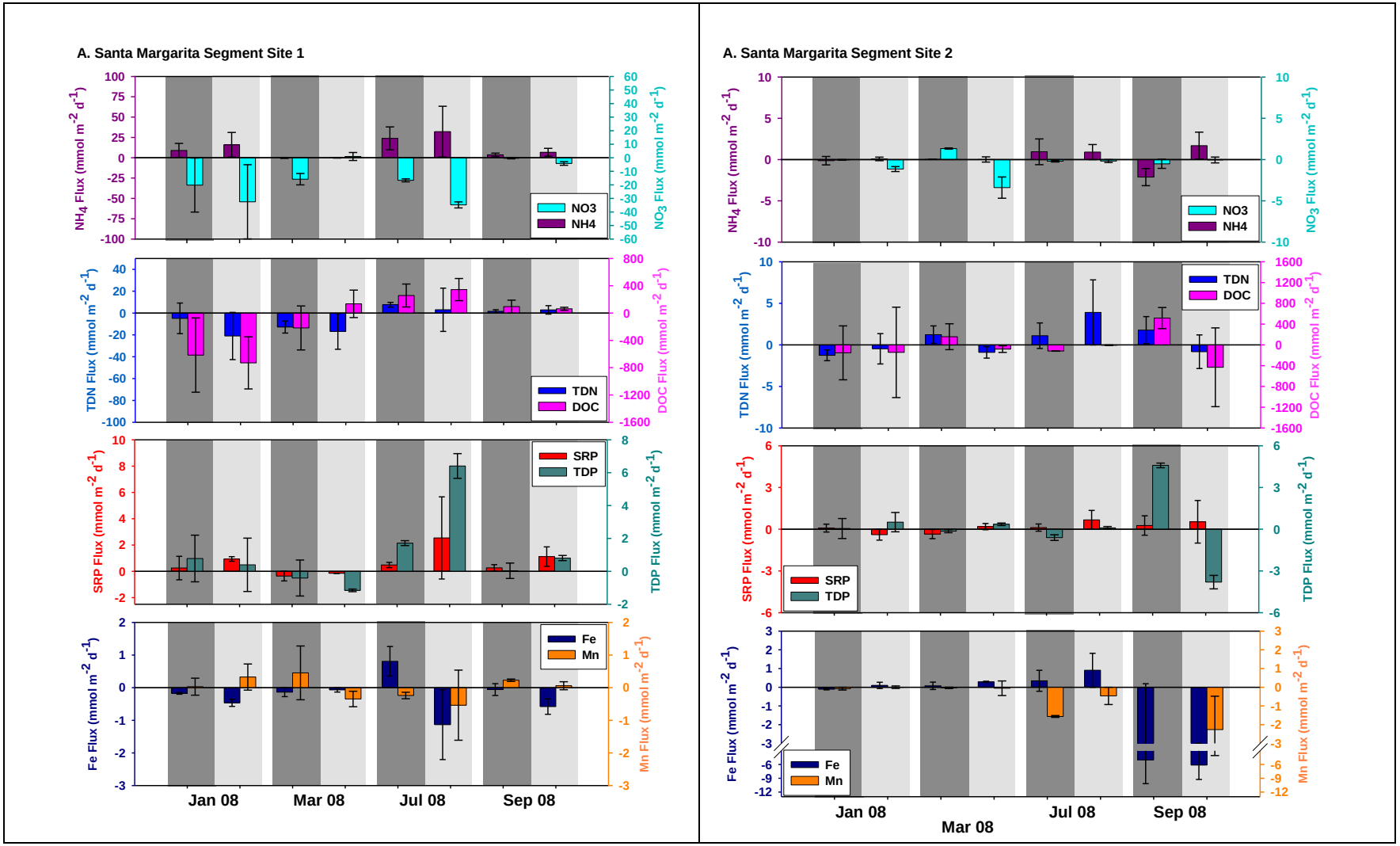


Figure 3.9. Segment 1 and Segment 2 benthic NH_4, NO_3, TDN, DOC, SRP, TDP, Mn, and Fe fluxes for dark (dark grey bands) and light (light grey bands) by index period. Error bars represent the standard deviation between replicate chambers.

3.3.5 Benthic Infaunal Abundance

In Santa Margarita, the benthic infauna community appears to support a diverse group of benthic infauna (Figure 3.10). Abundances are typically low during the winter and spring and increase in the summer and fall. Abundances are also greater for Segment 2 than for Segment 1, where sediments were more sandy and had lower OC and lower TN.

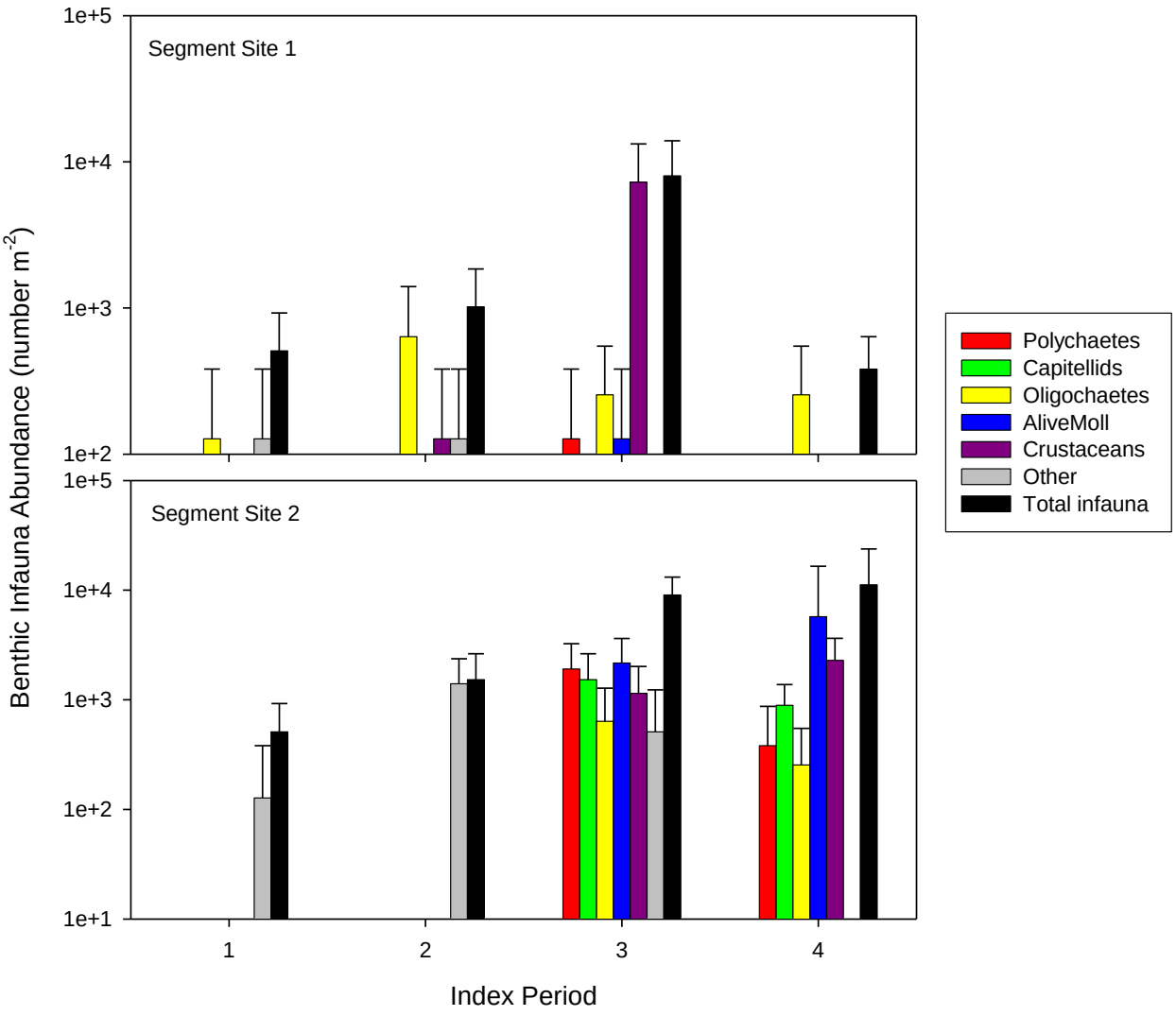


Figure 3.10. Benthic infauna abundance counts for Segment 1 and Segment 2. Functional groups are shown as different colored bars.

3.4 Discussion

Estuaries, at the terminus of watersheds, are typically subject to eutrophication due to high inputs of anthropogenic nutrient loads and hydromodification. Primary production in estuaries estuaries can be fueled by either "new" nutrients entering the system from the watershed or from "recycled" nutrients from the remineralization of particulate and dissolved organic matter that is brought into the estuary during rain events and transported to the water column via benthic flux. Shallow coastal lagoons with natural or anthropogenic muting of the tidal regime are particularly susceptible, because restricted exchange increases the residence time of water and thus the amount of time nutrients are available for uptake by primary producers (Sundbäck and McGlathery 2005).

Overall, this component of the study documented two principal findings:

1. Averaging over season and segment, benthic flux appears to provides net source of NH_4 (4.4 mmol m^{-2} hr^{-1}) and SRP (0.3 mmol m^{-2} hr^{-1}) to surface waters. Mean annual influx of NO_3 into the sediment was high (-10 mmol m^{-2} hr^{-1}). Measured rates of denitrification were 2 orders of magnitude lower than this rate (T. Kane, UCLA Dissertation) and thus can only partially explain the fate of this influx of NO_3 into the sediments. A more likely explanation is that some portion of this NO_3 is being reduced to NH_4 through DNR and is cycling back up to surface waters as NH_4. Dissimilatory nitrate reduction is a pathway that is favored under anoxic sediment conditions.
2. On average, estuary metabolism tends to tip from net autotrophic (net positive flux of O_2 to surface waters) in spring to net heterotrophic (net uptake of O_2 by sediments) in the fall. These rates of O_2 uptake were moderate relative to other eutrophic estuaries (e.g., Ferguson *et al.* 2003, 2004; Eyre and Ferguson 2005). High net TCO_2 effluxes are typically driven by respiration of accumulated dead or decaying biomass (organic matter accumulation) in the sediments rather than respiration of live biomass. While SMRE had among the highest peak biomass of macroalgae documented, this biomass does not appear to accumulate in SMRE sediments from season to season. Surficial sediments were primary sandy, had surface C:N values <10, indicative of algal carbon sources, but C:N values increased with depth, typically with non-detect with respect to N, indicating that organic matter is not accumulating with depth. In fluvially-dominated river mouth estuaries such as SMRE, this lack of interannual organic matter accumulation would make them less susceptible to eutrophication and is a factor responsible for the lower sediment O_2 demand, given the high abundances of algal biomass.

3.4.1 Significance of Rates of Benthic Oxygen and Total Carbon Dioxide

Eutrophication is typically defined by excess organic matter that fuels the development of hypoxia (i.e. low surface water DO concentration) as the organic matter is respired (Diaz 2001). When the consumption of O_2 exceeds the rate of resupply (decomposition of excessive amounts of organic matter exceeds diffusion/mixing of O_2 to bottom waters), O_2 concentrations can decline below the limit for survival and reproduction of organisms (Stanley and Nixon 1992, Borsuk *et al.* 2001, Diaz 2001). The consequence of this is often a cascade of effects including loss of habitat and biological diversity, development of foul odors and taste, and altered food webs (Sutula *et al.* 2007). Dissolved O_2 levels

that fall below 5 mg L^{-1} can be a stressor to aquatic life, and levels below 1 to 2 mg L^{-1} for more than a few hours can be lethal to both fish and benthic invertebrates (USEPA 2000, 2003). The basin plan water quality objective for the SMRE states that DO shall be greater than or equal to 5 mg L^{-1}. The Bight '08 Eutrophication Survey documented DO concentrations below 5 mg L^{-1} approximately 22% of the year with brief periods of hypoxia, driven by muted tidal hydrology during neap tides and, to some extent, reduced freshwater flow and tidal inlet restrictions during the summer and fall.

Shallow estuaries, such as the SMRE, can develop hypoxia typically through one of three main processes: 1) as episodic events driven by primary producer blooms (net autotrophy, where production greater than decomposition) and decomposition (net heterotrophy, where decomposition is greater than production; McGlathery *et al.* 2007), 2) chemical O_2 demand driven by sediment heterotrophic bacteria or redox reactions, and/or 3) during density-driven stratification which develops during intermittent closure to tidal exchange when the estuaries "trap salt" and preclude diffusion and mixing of O_2 to bottom waters (Largier *et al.* 1991). In Santa Margarita, the first two of these processes appear to contribute DO dynamics, with Segments 1 and 2 seasonally behaving in opposite fashions. Dissolved oxygen fluxes in Segment 1 show this region of the estuary to be mildly net heterotrophic during the winter index period, indicating that the lagoon at this time was decomposing more organic matter than producing it at the time of sampling (Eyre and Ferguson 2002a, 2002b). By summer, the continuous data show that small or positive DO fluxes, indicating that production is generally balancing respiration. In contrast, net benthic O_2 and TCO_2 data suggest that the sediments of Segment 2 are net autotrophic during the winter and spring, moving toward to heterotrophic during the summer and fall. Despite high cover and biomass of macroalgae during the summer and fall, large diurnal swings are not evident Segment 2 continuous data and periodicity appears more related to tidal hydrology. Time series analysis is required to better separate the effects of primary productivity versus tidal hydrology on O_2 signatures; this analysis is being conducted as a part of the Bight '08 Eutrophication Assessment and will be reported elsewere (McLaughlin *et al.* 2012).

Interestingly, comparison of O_2 and TCO_2 fluxes with *in situ* measurements in other systems indicate that SMRE fluxes are generally lower than those found in most eutrophic estuaries (Table 3.5). High <u>net</u> TCO_2 fluxes are typically driven by respiration of accumulated dead or decaying biomass (organic matter accumulation) in the sediments rather than respiration of live biomass. While SMRE had among the highest peak biomass of macroalgae documented, this biomass does not appear to accumulate in SMRE sediments from season to season. Surficial sediments were primary sandy, had surface C:N values <10, indicative of algal carbon sources, but these values increased dramatically with depth and with often non-detect with respect to N, indicating that organic matter burial and accumulation is not occurring with depth. A similar pattern was documented in Loma Alta Slough. Thus SMRE and Loma Alta Slough appear to be more dominated by fluvial process that scour fine-grained sediments rather than deposit them. In fluvially-dominated river mouth estuaries such as SMRE, this lack of interannual organic matter accumulation would make them less susceptible to eutrophication (Schubel and Kennedy 1984, Paerl *et al.* 1998, Bate *et al.* 2004).

Table 3.5. Comparison of fluxes from the Santa Margarita River Estuary to other estuarine environments.

Site	O_2	TCO_2	SRP	NH_4	NO_3
Santa Margarita (this study)					
Segment 1	4.5±66.5	-4.2±14.7	0.5±1.3	8.5±11.2	-13.9±14.3
Segment 2	-6.5±33.1	-3.1±23.8	0.1±0.4	0.2±0.9	-6.4±10.4
Loma Alta Slough (this study)	46.0±63.8	-6.7±58.0	0.1±0.2	1.8±4.9	-0.6±2.9
San Elijo Lagoon (this study)					
Segment 1	-12.3±17.9	28.6±21.7	0.4±0.3	0.9±0.3	-8.1±8.5
Segment 2	-51.5±26.8	98.1±36.4	0.8±0.3	11.8±2.3	-4.4±2.8
Buena Vista Lagoon (this study)					
East Basin	-4.6±28.5	13.4±14.8	-0.3±0.6	0.3±2.2	-5.9±13.0
Central Basin	-145.02±48.0	50.9±26.0	0.9±2.4	2.0±18.0	-1.2±4.3
Famosa Slough (this study)	-43.8±17.7	58.9±46.4	-0.2±0.2	1.0±1.4	-0.2±0.5
Shallow SE Australian Lagoons (Eyre and Ferguson 2002)	-50 to 0	10 to 100		-3.4 to 0.3	0 to -60
Hog Island Bay (Tyler *et al.* 2003)	-0.003 to +0.012			-0.33 to + 0.42	-0.12 to +0.009
Shallow NE Australian Lagoons (Ferguson *et al* 2004)				-0.2±0.3	-0.4 ± 0.3
Newport Bay (Sutula *et al.* 2006)	-43 ± 20	107 ± 81	0.36 ± 0.52	5.7 ± 2.7	-3.0 ± 5.3
Los Angeles Harbor (Berelson unpublished)	-18.9 ± 6.3	39 ± 29	0.33 ± 0.40	3.9 ± 2.9	-0.19 ± 0.18
San Francisco Bay (Hammond *et al.* 1985)	-30 ± 7	24 ± 8	0.10 ± 0.50	1.1 ± 0.1	-0.5 ± 0.6
Monterey Bay (Berelson *et al.* 2003)	-9.1 ± 2.4	9.9 ± 2.7	0.11 ± 0.07	0.56 ± 0.24	-0.57 ± 0.48
Chesapeake Bay (Callender and Hammond 1982, Cowan and Boynton 1996)	-49		0.8	10.2	-2.9 to 0.2
San Quentin Bay, Baja CA (Ibarra-Obando *et al.* 2004)	-23.4 ± 10.7	31 ± 22.9	0.114 ± 0.140	2.15 ± 1.39	
Tomales Bay (Dollar *et al.* 1991)	-9.37 ± 9.56	20.7 ± 24.4	0.24 ± 0.40	1.96 ± 2.39	-0.01 ± 0.17
Plum Island Sound (Hopkinson *et al.* 1999)	-33 to -170	23 to 167	-0.25 to 1.5	4.8 to 21.2	

3.4.2 Seasonal Patterns of Nutrient Fluxes and Benthic Metabolism

In shallow coastal lagoons such as the SMRE, trends in benthic metabolism and nutrient flux are typically regulated by temporal changes in the primary producer community as well as process of diagenesis and cycling within the sediments (Sundbäck and McGlathery 2005). Porewater nutrient concentrations are controlled by a variety of factors, including exchange via the sediments, denitrification, nitrification, dissimilatory NO_3 reduction, decomposition and uptake by organisms (Figure 3.11). Exchange with the surface waters can be driven by diffusive or advective processes such as tidal pumping, groundwater input, etc. Thus interpretation of porewater profiles and in situ benthic fluxes can yield rich information about the redox status and dominant processes controlling nutrients cycling witin the sediments and the degree to which they provide a net source of nutrients to support primary producers in the surface waters.

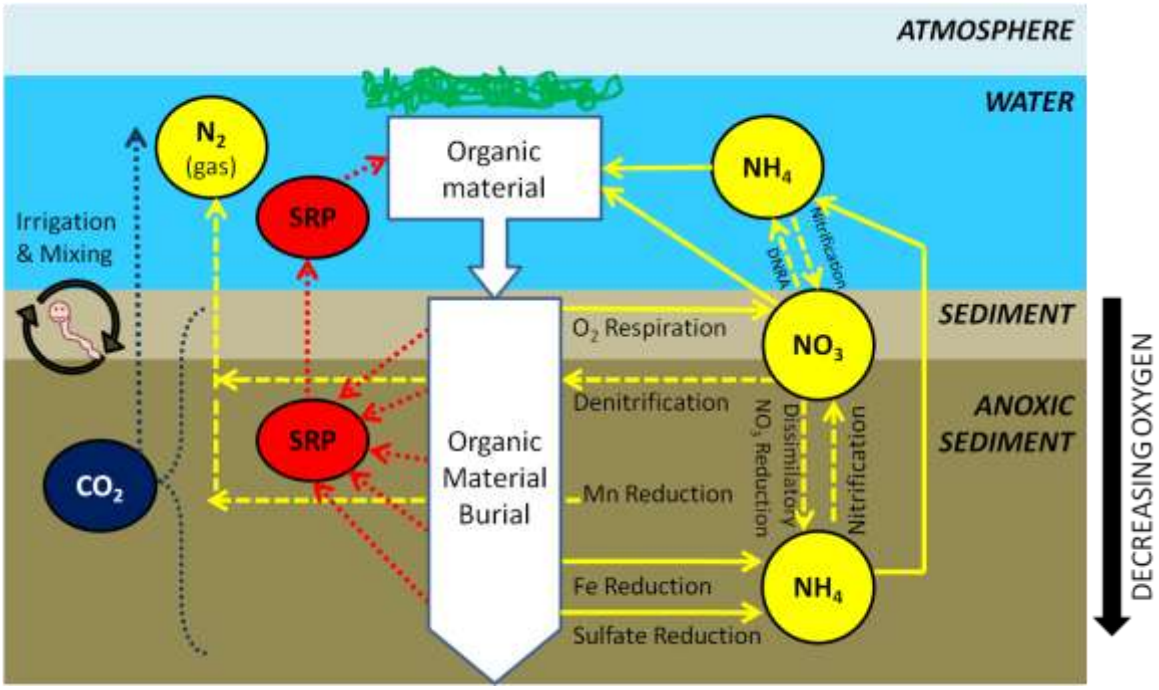


Figure 3.11. Pathways for nutrient cycling and decomposition of organic matter in the sediments.

For estuaries with high inputs of NO_3, the balance between denitrification and dissimilatory NO_3 two processes are important for the efficiency of N cycling and eutrophication in an estuary. Denitrification is the microbially-mediated conversion of NO_3 to N gas, a process that occurs in moderately reduced (low O_2) sediments and represents an important permanent loss of N from an estuary (Seitzinger 1988). Dissimilatory nitrate reduction (DNR) is the microbially mediated conversion of NO_3 to NH_4, a process which occurs in anoxic sediments (An and Joye 2006) and by which N can be recycled to surface waters and available for biological uptake. Averaging over segments and seasons, mean benthic flux appears to provides net source of NH_4 (4.4 mmol m^{-2} hr^{-1}) to surface waters. Interestingly, the magnitude of these NH_4 fluxes are among the highest documented in the literature (Table 3.6), despite very low and often

non-detectable sediment % N content. This suggests that one source of this sediment NH_4 flux is DNR. Mean influx of NO_3 into the sediment was high (-10 mmol m^{-2} hr^{-1}). Measured rates of denitrification in undisturbed cores were 2 orders of magnitude lower than this rate (7 to 10 µmol m^{-2} hr^{-1}; Table 3.3), 5 to 25X lower than the range of published rates in eutrophic estuaries (50 to 250 µmol m^{-2} hr^{-1}; Seitzinger 1988) and thus can only partially explain the fate of this influx of NO_3 into the sediments. A more likely explanation is that majority of this NO_3 is being reduced to NH_4 through DNR and is cycling back up to surface waters as NH_4. The porewater profiles provide additional evidence of DNR; with depth, NH_4 increases, with a corresponding decrease in NO_3, signaling the DNR may be a dominant process (An and Gardner 2002, Gardner et al. 2006, Porubsky *et al.* 2009). This may be a dominant process in sediments of Segment 1 and Segment 2 during the summer and fall. Peak NH_4 values coincided with higher SRP values and often with peaks in sulfide concentrations up to 9000 µM, signaling that sediments in an anoxic state and thus would favor DNR over denitrification. Denitrification may be playing a large role during the winter and spring time when sediments are better flushed and oxygenated (Seitzinger 1988). Thus in the winter and spring, the SMRE is better able to assimilate external DIN inputs through denitrfication, but as the estuary becomes more eutrophic during summer and fall, the efficiency of N loss is greatly reduced.

Table 3.6. Denitrification Rates Measured in the Santa Margarita River Estuary Subtidal Sediments on intact cores. All rates in µmol m^{-2} hr^{-1} (T. Kane, UCLA Dissertation 2011).

Segment	January 2008	March 2008	July 2008	August 2008
2	0.1	7.6	0	0.1
1	10.8	0	0	2.1

Averaging over index periods, sediments of the SMRE appear to be source of SRP (0.5 to 0.1 mmol SRP m^{-2} hr^{-1}). During winter and spring, sediments are acting as a sink for SRP. Sediments in this area appear more oxic, thus trapping P in particulate form associated with iron- and aluminum-oxides (Roden and Edmonds 1997). During the summer and fall index periods, sediments appear to act as a source to surface waters. The consequences of sulfate reduction for P cycling and fluxes, as indicated by peak sulfide concentrations, is important. As sulfate is reduced, Fe(II) is converted to iron-sulfides (Roden and Edmonds 1997). Because iron-sulfides cannot bind SRP, SRP adsorbed to Fe(II) are released, producing high porewater concentrations and net effluxes to surface waters.

In the SMRE, sediment % fines, OC, N and P content were major factor driving differences in the magnitude and direction of benthic fluxes observed between Segments 1 and 2. Porewater concentrations were orders of magnitude higher at Segment 1 then at Segment 2. Porewater TN at Segment 1 (413 to 1168 uM) was dominated by NH_4 throughout all sampling periods, while Segment 2 sediment TDN porewaters (49 to 114 uM) were dominated by NO_3+NO_2 and DON during the first 2 sampling periods and by NH_4 and DON during the last two, when NO_3+NO_2 was non-detect. With respect to in situ benthic fluxes, NH_4, NO_3 and SRP fluxes were typically 1 to 2 orders of magnitude lower at Segment 2 than Segment 1. Ultimately, the differences between these segments are driven by

hydrology. High percentages of sand content and the low concentrations of redox indicators (NO_3, Mn, Fe, Sulfide, and SRP) during the winter and spring indicate that sediments at Segment 2 appear well flushed and irrigated, consistent dominant fluvial hydrology of this site (Figure 3.12). In comparison, down estuary of I-5, the estuary becomes more depositional, which would explain the higher organic matter and nutrient content of the bulk sediments and porewater and, ultimately, higher magnitude of nutrient fluxes.

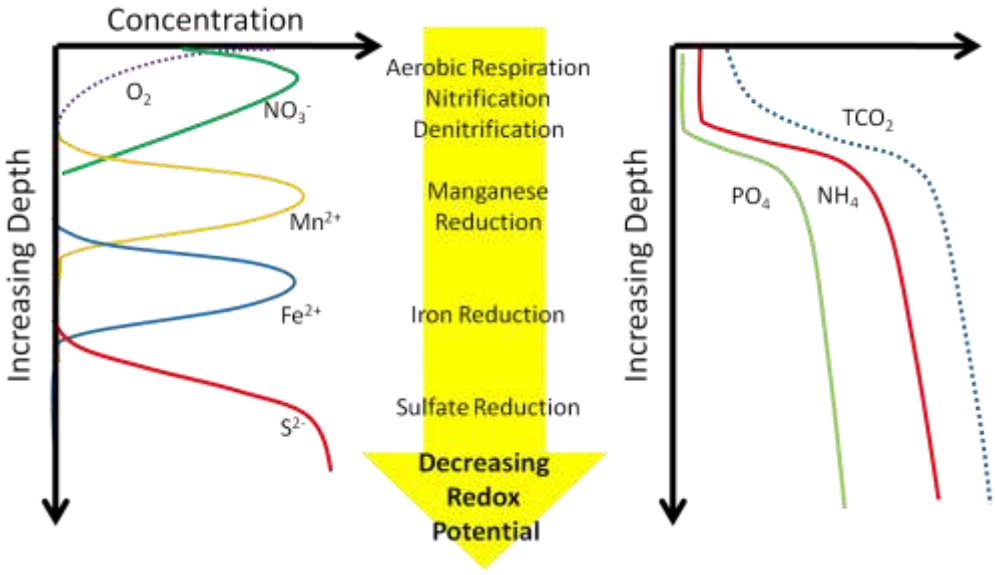


Figure 3.12. Sediment porewater profiles reflect redox status of the sediment.

Patterns of benthic nutrient cycling shifted seasonally, as can be observed from data representing the four index periods. The winter index period was characterized by frequent storm events. Peak flows during storm events in the winter index period would be expected to provide a subsidy of nutrients and particle-or organic matter-bound nutrients as well as an environment dominated by physical mixing of the surface waters and sediments (Smith *et al.* 1996, Correll *et al.* 1999, Paerl 2006). As evidence of this, surface sediments at both segments during this period contained the highest %fines of any of the four index periods (11 to 32% fines) and %OC and % N at Segment 1 (1% OC and 0.5% N) was an order of magnitude higher than the other index periods. Higher net sediment O_2 demand at Segment 2 is consistent with fresh input of labile organic matter. However, sediments were well flushed, as demonstrated by flat and near-nondetect profiles of SRP, NH_4, and sulfide (Froelich *et al.* 1979) and thus sediment O_2 demand was moderate. As a result, primary producer biomass was low and fluxes may have been controlled to a greater extent by advective processes (Sutula *et al.* 2004, Sutula *et al.* 2006). Ammonium and SRP fluxes are low and generally not signicantly different from zero, while NO_3 fluxes are large and negative (into the sediment), suggesting denitrification maye occurring. Interestingly, porewater NO_3 concentrations were relatively high during the spring index period at Segment 1. Peaks were observed in the vertical profiles of NO_3 and coincided with elevated Mn and Fe porewater

concentrations and low sulfide, TCO_2, NH_4 and SRP concentrations (Figure 3.6), suggesting that the shallow surface sediments were perched at higher redox levels (Roden and Edmonds 1997). It is likely that denitrification is occurring during this time.This concept is supported by independent measures of denitrification in SMRE sediments, which showed peak rates in the winter and spring (Table 4.3).

During the spring sampling period, O_2 effluxes out of the sediment and $TC0_2$ influxes peak, indicating net autotrophy (Eyre and Ferguson 2002a, 2005). As with the winter index period, NH_4, SRP, and NO_3 fluxes are low and into the sediment and porewater profiles indicate that the sediments are well flushed. Microphytobenthos biomass, increasing from winter time lows, in combination with well irrigated sediments, maybe responsible for this net autotrophy. Microphytobenthos can act to decouple nutrient turnover in the sediments from the overlying water column by acting as a "filter" for nutrient efflux from the sediments, at times completely intercepting nutrient fluxes across the sediment-water interface (McGlathery *et al.* 2004, McGlathery *et al.* 2007). Low fluxes of DIN compared to other eutrophic systems (Table 3.5), coupled with peak net O_2 efflux and $TC0_2$ influx, are an indication that this phenomenon may be occurring.

During the summer and fall index periods, macroalgae replaced MPB as the dominant primary producer. Macraolgae have been shown to control the biomass of other primary producer communities, including benthic microalgae. Macroalgae have been shown to control the biomass of other primary producer communities, including benthic microalgae, because of a competitive advantage in nutrient uptake rate (Fong *et al.* 1993, Fong *et al.* 2003). While MPB has been shown to enhance the O_2 penetration of sediments, macroalgal biomass is know to shallow the depth of sulfate reduction, resulting in high porewater concentrations near the surface (Tyler *et al.* 2003). Sulfide reached peak concentrations surficial sediments and porewater sulfide and SRP were at their peak. Previous studies have suggested that macroalgae can drive an increased efflux of dissolved inorganic nutrients from sediments by drawing down surface water concentration, thereby increasing the concentration gradient (Tyler *et al.* 2003, Sutula *et al.* 2006). As these nutrients are trapped as biomass, macroalgae become an effective mechanism to retain and recycle nutrients within an estuary, diverting loss from denitrification or tidal outflow. This concept is supported by low to non-detectable rates of denitrification in the SMRE during this index period. Both NO_3 uptake associated with primary production (MPB or macroalgae) as well as DNR may have limited denitrification through competition for NO_3 (Rysgaard *et al.* 1995, An and Joye 2001, Dalsgaard 2003, McGlathery *et al.* 2007). Denitrification is thought to be an unimportant sink for N in shallow coastal lagoons because primary producers typically outcompete bacteria for available NO_3 (McGlathery *et al.* 2007).

4 Santa Margarita River Estuary Nitrogen and Phosphorus Budgets

4.1 Introduction

Nutrient cycling is one of the critical functions of estuaries (Day *et al.* 1989). The net balance of nutrient sources, transformations and losses from the estuary dictate the biomass and community structure of primary producers and bacteria, which forms the foundation for the estuarine food webs and dictates the habitat quality for benthic and pelagic fauna. One means of evaluating the efficiency of nutrient cycling within an estuary is to estimate its N and P budgets (Sutula *et al.* 2001). Budgets are a useful method to assess the relative importance of allochthonous inputs ("new" nutrients) versus internal recycling ("recycled" nutrients) on primary productivity (Mitsch and Gosselink 1993) – the main symptom of eutrophication.

The purpose of this section is to estimate SMRE N and P sources, losses, and change in storage for those terms which are readily estimated. The estuarine hydrodynamic and water quality models will be used in the future to develop refined nutrient budgets for the SMRE. However, in the interim, coarse estimates of nutrient budgets can be derived. This information, in conjunction with data estimating the change in storage, can shed light on the efficiency of nutrient cycling, identify potential sources that are unaccounted for and inform potential management actions in the SMRE.

4.2 Methods

Budgets are estimated by determining the sum of source and loss terms from an estuary during the time period of interest (Figure 4.1). The sum of the source and loss terms, plus the change in "storage" of nutrients within specific compartments within the estuary (e.g. sediments, surface water, primary producers), should be equal to zero (Equation 4.1). Table 4.1 gives a summary of all the possible nutrient source, loss, and change in storage terms for an estuary and which of these were measured in the SMRE.

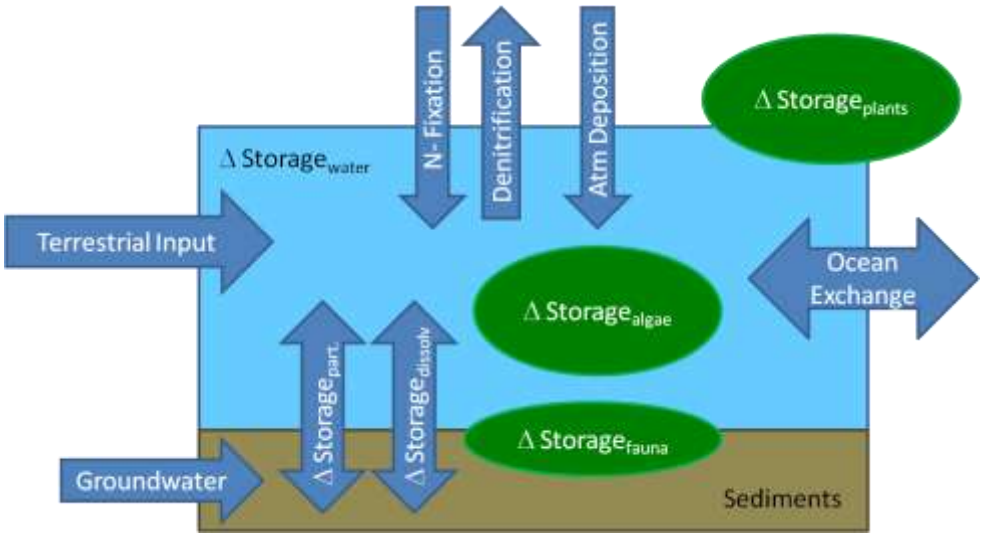


Figure 4.1. Conceptual model for development of budget estimates.

$$Load_{watershed} \pm Load_{ocean} \pm Load_{groundwater} + Atmospheric\ Deposition - Denitrification + N\ fixation - \Delta Storage_{algae} - \Delta Storage_{plants} - \Delta Storage_{fauna} + \Delta Storage_{part} + \Delta Storage_{dissolv} - \Delta Storage_{water} + Residual = 0 \quad \textbf{Eq. 4.1}$$

Table 4.1. Summary of nutrient budget terms: sources, losses and change in storage.

Budget Term	Nitrogen	Phosphorus
Sources		
Terrestrial Runoff (wet and dry weather)	CDM	CDM
Groundwater efflux	Unquantified	Unquantified
Atmospheric Deposition	Literature values	Literature values
Tidal surface water inflow	Unquantified	Unquantified
Benthic nitrogen fixation	UCLA Study	N/A
Losses		
Tidal surface water outflow	Unquantified	Unquantified
Grounwater influx	Unquantified	Unquantified
Denitrification	UCLA Study	N/A
Sediment burial	LSU	
Change in Storage		
Benthic exchange of nutrients with surface waters	SCCWRP	SCCWRP
Plant/algal uptake/ release	Residual of Sum of Sources, Losses and Change in Storage Terms	
Sediment deposition/resuspension of particulate nutrients	LSU	LSU
Faunal uptake and release	Assumed negligible	Assumed negligible

Nutrient sources to the SMRE include: terrestrial runoff (wet and dry weather from creeks and storm drains), groundwater efflux, atmospheric deposition, ocean water inflow, and N fixation (Table 4.1). Nutrient losses to include: groundwater recharge, ocean water outflow, sediment burial, and denitrification. Change in storage includes benthic exchange with surface waters, aquatic primary producer biomass, sediment mass accumulation or loss, and faunal uptake and release.

These terms were estimated from monitoring data or from literature values for the period of November 1, 2007 through October 31, 2008 (Table 4.1 and Appendix 2).

Terrestrial runoff was estimated from wet and dry weather runoff monitoring conducted by CDM, Inc. (2009). Benthic N fixation and denitrification were measured during each of the index periods at each segment site (personal communication, T. Kane, UCLA Department of Biological Sciences Doctoral Dissertation).

Atmospheric deposition rates were not estimated in this study and no local data were available. Atmospheric deposition rates are estimated from a National Atmospheric Deposition Program site in the San Bernadino Mountains during 2007. Dry deposition for NH_4 and NO_3 for this site was 2.6 kg ha^{-1} $year^{-1}$ while wet deposition was 1.5 kg ha^{-1} $year^{-1}$. Fewer data are available for atmospheric deposition of P;

data from south Florida indicate total (wet+dry) P fluxes ranging from 0.1 to 0.4 kg ha^{-1} $year^{-1}$, with an average of 0.3 kg ha^{-1} $year^{-1}$ (Redfield 2000, Ahn and James 2001). Typically ratios of dry:wet P deposition are 3:1. These numbers were used to estimate annual atmospheric loads for the SMRE, but are acknowledged to be highly uncertain.

Sediment mass accumulation and loss was estimated from long-term annual deposition rates measured by Louisiana State University (see Section 2). However, while these terms are important to the overall mass balance of nutrients, they were not included in the calculation of the residual because of lack of certainty on the net sediment transport through the estuary and because particulate nutrients are less biologically active then dissolved forms. Benthic flux accounts for sediment exchange with the surface waters, and thus incorporates the short-term effects of particulate nutrient deposition.

Groundwater interactions and the change in storage associated with faunal and emergent vegetation contributions were not quantified. Tidal surface water inflow and outflow cannot be estimated through a spreadsheet exercise, but rather throught the development of a hydrodynamic model for the estuary. Thus, net exchange with the coastal ocean is included in the residual budget term. However, concentrations of nutrients in the ocean are very low, so as an approximation, we assumed that ocean inputs of nutrients to the estuary are negligible.

In order to construct coarse budgets, a number of assumptions were necessary. First, benthic nutrient flux, denitrification and N fixation rates were extrapolated for the quarter over which the index period represents and the area of habitat available in the estuary. As these rates are expressed in a per square meter basis, the rates were multiplied by the representative area of intertidal and subtidal habitat in each of segment. It was assumed that only the mudflat and subtidal habitat in the main channel is subject to tidal hydrology. The large expanse of salt panne habitat west of the I-5 is infrequently inundated and therefore excluded from calculations. For the purposes of estimating benthic flux, it was assumed that nutrient exchange with the emergent marsh habitat was negligible and that the 102,191 m^2 of mudflat habitat was inundated ½ of the time, so the representative area of mudflat used was 51,096 m^2. Likewise, estimates of primary producers that are expressed on an areal basis (MPB and macroalgae) were multiplied by the total area of mudflat (102,191 m^2) and subtidal habitat (455,551 m^2). Table 4.2 presents the literature and assumptions were used to convert primary producer biomass to N and P.

Table 4.2. Literature values for Chla:C and C:N:P ratios of primary producer communities and assumptions to convert biomass to areal estimates of N and P associated with biomass.

Community	Stoichiometry (C:N:P)	Reference
Phytoplankton, assumed 1.5 m water depth	chl a: C Ratio of 30:1 C:N:P = 106:16:1	(Cloern *et al.* 1995), Redfield Ratio (Redfield 1958, Anderson and Sarmiento 1994)
Cyanobacteria mats	50% C by dry wt C:N:P = 550:30:1	Study data (Atkinson and Smith 1983)
Macroalgae	22% C by dry wt C:N:P = 80:5:1	Study data, (Eyre and McKee 2002)
Benthic microalgae	chl a: C ratio of 30:1 C:N:P = 90:15:1	(Sundbäck and McGlathery 2005) (Eyre and McKee 2002)

4.3 Results and Discussion

Coarse seasonal N and P budgets for the SMRE provide order of magnitude estimates of nutrients available for primary productivity and can be used interpret the importance of external loads versus internal biological recycling in supporting it.

Wet weather and total dry weather terrestrial inputs, as measured at the ME site, were equal in magnitude (Table 4.3). Most of the dry weather input was concentrated during the Winter (Nov-Jan, 41,627 kg TN), representing 36% of the total annual export. Terrestrial inputs during summer and fall were low (535 to 0 kg TN respectively).

With respect to relative sources, terrestrial TN input overwhelmed all other sources[2] during the wet season, but during the summer and fall estimated terrestrial input only represented 0-25% of TN loads to the surface waters (Table 4.4). In contrast, benthic flux ranged acted as a sink for about 10% of the terrestrial N during the winter index period but then became a dominant source during the summer and fall (79% to 97% of TN sources), the periods of peak primary producer biomass. Direct atmospheric deposition and benthic N fixation are negligible sources. Denitrification rates measured on undisturbed cores were low (see Table 4.3; T. Kane, UCLA Doctoral Dissertation 2011). However, rates were higher on slurried cores during the spring (mean of 114 µmol m^{-2} hr^{-1}; T. Kane, UCLA Doctoral Dissertation 2011). This rate would produce loss from denitrification on the order ~ 1000 kg N, a term on the same order of magnitude as NO_3 fluxes during this period.

Table 4.3. Comparison of estimated nitrogen source, loss and change in storage terms in the SMRE during dry weather periods (kg N). Positive and negative under "source and loss" terms indicates source and loss to the SMRE respectively. Positive and negative numbers in change of storage terms indicate gain and loss from compartment respectively. Residual is the sum of source and loss terms, minus the change in storage.

Budget Term	Wet Weather	Dry Weather Nov-Jan	Dry Weather Feb-Apr	Dry Weather May-Jul	Dry Weather Aug-Oct	Annual (Wet +Dry)
Source and Loss Terms						
Terrestrial runoff	39,278	30,255	10,837	535	0	80,905
N - Fixation	--	189	27	50	45	311
Atmos. Deposition	68	30	30	30	30	187
Denitrification	--	-68	-47	0	-14	-128
Source + Loss Terms	39,346	30,406	10,847	614	61	81,274
Change in Storage						
Benthic N Flux	--	-3,210	-3,475	1,702	617	-4,366
1^0 Producer N	--	0.1	1	484	1,114	1,600
Residual	39,346	27,196	7,370	1,832	-436	75,308

[2] The net exchange of groundwater is unknown.

Table 4.4. Comparison of loads from watershed versus benthic nutrient flux (kg).

kg	Wet Weather	Index Period 1		Index Period 2		Index Period 3		Index Period 4		Annual (Wet+ Dry)	
		Water-shed	Benthic Flux	Water-shed	Benthic Flux	Water-shed	Benthic Flux	Water-shed	Benthic Flux	Water-shed	Benthic Flux
TN	**39,278**	**30,255**	**--**	10,837		535		0		80,905	--
TDN	**0**	**0**	-3210	0	-3475	0	1702	0	617	0	-4,366
NH_4	**5,143**	**303**	4250	841	-96	13	9705	0	1724	6,300	15,583
NO_3	**26,581**	**26,163**	-8981	7,051	-2721	7	-8807	0	-837	59,801	-21,346
TP	**5,255**	**1,279**	**--**	1,274	**--**	328	**--**	0	**--**	8,137	--
TDP	**3,425**	**1,055**	189	1,153	-166	214	918	0	169	5,847	1,109
SRP	**1,642**	**1,054**	147	716	-29	157	666	0	140	3,569	923

A closer inspection of the balance between NO_3, NH_4 and TDN fluxes during each of the index periods is helpful in understanding the relative importance of two pathways of N cycling: denitrification and DNR (Table 4.4). Denitrification is the microbially-mediated conversion of NO_3 to N gas, a process that occurs is moderately reduced (low O_2) sediments and represents an important permanent loss of N from an estuary (Seitzinger 1988). Dissimilatory nitrate reduction is the microbially mediated conversion of NO_3 to NH_4, a process which occurs in anoxic sediments (An and Joye 2006) and by which N can be recycled to surface waters and available for biological uptake. During the winter and early spring index periods, sediments appeared to be a net sink for TDN (~ 6685 kg TDN over 6 months), driven by large NO_3 fluxes into the sediment (-11,702 kg TN over 6 months). During the Nov-Jan index period, these NO_3 fluxes were counteracted by a flux of NH_4 out of the sediments, while in the Feb-Apr index period NH_4 fluxes were negligible. During the 6-month summer and fall index period, TDN fluxes out of the sediment (~ 2319 kg TN) are driven by NH_4 fluxes (11,428 kg TN), which are greater than NO_3 fluxes into the sediments (-9,644 kg TN). The patterns illustrate that denitrification may be playing a large role during the winter and spring time when sediments are better flushed and oxygenated (Seitzinger 1988). Dissimilatory nitrate reduction is clearly a dominant pathway during the summer time and is likely responsible for the large NH_4 fluxes observed during these periods. Thus in the winter and spring, the SMRE is better able to assimilate external DIN inputs through denitrfication, but is overwhelmed during summer and fall.

This budget shows that during peak periods of macroalgal blooms, benthic flux of NH_4 is 1.5 to 19X the N required to grow the abundance of macroalgae observed (9705 and 1704 kg NH_4 vs 484 and 1114 kg algal N for summer and fall respectively). Macroalgae is an efficient trap for DIN and has been shown to intercept benthic nutrient effluxes and can even increase the net flux by increasing the concentration gradient between sediments and surface waters (Tyler *et al.* 2001, 2003; Sutula *et al.* 2006). The storage of large quantities of N as algal biomass thus diverts N loss from denitrification and providing a mechanism for N retention and recycling within the estuary (Krause-Jensen *et al.* 1999, Fong and Zedler 2000). Denitrification is thought to be an unimportant sink for N in eutrophic, shallow coastal lagoons because primary producers typically outcompete bacteria for available N, and partitioning of NO_3

reduction will shift to DNR to NH_4 in later stages of eutrophication (Risgaard-Petersen and Ottosen 2000, An and Gardner 2002, Dalsgaard 2003, McGlathery *et al.* 2007).

Two types of data suggest an external source of DIN to the estuary not accounted for in the estimate of terrestrial loads from the ME site. First, mixing diagrams of NO_3 suggest a source NO_3 in the 1 to 5 ppt range in the mixing diagrams during the Nov-Jan index period. This coincides with proximity to agricultural fields which may be running off into the lagoon near this location and may be responsible for the observed trends. Second, comparison of mass emission sources of NO_3 versus benthic influxes of NO_3 during the summer and fall show that SMRE surface waters has more NO_3 than can be predicted by inputs from the ME site. These data indicate that there are additional sources, such as lateral groundwater inputs of NO_3. This is a reasonable assumption, given the proximity of intensive, irrigated agriculture that was occurring at the time of sampling and permeable, sandy substrates which dominate the estuary.

Wet weather terrestrial runoff of TP constituted the majority (65%) of annual terrestrial input from the ME site (Table 4.5). Eighty-eight percent of the total annual dry weather runoff (2,882 kg) occurred over the winter and spring index periods. Terrestrial TP loads during summer and fall were low (328 to 0 kg TP, respectively). Wet weather terrestrial TP runoff was mostly 52% particulate P, while dry weather terrestrial loads ranged from 62 to 99% SRP (Table 4.4).

Table 4.5. Comparison of estimated phosphorus source and loss terms in the SMRE during dry weather periods (kg P). Positive and negative under "source and loss" terms indicates source and loss to the SMRE respectively. Positive and negative numbers in change of storage terms indicate gain and loss from compartment respectively. Residual is the sum of source and loss terms, minus the change in storage.

P Budget Term	Wet Weather	Dry Weather Nov-Jan	Dry Weather Feb-Apr	Dry Weather May-Jul	Dry Weather Aug-Oct	Annual (Dry Weather Only)
Source and Loss Terms						
Terrestrial runoff	5,255	1,279	1,274	328	0	8137
Atmos. Deposition	3	3	3	3	3	14
Source + Loss Terms	5,259	1,282	1,276	331	3	8150
Change in Storage						
Benthic N Flux	--	189	-166	918	169	1109
1^0 Producer P	--	0.0	0.6	215	975	1145
Residual	5,259	1,470	1,110	1,034	-803	8,115

With respect to relative sources, terrestrial TP input overwhelmed all other sources[3] during the wet season, but during the summer and fall estimated terrestrial loads only represented 0 to 32% of TP loads to the surface waters (Table 4.4). In contrast, benthic flux acted as a sink for about 10% of the terrestrial P during the spring index period but then became a dominant source during the summer and fall (75 to 97% of TP sources), the periods of peak primary producer biomass. Direct atmospheric deposition is a negligible source.

[3] The net exchange of groundwater is unknown.

The P budget shows that during peak periods of macroalgal blooms, benthic flux of TP is 17 to 400% the P required to grow the abundance of macroalgae observed (917 kg TDP and 169 kg TDP vs 215 kg and 275 kg of algal P for summer and fall, respectively). As with N, macroalgae is an efficient trap for PO_4 and has been shown to intercept benthic nutrient effluxes and can even increase the net flux by increasing the concentration gradient between sediments and surface waters (Tyler *et al.* 2001, 2003; Sutula *et al.* 2006). Macroalgae can change redox condition directly under the mat, causing PO_4 to solublize and become a source to surface waters (Roden and Edmonds 1997).

As with N, two types of data suggest an external source of PO_4 to the estuary not accounted for in the estimate of terrestrial loads from the ME site. First, mixing diagrams of NO_3 suggest show a source of PO_4 during all sampling periods. Second, the quantity of P required to grow macroalgae during the fall sampling period (975 kg TP) is not met by measured sources of terrestrial loads (0 kg TP) nor benthic flux (169 kg TDP). These data indicate that there are additional sources, such as lateral groundwater inputs of PO_4, that are occuring.

Interestingly, both N and P appear to be seasonally limiting in the SMRE. Surface water nutrients were P limited during the winter, and N limited during the summer and fall (Figure 4.2). Thus management of both N and P sources and the ratios available for primary productivity is critical for managing eutrophication.

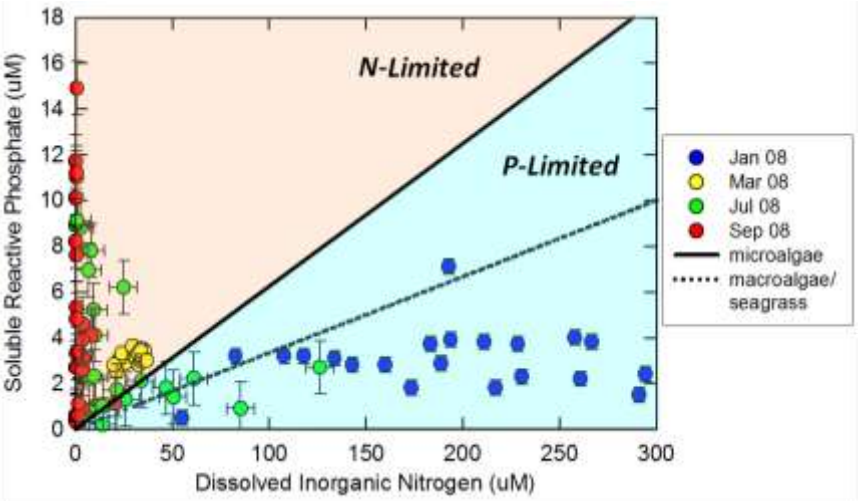


Figure 4.2. Ambient soluble reactive phosphorus versus dissolved inorganic nitrogen (nitrate, nitrite, and ammonium) from transect data taken in the northern channel (transect station # 11-15) and the southern basin (transect station # 1-10). The solid black line indicates the N and P requirements for both phytoplankton and benthic microalgae (N:P = 16:1), and the dotted black line indicates the N:P ratio for macroalgae and seagrasses (N:P = 30:1). If ambient values fall above these lines the communities are N limited. If values fall below, the communities are P limited.

4.4 Management Options to Reduce Eutrophication

The SMRE has the advantage, as a river mouth estuary, that sediments do not appear to have accumulated excessive organic matter with depth. Hypoxia was present in the estuary, but not chronic. Therefore, options for management of eutrophication in the SMRE are aimed at reducing the availability of nutrients for primary production during the growing season and increasing tidal exchange in order to increase availability of DO and enhance denitrfication. Three types of options could be considered:

1. Reduce terrestrial loads in order to limit primary productivity. Emphasis should be placed on reducing both P as well as N from the watershed. **Because sources during the growing season appear to be lateral inputs rather than those estimated by the ME site, minimizing these loads will be a critical and effective management strategy.**
2. Increase flushing during peak periods of primary productivity, particularly when SMRE has reduced tidal exchange to surface water exchange with ocean during summer. Clearly this is a trade off with the need preserve available tidewater goby habitat during summer. Improved circulation during closed condition could help to limit stratification and therefore ameliorate, to a minor extent, problems with hypoxia.
3. Restoration to improve exchange with expansive area of wetland habitat west of I-5. Denitrification rates are typically highest in wetland habitats (Day *et al.* 1989). Restoration to increase connectivity and exchange of surface waters with the large expanse of intertidal habitat south of the main channel would help to divert excessive NO_3 available during dry season from DNR towards denitrification and permanent loss. This could be accomplished through grading of portions of the natural levee with separates this the central channel from the wetland area.

5 References

Ahn, H. and R.T. James. 2001. Variability, uncertainty, and sensitivity of phosphorus deposition load estimates in South Florida. *Water, Air, & Soil Pollution* 126:37-51.

An, S. and W.S. Gardner. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). *Marine Ecology Progress Series* 237:41-50.

Anderson, L.A. and J.L. Sarmiento. 1994. Redfield ratios and remineralization determined by nutrient data analysis. *Global Biogeochemical Cycles* 8:65-80.

Atkinson, M.J. and S.V. Smith. 1983. C:N:P ratios of benthic marine plants. *Limnology and Oceanography* 28:568-574.

Bate, G.C., A.K. Whitfield, J.B. Adams, P. Huizinga and T.H. Wooldridge. 2004. The importance of the river-estuary interface (REI) zone in estuaries. *Water SA* 28:271.

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

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

Berelson, W.M., T. Townsend, D.T. Heggie, P. Ford, A.R. Longmore, G.W. Skyring, T. Kilgore and G.J. Nicholson. 1999. Modelling bio-irrigation rates in the sediments of Port Phillip Bay. *Marine and Freshwater Research* 50:573-580.

Bergamasco, A., L. De Nat, M.R. Flindt and C.L. Amos. 2003. Interactions and feedbacks among phytobenthos, hydrodynamics, nutrient cycling and sediment transport in estuarine ecosystems. *Continental Shelf Research* 23:1715-1741.

Borsuk, M.E., C.A. Stow, J. R. A. Luettich, H.W. Paerl and J.L. Pinckney. 2001. Modelling oxygen dynamics in an intermittently stratified estuary: Estimation of process rates using field data. *Esturine, Coastal and Shelf Science* 52:33-49.

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

Boynton, W.R., W.M. Kemp and C.G. Osborne. 1980. Nutrient fluxes across the ediment-water interface in the turbid zone of a coastal plain estuary pp. 93-109 *in*: V. S. Kennedy (Ed.), Estuarine Perspectives. Academic Press. New York, NY.

Brandl, H. and K.W. Hanselmann. 1991. Evaluation and application of dialysis porewater samplers for microbiological studies at sediment-water interfaces. *Aquatic Sciences* 53:54-73.

Burdige, D.J., W.M. Berelson, K.H. Coale, J. McManus and K.S. Johnson. 1999. Fluxes of dissolved organic carbon from California continental margin sediments. *Geochimica et Cosmochimica Acta* 63:1507-1515.

Caffrey, J.M. 2004. Factors controlling net ecosystem metabolism in US estuaries. *Estuaries* 27:90-101.

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

Clavero, V., J.J. Izquierdo, J.A. Fernandez and F.X. Niell. 2000. Seasonal fluxes of phosphate and ammonium across the sediment-water interface in a shallow small estuary (Palmones River, southern Spain). *Marine Ecology Progress Series* 198:51-60.

Cloern, J.E., C. Grenz and L. VidergarLucas. 1995. An empirical model of the phytoplankton chlorophyll:carbon ratio - The conversion factor between productivity and growth rate. *Limnology and Oceanography* 40:1313-1321.

Correll, D.L., T.E. Jordan and D.E. Weller. 1999. Transport of nitrogen and phosphorus from Rhode River watersheds during storm events. *Water Resources Research* 35:2513-2521.

Cowan, J.W. and W.R. Boynton. 1996. Sediment-water oxygen and nutrient exchanges along the longitudial axis of Chesapeake Bay: Seasonal patterns, controlling factors and ecological significance. *Estuaries* 19:562-580.

Dalsgaard, T. 2003. Benthic primary production and nutrient cycling in sediments with benthic microalgae and transient accumulation of macroalgae. *Limnology and Oceanography* 48:2138-2150.

Day, J.W., C.A.S. Hall, W.M. Kemp and A. Yaez-Arancibia. 1989. Estuarine Ecology. Wiley Interscience. New York, NY.

Diaz, R.J. 2001. Overview of hypoxia around the world. *Journal of Environmental Quality* 30:275-281.

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

Elrod, V.A., W.M. Berelson, K.H. Coale and K.S. Johnson. 2004. The fulx of iron from continental shelf sediments: A missing source for global budgets. *Geophysical Research Letters* 31:L12307.

Eyre, B.D. and A.J.P. Ferguson. 2002a. Comparison of carbon production and decompostion, benthic nutrient fluxes and denitrification in seagrass, phytoplankton, benthic microalgae- and macroalgae- dominated warm-temperature Australian lagoons. *Marine Ecology Progress Series* 229:43-59.

Eyre, B.D. and A.J.P. Ferguson. 2002b. Sediment biogeochemical indicators for defining sustainable nutrient loads to coastal embayments. Paper presented at the Proceedings of Coast to Coast - "Source to Sea", Tweed Heads.

Eyre, B.D. and A.J.P. Ferguson. 2005. Benthic metabolism and nitrogen cycling in subtropical east Australian estuary (Brunswick): Temporal variability and controlling factors. *Limnology and Oceanography* 50:81-96.

Eyre, B.D. and L.J. McKee. 2002. Carbon, nitrogen, and phosphorus budgets for a shallow subtropical coastal embayment (Moreton Bay, Australia). *Limnology and Oceanography* 47:1043-1055.

Ferguson, A.J.P., B.D. Eyre and J.M. Gay. 2003. Organic matter and benthic metabolism in euphotic sediments along shallow sub-tropical estuaries, northern New South Wales, Australia. *Aquatic Microbial Ecology* 33:137-154.

Ferguson, A.J.P., B.D. Eyre and J.M. Gay. 2004. Benthic nutrient fluxes in euphotic sediments along shallow sub-tropical estuaries, northern New South Wales, Australia. *Aquatic Microbial Ecology* 37:219-235.

Fong, P., K.E. Boyer, K. Kamer and K.A. Boyle. 2003. Influence of initial tissue nutrient status of tropical marine algae on response to nitrogen and phosphorus additions. *Marine Ecology-Progress Series* 262:111-123.

Fong, P., K.E. Boyer and J.B. Zedler. 1998. Developing an indicator of nutrient enrichment in coastal estuaries and lagoons using tissue nitrogen content of the opportunistic alga, Enteromorpha intestinalis (L. Link). *Journal of Experimental Marine Biology and Ecology* 231:63-79.

Fong, P. and J.B. Zedler. 2000. Sources, sinks and fluxes of nutrients (N + P) in a small highly modified urban estuary in southern California. *Urban Ecosystems* 4:125-144.

Fong, P., J.B. Zedler and R.M. Donohoe. 1993. Nitrogen vs. phosphorus limitation of algal biomass in shallow coastal lagoons. *Limnology and Oceanography* 38:906-923.

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

Gardner, W.S., M.J. McCarthy, S. An, D. Sobolev, K.S. Sell and D. Brock. 2006. Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries. *Limnology and Oceanography* 51:558-568.

Granek, E.F., S. Polasky, C.V. Kappel, D.J. Reed, D.M. Stoms, E.W. Koch, C.J. Kennedy, L.A. Cramer, S.D. Hacker, E.B. Barbier, S. Aswani, M. Ruckelshaus, G.M.E. Perillo, B.R. Silliman, N. Muthiga, D. Bael and E. Wolanski. 2010. Ecosystem services as a common language for coastal ecosystem-based management. *Conservation Biology* 24:207-216.

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

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

Hammond, D.E., P. Giordani, W.M. Berelson and R. Poletti. 1999. Diagenesis of carbon and nutrients and benthic exchange in sediments of the Northern Adriatic Sea. *Marine Chemistry* 66:53-79.

Hesslein, R.H. 1976. An in situ sampler for close interval pore water studies. *Limnology and Oceanography* 21:912-914.

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

Howarth, R.W. 1988. Nutrient limitation of primary production in marine ecosystems. *Annual Review of Ecology and Systematics* 19:89-110.

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

Jahnke, R.A., C.R. Alexander and J.E. Kostka. 2003. Advective pore water input of nutrients to the Satilla River Estuary, Georgia, USA. *Estuarine Coastal and Shelf Science* 56:641-653.

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

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

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

Koroleff, F. 1985. Simultaneous oxidation of nitrogen and phosphorus by persulfate. *in*: K. Grasshoff , M. Eberhardt and K. Kremling (Eds.), Methods of Seawater Analysis, 2nd Edition. Verlang Chemie. Weinheimer, Germany.

Krause-Jensen, D., P.B. Christensen and S. Rysgaard. 1999. Oxygen and nutrient dynamics within mats of the filamentous macroalga *Chaetomorpha linum*. *Estuaries* 22:31-36.

Largier, J.L., J.H. Slinger and S. Taljaard. 1991. The stratified hydrodynamics of the Palmiet-- A prototypical bar-built estuary. pp. 135-153 *in*: D. Prandle (Ed.), Dynamics and Exchanges in Estuaries and the Coastal Zone. American Geophysical Union. Washington, DC.

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

Loneragan, N.R. and S.E. Bunn. 1999. River flows and estuarine ecosystems: Implications for coastal fisheries from a review and a case study of the Logan River, southeast Queensland. *Australian Journal of Ecology* 24:431-440.

MACTEC. 2009. Carslbad Hydrologic Unit (CHU) Lagoon Monitoring Report. MACTEC Engineering and Consulting, Inc. San Diego, CA.

McGlathery, K., K. Sundbäck and I.C. Anderson. 2004. The importance of primary producers for benthic N and P cycling. *in*: S. L. Nielsen , G. M. Banta and M. F. Pedersen (Eds.), The Influence of Primary Producers on Estuarine Nutrient Cycling. Kluwer Academic. Dusseldorf, Germany.

McGlathery, K.J., K. Sundback and I.C. Anderson. 2007. Eutrophication in shallow coastal bays and lagoons: the role of plants in the coastal filter. *Marine Ecology-Progress Series* 348:1-18.

McLaughlin, K., M. Sutula and K. Schiff. 2007. San Diego Lagoons TMDL Monitoring Workplan. SCCWRP. Costa Mesa, CA.

Mitsch, W.J. and J.G. Gosselink. 1993. Wetlands (ed.). Van Nostrand Reinhold. New York, NY.

Neto, J.M., M.R. Flindt, J.C. Marques and M. Pardal. 2008. Modelling nutrient mass balance in a temperate meso-tidal estuary: Implications for management. *Estuarine, Coastal and Shelf Science* 76:175-185.

Paerl, H.W. 2006. Assessing and managing nutrient-enhanced eutrophication in estuarine and coastal waters: Interactive effects of human and climatic perturbations. *Ecological Engineering* 26:40-54.

Paerl, H.W. 2009. Controlling Eutrophication along the Freshwater-Marine Continuum: Dual Nutrient (N and P) Reductions are Essential. *Estuaries and Coasts* 32:593-601.

Paerl, H.W., J.L. Pinckney, J.M. Fear and B.L. Peierls. 1998. Ecosystem responses to internal and watershed organic matter loading: consequences for hypoxia in the eutrophying Neuse River Estuary, North Carolina, USA. *Marine Ecology Progress Series* 166:17-25.

Peckol, P. and J.S. Rivers. 1995. Contribution by macroalgal mats to primary production of a shallow embayment under high and low nitrogen loading rates. *Estuarine Coastal and Shelf Science* 44:451-465.

Pedersen, M.F. and J. Borum. 1997. Nutrient control of estuarine macroalgae: growth strategy and the balance between nitrogen requirements and uptake. *Marine Ecology Progress Series* 161:155-163.

Porubsky, W.P., N.B. Weston and S.B. Joye. 2009. Benthic metabolism and the fate of dissolved inorganic nitrogen in intertidal sediments. *Estuarine Coastal and Shelf Science* 83:392-402.

Qu, W., R.J. Morrison, R.J. West and C. Su. 2005. Diagenetic stoichiometry and benthic nutrient fluxes at the sediment–water interface of Lake Illawarra, Australia. Hydrobiologia 537:249-264.

Redfield, A.C. 1958. The biological control of chemical factors in the environment. *American Scientist* 46:205-221.

Redfield, G.W. 2000. Ecological research for aquatic science and environmental restoration in south Florida. *Ecological Applications* 10:990-1005.

Risgaard-Petersen, N. and L.D.M. Ottosen. 2000. Nitrogen cycling in two temperate *Zostera marina* beds: seasonal variation. *Marine Ecology Progress Series* 198:93-107.

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

Rountree, R.A. and K.W. Able. 2007. Spatial and temporal habitat use patterns for salt marsh nekton: implications for ecological functions. *Aquatic Ecology* 41:25-45.

Schubel, J.R. and V.S. Kennedy. 1984. Estuary as a Filter. Academic Press. Orlando, FL.

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

Shervette, V.R. and F. Gelwick. 2008. Seasonal and spatial variations in fish and macroinvertebrate communities of oyster and adjacent habitats in a Mississippi estuary. *Estuaries and Coasts* 31:584-596.

Smith, S.V., R.M. Chambers and J.T. Hollibaugh. 1996. Dissolved and particulate nutrient transport through a coastal watershed--estuary system. *Journal of Hydrology* 176:181-203.

Stanley, D.W. and S.W. Nixon. 1992. Stratification and bottom-water hypoxia in the Pamlico River Estuary. *Estuaries* 15:270-281.

Sundbäck, K. and K.J. McGlathery. 2005. Interaction between benthic macro- and microalgae in the marine environment. *in*: E. Kristensen , J. E. Kostka and R. H. Haese (Eds.), Interaction between Benthic Macro- and Microalgae in the Marine Sediments. American Geophysical Union. Washington, DC.

Sutula, M., C. Creager and G. Wortham. 2007. Technical Approach to Develop Nutrient Numeric Endpoints for California Estuaries. Southern California Coastal Water Research Project. Costa Mesa, CA.

Sutula, M., J.W. Day and J. Cable. 2001. Hydrological and nutrient budgets of freshwater and estuarine wetlands of Taylor Slough in Southern Everglades, Florida (USA). *Biogeochemistry* 56:287-310.

Sutula, M., K. Kamer and J. Cable. 2004. Sediments as a Non-point Source of Nutrients to Malibu Lagoon, California (USA). Technical Report 441. Southern California Coastal Water Research Project. Westminster, CA.

Sutula, M., K. Kamer, J. Cable, H. Collis, W. Berelson and J. Mendez. 2006. Sediments as an Internal Source of Nutrients to Upper Newport Bay, California. Southern California Coastal Water Research Project. Westminster, CA.

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

United States Environmental Protection Agency. USEPA. 2000. Ambient Aquatic Life Water Quality Criteria for Dissolved Oxygen (Saltwater): Cape Cod to Cape Hatteras. USEPA. Washington, DC.

USEPA. 2003. Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity, and Chlorophyll a for Chesapeake Bay and Its Tidal Tributaries. USEPA. Washington, DC.

Valiela, I., K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-Andreson, C. D'Avanzo, M. Babione, C. Sham, J. Brawley and K. Lajtha. 1992. Couplings of Watersheds and Coastal Waters: Sources and Consequences of Nutrient Enrichment in Waquoit Bay, Massachusetts. *Estuaries* 15:433-457.

Valiela, I., J. McClelland, J. Hauxwell, P.J. Behr, D. Hersh and K. Foreman. 1997. Macroalgal blooms in shallow estuaries: Controls and ecophysiological and ecosystem consequences. *Limnology and Oceanography* 42:1105-1118.

Webb, A.P. and B.D. Eyre. 2004. The effects of two benthic chamber stiffing systems on the diffusive boundary layer, oxygen flux, and passive flow through model macrofauna burrows. *Estuaries* 27:352-361.

Welsh, D.T., M. Bartoli, D. Nizzoli, G. Castaldelli, S.A. Riou and P. Viaroli. 2000. Denitrification, nitrogen fixation, community primary productivity and inorganic-N and oxygen fluxes in an intertidal *Zostera noltii* meadow. Vol. 208:65-77.

Weston Solutions, Inc. 2009. TMDL Monitoring for Eutrophication in Famosa Slough In Response to Investigative Order R9-2006-0076. Carlsbad, CA.

Appendix 1 - Quality Assurance Documentation

This section presents the results of the QA/QC procedures conducted throughout the sampling period at the SMRE.

Sampling Equipment Maintenance

Benthic chambers, porewater peepers and sediment cores were inspected prior to each deployment for cracks and/or deformities. Chambers were "re-plumbed" with new tubing and make-up bags during each index period and the diffuser bars were scrubbed internally and flushed with distilled water to make sure they were not clogged with sediment. Dark chambers were further inspected to make sure they were completely covered and no light was transmitted to the chamber. Peepers were cleaned and scrubbed with ethyl alcohol (to kill algae and microbial growth), rinsed in a 5% hydrochloric acid bath, then rinsed three times with distilled water prior to assembly to minimize contamination.

Data Sondes: Calibration, Drift, and Logging

Data sondes deployed in each benthic chamber and in the ambient surface water were calibrated not more than four days prior to deployment and a drift check was completed after deployment. No calibration problems or drift were apparent in any of the sonde maintenance events. During index period 1 sondes in chambers 3 and 4 failed to log data and during index period 3 the sonde in chamber 1 failed to log data. Reason for the lost data was due to a failure of the power supply.

Holding Times Violations

All water and sediment samples met the required holding times for benthic flux study in the SMRE SCCWRP special studies. Porewater samples had holding times violations for dissolved inorganic nutrients (NH_4, NO_3, NO_2, and SRP) by UCSB for two periods: samples collected on 4/3/08 were not analyzed until 5/5/08 and exceeded the holding times by four days, and samples collected on 7/23/08 were run on 8/27/08 and exceeded the holding time by six days. These were considered minor violations and the data were used in calculations.

Laboratory Blanks

All of the laboratory blanks were reported to be below the level of detection, suggesting no bias from analytical techniques.

Field Blanks

One field blank was collected for each analyte during each benthic flux study and during each porewater peeper study. Field blank samples were collected using the same sample handling and collection equipment as field samples, except distilled- deinonized water was processed instead of sample water to assess possible contamination issues. Field blanks for total dissolved nitrogen, ammonium, total carbon dioxide and iron had a small percentage of samples fall outside the acceptable range. All other field blanks were below the minimum detection limit.

Laboratory Control Standards

All of the laboratory control standards were met acceptance criteria for percent recovery.

Laboratory Duplicates

Laboratory duplicates were processed by all analytical laboratories. A subset of samples (~5%) were randomly selected by the technician, split in the laboratory, and run separately to assess the comparability of the sample analysis process. All laboratory duplicates were within the analytical reporting limits for each analyte.

Field Duplicates

One field duplicate was collected for each analyte during each benthic flux study and during each porewater peeper study. Ammonium, NO_3+NO_2, and TDP had a small percentage of samples fail to meet the acceptance criteria. Field duplicates for all other analytes fell within the acceptance criteria.

Laboratory Matrix Spikes

Matrix spike samples were processed in the laboratory by adding a known concentration of a specific analyte to a field sample. The sample was analyzed prior to addition of the spike and again after addition. The calculated analyte concentration was prepared and compared to the analytical concentration. Matrix spike results are acceptable when the percent recovery is between 80 and 120%. All of the matrix spike results were within the acceptable range for the the SMRE special studies.

Table A1.1 QA/QC analysis for the SMRE Data Set.

Constituent	Lab Blanks >MDL	Field Blanks >MDL	Lab Duplicates> 25% RPD	Field Duplicates >25% RPD	Holding Time Violation
Water Analyses					
TN	0%	0%	0%	0%	0%
TDN	0%	12%	0%	0%	0%
NH_4	0%	12%	0%	12%	15%
NO_3 + NO_3	0%	0%	0%	12%	15%
NO_3	0%	0%	0%	0%	15%
TP	0%	0%	0%	0%	0%
TDP	0%	0%	0%	12%	0%
SRP	0%	0%	0%	0%	15%
TCO_2	0%	12%	0%	0%	0%
Fe	0%	12%	0%	0%	0%
Mn	0%	0%	0%	0%	0%
S^{-2}	0%	0%	0%	0%	0%
Suspended chl a	0%	0%	0%		0%
Sediment Analyses					
%OC	0%	NA	0%	0%	0%
%TN	0%	NA	0%	0%	0%
%TP	0%	NA	0%	0%	0%
Grain Size	NA	NA	NA	0%	0%
Benthic chl a	0%	NA	0%		0%

Appendix 2 - Summary of Data to Support Modeling Studies

This appendix provides SCCWRP data in tabular format to facilitate use of the data for the development and calibration of the water quality model for the SMRE.

Mass Emissions

Table A2.1. Summary of mass emission site data by analyte for each storm event.

Storm	Date	NH4 (mg/L)	CBOD (mg/L)	CHLa (mg/m^3)	NO3+NO2 (mg/L)	NO2 (mg/L)	SRP (mg/L)	TDN (mg/L)	TDP (mg/L)	TN (mg/L)	TP (mg/L)	TSS (mg/L)
1	5-Jan-08	0.0124	1.01	43.6	1.18	0.01	0.09	7.83	0.12	2.13	0.2	74.4
2	27-Jan-08	0.6824	ND	21.2	1.27	0.03	0.13	2.77	0.23	2.24	0.32	255
3	26-Nov-08	0.0046	ND	1.2	0.33	0	0.11	0.5	0.17	0.44	0.17	-0.2

Table A2.2. Summary of mass emissions data by analyte for each index period.

Analyte (mg/L)	Index Period 1 Winter Nov-Jan			Index Period 2 Spring Feb-Apr			Index Period 3 Summer May-July			Index Period 4 Fall Aug-Oct		
	Mean		Stdev	Mean		Stdev	Mean		Stdev	Mean		Stdev
TSS	13.3909	±	9.6410	9.0000	±	4.2426	0.2500	±			±	
TN	3.1332	±	0.6086	1.1215	±	0.1608	0.3247	±	0.0586		±	
TDN												
NH4	0.0314	±	0.0295	0.0871	±	0.1509	0.0077	±	0.0044		±	
NO3 + NO2	2.7202	±	0.6786	0.7391	±	0.0467	0.0081	±	0.0007		±	
NO2	0.0108	±	0.0013	0.0095	±	0.0015	0.0039	±	0.0007		±	
TP	0.1325	±	0.0369	0.1318	±	0.0175	0.1994	±	0.0315		±	
TDP	0.1093	±	0.0443	0.1193	±	0.0098	0.1299	±	0.0391		±	
SRP	0.1092	±	0.0341	0.0741	±	0.0327	0.0952	±	0.0120		±	

Sediment Deposition

Table A2.3. ^{7}Be Inventory (I) and mass flux (ψ) calculation data.

Date	Depth in Core (*z, cmbsf*)	Core Section Thickness (*h, cm*)	Wet Bulk Density (*ρ, g/cm3*)	Be-7 Activity (*A, dpm/g*)	Be-7 Inventory (I, *dpm/cm^2*)	Total Inventory (I_T, *dpm/cm^2*)	Time Elapsed (*days*)	Residual Inventory (I_R, *dpm/cm^2*)	New Inventory (I_N, *dpm/cm^2*)	Mean Activity	Mass Flux (*g/cm^2*)	Mass Flux (*g/cm^2/day*)
Santa Margarita Segment Site 1												
15-Nov-07	0-1	1	1.208	0.157	0.19	1.71	initial					
	1-2	1	1.001	0.683	0.68							
	2-3	1	1.023	-0.742	0.00							
	3-4	1	1.146	0.731	0.84							
13-Dec-07	0-1	1	1.208	-0.155	0.00	0.00	28	1.189	-1.189	0.000		
21-Jan-08	0-1	1	1.208	2.141	2.59	2.99	39	0.000	2.989	0.636	4.704	0.121
	1-2	1	1.001	0.312	0.31							
	2-3	1	1.023	-0.448	0.00							
	3-4	1	1.023	0.087	0.09							
28-Feb-08	0-1	1	1.208	2.071	2.50	4.27	38	1.824	2.446	1.276	1.917	0.050
	1-2	1	1.001	1.315	1.32							
	2-3	1	1.023	0.440	0.45							
3-Apr-08	0-1	1	1.001	-0.666	0.00	0.25	34	2.744	-2.495	0.122	20.459	0.602
	1-2	1	1.023	0.243	0.25							
14-May-08	0-1	1	1.208	0.995	1.20	1.20	41	0.146	1.056	0.996	1.061	0.026
	1-2	1	1.001	-0.744	0.00							
	2-3	1	1.023	-0.196	0.00							
	3-4	1	1.023	-0.6191	0.00							
24-Jul-08	0-1	1	1.208	0.6250	0.75	1.11	71	0.478	0.632	0.490	1.291	0.018
	1-2	1	1.001	0.3547	0.36							
	2-3	1	1.023	-0.9824	0.00							
20-Aug-08	0-1	1	1.208	1.4248	1.72	3.11	27	0.781	2.333	1.409	1.657	0.061
	1-2	1	1.001	1.3923	1.39							
	2-3	1	1.023	-1.4336	0.00							
30-Sep-08	0-1	1	1.208	-1.3572	0.00	0.00	41	1.827	-1.827	0.000		

Table A2.3. Continued

Date	Depth in Core (*z, cmbsf*)	Core Section Thickness (*h, cm*)	Wet Bulk Density (*ρ, g/cm3*)	Be-7 Activity (*A, dpm/g*)	Be-7 Inventory (I, dpm/cm^2)	Total Inventory (I_T, dpm/cm^2)	Time Elapsed (*days*)	Residual Inventory (I_R, dpm/cm^2)	New Inventory (I_N, dpm/cm^2)	Mean Activity	Mass Flux (g/cm^2)	Mass Flux ($g/cm^2/day$)
Santa Margarita Segment Site 2												
15-Nov-07	0-1	1	0.982	-0.3511	0.00	0.18	initial					
	1-2	1	1.194	-0.0199	0.00							
	2-3	1	1.140	0.1587	0.18							
	3-5	2	1.160	-0.4501	0.00							
21-Jan-08	0-1	1	0.982	0.8194	0.80	0.80	67	0.076	0.729	0.819	0.889	0.013
	1-2	1	1.194	-0.4125	0.00							
	1-2	1	1.194	-0.3433	0.00							
28-Feb-08	0-3	3	0.982	0.4289	1.26	1.26	38	0.491	0.772	0.429	1.801	0.047
3-Apr-08	0-1	1	0.982	1.0534	1.03	1.35	34	0.812	0.535	0.658	0.814	0.024
	1-2	1	1.194	0.2619	0.31							
14-May-08	0-1	1	0.982	-0.4110	0.00	0.00	41	0.790	-0.790	0.000	#DIV/0!	#DIV/0!
	1-2	1	1.194	-1.0728	0.00							
	2-3	1	1.140	-0.4046	0.00							
	2-3	1	1.140	-0.1276	0.00							
24-Jul-08	0-1	1	0.982	-0.0409	0.00	0.00	71	0.000	0.000	0.000	#DIV/0!	#DIV/0!
	1-2	1	1.194	-0.2138	0.00							
20-Aug-08	0-1	1	0.982	0.2334	0.23	0.23	27	0.000	0.229	0.233	0.982	0.036
	1-2	1	1.194	-0.3920	0.00							
30-Sep-08	0-1	1	0.982	0.2832	0.28	3.06	41	0.134	2.922	0.887	3.295	0.080
	1-2	1	1.194	1.2755	1.52							
	2-3	1	1.140	1.1012	1.26							
	3-4	1	1.160	-0.0884	0.00							
	4-5	1	1.142	-4.1774	0.00							

Sediment Bulk Characteristics by Index Period: C, N, P

Table A2.4. Sediment bulk characteristics for each index period.

Index Period	Site	Sample Depth	% Organic C	% Total N	% Total P	OC:N (molar)	OC:P (molar)	N:P (molar)	% Fines
Pre-liminary Sampling	Segment 1	0 – 1 cm	1.2	0.13	0.0556	10.8	55.8	5.2	43.9
		1 – 2 cm	0.95	0.11	0.0516	10.1	47.6	4.7	48.3
		2 – 3 cm	0.92	0.12	0.0528	8.9	45.0	5.0	50.3
		3 – 4 cm	1.1	0.13	0.0489	9.9	58.1	5.9	51.5
		4 – 6 cm	0.98	0.12	0.052	9.5	48.7	5.1	78.3
		6 – 8 cm	1.3	0.18	0.0525	8.4	64.0	7.6	81.8
		8 – 10 cm	1.0	0.12	0.0494	9.7	52.3	5.4	77.6
Index Period 1 - Winter		0 – 1 cm	1.6	0.22	0.0695	8.5	59.5	7.0	51.1
		1 – 2 cm	1.2	0.16	0.0506	8.8	61.3	7.0	50.0
		2 – 3 cm	1.0	0.12	0.036	9.7	71.8	7.4	52.0
		3 – 4 cm	1.2	0.17	0.024	8.2	129.2	15.7	54.8
		4 – 5 cm	0.84	0.13	0.045	7.5	48.2	6.4	55.8
		5 – 6 cm	2.3	0.28	0.025	9.6	237.7	24.8	65.0
		6 – 8 cm	1.9	0.24	0.0801	9.2	61.3	6.6	62.2
		8 – 10 cm	1.3	0.20	0.0138	7.6	243.4	32.1	53.2
		10 – 12 cm	0.90	0.13	0.0191	8.1	121.7	15.1	
		12 – 14 cm	1.3	0.14	0.0167	10.8	201.1	18.6	55.1
Index Period 2 - Spring		0 – 1 cm	0.54	0.07	0.0477	9.0	29.2	3.2	31.2
		1 – 2 cm	0.34	0.00	0.0394		22.3	0.0	13.3
		2 – 3 cm	0.28	0.00	0.0380		19.0	0.0	14.5
		3 – 4 cm	0.33	0.00	0.0445		19.2	0.0	15.2
		4 – 5 cm	0.55	0.00	0.0420		33.9	0.0	16.9
		5 – 6 cm	0.00	0.00	0.0554		0.0	0.0	22.6
		6 – 8 cm	1.2	0.13	0.0643	10.8	48.2	4.5	56.7
		8 – 10 cm	1.1	0.14	0.0681	9.2	41.7	4.6	55.5
		10 – 12 cm	1.1	0.14	0.0633	9.2	44.9	4.9	53.5
Index Period 3 - Summer		0 – 1 cm	0.58	0.04	0.0460	16.9	32.6	1.9	21.0
		1 – 2 cm	0.24	0.00	0.0317		19.6	0.0	12.5
		2 – 3 cm	0.16	0.00	0.0333		12.4	0.0	8.5
		3 – 4 cm	0.15	0.00	0.0298		13.0	0.0	8.2
		4 – 5 cm	0.12	0.00	0.0350		8.8	0.0	9.9
		5 – 6 cm	0.12	0.00	0.0286		10.8	0.0	9.9
		6 – 8 cm	0.94	0.11	0.0374	10.0	65.0	6.5	14.5
		8 – 10 cm	0.41	0.00	0.0440		24.1	0.0	22.0
		10 – 12 cm	0.61	0.06	0.0552	11.9	28.5	2.4	37.0
Index Period 4 - Fall		0 – 1 cm	0.34	0.00	0.4931		1.8	0.0	30.3
		1 – 2 cm	0.81	0.09	0.0572	10.5	36.6	3.5	31.9
		2 – 3 cm	1.0	0.13	0.0542	8.8	46.9	5.3	55.8
		3 – 4 cm	1.3	0.16	0.0639	9.8	54.2	5.5	64.5
		4 – 5 cm	1.2	0.14	0.0633	9.7	47.4	4.9	72.6
		5 – 6 cm	0.95	0.14	0.0575	7.9	42.7	5.4	70.9
		6 – 8 cm	0.76	0.12	0.0610	7.4	32.2	4.4	62.7
		8 – 10 cm	0.85	0.12	0.0567	8.3	38.7	4.7	63.4
		10 – 12 cm	0.32	0.00	0.0380		21.8	0.0	51.7

Table A2.4. Continued

Index Period	Site	Sample Depth	% Organic C	% Total N	% Total P	OC:N (molar)	OC:P (molar)	N:P (molar)	% Fines
Pre-liminary Sampling	Segment 2	0 – 1 cm	0.56	0.07	0.0404	9.3	35.8	3.8	20.4
		1 – 2 cm	0.45	0.00	0.0342		34.0	0.0	30.0
		2 – 3 cm	0.25	0.00	0.0245		26.4	0.0	34.4
		3 – 5 cm	0.26	0.00	0.021		32.0	0.0	1.7
		5 – 7 cm	0.26	0.00	0.022		30.5	0.0	1.6
		7 – 9 cm	0.37	0.00	0.0224		42.7	0.0	1.6
Index Period 1 - Winter		0 – 1 cm	0.15	0.00	0.0624		6.2	0.0	1.6
		1 – 2 cm	0.15	0.00	0.0627		6.2	0.0	1.7
		2 – 3 cm	0.11	0.00	0.0396		7.2	0.0	2.1
		3 – 4 cm	0.12	0.00	0.035		8.9	0.0	1.2
		4 – 5 cm	0.10	0.00	0.021		12.3	0.0	1.3
		5 – 6 cm	0.15	0.00	0.05		7.8	0.0	1.7
		6 – 8 cm	0.11	0.00	0.095		3.0	0.0	1.2
		8 – 10 cm	0.13	0.00	0.084		4.0	0.0	2.6
		10 – 12 cm	0.12	0.00	0.031		10.0	0.0	1.6
Index Period 2 - Spring		0 – 1 cm	1.2	0.11	0.0542	12.7	57.2	4.5	23.3
		1 – 2 cm	1.8	0.13	0.0253	16.2	184	11.4	26.0
		2 – 3 cm	0.46	0.00	0.0259		45.8	0.0	17.4
		3 – 4 cm	0.15	0.00	0.0231		16.8	0.0	5.56
		4 – 5 cm	0.24	0.00	0.0281		22.1	0.0	3.44
		5 – 6 cm	0.19	0.00	0.0195		25.1	0.0	4.19
		6 – 8 cm	0.09	0.00	0.0112		20.8	0.0	2.56
		8 – 10 cm	0.14	0.00	0.0239		15.1	0.0	1.36
		10 – 12 cm	0.09	0.00	0.0116		20.1	0.0	1.17
Index Period 3 - Summer		0 – 1 cm	0.20	0.00	0.0158		32.6	0.0	1.52
		1 – 2 cm	0.2	0.00	0.0261		19.8	0.0	1.70
		2 – 3 cm	0.09	0.00	0.0170		13.7	0.0	1.51
		3 – 4 cm	0.11	0.00	0.0138		20.6	0.0	0.89
		4 – 5 cm	0.00	0.00	0.0148		0.0	0.0	1.05
		5 – 6 cm	0.00	0.00	0.0101		0.0	0.0	1.43
		6 – 8 cm	0.00	0.00	0.0081		0.0	0.0	1.28
		8 – 10 cm	0.00	0.00	0.0127		0.0	0.0	1.24
		10 – 12 cm	0.00	0.00	0.0084		0.0	0.0	1.54
Index Period 4 - Fall		0 – 1 cm	0.14	0.00	0.0313		11.5	0.0	5.19
		1 – 2 cm	0.08	0.00	0.0170		12.2	0.0	1.64
		2 – 3 cm	0.00	0.00	0.0159		0.0	0.0	3.87
		3 – 4 cm	0.00	0.00	0.0148		0.0	0.0	3.31
		4 – 5 cm	0.00	0.00	0.0120		0.0	0.0	0.83
		5 – 6 cm	0.00	0.00	0.0137		0.0	0.0	2.70
		6 – 8 cm	0.00	0.00	0.0238		0.0	0.0	2.26
		8 – 10 cm	0.00	0.00	0.0088		0.0	0.0	1.58
		10 – 12 cm	0.00	0.00	0.0135		0.0	0.0	2.05

Sediment Porewater Concentrations

Table A2.5. Porewater constituent analysis for each index period. Constituent values in µM.

Segment 1												
	Depth	**TDN**	**NH_4**	**NO_3 + NO_2**	**NO_2**	**TDP**	**SRP**	**TCO_2**	**S^{-2}**	**DOC**	**Fe**	**Mn**
Index Period 1 – Winter 1/21/2008	Bottom water	36.0	6.3	8.1	0	4.69	1.8	1180	1.55	183	0.349	3.56
	0–1 cm	44.9	7.4	2.8	0	5.04	1.6	2770	1.35	290	2.15	7.46
	1–2 cm	393	410	3.4	1	5.95	2.8	3830	1.42	900	8.24	27.3
	2–3 cm	636	7.4	2.6	0	14.2	14.6	6030	1.35	783	4.48	67.3
	3–4 cm	599	724	3.2	0	59.4	82.4	4610	10.3	738	47.5	65.5
	4–5 cm	597	688	3	0	91.3	95.2	3000	6.82	685	53.7	54.6
	5–6 cm	588	650	2.4	2.2	96.7	105	2120	13.2	653	51.9	51.0
	7–8 cm	522	530	8.8	1	95.9	106	1740	8.78	683	37.6	49.1
	10–11 cm	310	330	21	0	41.2	50.6	1070	5.74	650	32.2	18.2
	13–14 cm	275	318	5.4	0.8	47.4	57.2	1050	5.41	600	26.9	10.4
Index Period 2 – Spring 4/3/2008	Bottom water	35.5	3.35	12.3	0	2.02	1.5	1060	0	276	1.40	3.50
	0–1 cm	1370	18.4	3.6	0	105	12.4	971	0.969	1300	129	9.47
	1–2 cm	192	9.2	4.6	1	11.6	2.8	1520	0	927	75.2	17.1
	2–3 cm	434	292	6.4	0.4	2.64	1.2	2350	0	996	39.4	98.3
	3–4 cm	900	770	6.8	0	0.282	0	2680	0	1930	94.9	237
	4–5 cm	1210	1080	15.6	0	1.43	1	5030	0.277	1360	62.7	162
	5–6 cm	1650	1410	11.4	0	6.43	1.8	5910	0	1290	127	182
	7–8 cm	2000	1680	5.4	0	188	110	5670	17.2	1360	448	138
	11–12 cm	1520	1160	6.6	0	208	188	4250	378	1090	75.2	52.8
	13–14 cm	1160	894	4.8	0	152	10	3270	17.2	997	106	102
Index Period 3 – Summer 7/22/2008	Bottom water	22.0	1.9	11.7	0	1.43	1	396	0	283	0.492	0.319
	0–1 cm	0	716	11.8	0	0	127	2550	85.3	595	23.3	29.1
	1–2 cm	1070	772	27.6	1.6	135	117	2330	59.9	585	62.7	30.0
	2–3 cm	1100	846	24.2	0	124	114	2170	90.1	550	48.3	30.9
	3–4 cm	1210	922	24	0	129	109	2560	135	578	68.0	34.6
	4–5 cm	1460	1190	40.2	0	156	138	3110	181	628	66.3	43.7
	5–6 cm	1570	1290	14.6	0	162	145	3320	591	618	17.9	41.9
	6–7 cm	1880	1590	70.4	0	196	168	3580	154	738	25.1	40.0
	9–10 cm	1740	1460	43.2	0	178	159.2	3950	54.5	734	60.9	25.5
	13–14 cm	1390	1140	49.2	0	172	150	3410	25.3	685	25.1	25.5
Index Period 4 – Fall 9/29/2008	Bottom water	18.0	2.97	2.33	0.2	0.535	1.1	6.08	0	72.9	2.69	0.328
	0–1 cm	27.5	17.0	2.8	0	5.31	4.4	2810	0	103	26.9	3.82
	1–2 cm	204	242	0	0	37.9	40.8	3680	482	72.5	15.6	12.2
	2–3 cm	998	1340	0	0	140	159	3900	5550	200	26.9	21.8
	3–4 cm	1490	1870	0	0	177	232	861	9180	294	34.0	21.8
	4–5 cm	1640	2200	0	0	206	159	4670	8010	313	34.0	27.3
	5–6 cm	1060	2266	0	0	166	171	4130	7360	458	32.2	38.2
	7–8 cm	2360	2750	0	0	219	308	0	7430	298	35.8	58.2
	10–11 cm	1660	2740	0	0	182	138	0	5050	365	68.0	61.9
	13–14 cm	1620	2070	0	0	149	176	0	4240	313	23.3	36.4

Table A2.5. Continued

Segment 2												
	Depth	**TDN**	**NH_4**	**$NO_3 + NO_2$**	**NO_2**	**TDP**	**SRP**	**TCO_2**	**S^{-2}**	**DOC**	**Fe**	**Mn**
Index Period 1 – Winter 1/21/2008	Bottom water	28.6	3.45	12.3	0	2.14	1.3		1.45	295	0.596	2.55
	0–1 cm	102.2	4.2	22.8	2.6	6.88	4	321	2.70	693	1.97	1.55
	1–2 cm	65.3	5.6	35.8	1.4	6.07	1.6	958	1.28	260	1.34	0.928
	2–3 cm	67.7	3.2	27.8	0	2.50	1.2	875	1.55	434	1.18	1.07
	3–4 cm	54.1	4.2	21.6	0	1.28	1.2	919	1.69	423	0.752	0.710
	4–5 cm	5.0	4.4	27	0	0.787	1.4	932	1.42	525	0.752	1.02
	5–6 cm	43.6	4.2	13.8	0	4.13	1.2	809	1.35	585	0.859	0.510
	7–8 cm	42.0	5.2	2.8	0	1.4	1.4	642	1.22	448	0.627	0
	10–11 cm	33.9	4.6	3.8	0	4.08	2.2	721	1.49	560	0.985	0
	14–15 cm	61.7	2.6	31	1.2	5.48	4	777	1.49	618	0.394	0
Index Period 2 – Spring 4/3/2008	Bottom water	39.2	5.5	14.8	0	3.58	2.07	1630	0	470	1.32	8.01
	0–1 cm	36.9	3	11.2	0	1.08	0	585	0	467	3.40	0.158
	1–2 cm	57.6	2	21.6	0	0.293	0	791	0	485	3.76	0.162
	2–3 cm	53.7	5.2	21	0	1.55	1.6	860	0	672	4.30	0.076
	3–4 cm	52.0	1.6	18.4	0	1.33	1.6	850	0	1150	2.15	0.075
	4–5 cm	49.8	4.4	20.6	0	0.527	1.4	907	0	747	3.40	0.124
	5–6 cm	54.7	3.8	20.6	0	0.121	0	853	0	504	1.97	0.098
	7–8 cm	52.2	13.2	20.8	2.8	0.880	0	817	0	785	2.33	0.510
	10–11 cm	71.9	12.8	40	15.2	0.112	0	844	0	824	2.69	17.5
	13–14 cm	136	77	23.9	3	1.55	1.7	882	0	630	5.91	124
Index Period 3 – Summer 7/22/2008	Bottom water	29.5	3.5	4.6	0.65	5.29	4.35	699	0.262	450	0.716	0.528
	0–1 cm	66.7	45.8	15.0	0	17.7	16	795	1.01	473	19.7	49.1
	1–2 cm	87.3	58	19.0	0	32.5	32.2	789	0.794	415	34.0	47.3
	2–3 cm	155	101	13.8	0	44.6	44.6	948	0.902	410	19.7	43.7
	3–4 cm	138	92.2	12.4	0	28.9	22.6	927	71.9	430	9.94	21.8
	4–5 cm	151	104	13.0	0	34.6	29.2	933	68.0	433	8.42	38.2
	5–6 cm	171	105	7.8	0	42.3	47	1070	81.0	433	6.45	49.1
	7–8 cm	196	153	7.4	0	52.3	47	1160	55.8	398	8.24	61.9
	10–11 cm	165	120	9.2	0	36.3	49.2	1080	5.49	435	49.2	69.2
	13–14 cm	131	97.2	10.8	0	27.6	44	1080	2.20	440	51.9	65.5
Index Period 4 – Fall 9/29/2008	Bottom water	24.8	1.7	0	0	6.24	7.3	702	0	219.5 833	2.06	5.82
	0–1 cm	103	60.4	0	0	22.3	24	568	62.4	90	5.01	104
	1–2 cm	126	82.6	0	0	26.6	27	635	90.2	82.5	6.98	51.0
	2–3 cm	25.5	22.8	0	0	6.67	14.3	456	7.66	87.5	43.0	44.0
	3–4 cm	69.0	62.4	3	0	15.9	27.3	554	18.3	204	7.70	45.5
	4–5 cm	137	109	2.7	0	45.0	42.1	553	4.39	92.5	25.1	71.0
	5–6 cm	124	126	0	0	33.6	49.2	683	0.375	75.0	43.0	96.5
	7–8 cm	125	168	2	0	36.4	59.8	769	1.89	130	35.8	96.5
	10–11 cm	192	176	2.4	0	64.0	57.2	912	4.21	67.5	23.3	95.0
	13–14 cm	181	147	2	0	64.6	52.2	659	16.8	138	9.49	76.4

Water Column Transect Data

Table A2.6. Transect data for each index period during ebb tide (constituents are in mmol/L, except for chlorophyll a, which is in µg/l).

	Site #	TN	TDN	NH_4	$NO_3 + NO_2$	NO_2	TP	TDP	SRP	TSS	Chl *a*
Index Period 1 Winter	1	216.3	315.3	3.78	130.0	0.571	3.52	3.71	3.10	42.3	10.0
	2	92.3	185.0	9.92	133.0	0.714	3.07	3.26	2.81	34.3	8.5
	3		497.5							47.3	4.5
	4	200.0	224.8	66.8	193.9	0.928	2.55	3.36	2.19	3.3	7.1
	5	231.6	403.3	3.00	207.9	1.21	3.75	3.68	3.81	9.1	-1.0
	6	155.1	324.8	108.0	218.0	1.00	2.36	3.80	1.61	12.0	5.3
	7			1.78	106.0	0.571	2.29	2.58	3.19	45.0	6.2
	8	197.6	1136	2.42	226.0	1.21	3.75	3.52	3.71	8.3	6.2
	9	181.6	395.1	2.18	190.5	0.785	2.58	3.94	7.10	7.5	6.2
	10	217.0	394.6	1.43	229.0	1.00	3.52	3.81	2.29	4.7	3.6
	11	122.4	532.9	2.43	171.0	0.785	2.78	5.04	1.81	13.0	4.5
	12	161.8	408.7	70.5	224.0	1.50	2.42	3.78	2.39	9.7	-1.0
Index Period 2 Spring	1	54.6	79.0	3.71	22.4	0.428	3.87	3.16	2.90	3.0	13.4
	2	52.2	64.3	3.50	19.2	0.286	3.61	3.32	3.09	3.7	9.3
	3	52.1	75.4	3.43	20.3	0.357	4.22	3.84	3.29	3.0	9.3
	4	49.3	73.7	2.93	26.4	0.500	4.22	4.03	3.61	2.7	12.7
	5	62.9	76.3	2.00	32.1	0.571	4.39	4.10	3.29	7.7	12.9
	6	55.4	75.0	2.21	30.7	0.500	4.13	3.77	3.00	3.3	42.7
	7	62.0	66.9	1.93	31.9	0.500	4.08	3.72	3.45	7.3	20.0
	8	54.9	56.7	2.43	32.4	0.500	4.29	4.39	3.39	2.3	10.2
	9	52.4	36.5	2.00	32.1	0.500	4.16	4.19	3.48	3.1	11.3
	10	53.1	51.1	1.78	30.4	0.500	3.45	3.61	3.29	2.4	10.2
	11	56.7	45.1	1.43	34.2	0.500	3.90	4.03	3.39	1.7	10.2
	12	46.8	39.5	1.07	35.5	0.500	3.87	3.81	3.00	2.1	10.7
Index Period 3 Summer	1	11.4	197.8	12.8	1.30	0.000	0.736	0.588	0.200	2.3	2.7
	2	13.1	47.6	83.7	1.60	0.000	0.610	0.604	0.900	3.2	2.2
	3	11.2	293.4	0.00	0.00	0.000	0.488	0.694	0.400	2.3	2.2
	4	9.26	69.2	3.10	0.00	0.000	0.839	0.965	0.600	3.0	2.7
	5	68.9	1131	11.8	2.40	0.200	1.09	0.962	1.00	3.5	4.9
	6	23.4	96.3	19.1	6.70	0.400	1.48	1.23	1.30	5.3	10.2
	7	31.1	87.4	44.3	6.20	0.500	1.90	1.97	1.40	4.0	10.1
	8	38.6	91.3	36.4	10.4	0.850	2.92	1.99	1.80	4.0	12.9
	9						6.55			5.5	16.9
	10	45.3	141.9	44.4	16.8	1.30	2.89	2.07	2.20	6.3	13.4
	11	52.9	146.0	106.0	20.2	1.40	3.49	3.36	2.70	7.0	14.7
	12	49.8	116.5	17.2	16.8	1.40	3.52	3.74	2.10	3.3	14.7
Index Period 4 Fall	1	46.9	49.2	18.5	2.20	0.300	1.99	1.74	1.10	3.7	1.6
	2	20.3	38.8	2.90	0.600	0.000	2.18	1.71	0.900	6.0	2.2
	3	24.9	42.8	1.60	0.000	0.000	2.29	1.88	1.10	4.5	3.6
	4	28.2	24.9	0.500	0.000	0.000	4.18	3.58	2.70	2.7	8.0
	5	43.1	36.3	0.900	3.20	0.000	4.63	3.95	3.10	1.7	4.9
	6	36.4	49.1	2.00	1.90	0.200	3.45	3.01	2.60	6.0	5.3
	7	35.3	56.9	1.90	1.50	0.000	4.97	4.68	3.90	3.0	6.2
	8	51.2	56.7	0.550	3.15	0.200	6.27	6.26	4.60	3.2	3.4
	9	35.5	56.6				8.21	11.7	10.1		
	10	39.7	57.7	0.500	0.000	0.000	9.28	9.54	7.60	4.0	6.2
	11	38.7	36.9	0.100	0.000	0.000	11.2	10.4	8.20	2.4	4.5
	12	44.3	32.6	0.500	0.000	0.000	12.4	12.5	11.2	4.7	5.8

Table A2.7. Transect data for each index period during flood tide.

	Site #	TN	TDN	NH_4	$NO_3 + NO_2$	NO_2	TP	TDP	SRP	TSS	Chl *a*
Index Period 1 Winter	1	31.1	31.9	0.21	1.85	0.143	0.161	0.048	0.613	6.4	13.7
	2	158.6	566.4	1.99	157.9	0.571	1.10	4.81	2.80	7.5	5.0
	3	182.3	169.8	98.76	167.9	0.785	3.23	2.64	3.81	5.0	6.2
	4	161.3	610.3	120.0	138.0	0.714	2.00	2.03	4.00	6.7	86.3
	5	280.2	188.6	78.1	212.9	1.00	2.81	3.58	1.48	8.0	5.3
	6	248.1	400.0	0.714	81.8	0.428	3.52	3.55	3.19	8.3	8.0
	7	206.9	655.6	14.1	202.9	1.07		3.06	1.80	41.7	6.7
	8	135.0	403.3	10.8	182.9	1.07	4.71	4.45	3.90	9.0	1.9
	9	192.2	721.2	1.93	186.9	0.928	3.29	5.32	2.85	10.0	1.8
	10	176.5	213.0	1.28	181.9	1.21	4.19	3.19	3.71	10.3	4.7
	11	151.8	193.6	1.78	116.0	0.500	4.58	2.55	3.19	9.0	7.7
	12	251.1	400.8	2.21	52.8	0.214	4.00	3.42	0.484	10.5	7.1
Index Period 2 Spring	1	21.9	15.9	1.28	3.28	-0.071	1.16	0.743	0.710	8.0	10.2
	2	42.5	54.0	4.21	16.92	0.428	3.16	2.87	2.48	7.3	16.0
	3	50.4	54.4	3.28	16.71	0.286	3.45	3.24	2.80	20.2	28.9
	4	59.6	75.8	2.49	27.6	0.428	4.39	4.16	3.19	9.0	15.4
	5	50.8	76.9	1.49	32.9	0.500	3.61	3.93	3.19	3.5	14.2
	6	58.6	51.6	1.57	29.7	0.428	3.51	3.87	3.19	9.7	10.2
	7	55.7	49.3	1.21	29.9	0.428	4.00	3.84	3.09	5.3	11.1
	8	59.9	81.5	1.42	31.1	0.500	4.32	3.87	2.80	4.7	19.6
	9	64.9	60.8	1.49	31.6	0.428	3.68	4.13	3.00	2.0	11.1
	10	71.3	63.4	1.21	32.9	0.428	4.13	4.26	3.09	0.7	11.6
	11	60.9	58.6	0.928	33.1	0.286	3.61	3.93	3.19	3.4	11.1
	12	62.3	56.4	1.00	32.7	0.286	3.94	3.71	3.39	5.4	11.6
Index Period 3 Summer	1	34.0	41.3	0.800	9.50	0.500	1.71	1.65	1.00	3.4	5.6
	2	66.8	50.0	0.700	20.5	0.900	3.33	2.96	1.70	3.5	7.1
	3	43.0	39.3	1.00	6.00	0.600	4.27	3.43	2.20	4.0	6.2
	4	42.5	45.6	0.600	9.00	0.900	3.91	1.69	2.30	12.3	15.5
	5	40.3	32.5	2.10	7.10	1.50	5.06	3.19	5.20	9.5	9.3
	6		33.1	2.80	7.10	1.50	4.65	4.14	4.10	4.1	7.6
	7	56.1	64.9	4.20	20.6	2.00	6.53	7.06	6.20	5.5	11.1
	8	45.9	38.9	6.90	1.00	0.700	7.98	7.47	7.80	2.8	8.5
	9	42.2	43.6	6.00	0.600	0.500	7.73	7.21	6.95	7.5	7.3
	10	36.5	43.7	2.50	0.000	0.300	6.29	6.42	8.80	13.5	8.9
	11	35.2	39.0	0.200	0.000	0.200	7.58	6.84	8.90	4.0	12.0
	12	40.9	33.8	0.900	0.000	0.300	8.29	7.01	9.10	3.0	12.9
Index Period 4 Fall	1	10.7	8.4	0.400	0.000	0.000	0.96	1.02	0.300	68.5	1.8
	2	14.4	12.5	0.000	0.000	0.000	1.61	1.33	0.600	6.3	3.6
	3	13.5	31.6	1.10	0.000	0.000	1.29	0.904	0.600	13.7	3.1
	4	47.5	20.2	0.200	0.000	0.000	4.56	3.91	2.70	2.5	6.7
	5	33.2	44.9	0.500	0.000	0.000	4.87	3.86	3.30	3.0	8.9
	6	34.6	29.6	1.60	0.000	0.000	6.07	5.30	3.40	8.0	10.7
	7	49.6	51.1	3.60	4.70	0.900	6.23	4.98	4.10	4.2	2.2
	8	34.1	31.0	0.500	0.000	0.000	6.83	7.01	5.30	1.3	5.3
	9	43.0	34.3	0.400	0.000	0.000	12.7	5.472	4.80	3.9	5.8
	10	43.5	41.2	0.400	0.000	0.000	13.3	12.9	11.0	4.3	4.5
	11	54.7	47.8	0.200	0.000	0.000	16.7	14.8	11.7	4.0	5.3
	12	43.9	65.1	0.700	0.000	0.000	18.6	16.8	14.9	3.7	3.1

Primary Producer Biomass and/or Percent Cover

Table A2.8. Means and standard deviations of suspended chlorophyll *a* and benthic chlorophyll *a* concentrations during each index period.

Index Period	Site	Mean Suspended Chlorophyll a (mg/m^3)
1 Winter	Segment 1	3.65 ± 0.96
2 Spring		1.91 ± 0.17
3 Summer		10.95 ± 1.63
4 Fall		4.76 ± 0.37
1 Winter	Segment 2	5.49 ± 0.34
2 Spring		1.92 ± 0.76
3 Summer		5.60 ± 0.44
4 Fall		1.01 ± 0.01

Table A2.9. Macroalgae total percent cover and biomass by species during each index period.

Site	Date	Dry Biomass (g/m^2)								Total % Cover	
		Ulva intestinalis		Ulva expansa		Cyanobacteria		Total Biomass			
		avg	SE	avg	SE	avg	SE	avg	SE	avg	SE
Segment 1	1/22/08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4/11/08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7/21/08	46.53	43.48	7.76	5.26	0.00	0.00	54.29	48.19	81.67	16.98
	9/29/08	0.00	0.00	175.10	93.49	63.27	44.54	238.37	88.19	100.00	0.00
Segment 2	1/22/08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4/11/08	0.56	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7/21/08	0.00	0.00	14.69	9.14	0.00	0.00	14.69	9.14	33.33	12.64
	9/29/08	0.41	0.41	40.82	12.07	0.00	0.00	41.22	12.30	98.33	1.11

Rates of Exchange Between Surface Waters and Sediments – Benthic Flux

Table A2.10. Benthic fluxes by index period and light/dark regime

	Index Period	Regime	Type	DO	TCO_2	TDN	TDP	DOC	Fe	Mn	NH_4	NO_3	SRP
Segment Site 1	1 Winter	light	avg	28.7	-145	-20.97	0.40	-729	-0.46	0.33	15.95	-32.49	1.27
			stdev	120	53.3	30.5	2.29	539.	0.15	0.56	21.44	38.73	2.98
		dark	avg	-164	183	-4.85	0.78	-615	-0.17	0.03	9.01	-20.18	0.20
			stdev	138	109	19.79	2.01	770	0.04	0.37	12.17	28.16	0.51
	2 Spring	light	avg	234	-78.4	-16.78	-1.16	134	-0.07	-0.35	-0.25	0.94	-0.02
			stdev		33.7	23.15	0.11	284	0.10	0.34	0.24	4.14	0.03
		dark	avg	-11.0	37.3	-12.81	-0.41	-217	-0.14	0.24	-0.33	-15.83	-0.11
			stdev	10.5	0.68	7.76	1.55	455	0.19	0.87	0.69	5.93	0.68
	3 Summer	light	avg	33.4	-60.7	3.03	6.41	343	-1.14	-0.54	32.15	-34.79	3.70
			stdev		24.2	28.01	1.06	229	1.51	1.52	44.12	3.13	5.24
		dark	avg	-85.1	38.0	7.62	1.72	257	0.81	-0.24	23.81	-16.67	1.33
			stdev		4.41	3.03	0.21	238	0.64	0.14	19.94	1.56	1.57
	4 Fall	light	avg	29.6	-21.2	2.95	0.81	62.8	-0.58	0.06	6.75	-4.23	0.60
			stdev	38.0	5.26	5.45	0.22	31.1	0.33	0.17	6.81	1.88	0.38
		dark	avg	-28.9	12.7	1.55	0.04	94.6	-0.06	0.23	3.59	-0.38	-0.01
			stdev	3.81	4.59	2.10	0.66	133	0.26	0.05	2.99	0.59	0.11
Segment Site 2	1 Winter	light	avg	57.4	-6.06	-0.47	0.51	-144	0.10	0.00	0.08	-1.15	-0.39
			stdev	4.58	4.70	2.58	0.98	1229	0.24	0.09	0.30	0.42	0.56
		dark	avg	-14.2	10.8	-1.25	0.05	-153	-0.10	-0.07	-0.14	-0.04	0.08
			stdev	19.1	0.57	0.92	1.02	733	0.05	0.10	0.72	0.06	0.40
	2 Spring	light	avg	48.1	-35.4	-0.90	0.36	-81.0	0.29	-0.05	0.01	-3.40	0.19
			stdev	36.8	5.72	0.98	0.13	90.9	0.04	0.55	0.45	1.82	0.32
		dark	avg	-3.14	13.3	1.23	-0.14	157	0.08	-0.03	0.01	1.33	-0.35
			stdev	1.47	7.03	1.49	0.16	352	0.28	0.05	0.00	0.11	0.47
	3 Summer	light	avg	69.4	-62.5	3.91	0.10	-5.74	0.91	-0.46	0.91	-0.18	0.68
			stdev		84.43	5.53	0.14	8.12	1.28	0.65	1.29	0.26	0.96
		dark	avg	-37.9	61.50	1.10	-0.60	-119	0.35	-1.56	0.94	-0.20	0.12
			stdev	11.5	1.05	2.17	0.29	2.40	0.79	0.07	2.20	0.13	0.37
	4 Fall	light	avg	-30.0	34.6	-0.82	-3.80	-431	-6.12	-2.26	1.69	-0.05	0.53
			stdev	63.3	203	2.86	0.69	1071	4.43	2.53	2.31	0.50	2.17
		dark	avg	-93.6	66.8	1.78	4.59	516	-4.99	0.00	-2.12	-0.52	0.27
			stdev	7.63	44.8	2.30	0.24	286	7.32	0.00	1.47	0.78	0.98

Data on Additional Factors Controlling Benthic Flux

Table A2.11. Number of benthic infauna in each chamber by index period, along with chamber light/dark regime, site average, and standard deviation.

Index Period		Chamber	Polychaetes (individuals/ m^2)	Capitellids (individuals/ m^2)	Oligochaetes (individuals/ m^2)	Mollusks (individuals/ m^2)	Crustaceans (individuals/ m^2)	Other (individuals/ m^2)	Total Polychaetes (individuals/ m^2)	Total Infauna (individuals/ m^2)
Segment 1	1 Winter	Chamber 1 (light)	0	0	0	0	0	509	0	509
		Chamber 2 (dark)	0	0	509	0	0	0	0	1019
		Chamber 3 (light)	0	0	0	0	0	0	0	509
		Chamber 4 (dark)	0	0	0	0	0	0	0	0
		Average	0	0	127	0	0	127	0	509
		Standard Deviation	0	0	255	0	0	255	0	416
	2 Spring	Chamber 1 (light)	0	0	0	0	0	0	0	0
		Chamber 2 (dark)	0	0	0	0	509	0	0	1019
		Chamber 3 (light)	0	0	1019	0	0	0	0	1019
		Chamber 4 (dark)	0	0	1528	0	0	509	0	2037
		Average	0	0	637	0	127	127	0	1019
		Standard Deviation	0	0	764	0	255	255	0	832
	3 Summer	Chamber 1 (light)	0	0	0	0	3056	0	0	3056
		Chamber 2 (dark)	509	0	509	0	1528	0	509	3056
		Chamber 3 (light)	0	0	0	509	14260	0	0	14770
		Chamber 4 (dark)	0	0	509	0	10186	0	0	11205
		Average	127	0	255	127	7257	0	127	8021
		Standard Deviation	255	0	294	255	6003	0	255	5916
	4 Fall	Chamber 1 (light)	0	0	0	0	0	0	0	509
		Chamber 2 (dark)	0	0	509	0	0	0	0	509
		Chamber 3 (light)	0	0	509	0	0	0	0	509
		Chamber 4 (dark)	0	0	0	0	0	0	0	0
		Average	0	0	255	0	0	0	0	382
		Standard Deviation	0	0	294	0	0	0	0	255
Segment 2	1 Winter	Chamber 1 (light)	0	0	0	0	0	0	0	1019
		Chamber 2 (dark)	0	0	0	0	0	509	0	509
		Chamber 3 (light)	0	0	0	0	0	0	0	0
		Chamber 4 (dark)	0	0	0	0	0	0	0	509
		Average	0	0	0	0	0	127	0	509
		Standard Deviation	0	0	0	0	0	255	0	416
	2 Spring	Chamber 1 (light)	0	0	0	0	0	2037	0	2546
		Chamber 2 (dark)	0	0	0	0	0	0	0	0
		Chamber 3 (light)	0	0	0	0	0	2037	0	2037
		Chamber 4 (dark)	0	0	0	0	0	1528	0	1528
		Average	0	0	0	0	0	1401	0	1528
		Standard Deviation	0	0	0	0	0	964	0	1100
	3 Summer	Chamber 1 (light)	2037	3056	509	4074	2037	0	5093	13751
		Chamber 2 (dark)	0	1528	0	1019	1528	1528	1528	6112
		Chamber 3 (light)	2546	509	509	1019	0	509	3056	5093
		Chamber 4 (dark)	3056	1019	1528	2546	1019	0	4074	11205
		Average	1910	1528	637	2165	1146	509	3438	9040
		Standard Deviation	1339	1100	641	1463	870	720	1521	4124
	4 Fall	Chamber 1 (light)	1019	1528	509	21900	2037	0	2546	29539
		Chamber 2 (dark)	0	1019	509	0	3565	0	1019	8149
		Chamber 3 (light)	509	509	0	1019	3056	0	1019	5602
		Chamber 4 (dark)	0	509	0	0	509	0	509	1528
		Average	382	891	255	5730	2292	0	1273	11205
		Standard Deviation	488	488	294	10791	1347	0	882	12524

Appendix 3 - Graphs of Segment 1 and Segment 2 2007-2008 Continuous Data (From CDM, Inc. 2009)

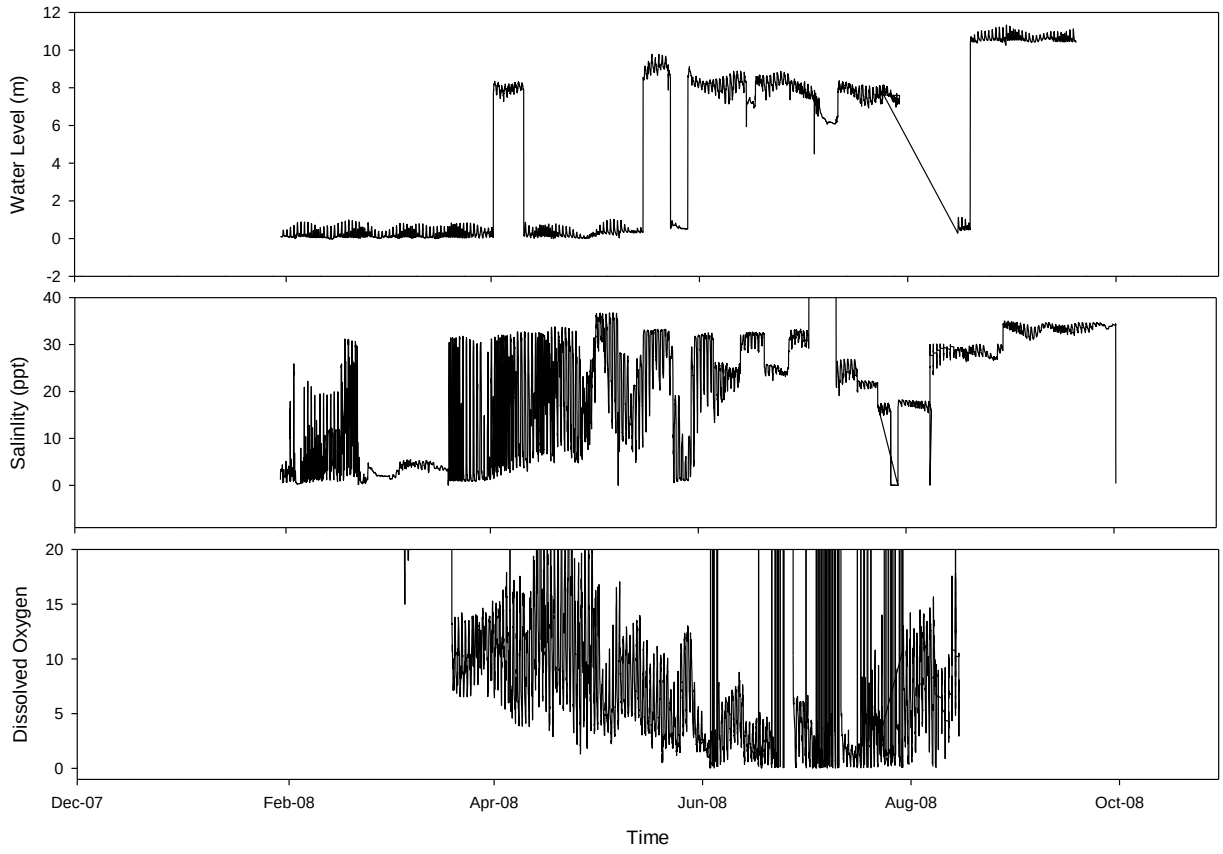


Figure A3.1. Continuous water level, salinity, and dissolved oxygen data over December 2007-October 2008 for Segment One (upstream; CDM 2009).

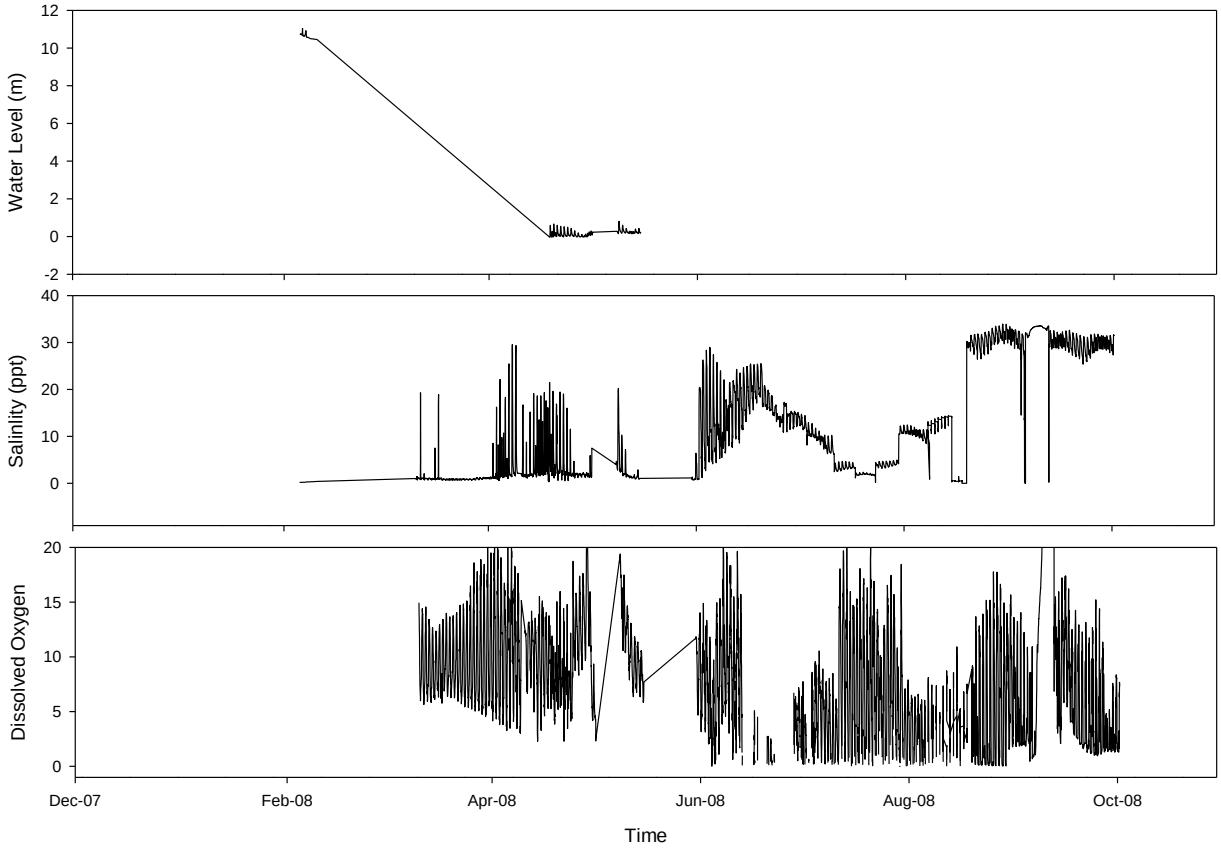


Figure A3.2. Continuous water level, salinity, and dissolved oxygen data over December 2007-October 2008 for Segment Two (downstream; CDM 2009).