

NUTRIENT DYNAMICS IN TIDALLY RESTRICTED REGIONS OF
THE ELKHORN SLOUGH NATIONAL ESTUARINE RESEARCH RESERVE

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NUTRIENT DYNAMICS IN TIDALLY RESTRICTED REGIONS OF
THE ELKHORN SLOUGH NATIONAL ESTUARINE RESEARCH RESERVE



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by

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DEDICATION

I dedicate this research to the lifelong pursuit of untying the mysteries of the natural world. I hope these findings can impact the world for the better with further understanding of our precious coastal systems. I dedicate this furthermore to the pursuit of what sets your soul on fire - to following passion and desire in life, and to taking giant leaps of faith into the unknown in search for answers and understanding.

“Wilderness is not a luxury, but a necessity of the human spirit” – Edward Abbey

47X

ABSTRACT

Nutrient Dynamics In Tidally Restricted Regions Of The Elkhorn Slough National
Estuarine Research Reserve

By

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Masters of Science in Marine Science

Moss Landing Marine Laboratories

California State University Monterey Bay, 2017

The Elkhorn Slough, in the heart of the Monterey Bay, includes water bodies that have been isolated from tidal flushing cycles by dikes, levees, roads and train tracks. This partitioning has changed the functionality of these systems primarily through reduced circulation and increased eutrophication. The Elkhorn Slough is surrounded by a patchwork of lands under varied land-uses, including open space, developed properties, and extensive agriculture, that results in high and variable nutrient loading into the surrounding aquatic habitat. Water bodies of restricted flow disproportionately exhibit impacts due to this loading. In this study, nutrient concentrations were measured using both discrete water column sampling methods and *in situ* continuous osmotic sampling techniques. Fluxes were measured using water column nutrient determinations, flow measurements, ground water flux correlations, benthic chambers, modeled pore water gradients and estimates of *Ulva* uptake. These measurements were used to quantify the cycling of nitrate, ammonium and phosphate in these pocket regions and have identified systemic nutrient drivers to be surface water flow, *Ulva* uptake and groundwater inputs. A box model approach was used to determine the degree to which these drivers contributed to overall nutrient concentrations on a seasonal timescale. The systems of study were all in dynamic disequilibrium, rather than steady-state. Nitrate varied from 355.5 μM to 0.0 μM on timescales as short as one month. Ammonium varied from 199.3 μM to 0.0 μM and phosphate varied from 22.7 μM to 0.0 μM on similar timescales. These variations were large compared to the same nutrients in the adjacent Elkhorn Slough. Such variability is significant when characterizing these systems, as it is indicative of the nature of nutrient flux in tidally restricted ecosystems and the rapid extremes in chemical composition experienced by the resident biota. The dominant sources of nutrients in these restricted areas also varied in time with surface runoff dominating in the wet season, and ground water inputs (possibly due to agricultural irrigation) dominating in the dry season. *Ulva* uptake and advective flow were the largest loss terms and these too varied significantly in time. Understanding the key nutrient drivers, as well as the degree to which these drivers influence biogeochemical cycling of nutrients in these systems, informs mitigation projects for best management of estuarine regions with structural barriers inhibiting natural flow, an increasingly common feature of the coastal landscape. In addition, in this thesis, I suggest that variability itself is a niche/ecosystem characteristic that forces the structure of resident biota such as *Ulva*.

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Introduction

The coastal ecosystem is a dynamic environment responding to physical, biological, geological, anthropogenic and chemical forcing functions that act at the interface between land, sea and atmosphere. Dominant features of this interface are estuaries that are found globally and are considered some of the most productive environments in the world (Kamer *et al.*, 2001; Pomeroy and Stockner 1976; Valiela *et al.*, 1997). Species diversity and productivity in estuaries are controlled by variable environmental factors such as water temperature, oxygen, turbidity, light, nutrient loading and salinity (Fong *et al.*, 1996; Martins *et al.*, 2001; Pregnall and Rudy 1985; Su *et al.*, 2004). Estuaries are particularly susceptible to human impact due in part to their proximity to highly modified terrestrial systems, large human populations that typically bound them, and anthropogenic runoff all along the watersheds that feed them. Anthropogenic impacts such as increased nutrient loading, is often a result of changes in land use (e.g., urbanization, agriculture, etc.). Along the central California coast, land use has changed significantly and hydrological modifications have often resulted in habitat and water quality degradation.

The Elkhorn Slough, located in the heart of the Monterey Bay, hosts an immense diversity of biological, geological and chemical qualities making it a vibrant and complex ecosystem. Located northwest of Salinas in Monterey County, CA, the Elkhorn Slough is surrounded by large-scale agriculture. In 2015, Monterey County ranked number 4 in California's top 10 agricultural counties (CDFA statistics report, 2015). The Elkhorn Slough watershed is surrounded by approximately 24% cultivated agriculture regions (Elkhorn Slough Foundation). Five subwatersheds make up the Elkhorn Slough watershed, and each watershed uniquely impacts nutrient loading and freshwater input seasonally to Monterey Bay (Fig. 1). Substantial fertilizer usage on these lands has led to extreme eutrophication of many regions of the Elkhorn Slough, particularly where tidal flushing is minimal.

The Elkhorn Slough is a tidal wetland system that was historically subject to episodic flooding by the Salinas, Carneros and Pajaro Rivers before land use was

significantly modified and water was controlled. Wetland changes in the Elkhorn Slough started directly after the Gold Rush in California (Van Dyke & Wasson 2005).

Historically, the Elkhorn Slough region was used for grazing until water control (i.e. diking) allowed wetlands to be drained for row crops (Caffrey *et al.*, 2002). Major changes have been documented since 1870 with the majority of salt marsh changes and degradation occurring during periods of diking. This diking resulted in the reduction or complete removal of tidal exchange in the region's wetlands (Caffrey *et al.*, 2002; Van Dyke & Wasson 2005). By 1940, about 50 percent of the Elkhorn Slough wetlands were converted to farmland (Browning *et al.*, 1972). Today, a staggering 91% of California's historic wetlands have been lost (Dahl, 1990) making Elkhorn Slough National Estuarine Research Reserve a unique study region that may act as a proxy for other such environments in California.

In its transition from predominantly freshwater to brackish water, the Elkhorn Slough is now home to ecologically-important species such as the leopard shark, sea otter, harbor seal and juvenile invertebrate and vertebrates, as it is a coastal nursery habitat. There have been 102 species of fish from 43 families, as well as 265 bird species and 59 mammal species recorded in this region (Ramer *et al.*, 1991; Roberson 1991). A decline in faunal communities such as shore crabs, song sparrows, clapper rail and brackish-water snails have been associated with the degradation of the Elkhorn Slough's marshlands over the past century (Wasson *et al.*, 2002; Zedler 1996).

The reclamation of wetlands in central California involved constructing levees, dikes, berms, and drains to restrict and divert water flow so the land could be cultivated. Hydrologic changes along the coast even involved diverting the mouth of the Salinas River, a major river that converges with Elkhorn Slough. The partitioning of wetlands for hydrodynamic control or transportation purposes result in bodies of water that are trapped behind roads, railways and levees. These water bodies have restricted flow and tidal flushing, which modifies the chemical cycling of nutrients within the system.

Changing the hydrologic regime and landscape allowed central California to become one of the most important agricultural regions in the United States, producing over a third of the country's vegetables and two-thirds of the country's nuts and fruits (California Department of Food and Agriculture, 2015). The result of high levels of

agriculture and loss of wetlands was significant water quality degradation within the region. With decades of farming and nutrient fertilizer application, eutrophication has become a persistent problem in central California coastal environments. Directives have been given to farmers to decrease nutrient laden farm runoff into the surrounding watersheds (Sharpley *et al.*, 2006). Although farmers are changing to best management practices for irrigation and fertilizer application, nutrient concentrations in many coastal waterways still exceed drinking water standards. Nutrient runoff is a major concern in this region as increased nutrients has cascading effects on coastal marine and freshwater systems (Rabalais and Turner, 2001; Smith *et al.*, 1992; Caffrey *et al.*, 2006). These impacts may be exacerbated and intensified in regions of restricted flow as they are often the receiving waters of these inputs and comprise water bodies of smaller volume, where loading can become more concentrated and responses, amplified.

Nutrients (nitrogen and phosphorus species) drive primary productivity in aquatic systems, which can have lasting effects of ecosystem diversity and overall health by supporting consumers when nutrients are at a moderate level, but can induce anoxic events when nutrients are high and eutrophication results (Cebrian *et al.* 2014; Chapin *et al.* 2004). Increased nutrient loading can result in vast areas of coastal eutrophication, suboxic or anoxic dead zones, and increase the prevalence and frequency of harmful algal blooms (Kamer, 2001; Nixon, 1995; Rabalais *et al.*, 1996). Dinoflagellate and diatom blooms in the Monterey Bay have been seen to occur during upwelling events, and are considered a local phenomenon in the area, yet they have also been traced to runoff events as well (Horner *et al.*, 1997; Ryan *et al.*, 2009).

In addition to algal blooms found in the Monterey Bay, there are extensive blooms of the green algae *Ulva* spp. that blooms widely across central California at times. *Ulva* spp. is a common, ubiquitous estuarine alga that thrives on pulses of nutrients, and is considered to be opportunistic, as it is able to uptake nutrients and build biomass quickly (Abbott and Hollenberg, 1976; Lavery *et al.*, 1991; Pregnall and Rudy, 1985; Thom *et al.*, 1984). This species is found in shallow waters worldwide and has been shown to contribute as a primary trophic producer (Horn 1983) as well as a bioindicator for eutrophication in coastal environments (Kozhenkova *et al.*, 2006). Studies have shown that increasing nutrient input leads to overabundance of opportunistic macroalgal

blooms. Up to 30% of total primary production in an estuary can occur from *Ulva* spp., which can also grow faster than almost any other estuarine macroalga (Owens and Stewart 1983; Pomeroy and Stockner 1976; Pregnall and Rudy 1985). Once maximum growth has been reached (nutrients diminish or growth parameters become limited), decomposition of the algae releases nutrients back into the water column resulting in a nutrient flux (Beck *et al.*, 2000; Kamer *et al.*, 2001). This biological decomposition results in decreased oxygen levels in the water column that can affect fish and benthic communities. Primary producers as well as primary consumers depend on healthy benthic communities to survive (Levin *et al.*, 2009; Llanso 1992). This also impacts the survival of larger animals such as otters and other secondary consumers that are dependent on food availability in these regions (Hughes *et al.*, 2010; Sutula *et al.*, 2014). *Ulva* spp. can grow to expansive blooms that eventually cease to thrive. The decomposition of algae affects the cycling of nutrients greatly within a system (Hanisak 1993; Sfriso *et al.*, 1987).

The cycling and transport of nutrients from groundwater, surface water, sediments and biota is poorly understood in this region. In this study, the role and distributions of nutrients (nitrate, nitrite, ammonium, and phosphate) with measurements of flow and algal (*Ulva* spp.) coverage in four semi-restricted flow areas were investigated. Knowledge of each location's unique biogeochemical behavior helps quantify the processes responsible for the cycling of nutrients and the extent to which algae such as *Ulva* spp. can respond to nutrient loading and removal from the water body. The results of the fate and cycling of nutrients through highly eutrophic, tidally-restricted regions in the Elkhorn and Moro Cojo watersheds along the central California coast, provide useful models to inform nutrient dynamics and future mitigation strategies. *The primary goal of this study is to quantify nutrient flux dynamics, including sources and sinks, in tidally-restricted regions of the Elkhorn Slough and investigate the role of Ulva spp. in modulating nutrients in these systems.*

Study Site Description

In order to address the inputs, exports, cycling and impacts of nutrients in restricted flow regions, four sites were selected for this study (Fig. 2, 3). Sites were

targeted specifically based on flow characteristics, which alter biogeochemical processes within the region. All four sites are located behind physical barriers, which decreases flushing rates and increases residence times within the system. The sites used for this study were located in the Elkhorn Slough, outside of the main channel, where tidal exchange has been restricted due to roads, train tracks or culverts that separate small pocket regions from the main channel of the slough (Fig. 2).

North Azevedo Pond (Fig. 3), located in the upper portion of Elkhorn Slough near Kirby Park, has a total area of 31,449 square meters and lies behind the Southern Pacific rail line. Its average depth is 0.26 meters, and the flow is controlled by weirs and culverts in dikes at the northern and southern portions, which allows some flushing to occur on a tidal basis. The estimated volume was calculated by multiplying total area by average depth and resulted in approximately 8,365 m³. Strawberry and seasonal flower fields surround North Azevedo Pond. These fields are owned by The Nature Conservancy and managed by Elkhorn Slough Foundation, who then lease the land to private land owners (Elkhorn Slough Foundation).

Estrada marsh (Fig. 3) is located in the upper portion of Elkhorn Slough. Estrada marsh is a pocket region of the much larger North Marsh, located behind the Southern Pacific Rail line. It is the shallowest of the four sites at 0.25 meters deep and comprises a total area of 108,111 square meters, resulting in an estimated volume of approximately 27,136 m³. Estrada is separated from North Marsh by a dirt levee. The levee allows both inflow and outflow of water in Estrada through one gap in the levee that is approximately 3.5 m in length. Surrounding Estrada on the one side is North Marsh, with the other three sides bordered by Elkhorn Road, train tracks and a mudflat region surrounded by pickle weed. Tidal flushing is very dampened in this region because it is blocked by the train tracks and a dirt levee.

East Bennett Slough (Fig. 3) is located closer to the mouth of the Elkhorn Slough near the northern region of Moss Landing Harbor. This site is located east of Highway 1 and is restricted on two ends by culverts that run under the highway. East Bennett is 75,847 m² and has an average depth of 0.5 m in depth at mean tide, that results in an estimated volume of 39,137 m³. This site is surrounded by the Moss Landing Wildlife Area and strawberry farming in the northwestern regions. East Bennett has direct contact

with Struve Pond through a culvert, which receives nutrients via row-crop irrigation drainage. The other region of influence is through West Bennett slough, which drains directly to the Moss Landing Harbor.

The Moro Cojo Slough (Fig. 3) is the most southwestern of the four sites and is located between the Highway 1 and Moss Landing Road. This site is 18,832 m² and has an average depth of 0.65 m at mean tide which results in an estimated volume of 11,676 m³. This site is not surrounded by agriculture directly, yet is impacted by upstream flow under the Highway 1 culvert from the upper Moro Cojo. The surrounding region upstream is strictly agriculture and dairy farming that discharges nutrients to the study area. There is also saltwater intrusion into the slough under Moss Landing Road from Moss Landing Harbor via the leaking tide gates.

All four sites were chosen based on extreme tidal restriction due to anthropogenic barriers. Each site differs slightly with respect to size, perimeter, sediment type and total tidal flux but can be compared based on the common characteristic of the dampened tidal flushing from flow structures. Restricted tidal flushing has been determined to be a leading factor for eutrophication estuarine environments (Ritter *et al.*, 2008; Hughes *et al.*, 2011). Yet these structures also allow for a more quantitative assessment of nutrient flux, both into and out of these systems. Comparing study sites will clarify further drivers of nutrient cycling within these systems.

Methods

Water Column Characteristics

Each site was monitored weekly for one year (April 2015 – April 2016) to measure temperature, pH, salinity, dissolved oxygen and flow rates. Flow measurements were conducted at both the inflow and outflow regions of each site, using an OTT MF PRO[®] flow meter and following the USGS protocol for monitoring stream flow (Buchanan *et al.*, 1976). Multiple flow measurements were collected across the culvert opening of inflow into the slough and were averaged. Flow was measured during both incoming and outgoing tides to characterize water movement into and out of the sites from different sources. Physical parameters including temperature, salinity, pH and dissolved oxygen were measured on a weekly basis to characterize each system using a

handheld YSI® 556-01 Multi-parameter Meter (Yellow Springs Instruments) in conjunction with water quality collections. The YSI® meter was calibrated daily according to the manufacturers guidelines.

Nutrient Monitoring in Surface Waters

Water quality was measured by monitoring nutrients using two different methods, continuous integrated samples and discrete, or grab samples. In order to acquire continuous surface water samples, OsmoSampler pumps were deployed at each site for a composite collection series of surface water. This method is well established for deep-sea measurements (Jannasch *et al.*, 2004) and has been modified for this study by optimizing the deployment casings for shallow estuarine environments. Each OsmoSampler included a pump and coil with 0.079" OD FEP tubing for sample collection. Both the pump and the coil of tubing were connected and placed in a plastic bin that was enclosed with a lid. The bin was painted to decrease light impacts such as photosynthesis within the coil, resulting in utilization of nutrients in the water sample. The boxes were attached to t-stakes (metal fence posts) at each site and were resting on the bottom sediments to remain deep enough so the pump would not collect air at low tides. The OsmoSamplers were deployed starting in March 2015 and were collected every 2 months to process samples. The final sampling finished in March 2016. Upon collection each time, the Teflon tubing was cut into 1 m d⁻¹ long sections and the sample was drained into microcuvettes. Upon analysis, the contents of 5 microcuvettes were combined and analyzed for nutrients as one sample creating a 5-day composite sample. The pumps were resupplied with salt and deionized water and were attached to more Teflon tubing before being redeployed in the field. The OsmoSampler nutrient analysis was limited by required sample volume and therefore represents an integrated ~ 5 day time period. Samples were collected and kept at +4 °C until analysis that occurred within 24 hours.

To validate the OsmoSampler method, weekly grab samples for nutrient analysis were also collected at all four sites on an outgoing tide flow to capture water samples exiting the system. The goal for using grab sample method was to increase sampling confidence in the case of pump failure or vandalism. Weekly grab samples also enabled correlation with the weekly-integrated continuous Osmosamples to identify variability

between the two methods. All samples were collected in acid washed (10% HCl) 50 mL polypropylene Falcon[®] tubes and were filtered upon collection using a 0.7 μm Whatman[®] glass microfiber filter. Samples were kept on ice and in the dark in the field until returned to lab directly after collection. Samples were frozen prior to analysis. The samples were kept at -20°C , which has been shown to be a stable temperature to prevent degradation of nitrogen and phosphorous species (Gardolinski, 2001). All nutrient samples were analyzed on a Lachat QuickChem[®] 8000 series autoanalyzer for phosphate (PO_4^{3-}), nitrite (NO_2^-), nitrate+nitrite ($\text{NO}_3^-+\text{NO}_2^-$), and ammonium (NH_4^+). Nitrate+nitrite measurements will be referred to as nitrate for the remainder of this report. Nitrite was a small component of the total nitrite+nitrate signal so was not reported as an individual nitrogen species in this report.

Porewater and Sediment Characteristics

Porewater nutrient concentrations were measured seasonally at each site in order to determine the diffusional flux of nutrients between the sediments and the overlying water. The first three centimeters of sediments were sampled at each site with 10 cm push cores. Three cores were taken randomly at each site. The cores were sliced into the following sections: 0-0.5 cm, 0.5-1 cm, 1-2 cm, and 2-3 cm from the surface. Each section of sediment was placed in a Falcon[®] tube and transported on ice back to the laboratory. The sediment samples were centrifuged for 5 minutes at 500 rpm in order to extract the pore water. The extracted porewater was filtered with a 0.7 μm Whatman[®] glass fiber filter into an acid cleaned Falcon tube. These porewater samples were then frozen until analyzed for nutrients on the Lachat autoanalyzer. The diffusional flux across the sediment-water interface for each nutrient was calculated using the porewater nutrient concentrations and Fick's first law of diffusion (Petersen, 1965; van Brakel and Heertjes, 1974; Ullman and Aller, 1982). The following equation for diffusional flux (J) from Boudreau (1996) was used:

$$\text{Equation 1: } F_D = -(\phi D_w / \theta^2) (\delta C / \delta x)$$

where ϕ is the sediment porosity, θ is the tortuosity, D_w is the molecular diffusivity coefficient of $5 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, C is the concentration of nutrients in the pore waters, x is the sediment depth (Choe *et al.*, 2004). Gradients were linear with r^2 between 0.7 and 0.95. The value of θ^2 can be estimated from porosity using the relationship $\theta^2 = 1 - \ln(\phi^2)$ (Boudreau, 1996).

Cores for organic carbon analysis were taken seasonally in conjunction with the cores taken for porewater analysis in order to determine the amount of organic material that comprises the surface sediments. One 10 cm push core was taken at each site and was sectioned in the field in the same increments as were the porewater cores. The sectioned core samples were taken back to the lab and dried in pre-weighed porcelain crucibles at 100°C for 12 hours. The samples were weighed again, then combusted at 550°C for 4 hours (LacCore, 2013 National Lacustrine Core Facility). Samples were cooled in a desiccator before final weight was determined. The loss on ignition (LOI) or difference between initial dry weight and final weight using the following equation was used to estimate percent organic material:

$$\text{Equation 2: } \% \text{ OM} = \left(\frac{\text{pre-ignition weight (g)} - \text{post-ignition weight (g)}}{\text{pre-ignition weight (g)}} \right) * 100$$

This was used to determine how organic material changed in the benthic sediments seasonally at each site.

Benthic Flux Chambers

Benthic flux chambers were used to measure seasonal nutrient flux from the sediments at each site via *total respiration*. Two benthic flux chambers were deployed at each site for 3-5 hours. The benthic flux chambers were gently and securely pushed into the surface sediments to minimize sediment disturbance and to ensure that there was no surface water exchange with the contents of the chamber. The total volume of water inside the chamber was 7 L and an internal sediment surface area of 0.05m^2 . Hourly water samples were taken from the chambers, measuring 20 mL each in order to maintain a relatively constant volume within the chamber. All samples were filtered upon collection and

frozen before nutrient analysis. The rate of change in nutrient concentrations inside the chambers was converted to benthic fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$).

Groundwater

Groundwater discharge was quantified during the wet and dry season at each site using radon (^{222}Rn) as a tracer for total *advective flux*. Radon was measured continuously for ~6 hours at each site using a RAD7[®] (DurrIDGE Inc.) to capture variability in groundwater flux during high and low tides and different season. Information regarding the instrumentation can be found elsewhere (Burnett and Dulaiova 2003). Radon-222 in surface water was measured in 15-minute intervals and 6 L grab samples were collected from groundwater at each site. The following equation was used to determine the mass balance of ^{222}Rn in the water column and determine the advective water flux:

$$\text{Equation 3: } GW_{flux} = \{(A_{box} - A_{out})V_{box}/\tau\}/A_{PW}$$

The groundwater flux (GW_{flux} ; $\text{m}^3 \text{m}^{-1} \text{d}^{-1}$) is groundwater discharge (including freshwater and recirculated seawater) along one meter of pond circumference. A_{box} is the average ^{222}Rn activity of the coastal box where groundwater discharge occurs (dpm m^{-3}). A_{out} is the average activity outside the box (~5 m outside of the box; dpm m^{-3}). V_{box} is the volume of the box (m^3). τ is the water residence time (d; estimated to be 1 day). Radon-222 flux is then divided by the measured groundwater ^{222}Rn activity end-member (A_{PW} ; dpm m^{-3}) to obtain a discharge estimate ($\text{m}^3 \text{m}^{-1} \text{d}^{-1}$) required to supply the flux of ^{222}Rn assuming steady-state conditions. This simplified model is a snapshot of groundwater discharge and does not account for ^{222}Rn variability due to tidal water level fluctuations or atmospheric evasion of ^{222}Rn from wind. The flux of nutrients from advection can be derived by multiplying the groundwater flux and groundwater nutrient concentrations times the circumference of the water body.

Algal Biomass Dynamics

Algal biomass dynamics were measured using aerial photography overlaid with biomass surveys to estimate total algal biomass in each region on a monthly timescale.

1. Aerial Photography:

Monthly transects were conducted by flying an IRIS+ drone 80 m overhead at each site to estimate percent cover of floating algae using the acquired aerial images. The imagery was captured with a GoPro[®] Hero camera attached to the bottom of the drone. The aerial images were stitched together using the mosaic tools from AutoPanoGiga[®] software. Only algae seen from the surface was accounted for as to not bias regions with good water visibility. Once mosaic images of each site were created, the images were analyzed for percent cover using ArcGIS[®] software by creating polygons.

2. Biomass Surveys:

Monthly algal samples were collected to estimate total algal biomass at each site. A 0.3 m diameter core was used to collect randomized samples from patches of algae. Ten samples were collected randomly at each site per month. To reduce bias toward or away large algal patches, cores were spread throughout each site with samples coming from different patches of algae. The samples were transported back to the lab and rinsed in freshwater to remove debris and mud, and spun 5 times in a salad spinner to remove excess water. Wet weights were recorded for each of the ten samples from each site. The algae dried for 48-72 hours using heat-drying racks to obtain a dry weight measurement. From these measurements, an estimate of total algal biomass in each region was obtained using the equation:

$$\text{Equation 4: } \text{Algal Cover (m}^2\text{)} * \text{Algal Biomass (g m}^{-2}\text{)} = \text{Total Algae (g)}$$

Results

Water Column Characteristics & Field Measurements

All four sites showed seasonal trends in temperature fluctuations with a winter low in February 2016 being the coldest for all sites (9.66°C, 9.98°C, 10.2°C and 10.22°C at East Bennett Slough, North Azevedo Pond, Estrada Marsh and Moro Cojo Slough respectively). All sites except North Azevedo had highest seasonal averages during the summer with Estrada averaging 24.2°C, Moro Cojo averaging 20.66°C and East Bennett averaging 22.51 °C. North Azevedo had highest average temperatures during the fall with an average of 22.1°C (Table 1).

Salinity values included a wide range for both Moro Cojo Slough and East Bennett Slough ranging from 6.7-50.6 psu and 6.6-51.0 psu respectively. North Azevedo Pond and Estrada Marsh had more narrow ranges of salinities from 24.7- 40.2 and 22.3-58.4 psu respectively. Estrada Marsh, Moro Cojo Slough and North Azevedo Pond had highest salinity values during summer (48.1 psu, 33.94 psu and 36.65 psu), while East Bennett Slough reached 45.75 psu during the Fall (Table 1). Temperature and salinity showed a weak correlation for all sites ($r^2 = 0.27$).

East Bennett Slough showed the widest range in dissolved oxygen from 162.15 μM during the summer months to 391.18 μM during the winter (Table 1). Dissolved oxygen was highest during the winter season for all sites. DO levels drop to lows of 167.44 μM and 311 μM during Fall for Estrada Marsh and Moro Cojo Slough respectively. Summer yielded lowest DO averages for North Azevedo Pond (152.55 μM) and East Bennett Slough (162.15 μM DO). The four sites had comparable pH values with a range of 7.88 – 8.88 (Table 1).

Flow rates were measured at each site and each culvert, for both incoming and outflowing tides. Total discharge was calculated from these flow measurements and the area of each culvert (Table 2). Moro Cojo Slough had the largest flow rates of all four sites, reaching a peak flow of 64,696 $\text{m}^3 \text{d}^{-1}$ during January 2016 which was during the peak rain season. North Azevedo reached 58,409 $\text{m}^3 \text{d}^{-1}$ flow during October 2015. Estrada Marsh peaked in flow during July 2015 with 10,390 $\text{m}^3 \text{d}^{-1}$, and East Bennett Slough peaked during March 2016 with 726 $\text{m}^3 \text{d}^{-1}$, making it the site with the lowest flow. Moro Cojo and North Azevedo both reached their lowest flows during April 2015,

while Estrada and East Bennett Slough exhibited lowest flows during February 2016 and September 2015 respectively. On average, Moro Cojo Slough had the highest flows throughout the year, while East Bennett Slough had the lowest average flow rates of all four sites (Table 2). Flow rates were able to inform hydraulic residence times for each site. Calculating residence time (τ) = volume of reservoir (m^3) / flux (m^3/day), resulted in East Bennett Slough having the longest hydraulic residence time of 19.5 days, whereas Moro Cojo Slough and North Azevedo Pond both had residence times of 0.3 days. Estrada Marsh had a residence time estimate of 4.13 days (Table 2).

Surface Water Nutrients

Ammonium, nitrate, and phosphate were analyzed from water samples collected via osmotic sampler (OsmoSampler). These samples were compared to the corresponding grab samples in order to verify the accuracy of nutrient concentrations collected by the continuous, osmotic sampler. Comparing values for individual nutrient species between discrete grab samples and continuous osmotic samples resulted in r^2 values of 0.03, 5.2×10^{-6} , and 0.06 for nitrate, ammonium and phosphate respectively. The visible correlations between the methods are shown in Figures 4, 5 & 6. The nutrient samples collected via the OsmoSampler differ from those collected via grab samples due to two sampling variables. The OsmoSampler samples were not frozen upon collection, but were stored in Teflon tubing *in situ*. Secondly, the samples were not filtered prior to being analyzed. While this method allows for continuous sampling, it also allows for nutrient transformations due to microbial utilization and other biogeochemical alterations within the tubing. Therefore, the samples collected via OsmoSampler were analyzed for dissolved inorganic nitrogen (DIN) as a whole rather than individual nitrogen species (NO_3^- , NH_4^+) due to the low confidence for individual nitrogen species from transformations. The grab samples collected were frozen immediately which decreased nitrogen transformations within the samples, so individual nitrogen species (NO_3^- , NH_4^+) were analyzed separately with confidence. Grab samples were also used to quantify phosphate levels due to a low confidence interval in the Osmosampler data for phosphate.

Dissolved Inorganic Nitrogen

Dissolved inorganic nitrogen (DIN) was typically elevated during the warmer summer months as well as the rainy winter months (Fig.7, Table 3). The highest DIN level was measured at Moro Cojo Slough at 707.13 μM in May 2015. East Bennett followed with 506.98 μM DIN in July 2015. The highest DIN measurement in Estrada Marsh was 490.32 μM DIN in August 2015, and the highest for North Azevedo was 258.46 μM DIN in March 2016. Both East Bennett Slough and Estrada Marsh had their two highest monthly average DIN measurements during July and August 2015. Moro Cojo Slough and North Azevedo Pond peaked in DIN levels during the winter months (January – March 2016). DIN levels were at a minimum of 2.53 μM at Moro Cojo Slough in November 2015. Estrada Marsh reached a minimum of 1.67 μM DIN in June 2015. North Azevedo Pond reached the lowest DIN concentration in September 2015 with 2.81 μM , and East Bennett reached 4.85 μM DIN in December 2015 (Fig.7). Overall, for the sampling year, East Bennett had the highest DIN with an average of 124.62 μM DIN, while Moro Cojo had an average of 106.93 μM DIN. Estrada averaged 95.95 μM DIN, and North Azevedo averaged 31.42 μM DIN (Table 3).

Nitrogen Species

Nitrogen species varied in concentration between each site throughout the sampling year. East Bennett Slough had the highest nitrate levels during Spring 2015 at 272.66 μM with an average high of 129.9 ± 43 μM during May 2015 (Fig.8, Table 5). Nitrate levels reached a maximum during the spring for Moro Cojo as well, with a peak of 355.54 μM and reached the highest monthly average during May (160.7 ± 50.5 μM) (Fig. 9, Table 6). North Azevedo reached a high of 130.00 μM nitrate for a single grab sample in February 2016 and the highest average month for nitrate peaked at 33.8 ± 24 μM during February as well (Fig. 10, Table 7). Estrada Marsh also peaked to 19.0 μM nitrate in January 2016, when the average was 8.38 ± 5.3 μM during January 2016 (Fig. 11, Table 8). Nitrate concentrations exhibited the largest range of all nutrients measured (Table 4).

Ammonium concentrations peaked during the winter months for Estrada Marsh, Moro Cojo Slough, and North Azevedo, while East Bennett Slough followed in late winter and early spring (Fig.8-11). Ammonium reached a maximum of 199.29 μM at Estrada Marsh in December 2015 with the highest monthly average reaching 132.4 \pm 41.5 μM (Table 8). Moro Cojo reached a maximum ammonium concentration in April 2016 at 107.1 μM , yet the highest monthly averaged was measured in January at 84.8 \pm 8.4 μM (Table 6). A peak of 77.86 μM at North Azevedo was measured in January 2016 with the highest monthly average being 39.5 \pm 19.3 μM during January as well (Table 7). East Bennett Slough peaked in spring 2016 with a high value of 69.0 μM measured and an average high of 37.4 \pm 31.6 μM both during March 2016 (Table 5). Ammonium concentrations dropped to low concentrations for North Azevedo, Estrada, and East Bennett Slough during the summer months, whereas low concentrations in the Moro Cojo slough were measured during the Spring. North Azevedo and East Bennett had the lowest average ammonium concentrations during July 2015 with 2.9 \pm 1.29 μM and 3.3 \pm 1.3 μM , respectively. Estrada Marsh had the lowest monthly average ammonium levels during June 2015 with 2.4 \pm 0.28 μM , and Moro Cojo dropped to 2.36 \pm 0.1 μM during Spring 2015 (Tables 5-8).

Phosphate

Phosphate levels varied among sites with North Azevedo Pond, East Bennett Slough and Moro Cojo Slough showing elevated phosphate levels during the late spring and summer months as well as the late fall and winter months. Moro Cojo had the highest average phosphate level while North Azevedo Pond had the lowest phosphate values over the sampling year. Estrada Marsh showed elevated phosphates primarily during the fall and winter months (Fig. 12). Phosphate levels reached a maximum peak during November 2015 at Estrada Marsh with 20.7 μM (Fig. 11). The highest monthly average at Estrada Marsh was also during November 2015 with an average of 20.32 \pm 18 μM . Phosphate levels peaked at East Bennett Slough during summer and winter months. East Bennett Slough hit a peak of phosphate during September 2015 at 22.76 μM phosphate,

and had a high monthly average during September 2015 ($15.26 \pm 5.89 \mu\text{M}$) (Fig. 8). Phosphate levels at Moro Cojo Slough were relatively high during most seasons with a decrease during the late summer months (Fig. 9). The highest peak in phosphate at Moro Cojo was during November 2015 with $17.08 \mu\text{M}$, and the highest monthly average was $14.82 \pm 0.79 \mu\text{M}$ during January 2016. North Azevedo phosphate levels peaked with a high of $10.59 \mu\text{M}$ during October 2015, and a highest monthly average of $6.72 \pm 1.46 \mu\text{M}$ during March 2016 (Fig. 10).

From the time-series data it appears that variability is the common feature of these systems. Table 4 represents the range of values found in these systems. This variation was sometimes observed over very short time periods. Large ranges in nutrient concentrations were shown to be characteristic of each system with nitrate values exhibiting a high range of variability, whereas phosphate values remained comparatively more constant (Table 4).

Benthic Flux

Flux Chambers

Benthic Flux chambers were deployed on a seasonal basis for all four sites starting in summer 2015 and ending in spring 2016 (Fig. 13). The rate of change in nutrient concentrations inside the chambers was converted to benthic fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$).

Nitrate fluxes varied between site and season, although the largest degree of flux was measured to be negative (sinks in the system) during the winter months at East Bennett Slough and North Azevedo Pond (Fig. 13b a,b). Nitrate fluxes from the benthic sediments reached a maximum rate of $6.84 \text{ mmol m}^{-2} \text{d}^{-1}$ in Moro Cojo Slough (Fig. 13c.), and $0.21 \text{ mmol m}^{-2} \text{d}^{-1}$ in Estrada Marsh (Fig. 13 d.), both during winter 2016. North Azevedo reached a maximum nitrate flux of $0.17 \text{ mmol m}^{-2} \text{d}^{-1}$ during Spring 2016 (Fig. 13b.). East Bennett Slough never had a positive nitrate flux from the sediments, but rather only exhibited nitrate removal (Fig. 13a.).

Ammonium exhibited the greatest degree of positive flux from the sediments among all four sites. All four sites showed a seasonal trend of positive ammonium fluxes during the winter season, but varied between ammonium flux and utilization throughout

the remaining months. Ammonium fluxes from the sediments peaked at Moro Cojo Slough during fall 2015 with a rate of $64.24 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 13c.). Estrada Marsh, East Bennett Slough and North Azevedo Pond all peaked in ammonium fluxes during winter 2016 with $23.24 \text{ mmol m}^{-2} \text{ d}^{-1}$, $11.41 \text{ mmol m}^{-2} \text{ d}^{-1}$, and $7.30 \text{ mmol m}^{-2} \text{ d}^{-1}$ respectively (Fig. 13d, a, b). Ammonium flux and dissolved oxygen levels had a weak correlation of ($r = 0.15$).

Phosphate fluxes were the smallest of the benthic fluxes measured, and were found to act as both sources and sinks in the systems, which varied by site. Phosphate flux levels peaked in Moro Cojo Slough in Fall 2015 with $11.78 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 13c.). East Bennett Slough exhibited high phosphate peaks in Summer 2015 with $1.58 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 13a.). Estrada Marsh peaked during winter 2015 with $1.42 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Fig. 13d.). North Azevedo never had a positive phosphate flux, but rather the sediments acted as a sink in the system.

Porewater Gradients/ Diffusive Flux

Diffusive fluxes were estimated based on vertical pore water gradients using Fick's first law of diffusion, modified for sediment porosity and tortuosity Boudreau (1996, Equation 1). The largest positive diffusive fluxes of all four sites were ammonium fluxes (Table 9). East Bennett Slough and Moro Cojo Slough peaked in ammonium fluxes during fall, while Estrada Marsh and North Azevedo Pond peaked during winter months. Estrada Marsh had the largest fluxes of all four sites in winter 2016 with $646.15 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$. North Azevedo also peaked in ammonium flux during winter 2016 with $188.55 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$. East Bennett Slough had a large ammonium flux during fall 2015 with $590 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$, and Moro Cojo had a flux of $420.98 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ in fall 2015 as well.

Nitrate fluxes were significantly less than ammonium fluxes for most sites (Table 9). East Bennett Slough exhibited large nitrate fluxes during winter 2016 with $234.02 \text{ } \mu\text{mol/m}^2/\text{day}$. Both Estrada Marsh and Moro Cojo had nitrate fluxes of $138.97 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ and $76.50 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ during fall 2015. North Azevedo peaked in spring 2016 with a nitrate flux of $0.40 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$. Estrada Marsh and North Azevedo Pond exhibited primarily negative fluxes of nitrate.

During Summer 2015, Estrada Marsh had a negative nitrate flux of $-78.66 \mu\text{mol m}^{-2} \text{d}^{-1}$, and similarly, had a flux of $-73.91 \mu\text{mol m}^{-2} \text{d}^{-1}$ in Spring 2016 (Table 9). Moro Cojo Slough had a negative nitrate flux of $-37.66 \mu\text{mol m}^{-2} \text{d}^{-1}$, and North Azevedo had a negative nitrate flux of $-2.15 \mu\text{mol m}^{-2} \text{d}^{-1}$ during Winter 2016.

Phosphate fluxes were highest in Estrada Marsh during Spring 2016 with $51.15 \mu\text{mol/m}^2/\text{day}$ (Table 9). East Bennett followed with $22.35 \mu\text{mol m}^{-2} \text{d}^{-1}$ during Spring 2016 as well. North Azevedo peaked in Winter 2016 with $18.71 \mu\text{mol m}^{-2} \text{d}^{-1}$ phosphate, and Moro Cojo Slough peaked in Summer 2015 with $3.27 \mu\text{mol m}^{-2} \text{d}^{-1}$ phosphate.

Groundwater Flux

Groundwater flux was measured based on California's wet/dry seasonal dichotomy. The largest groundwater flux was measured at Estrada Marsh during the wet season (March 2016) with a flux of $6775.52 \text{ m}^3\text{d}^{-1}$ (Table 10). North Azevedo Pond exhibited the smallest groundwater flux of the four sites during September 2015 with $880.6 \text{ m}^3\text{d}^{-1}$. There was an increase in groundwater discharge for all four sites when comparing the dry and wet seasons. Moro Cojo Slough and Estrada Marsh showed the largest range between wet season and dry season groundwater discharge measurements.

Algal Biomass, Percent Cover, Total Algae, and Organic Matter in Sediments

Algal Biomass Density

Algal biomass density (g/m^2) as well as algal cover (m^2) was measured monthly for 12 months (Fig. 14,15). Algal biomass density peaked during the spring and summer months and dissipated during the late fall and winter. December and February had the lowest measured algae, while March-September yielded high amounts of algae for most sites. North Azevedo had the largest biomass density measured of all four sites during March 2015 with $521.27 \text{ g dry algae m}^{-2}$. Estrada Marsh, Moro Cojo Slough, and East Bennett Slough all had their highest biomass densities measured during September 2015 with $292.44 \text{ g dry algae m}^{-2}$, $182.32 \text{ g dry algae m}^{-2}$, and $252.63 \text{ g dry algae m}^{-2}$ respectively. Inversely, January yielded no measureable algal biomass for Moro Cojo Slough, Estrada Marsh or North Azevedo Pond. East Bennett Slough measured $79.12 \text{ g dry algae m}^{-2}$ during January. Overall, there was a seasonal trend in algal biomass density

measurements with the vast majority of biomass measured during the late spring persisting until early fall, with the winter months yielding less algae, while some sites dropped to zero algae (Fig. 14).

Algal Cover

Algal percent cover was analyzed using AutoPano Giga 3.7 software along with ArcGIS imaging. Algal Percent cover ranged from 75% - 0% cover throughout the sites during the sampling year (Figure 15). On average, the most algal cover for all sites ranged from late spring through early fall. The late fall and winter months yielded far less algal cover (close to 0%) for most sites. The highest percent algal cover was measured in East Bennett Slough during April 2015 with 75% of the surface covered. North Azevedo Pond and Moro Cojo Slough had the highest measured monthly cover during October 2015 with 41.76% cover and 18.7% in October 2015. Estrada peaked in late spring with 18.14 % cover during May 2015. Moro Cojo had the longest time in which 0% algal cover was measured, which was during December 2015-March 2016. Likewise, Estrada Marsh had 0% cover from November 2015-January 2016 (Fig. 15).

Total algae was calculated by combining algal biomass density (g m^{-2}) x cover (m^2) (Fig. 16). There was a seasonal trend in total algal abundance for all sites with the majority of algae present from spring-fall and peaking during the early summer with smaller peaks in the fall months (Fig. 16). East Bennett Slough had the highest total algal measurements of all four sites with a maximum of 10611.8 kg dry weight during April 2015. Estrada Marsh peaked at half of East Bennett's total algae with 5029.3 kg during May 2015. North Azevedo reached peak algal biomass during November 2015 with 1669.3 kg. Moro Cojo also peaked during the fall months with 593.6 kg during September 2015 (Fig. 16).

Organic Carbon Sediment Cores

Cores were taken in the surface sediments (0-3 cm) in order to determine the extent to which organic material comprised the sediment composition, and its decomposition could lead to sediment nutrient fluxes. Estrada Marsh had the highest organic material in the sediments of all four sites during summer 2015 with 68% organic material at 2 cm depth (Fig. 17a.). North Azevedo had the second highest organic matter

content during spring 2016 with 39% organic matter at 3 cm depth (Fig. 17b). Moro Cojo Slough peaked in spring 2016 with 25% organic material in the surface sediments (Fig. 17c). East Bennett Slough peaked in fall 2015 with 18% organic material in the surface sediments (Fig. 17d).

Discussion

Nitrate, ammonium and phosphate are key nutrients that impact the health, growth and persistence of primary producers in estuarine systems (Conley and Malone, 1992; Conley, Schelske, and Stoermer 1993; Ryther and Dunstan 1971). Nitrogen species in particular are complex in that nitrification, denitrification and anaerobic ammonia oxidation reactions transform nitrogen species through the eight redox states and biological conditions. This nature of nitrogen species complicates the interpretation of nitrogen data from surface waters alone, especially when sampled intermittently. On the other hand, phosphate undergoes no change in its redox state.

OsmoSampler and Grab Surface Water Samples

Using the OsmoSampler method for surface water collection in addition to individual grab samples allowed for higher resolution measurements and comparisons could be made between the concentrations of individual nitrogen species in order to determine the accuracy of each method. Dissolved inorganic nitrogen (DIN) is at times used to quantify nitrogen species concentration as a whole when there is a high degree of nitrogen transformations within the OsmoSampler. Thus, the relationship between measured DIN concentrations between the grab samples and Osmosamples was much closer than the comparison of any single nitrogen species (Fig. 4 & 5). Between June and November (summer through fall), OsmoSampler and grab sample DIN concentrations had a much tighter relationship than for the winter and spring seasons (Fig. 4). The same trend is seen for nitrate values when comparing grab samples and OsmoSampler values, with a tight relationship between June and November, and more variability during the winter and spring months. This trend may be in part due to the wet/dry seasons that California is known for. The wet season for 2015/2016 started during November 2015 and lasted through April 2016 (Fig. 18). The high degree of variability between the grab

samples and the Osmosamples during this wet season may be attributed to the flashiness of these systems when rain events occur. While OsmoSamplers collect an average nutrient composition over a couple days, grab samples account for one specific nutrient concentration in time. In a system where surface flow is a major contributor to overall nutrient concentrations, the wet season variability is expected. Nutrient transformations also add to the variability between the two methods of collection, while Osmosamples may experience microbial induced nutrient transformations. The tighter relationship between the two sampling methods during the dry season may be attributed to a lower degree of flow, including a lower degree of variability in nutrient inputs to the system. Another aspect is that the OsmoSamplers sample water masses near the bottom sediments where the sampler is deployed, whereas the grab samples are near the surface. This difference can lead to variability in samples during the rainy season due to potential salinity stratification.

A linear regression between the OsmoSampler data and grab sample data for nitrate and ammonium concentrations at Moro Cojo Slough had an $r^2 = 0.05$ and $r^2 = 0.001$, respectively. This low level of correlation between the two methods when determining individual nitrogen species implies a significant level of nitrogen transformation, suggesting the method of sample collection as the determinant. The very low level ($r^2 = 0.001$) of correlation of ammonium values between the two methods is understandable since ammonium is a highly labile nutrient with an oxidation state of (-III). Ammonium is more readily utilized by plants and algae via nitrogen assimilation since less redox energy is required to utilize ammonium rather than a more oxidized form such as nitrate or nitrite.

Phosphate is less labile than nitrogen species with fewer transformations present in the phosphorous cycle. Remineralization, sedimentation and photosynthesis drive the phosphorous cycle, resulting in slower transformations between dissolved inorganic phosphorous and particulate organic phosphorous found in estuarine environments. The correlation found between the OsmoSampler data and the grab sample data ($r^2 = 0.06$) suggests different utilization of phosphates between the two methods or there was water column stratification, resulting in separated water bodies that were measured. Phosphates typically were closer in range during July – November, similar to the trends seen in the

nitrogen species samples (Fig. 6). Although the higher r^2 value indicates a closer relationship between these methods, it is not close enough to confidently account for phosphate levels using the OsmoSampler technique alone. Grab samples with filtering and freezing reduce nutrient transformations and in this case, were used to evaluate the magnitude of the sources and sinks in this system.

Nutrient Sources and Sinks

In tidally restricted estuarine systems, nutrient cycling differs from natural, tidally open systems due to altered inputs and outflows of water that can impact the residence time of nutrients in the system. Understanding the sources (addition processes) and sinks (removal processes) of nutrients in these systems helps to identify the system drivers, and whether the system is in steady state. A system at steady state would be indicated by sources equaling sinks. A box model approach was used in order to determine the sources and sinks as well as the primary nutrient drivers in these tidally restricted systems. This box model was utilized to understand these dynamics and is illustrated in the following schematic:

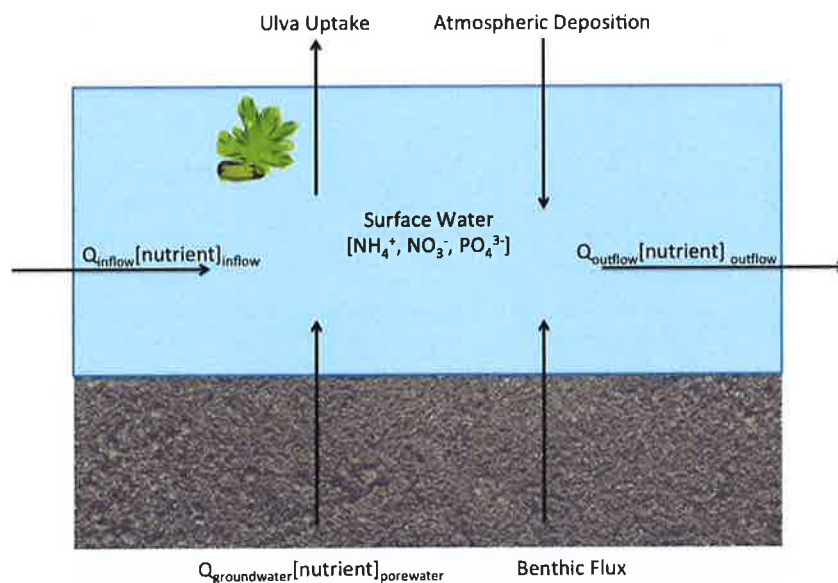


Fig.19: The water column processes investigated and quantified in the study were interpreted as follows:

Water Column processes = Sources – Sinks

Sources:

$Q_{\text{Inflow}}[\text{nutrient}]_{\text{Inflow}}$

$Q_{\text{Groundwater}}[\text{nutrient}]_{\text{Porewater}}$

Benthic Flux

Atmospheric Deposition

Sinks:

$Q_{\text{outflow}}[\text{nutrient}]_{\text{outflow}}$

Ulva Uptake

Variable Description:

Q_{inflow} = surface water flow into the system (liters or m³/sec)

Q_{outflow} = surface water flow out of the system (liters or m³/sec)

$[X]_{\text{inflow}}$ = nutrient concentration of flow into system (mol/liter)

$[X]_{\text{outflow}}$ = nutrient concentration of flow out of system (mol/liter)

Q_{GW} = groundwater flow into the system (liters or m³/sec)

$[X]_{\text{GW}}$ = nutrient concentration in groundwater (moles/liter)

Benthic flux = benthic flux of nutrients (moles/sec)

Ulva uptake/release (moles/sec)

For *Ulva* uptake and release, the Michaelis-Menten approach was used to calculate nutrient uptake as a function of ambient nutrient concentration (Pedersen *et al.*, 1997). For any given substrate concentration, given the mass of *Ulva* present, the uptake velocity (V) was calculated. V_{max} and K_m values were estimated based on literature values and were found to be consistent with these parameters measured on local species in the laboratory. For these experiments, values $V_{\text{max}} = 77.07, 270.90$ and 7.46 and $K_m = 15.86$,

31.73 and 8.67 were chosen for this study for nitrate, ammonium and phosphate respectively.

Equation 5:

$$V = V_{\max} (S) / K_m + (S)$$

V = Uptake Velocity (micromols/grams dry weight/hour)

V_{\max} = Maximum rate of uptake at saturating substrate concentration

K_m = Substrate concentration at which the reaction rate is half of V_{\max}

S = substrate concentration

Nitrate

Nitrate source inputs varied between sites. Moro Cojo Slough had the largest amount of nitrate entering the system of all four sites according to the box model results, reaching 907.9 Kmol N/month (12,710.6 Kg), with the dominant source of nitrate coming from flow into the system through culverts. The flow for the year accounted for 86% - 99.9% of all nitrate contributing to the overall nitrate concentration in the system (Fig. 20). Moro Cojo also had a short hydraulic residence time of 0.3 days, which influenced the time frame in which nitrate entering the system could be utilized (*Ulva* uptake, benthic flux sequestration, etc.) before exiting the system (Table 2). Nitrate also entered the system via groundwater flux and atmospheric inputs, however both were far less significant to the overall nitrate load. According to previous research by Chapin *et al.*, 2004, propagation of internal waves during high tides in the Elkhorn Slough accounted for up to 90% of nitrogen loading into the slough during the summer months and tidal cycling was the most influential nitrate source throughout the year (Chapin *et al.*, 2004). Although the Moro Cojo is a tidally restricted site, the nutrients delivered via flow from tidal surges is incorporated in the overall nitrate flow data in this model. Nitrate sinks, or removal processes, in the Moro Cojo Slough were driven primarily through flow, which comprised 82.8%-99.9% of total nitrate removal from the system (Fig. 21). Flow nitrate removal was primarily high during the spring and winter months with a peak of 917.5 Kmol nitrate removed from the system per month, accounting for up to 99.9% of all nitrate sink processes during the month of February 2016 (Fig. 21). *Ulva* uptake and benthic flux also added to the nitrate sinks for this site, up to 16.2% and 6.4%,

respectively (Fig. 21). When comparing sources and sinks in this system per month, there are only two months out of the year where nitrate sources are greater than nitrate sinks. During December 2015 and March 2016, the nitrate sources outweigh the nitrate sinks with 3.1 Kmol nitrate/month and 9.6 Kmol nitrate/month respectively. Balancing the sources and sinks for nitrate for the entire sampling year, the system has a sum of -163.14 Kmol/year in loss of nitrate from the system (Table 11). This result of greater nitrate sinks compared to nitrate sources indicates the system may utilize and/or export nitrate at a faster rate than nitrate is entering the system, therefore, a “nitrate losing” system. This system is dominated by flow for both sources and sinks of nitrate throughout the year, while benthic flux, groundwater inputs and *Ulva* uptakes contribute to far less as sources and sinks to the system. This fast flow rate and high level of nitrate removal from the system for the majority of the year indicates that this site is highly flushed.

North Azevedo was another site where flow measurements accounted for the major source of nitrate. Flow into North Azevedo Pond from the upper channels of the Elkhorn Slough (Kirby Park region) accounted for 93%-100% of the system's overall nitrate concentrations (Fig. 22). From July 2015 – January 2016, flow incorporated the most nitrate into the system (Fig. 22). The largest input of nitrate due to flow was during January 2015 with 66.52 Kmols/month. Benthic flux, flow and *Ulva* uptake all contributed to the total nitrate sink at North Azevedo. During March and April 2015, benthic flux contributed to the vast majority of nitrate sinks with 66.93 Kmols nitrate removal/month. This indicates a large utilization of nitrate by benthic sediments most likely by denitrifying bacteria, in anaerobic sediments, transforming nitrate into dinitrogen gases. Dissimilatory nitrate reduction, another anaerobic process, can transform nitrate into ammonium by heterotrophic bacteria, and then the reductants can flux from the sediments into the surface water (Caffrey *et al.*, 2002).

Flow was also a major sink of nitrate to North Azevedo during February 2016 with 67.6 Kmol/month. High flow rates during the rainy season at times allow for flushing of the system, which can act as a sink to the total nitrate concentrations within the system. From May – October, all three sinks (flow, *Ulva* uptake and benthic flux) remained relatively equal to one another. For the entirety of the sampling year, the nitrate sources were far less than the nitrate sinks in this system with a sum of -321.06

Kmol/year (Table 12). On a monthly scale, ~ 27 Kmole of nitrate to the system is not accounted for, which may be a single source, or multiple other sources attributing for this imbalance.

While flow dominated the nitrate source for Moro Cojo Slough and North Azevedo Pond, Estrada Marsh and East Bennett Slough nitrate sources peaked primarily due to groundwater input. Estrada Marsh nitrate input via groundwater peaked from August 2015-November 2015 with a maximum loading of 54.84 Kmole/month during November 2015 (Fig. 24). Overall, groundwater was the primary driver for nitrate loading in Estrada Marsh (Table 10). Furthermore, Estrada Marsh experienced the highest amount of organic matter comprising the surface sediments as seen in LOI measurements during the fall and summer of 2015 (Fig. 17a.) indicating organic matter decomposition may yield high nitrate concentrations via a series of reactions (ammonification → nitrification → nitrite oxidation to nitrate). According to previous research by Hanisak (1993), nitrogen release from decomposing *Ulva* can reach a maximum of $6.37 \pm 2.59 \text{ g N m}^{-2}\text{d}^{-1}$ under certain conditions (Hanisak, 1993). High levels of nitrate flux from the groundwater measurements is expected due to large LOI measurements, coupled with previous data indicating high nitrogen release from decomposing *Ulva* (Hanisak, 1993). East Bennett nitrate sources were also dominated by groundwater fluxes, comprising 73.9% - 98.9% of nitrate sources to the system during these high flux periods. The largest of these groundwater fluxes were during December 2015 and January 2016 with 72.6 Kmole/month input (Fig.25). Nitrate sinks in both of these systems were driven by *Ulva* uptake. Estrada Marsh nitrate sinks were vastly dominated by *Ulva* uptake from March 2015 – August 2015 with a peak nitrate removal rate of 30.15 Kmole/month (Fig. 26). East Bennett nitrate sinks peaked from October 2015 – January 2016 with January having the largest nitrate removal via *Ulva* uptake of 7.0 Kmole/month (Fig.27). While both East Bennett Slough and Estrada Marsh exhibited similar trends in the type of sources and sinks that dominated the system, the degree in which sources and sinks played roles in nutrient input and removal on a yearly timescale differed greatly. After summing the nitrate sources and sinks for East Bennett Slough, the yearly balance is – 347.22 Kmole (Table 14). This large negative balance indicates highly efficient nitrate removal from the system. Given that *Ulva* uptake is the major sink for nitrate in East Bennett Slough, the

degree to which *Ulva* is able to uptake and remove nitrate from the water is highly effective and drives the system to be nitrate-losing. As for Estrada Marsh, the nitrate balance is 49.15 Kmols (Table 13), resulting in higher sources than sinks. This could be in part due to the higher groundwater flux in the system that contributes to a greater amount of nitrate than the major sink (*Ulva*) is able to remove nitrate from the system.

It is understood through this box model that there is a constant flow of nitrate into the system by looking at the flow inputs, yet the utilization and flow of nutrients out of the system accounts for a net decrease in nutrients each month for many of the sites. The data suggests that outside processes such as agricultural practices dominate the variability in nutrient fluctuations into the systems because of the rapidly fluctuating surface water nutrient concentrations and the natural tidal influence is not the single driving force. On a broader timescale, this nitrate imbalance may level out, however an overarching theme of dynamic disequilibrium at these sites suggests that a steady state model may not characterize the systems accurately for nitrate. In addition, the disequilibrium can be attributed to a missing link of nitrate sources to the system. Without all nitrate sources accounted for, the box model approach illustrates Moro Cojo as a “nitrate losing” system. Possible sources of nitrate include water column processes such as nitrification, ammonium oxidation by aerobic nitrifying bacteria, transforming ammonium into nitrate in the presence of aerobic conditions, and surface water runoff (tile drains, etc.) from adjacent fields. Further investigation may be useful in determining possible nitrate sources that may not have been accounted for in this study.

Ammonium

Ammonium sources in the Moro Cojo Slough were primarily through surface water flow into the system. Flow peaked in February with 290 Kmols ammonium/month input into the system (Fig. 28). During the dry season (summer and fall), flow accounted for 3- 8.8 Kmols/month of ammonium input. Overall, flow ranged from 55.13% - 92.8% of the total ammonium source to the system during the sampling year. Groundwater flux was the primary source during the winter months of January 2016 – March 2016 with a peak of 17.15 Kmols ammonium/month. Ammonium sinks at Moro Cojo Slough consisted primarily of flow removal. Flow peaked in February 2016 with a flow removing 292.11

Kmol ammonium/month (Fig. 29). The wet season flow rates acted as the largest flow for the system overall (Fig. 29). *Ulva* uptake contributed slightly to ammonium removal during August 2015 – October 2015, but only comprised up to 59% of total ammonium sinks within the system during that short time. Benthic Flux acted as an ammonium sink during the winter months, contributing up to 52.5% of ammonium removal during December 2015. This may be in part due to ammonium oxidation or nitrification during aerobic conditions, which are found mostly in winter months. Summing the monthly ammonium totals, the Moro Cojo slough accounts for -16.84 Kmol ammonium per year. This indicates a net removal of ammonium over the sampling year. Systemic flow accounts for the majority of this ammonium sink, and characterizes this system as an ammonium sink for the Moro Cojo region. Tidal exchange and residence time within a system controls the processing of organic matter in sediments (Caffrey *et al.*, 2002). Moro Cojo Slough is the most highly flushed of the four sites, which allows for ammonium to be physically removed from the system without the long residence time needed for accumulation and saturation of ammonium in the sediment layers.

Ammonium sources in North Azevedo Pond were variable throughout the year with multiple sources contributing to overall ammonium concentrations (Fig.30). Benthic flux measurements as well as groundwater flux measurements accounted for the largest sources of ammonium to the system. Benthic flux reached a high of 37 Kmol ammonium/month in April and May 2015, and peaked again from September 2015- November 2015 with 36.3 Kmol ammonium/month, and rose again in March 2016 with 37 Kmol ammonium/month. From September 2015 – November 2015 there were relatively higher groundwater fluxes that mirrored the benthic flux measurements, indicating high porewater concentrations. Another large peak in groundwater was measured in January and February 2016 with 71.9 Kmol ammonium/month. This flux is measured during high rain events, which may cause this influx of groundwater to the system. Flow contributed to overall ammonium flux primarily during the late summer through winter months with the largest peak during the January rainy season. Benthic flux and groundwater fluxes peaking in late fall and then again in winter indicates the presence of algal decomposition in sediments (which is reflected in the high porewater concentrations at this time) as well as an increase in groundwater input during the wet

season. The ammonium sinks in North Azevedo Pond were driven by *Ulva* uptake and flow with alternating seasonality. *Ulva* uptake was the primary sink of ammonium from April 2015 until November 2015 with a peak during November 2015 (Fig. 31). As *Ulva* uptake decreased from the fall into winter, flow started to increase as a major ammonium sink. Flow accounted for 23.8 Kmol ammonium/month removal during February 2016 at its highest rate of ammonium removal (Fig. 31). As a sink, flow accounted for 2.5 – 100% of removal of ammonium throughout the sampling period. By compiling the ammonium budget throughout the sampling year, North Azevedo Pond totaled 397.57 Kmol of ammonium (Table 12), which suggests North Azevedo Pond is an ammonium source in the Elkhorn Slough. Estrada Marsh and North Azevedo Pond are ammonium saturated regions, following similar biogeochemical processes. High levels of algal biomass have been shown here to be followed by high levels of ammonium in the system which indicates algal decomposition within the sediment layers. This tradeoff between prime algal growth periods during the warmer seasons with a longer photoperiod and periods of high algal decomposition during the colder season with shorter photoperiods is a trend that is indicative of these shallow, highly eutrophic systems

Similar to inputs of nitrate, inputs of ammonium between East Bennett Slough and Estrada Marsh were mostly impacted by groundwater discharge. East Bennett Slough had very high groundwater ammonium inputs from August 2015-November 2015 accounting for a peak input of 175.4 Kmol/month during November 2015 (Fig. 32). Similarly, during August 2015 – October 2015 there was a large increase in benthic flux measurements of 75.4 Kmol/month. This simultaneous increase in groundwater ammonium flux as well as benthic flux is driven by high porewater concentrations, suggestive of ammonification via microbial transformation of organic amines in the soils. Additionally, a simultaneous increase in ammonium via groundwater and benthic flux suggests that porewater may be seeping from sediments via diffusional flux of these shallow water systems, rather than solely from groundwater discharge at the perimeter of shoreline. The extremely high diffusive flux rates during the fall season at East Bennett Slough ($590.5 \mu\text{mol}/\text{m}^2/\text{day}$), suggests that the increase in benthic flux and groundwater flux during this time is driven by this large nutrient concentration in sediments. Ammonium loading from sediments is a very common phenomenon due to the

biogeochemical conditions that are present in sediments during organic matter decay. When organic matter (the most dominant form is *Ulva*) dies and sinks to the sediments in these systems there is little, if any, transport of the decaying algal thallus out of the system via tidal flushing. Without removal, the organic material starts to decompose and release ammonium back into the surface water. Ammonium sinks in East Bennett Slough were driven throughout the sampling season by *Ulva* uptake (Fig. 33). April 2015 – September 2015 yielded the largest ammonium removal via *Ulva* uptake, peaking during May 2015 with 239.3 Kmols /month removed from the system. *Ulva* uptake averaged 86.2% of the total sink in East Bennett Slough throughout the sampling year, which was the highest of all four sites. Flow accounted for up to 55% of ammonium sink in East Bennett Slough, but typically was around 0.5-3% of the monthly total. Benthic flux did not act as a sink for this site, and only contributed to the overall ammonium concentrations. The ammonium balance for the year sums to 155.75 Kmols/year (Table 14), which indicates that the system's ammonium input outweighs the removal processes to yield a system that is ammonium saturated. This is made possible by conversion of nitrate to ammonium in this system. High ammonium saturation in a system may indicate a high level of microbial productivity due to ammonium release during decomposition of organic material.

Estrada Marsh ammonium sources were similarly driven by groundwater flux. August 2015 – February 2016 yielded the highest ammonium groundwater fluxes with maximum input values of 256.0 Kmols ammonium/month (Fig. 34). Groundwater ranged from 70.9%-99.3% of the total ammonium sources at Estrada Marsh. There were elevated ammonium benthic flux measurements from November 2015-January 2016. This directly coincided with a high level of diffusive flux measurements at 646.2 $\mu\text{mol}/\text{m}^2/\text{day}$ during the winter months, influencing such large fluxes from the benthos. Ammonium sinks in Estrada Marsh were driven by *Ulva* uptake, and nearly mirror the trends seen at East Bennett Slough (Fig. 35). *Ulva* ammonium uptake peaked in April 2015 – September 2015, accounting for 90%-99% of total ammonium sink during that time. The highest rate of uptake was during August 2015 with 100.47 Kmols ammonium/month. This uptake trend exhibits a seasonal pattern with light availability as well as nutrient abundance available for *Ulva* to build biomass while in turn removing ammonium from the aquatic

system. Totalling the monthly ammonium budget in the box model, Estrada Marsh exhibits the largest positive value of all four sites with 851.65 Kmol for the sampling year. This extremely high value identifies Estrada Marsh as a large ammonium source for nearby regions of the Elkhorn Slough. Looking into the physical characteristics of Estrada Marsh, this high level of ammonium production becomes an obvious, defining characteristic. Estrada Marsh is shallowest of all four sites, with an average depth of 0.25 meters. The flow is extremely low in and out of the site that was never measured to exceed $3283 \text{ m}^3\text{h}^{-1}$. In shallow, slow moving slough systems, photosynthesis becomes prevalent with abundance of sunshine throughout the water column. With high levels of photosynthesis and low levels of tidal flushing, ammonium is able to accumulate in the system via organic matter decomposition. Previous work has proven that as organic matter production increases in the water column or as water depth decreases, decomposition in sediments increases (Kemp *et al.*, 1992, Jorgensen 1996a.) Also, if the system becomes anoxic due to microbial decay, any nitrate that is present in the system can be transformed into ammonium via dissimilatory nitrate reduction, which can act as another source for ammonium production in this system (Tiedje, 1988). This may also be contributing to formation of nitrate losing systems. These findings also suggest that investigating the different forms of nitrogen may be important for overall nutrient loading and not just investigating nutrient concentrations.

Phosphate

According to previous research, sediments found in estuarine environments can act as a source or sink for phosphorous to overlying water. These fluxes are determined based on varying biogeochemical parameters (Pant & Reddy, 2000). Phosphate sources were driven in the box model primarily by groundwater flux and benthic flux for East Bennett Slough, Estrada Marsh and North Azevedo Pond, while surface water flow appeared to dominate the flux in the Moro Cojo Slough.

Moro Cojo Slough phosphate sources were driven primarily by flow. Flow inputs peaked during the summer months (July and August 2015) with a high of 58.9 Kmol/month, and again in February 2016 with a peak of 130.2 Kmol/month (Fig. 36). Flow accounted for close to 99% of all phosphate input during the entirety of the

sampling season. This suggests that there are major phosphate sources outside of the system than contribute to the phosphate concentrations more than sources within the system. Groundwater, benthic flux and atmospheric input measurements only contributed to a maximum of 23.9 %, 9.9% and 0.16% respectively. Seasonally, the largest phosphate sinks occurred during the early summer (June and July 2015) and then again in the winter (January and February 2016). Comparing the phosphate peak months of sources and sinks illustrates the same months with the highest peaks for both. Since this system is driven by flow rather than a biogeochemical process such as microbial decay within the sediments or *Ulva* uptake, during the same month the site experiences the highest input as well as export of phosphate. This physical trait of Moro Cojo Slough is crucial in determining how phosphate is driven through sources and sinks via flow. The yearly phosphate budget sums to -18.41 Kmols indicating that Moro Cojo acts as a phosphate sink for the system (Table 11). With flow acting as the primary source and sink to the system, it is understood that flow through the system allows for phosphate to exit the system at a faster rate than it enters.

North Azevedo Pond is the most variable of all four sites when characterizing phosphate sources and sinks. Groundwater, benthic flux and flow all contribute to the overall flux of phosphate into the system. Benthic flux and flow increase from zero input in the winter months to 1.73 Kmol/month from June – August 2015 accounting for up to 77% of total phosphate; while benthic flux peaks in the fall (September – November 2015) with 6.66 Kmol/month of phosphate input (Fig. 38). Source from flow also peaked during the fall with a high of 3.26 Kmol during November 2015. Groundwater input peaked during January-February 2016 with 7.12 Kmols/month (Fig. 38). The overall wide breadth of phosphate sources illustrates a dynamic system with multiple driving sources. The phosphate sinks were also very variable with flow, *Ulva* uptake and benthic flux as all major sinks throughout the sampling year (Fig. 39). During the winter months, benthic flux, *Ulva* uptake and flow all contributed significantly (65.6%, 20% and 79.9% respectively). High benthic flux and groundwater flux alludes to high porewater nutrient concentrations allowing for simultaneously high fluxes. The summer and fall months were dominated by flow and *Ulva* uptake, which is expected due to increase in flow from inland irrigation practices and more sunlight promoting photosynthetic. Flow and *Ulva*

uptake remained large sinks in the system throughout the fall, until *Ulva* uptake dropped in the winter months, accounting for only 0%-1% of the system's phosphate sink. As *Ulva* uptake dropped during the winter, benthic flux increased to account for up to 65% of total phosphate sinks. This mechanistic shift in phosphate sink drivers in the system may be linked to less *Ulva* in the system and consequentially less uptake, and also decaying *Ulva* via bacterial decay in the sediments that act as a sink in the system. Expanding the phosphate budget to the yearly scale, North Azevedo pond phosphate fluxes result in 25.63 Kmols. This is a large source of phosphate for the surrounding region and characterizes North Azevedo Pond as a source of phosphate to the larger slough system.

Phosphate peaked in East Bennett Slough primarily through groundwater flux throughout the year. The highest fluxes were measured from September – December 2015 with a high of 5.28 Kmol/month, and an even greater flux during the month of March 2016 with 7.99 Kmol/month (Fig. 40). Groundwater flux accounted for up to 97% of total phosphate sources to East Bennett Slough. High groundwater flux was coupled with elevated benthic flux measurements from September-November 2015. This trend was also seen with nitrate and ammonium measurements at times, which indicates a high level of porewater nutrient concentrations contributing to the flux measurements from the sediments. Elevated benthic flux and groundwater phosphate sources is expected due to the ecological pathways in which phosphate cycles in estuarine systems. Phosphate is transformed between the sediments into the water column and into plant matter before returning back to the sediments. The large inputs of phosphate measured from the benthos in the case of this box model, follows the natural pathway of phosphate cycling. Phosphate sinks in East Bennett Slough were driven by *Ulva* uptake (Fig. 41). *Ulva* uptake was highest in the spring of 2015 with the month of March accounting for phosphate removal via *Ulva* at 11.93 Kmol/month. Flow and benthic flux were very minor sinks in this system. East Bennett Slough exhibited a seasonal tradeoff between source and sink dominance within the system. From April 2015 – September 2015 (with an exception of June 2015), the sinks were greater than the sources in East Bennett Slough. From October 2015 through March 2016, sources outweighed the sinks in the system. These results suggest that during the spring and summer months the system has

an elevated ability to utilize and export the nutrients that are input into the system, while during the fall and winter, the system could not uptake and remove the nutrients at the same rate of nutrient input. Compiling the phosphate data over the entire sampling year, the system sums to 9.18 Kmol phosphate (Table 14), indicating that East Bennett Slough acts as a phosphate source for the surrounding regions of the Elkhorn Slough (North Harbor and the slough mouth).

Estrada Marsh phosphate sources were also dominated by groundwater flux and benthic flux. The highest groundwater flux measurements were during December 2015 – February 2016, with a peak input of 13.6 Kmol/month. September 2015 – November 2015 also had elevated groundwater fluxes of 5.8 Kmol/month (Fig. 42). During the large flux from December 2015 – February 2016 there was also a peak in benthic flux measurements. This same trend as East Bennett Slough indicates the high degree in which porewater nutrient concentration may influence these flux measurements (Fig. 42). Flow and atmospheric inputs were far smaller than the inputs by groundwater and benthic flux in this system. There is a seasonality of increasing groundwater and benthic flux inputs from fall into winter with the largest fluxes during the wet season starting in December. The major phosphate sink throughout the year in Estrada Marsh is *Ulva* uptake (Fig. 43). Estrada Marsh exhibited similar trends to East Bennett Slough in *Ulva* uptake ability. *Ulva* uptake peaked from April 2015 – July 2015 accounting for up to 97.1% of the total phosphate sinks in the system. Flow and benthic flux also acted as sinks for phosphate, peaking from May 2015 – August 2015. Benthic flux accounted for up to 14.3% of the phosphate sinks during this time, while flow accounted for 21% of the sinks at this time. Comparing the yearly system drivers in terms of total sources and sinks, Estrada Marsh has highest source inputs that outweigh sinks during the winter months (December 2015- February 2016), while sinks outweigh sources in the spring (May 2015) and summer (July – August 2016). This implies a seasonal trend in which part of the year the system utilizes and removes nutrients efficiently, whereas another part of the year the system is heavily inundated with nutrients and is unable to remove them to the degree in which they enter the system. For the entirety of the sampling year, Estrada Marsh has a net phosphate balance of 65.47 Kmol, indicating Estrada Marsh as a phosphate source in the Elkhorn Slough (Table 13).

Seasonal Nutrient Loading

The climate in the Monterey Bay is characterized as Mediterranean with warmer, dry summers and cool, wet winters (Caffrey *et al.*, 2014). Using the rain data provided by the Moss Landing Marine Laboratory Weather Station, there is a distinct wet season (November– April) and dry season (May– October) for the sampling period during this project. Variability in nutrient loading between the two seasons can be estimated using the box model approach by summing the sources within these seasonal time periods. These source values are shown in tables 11-14 for each site and each nutrient. *For each site and each nutrient, wet season nutrient loading was greater than dry season nutrient loading* (Figures 44-47). There was a significant difference in ammonium loading between the wet and dry seasons when performing a t-test at both Estrada Marsh ($p=0.032$) and North Azevedo Pond ($p=0.026$), and also for phosphate at Estrada Marsh (0.024) (Table 15). This piece of the puzzle is interesting in that the “dynamic disequilibrium” that was mentioned earlier can be “smoothed” with an overarching trend in the total loading of nutrients between the two seasons. Although nutrients are extremely dynamic in regions near human impact (Fong and Kennison, 2010; Castro *et al.*, 2007; Carlier *et al.*, 2008), the seasonality in which nutrient loading occurs is shown to follow a wet/dry cycle with greater loading in the wet season.

The DIN levels at each site yielded higher surface water values during the dry season compared to the wet season (Fig.7). Similar nutrient trends were seen when data from the Land/Ocean Biogeochemical Observation buoy in Elkhorn Slough main channel is compared with the DIN data collected in this study, but much higher DIN values occurred during the dry season in tidally restricted sites compared to nitrates in the main channel (Fig. 48 a,b). Taking into consideration the location of the study sites, surrounding land is heavily irrigated during the dry months. Furthermore, high DIN concentrations in surface waters correspond to high porewater nutrient concentrations and low groundwater discharge during the dry months. This high groundwater DIN input driven by high porewater nutrient concentrations during the dry season is also seen for

ammonium and phosphate, and is demonstrated over multiple sites. This suggests a flux of nutrients that is not precipitation (i.e. irrigation).

Similarly, *Ulva* biomass peaks during the dry season as well. *Ulva* is able to grow with the excessive nutrients during the dry season and the ample light. The timing of these *Ulva* blooms indicates *Ulva* as a response variable to nutrient fluxes in these systems. *Ulva* blooms are considered a dominant trait in these systems and has recently been shown to decrease marsh stability by increasing erosional rates (Wasson *et al.*, 2017). In a chain of events, nutrients influence *Ulva* blooms, which in turn increases marshland erosion, making nutrient effects extremely critical for marsh health and functionality.

This box model approach was intended to identify the major sources and sinks within the tidally restricted study sites. Identifying the trends of nutrient input, utilization and export are important in understanding changes in nutrient concentrations of these physically modified regions of the slough that are impacted by the surrounding environment. The state of each system, whether in excess or deficit of nutrients, changed throughout the year, indicating variability in the biogeochemical cycling of nutrients under dynamic conditions. The wet season nutrient sources were dominated by surface water flow, whereas the dry season was dominated by groundwater flux. The wet season nutrient sinks were dominated by surface water flow, whereas the dry season was dominated by *Ulva* uptake. There are restrictions to the box model in that there are more sources and sinks in each system than were quantified, and would require further research into these parameters. Also, the time scale in which this box model was utilized was restricted to one month. Understanding sources and sinks on a diel time scale may inform daily fluxes that are much more variable than on the monthly time scale.

Conclusion

The box model approach was useful in quantifying nutrient loads and identifying dominant sources and sinks that contributed to overall nutrient concentrations at each site over time. This is very useful in management plans in order to create total maximum daily load (TMDL) reports and identify target source areas to mitigate. Measuring nutrient concentrations using grab samples and Osmosamples is useful in tracking nutrient changes over time but concentrations alone provide little information about the total nutrients a system may receive. Measuring seasonal nutrient loading via the summing of sources provides information about the total nutrients entering and leaving the system at different times of the year. Each system was characterized according to sources, sinks, and total yearly nutrient budget. While each system varied in regards to the dominant nutrient sources and sinks, the systems were unanimously in a state of dynamic disequilibrium, rather than steady-state. While disequilibrium was a common trend on the monthly time scale for nutrient fluxes, nutrient loading showed clear trends between wet and dry seasons. During the dry season, sources were mainly driven by groundwater flux while sinks were dominated by *Ulva* uptake. During the wet season, sources and sinks were driven by surface water flow. On a larger scale, the source and sink ratio between wet and dry season indicates that sources dominate the nutrient fluxes during the wet season while sinks dominate the nutrient flux during the dry season. The seasonality of nutrient loading is integral when characterizing these systems, as it is indicative of the nature of nutrient flux in tidally restricted ecosystems. Previous work has shown similar trends of variable nutrient cycling and physical conditions between physically restricted estuaries in southern California as well (Kennison and Fong, 2014). According to a study by Caffrey *et al.* in 2002, the overarching character traits for nutrient concentrations in local estuarine environments is that they can differ greatly from nearby sites and from the average condition of the estuary.

The integration of biological, geological and chemical parameters influencing nutrient flux within tidally restricted regions of the Elkhorn Slough is proven necessary when characterizing these unique systems. The information discovered in this study is useful in the characterization of estuarine water bodies that have been physically constrained due to land use, transportation corridors, and tidal inundation restrictions

(hello global climate change!). The findings in this study can act as a representation of nutrient cycling occurring in other temperate estuarine environments worldwide.

It is critical to understand nutrient cycling and drivers of our coastal ecosystems worldwide in a time with increasing precipitation and rising seas (no this is not “fake news”). According to Sinha *et al* (2017), changes in precipitation patterns will greatly impact the nitrogen loading in the continental United States. These pattern shifts are shown to be compounded by an ever-increasing use of land, while these shifts may also contradict management practices that aim to reduce nitrogen loading (Sinha *et al.*, 2017). Understanding water quality parameters as well as the dynamics between the land-sea interface in tidally restricted regions of estuaries is imperative in the mitigation and management of our coastal estuarine ecosystems for now and most importantly, for the future.

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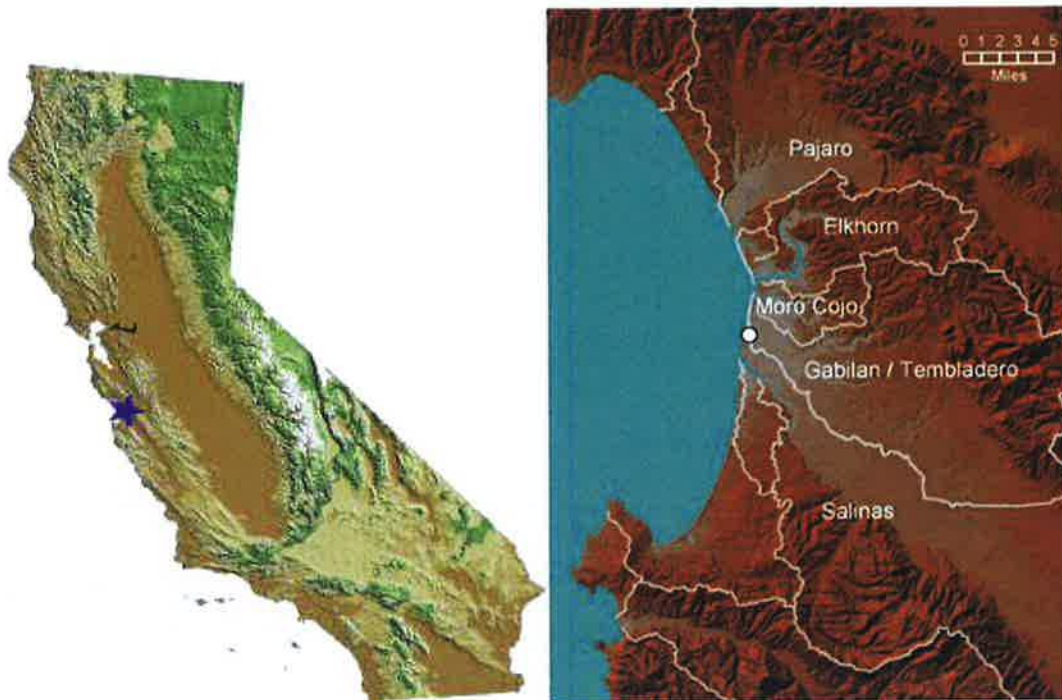


Figure 1. Elkhorn Slough in Relation to California Coastline (left); Elkhorn Slough Watershed (right).

ElkhornSlough.com

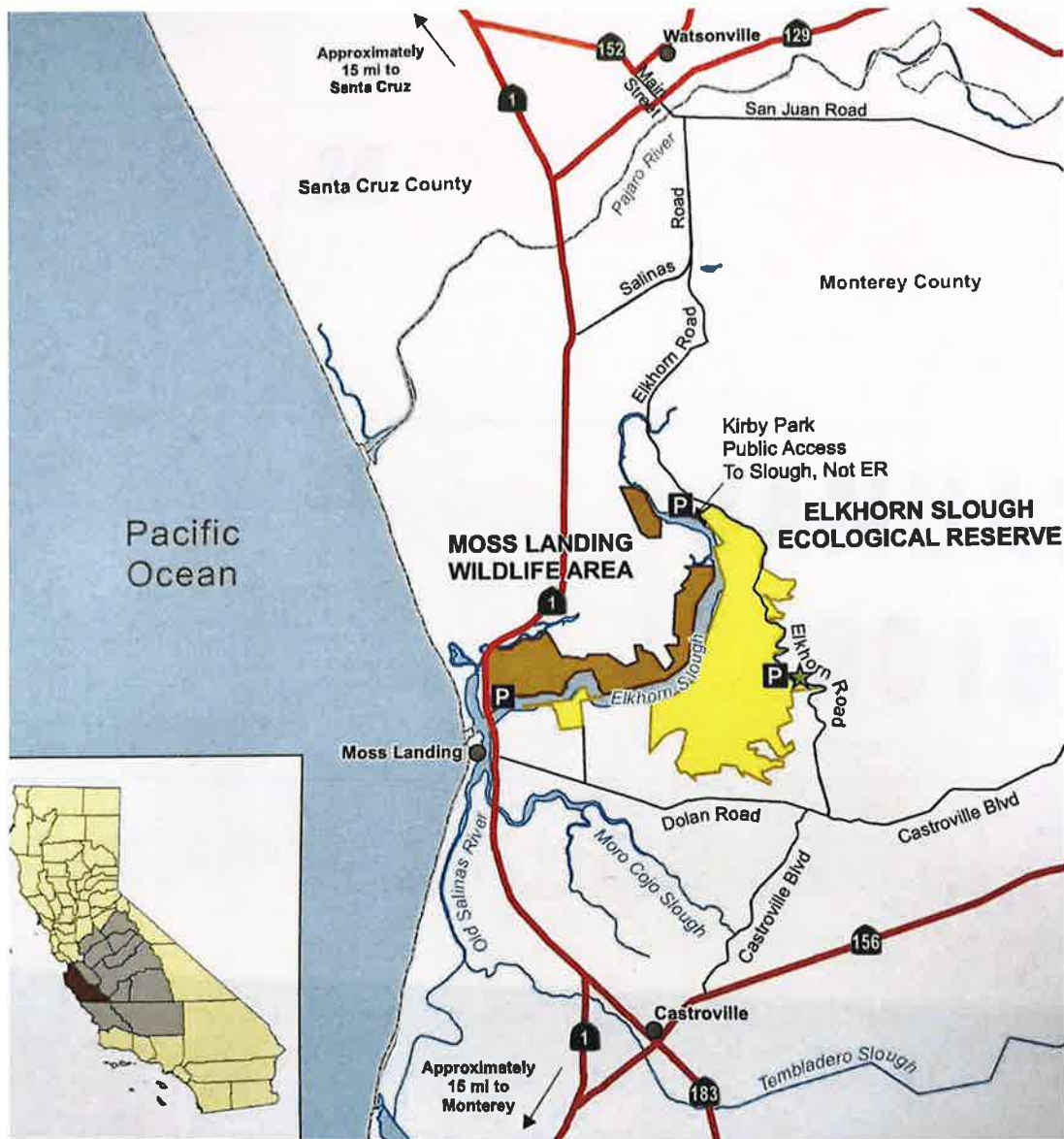


Figure 2: Site Map of the Elkhorn Slough Including Major Roads (Highway 1, Elkhorn Road) and Railways. Wildlife.ca.gov

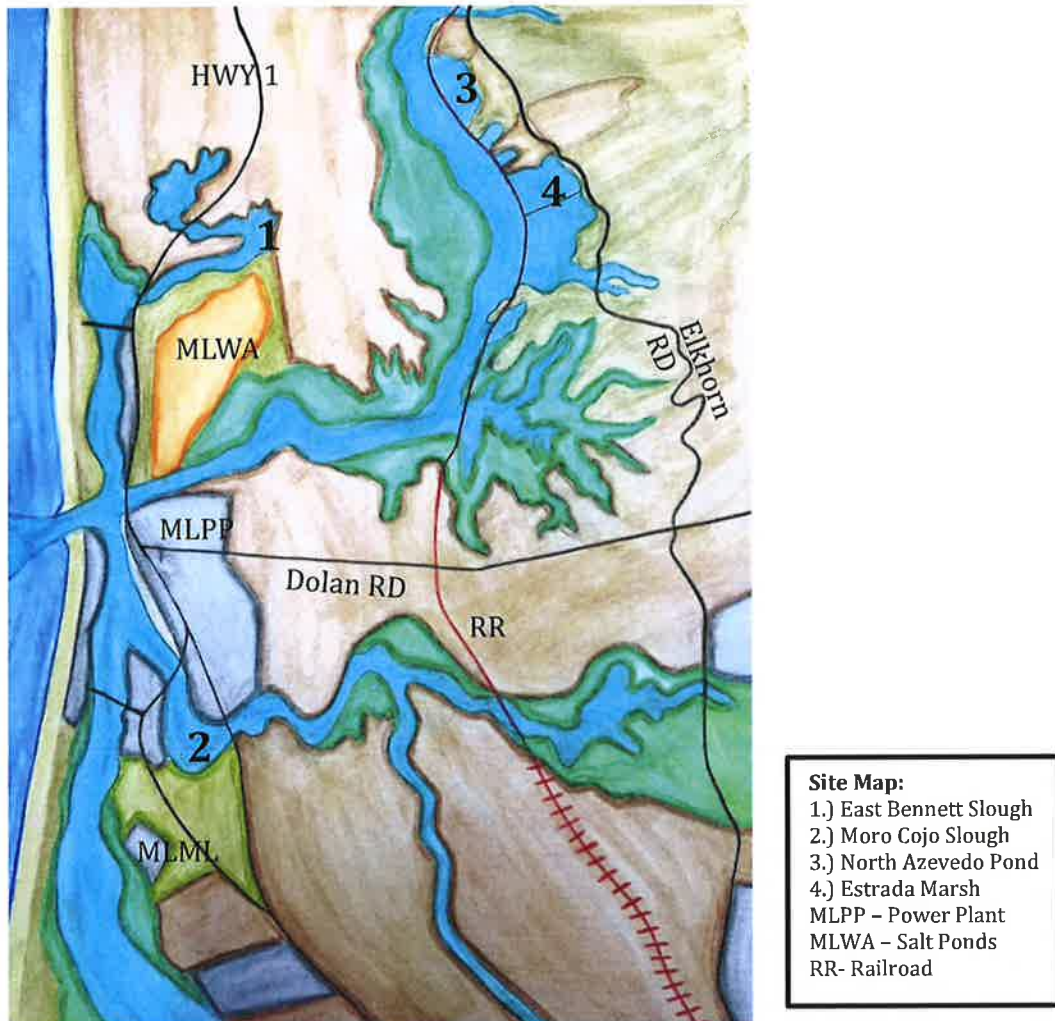


Figure 3: Site Map of East Bennett Slough, Moro Cojo Slough, North Azevedo Pond, and Estrada Marsh. Dimensions are Approximately 5 Km by 6 Km.
Image by Mo Wise

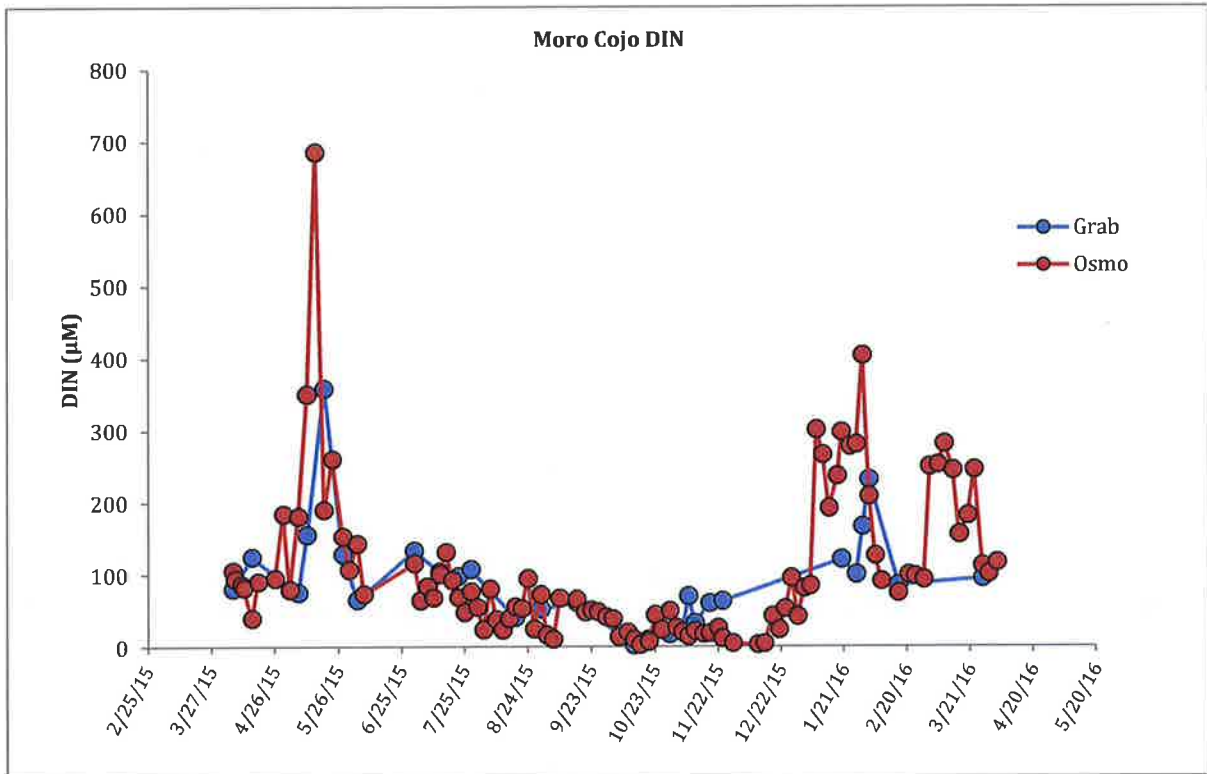


Figure 4. Moro Cojo Dissolved Inorganic Nitrogen (DIN) Levels Comparing Grab Samples with Osmosamples – Method Comparison.

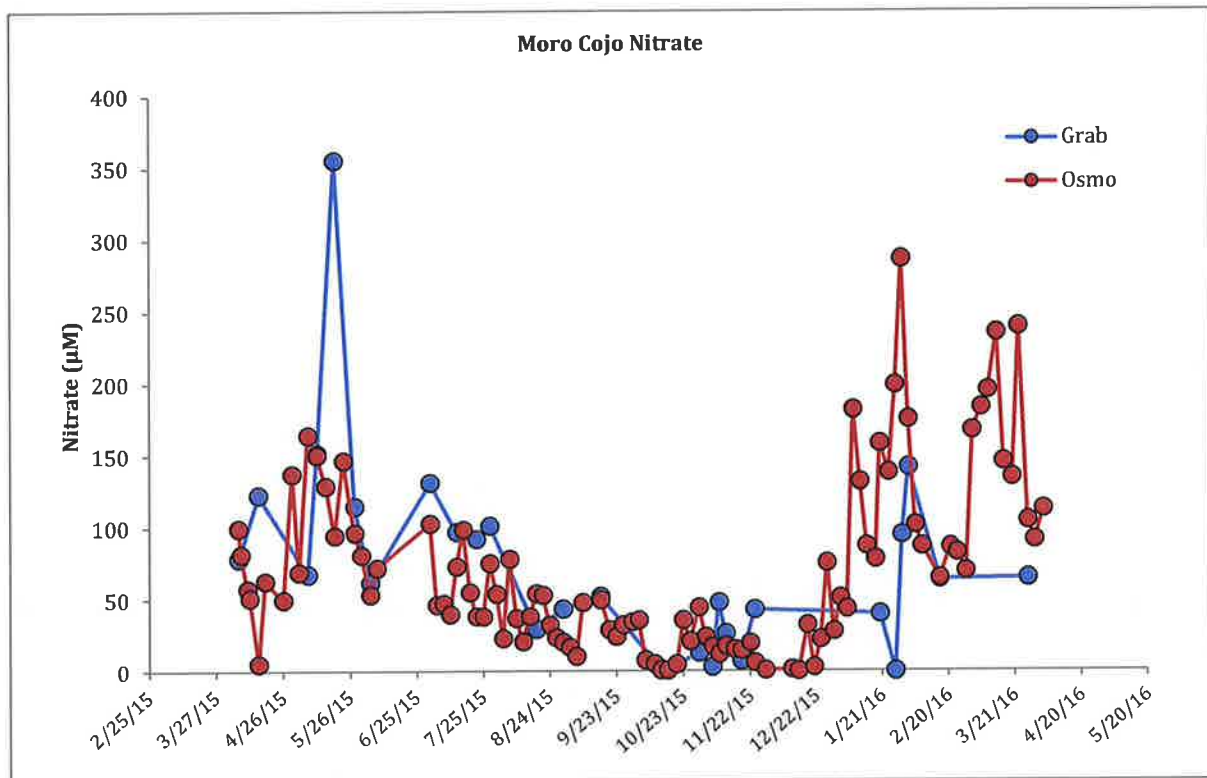


Figure 5. Moro Cojo Nitrate Levels Comparing Grab Samples with Osmosamples – Method Comparison

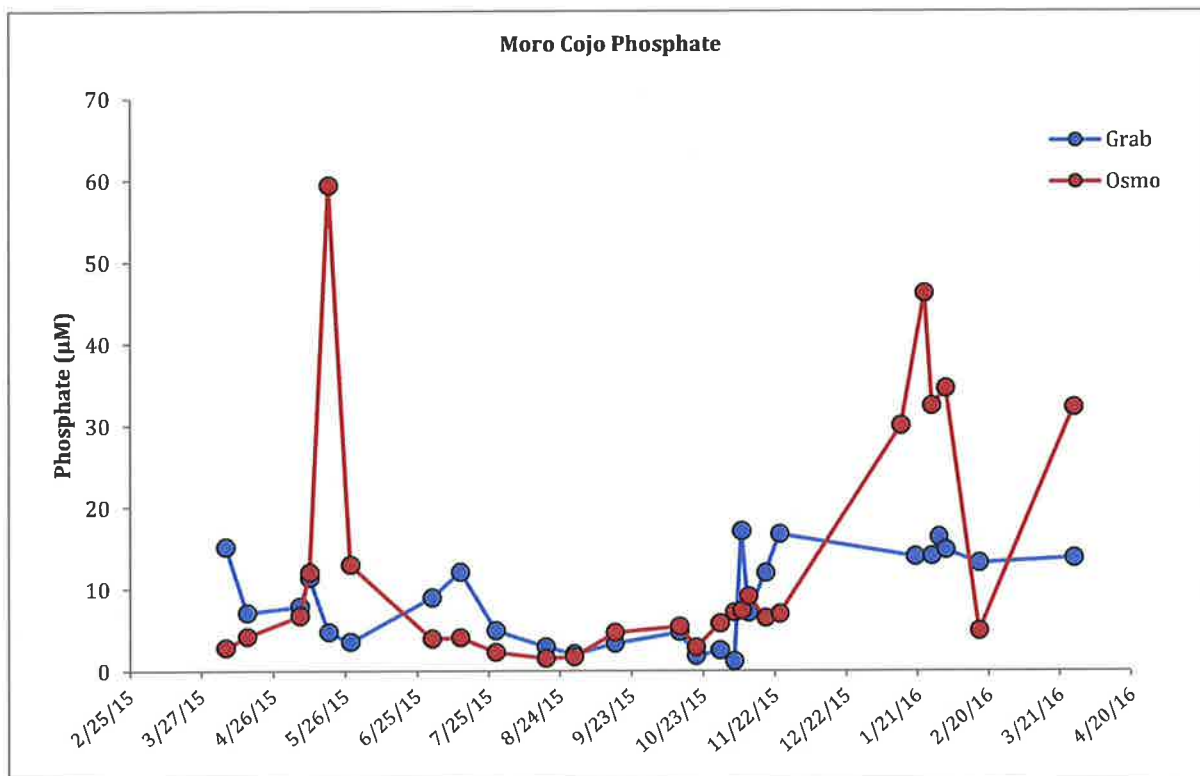


Fig. 6. Moro Cojo Phosphate Levels Comparing Grab Samples with Osmosamples – Method Comparison

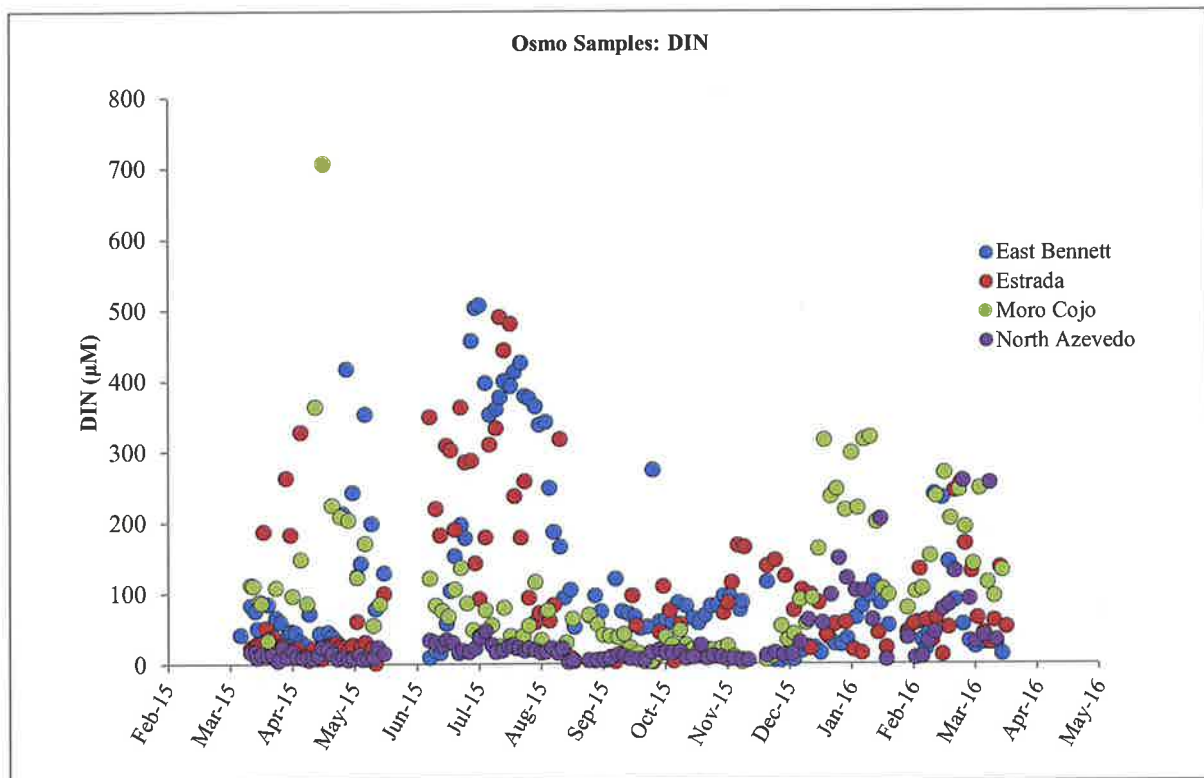


Figure 7. OsmoSampler Dissolved Inorganic Nitrogen (DIN) As a Function of Time. X-axis is Labeled by Month of 2015 and 2016. DIN is the sum of nitrate, nitrite and ammonium.

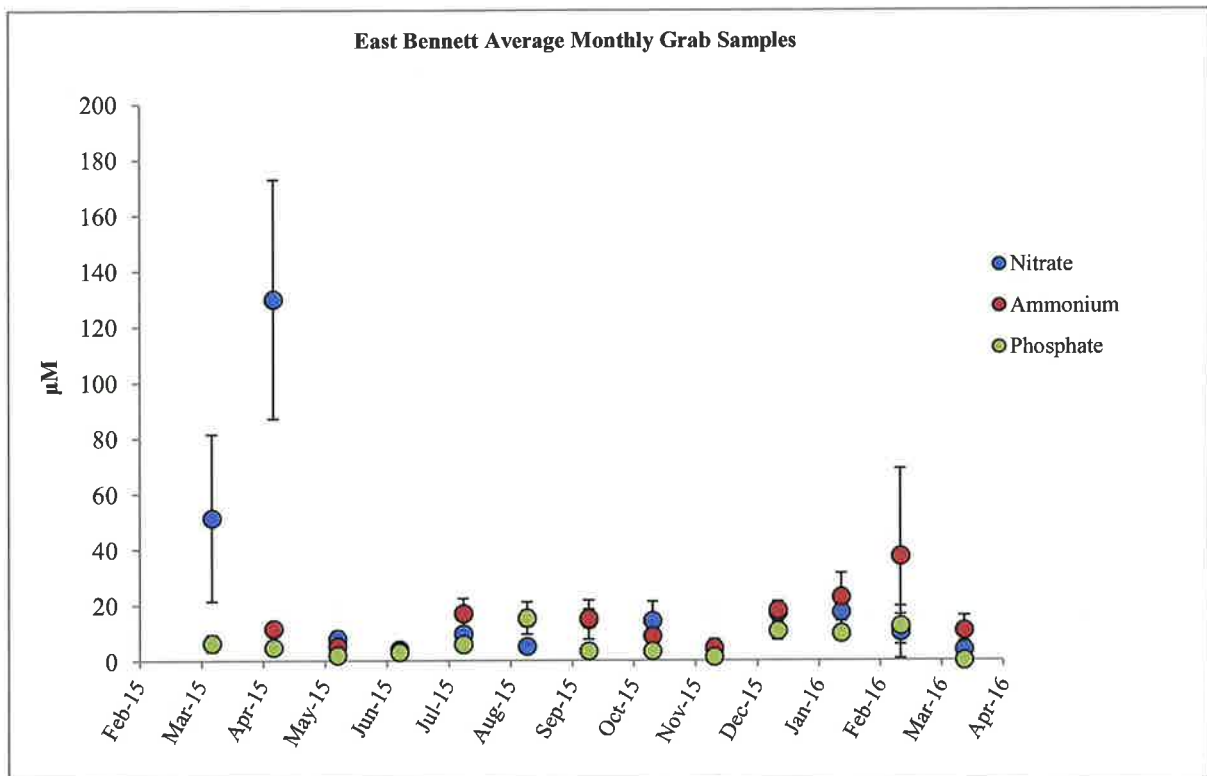


Figure 8. East Bennett Slough Averaged Monthly Grab Samples. X-axis is Labeled by Month of 2015 and 2016. Bars Represent Standard Error.

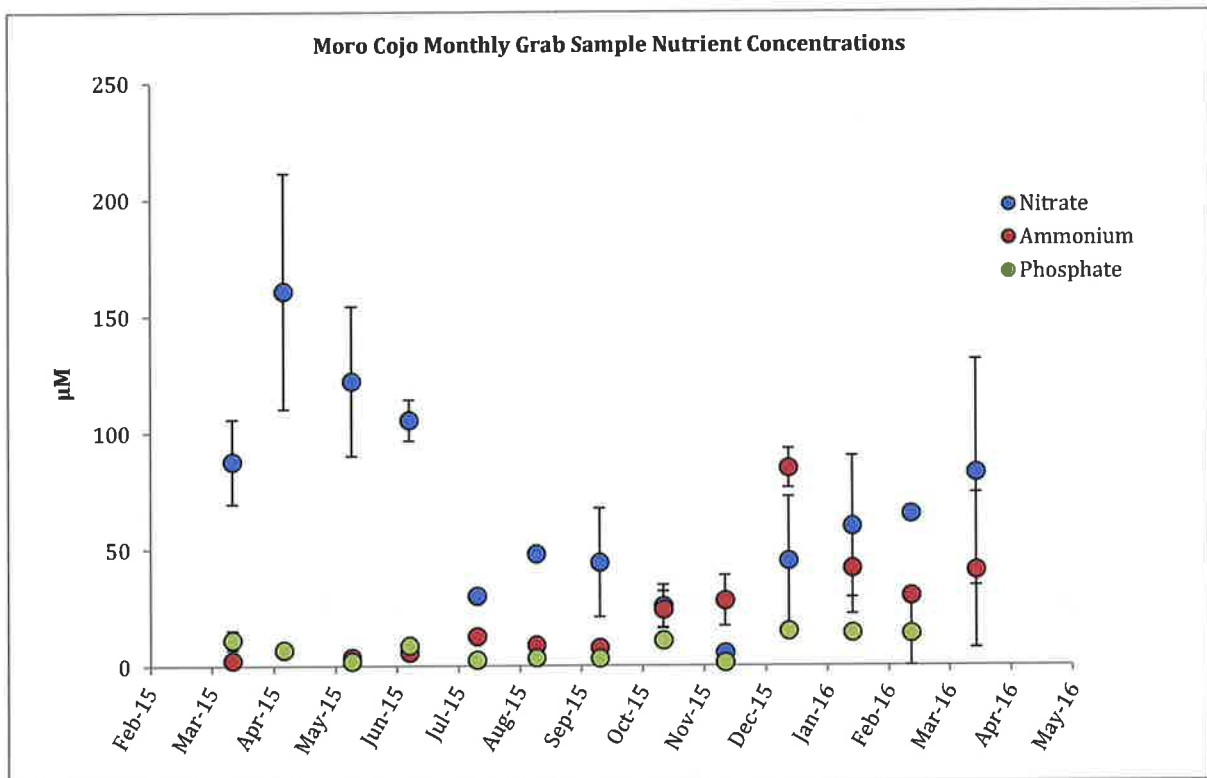


Figure 9. Moro Cojo Slough Averaged Monthly Grab Samples. X-axis is Labeled by Month of 2015 and 2016. Bars Shown Are Standard Error.

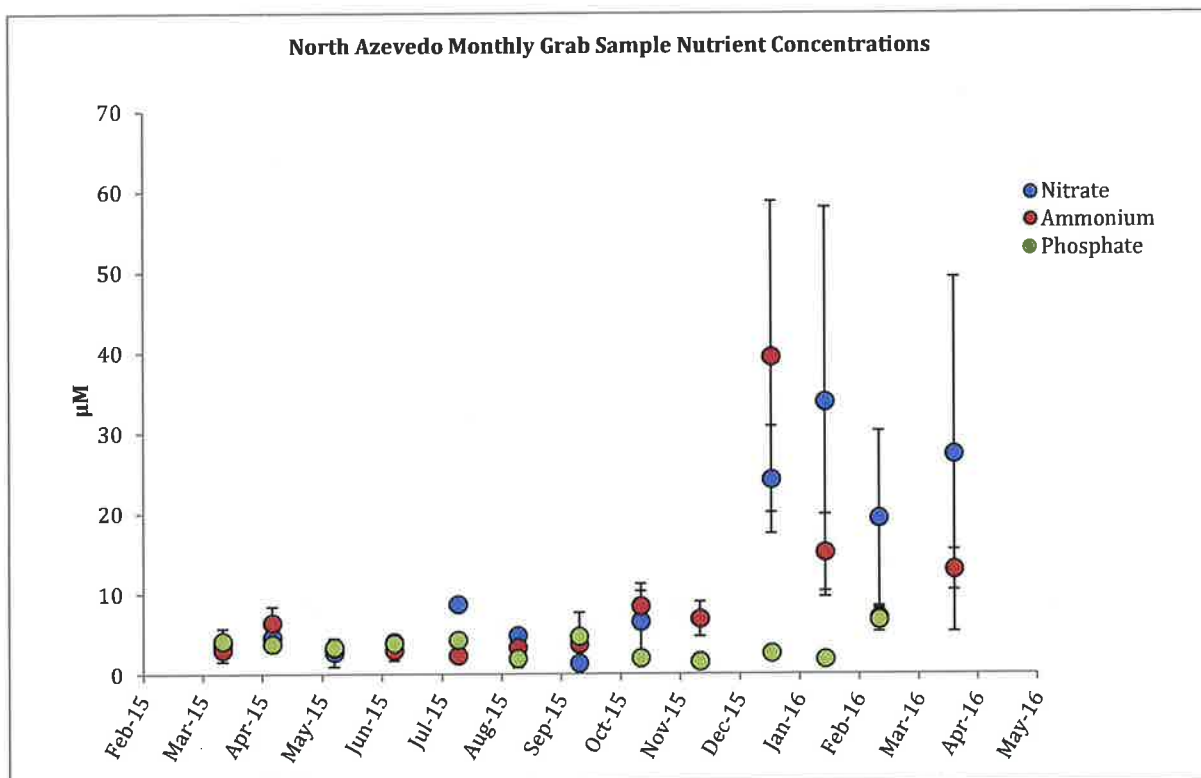


Figure 10. North Azevedo Pond Averaged Monthly Grab Samples. X-axis is Labeled by Month of 2015 and 2016. Bars Shown Are Standard Error.

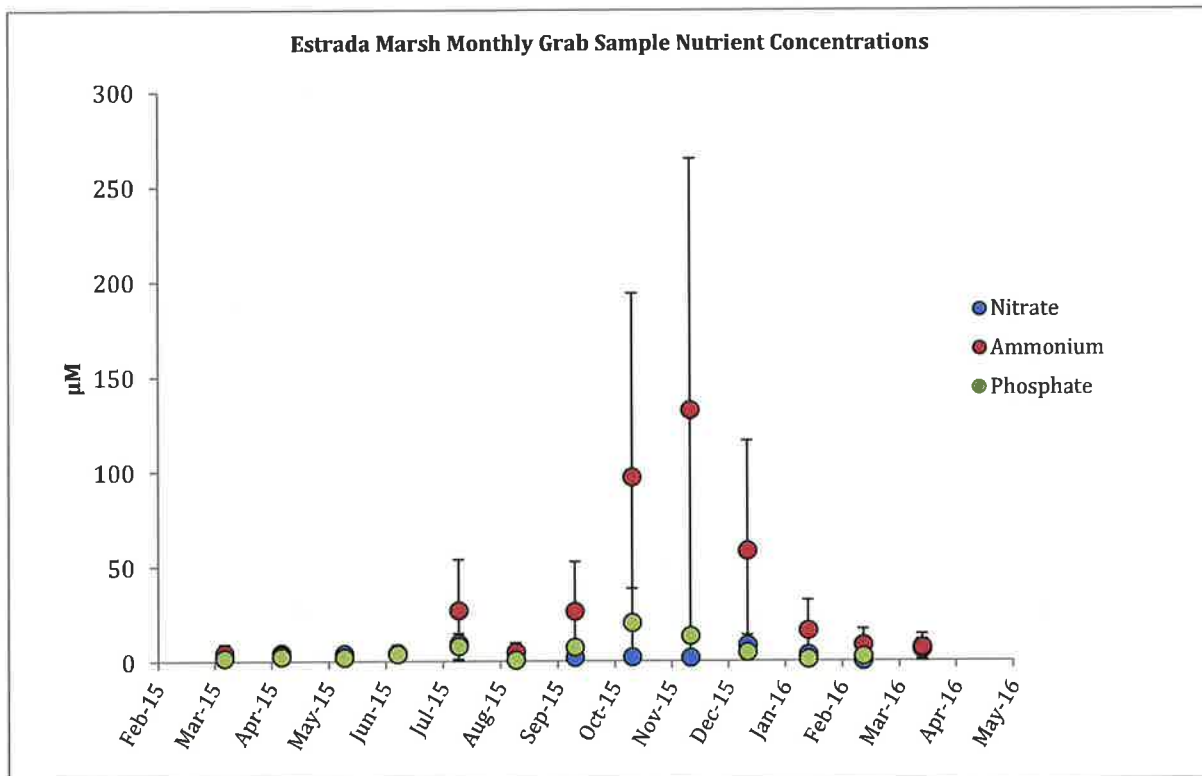


Figure 11. Estrada Marsh Averaged Monthly Grab Samples. X-axis is Labeled by Month of 2015 and 2016. Bars Shown Are Standard Error.

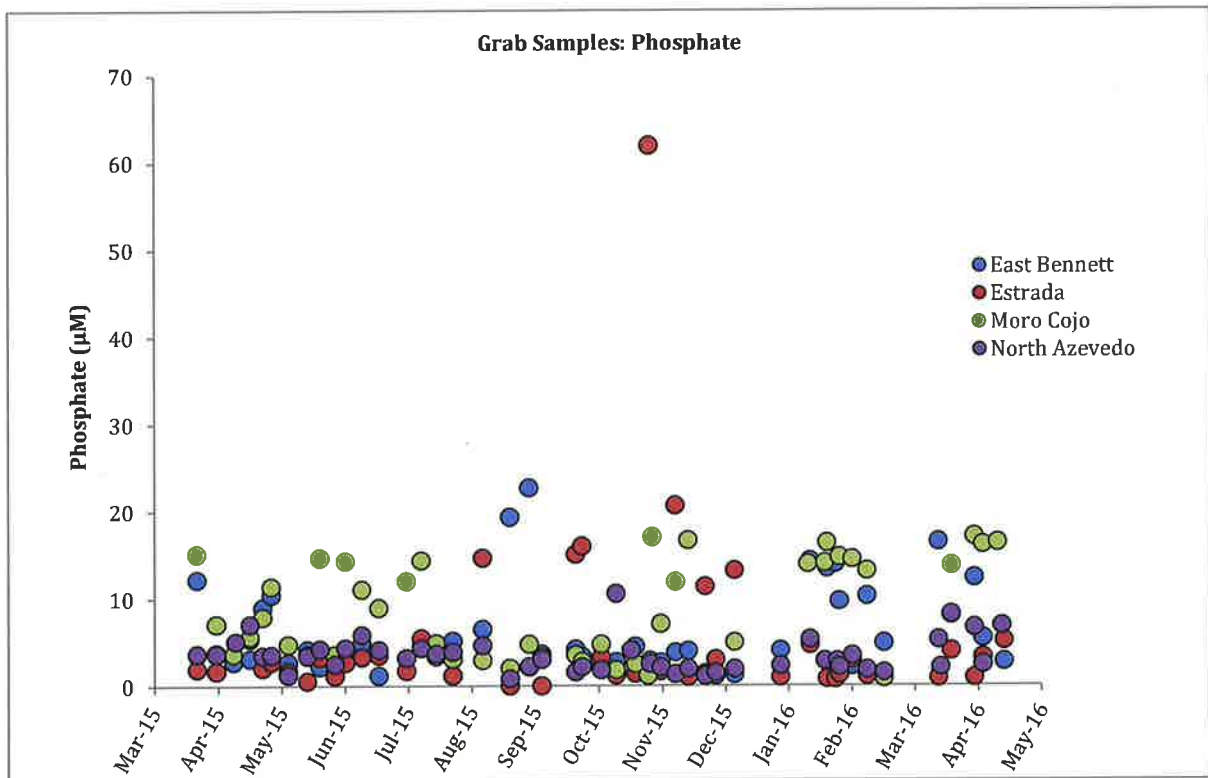


Figure 12. Phosphate Grab Samples as a Function of Time. X-axis is Labeled by Month of 2015 and 2016.

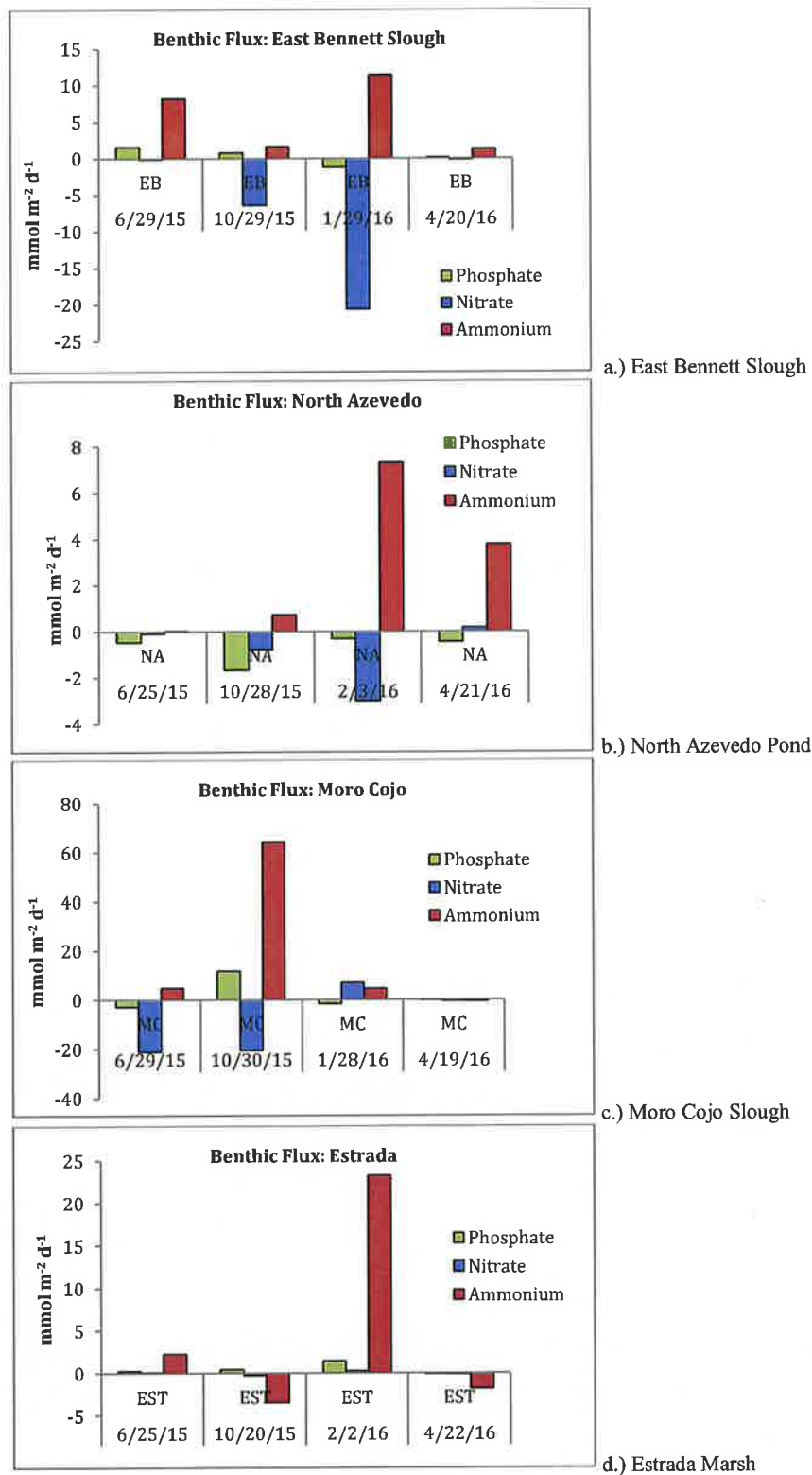


Figure 13. Seasonal Benthic Flux Measurements for Each Site (a-d).

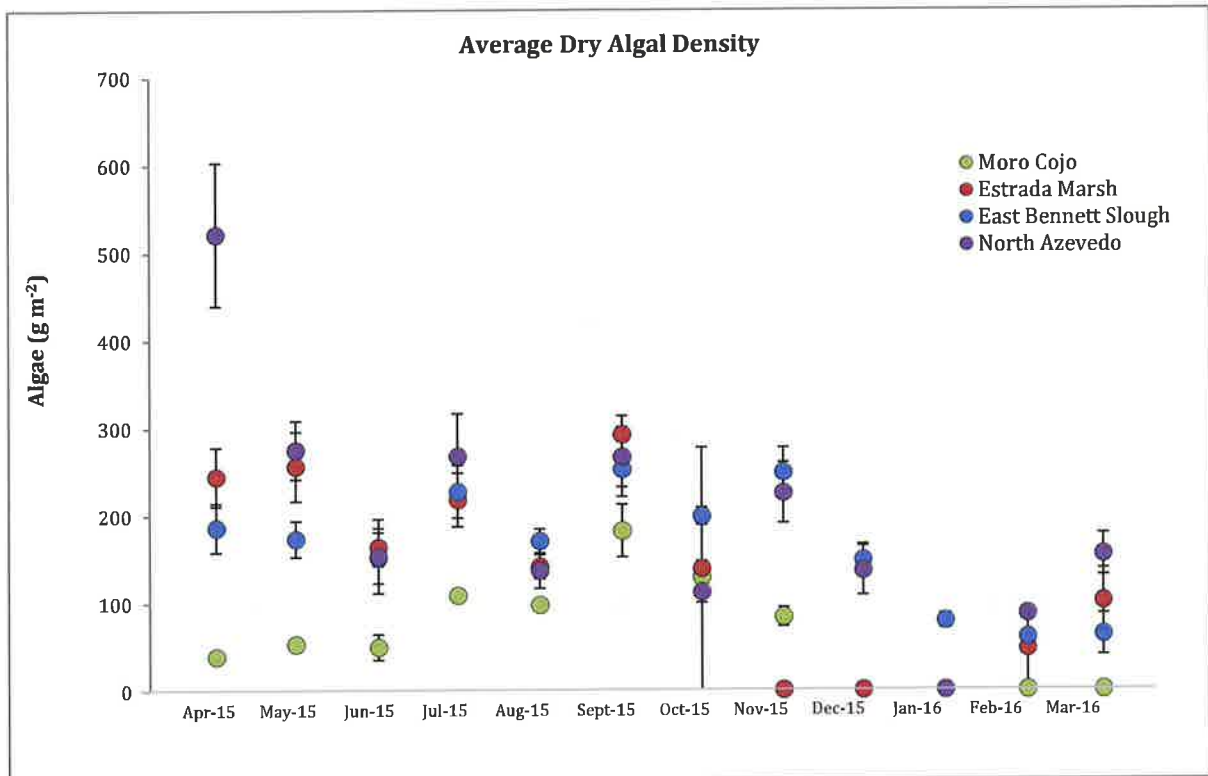


Fig. 14. Monthly Average Algal Biomass Density (Grams Dry Weight m⁻²). Bars Are Standard Deviation.

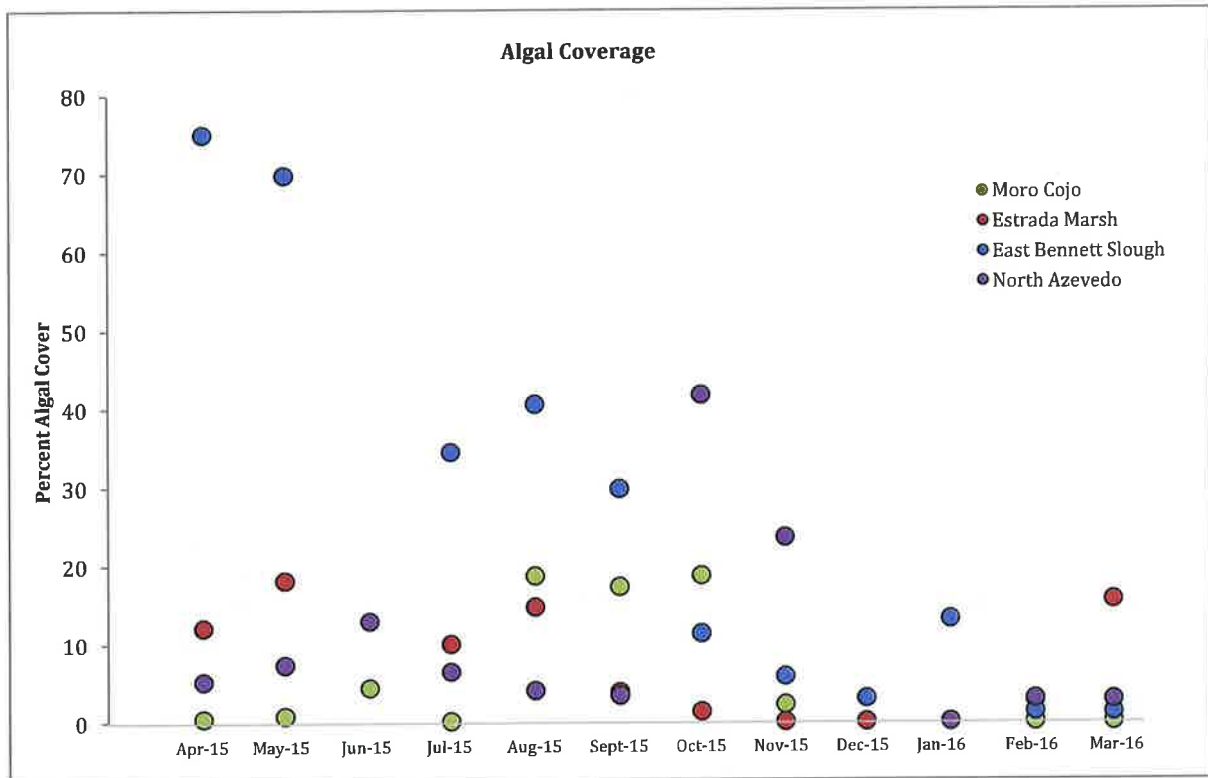


Figure 15. Monthly Algal Coverage (m²).

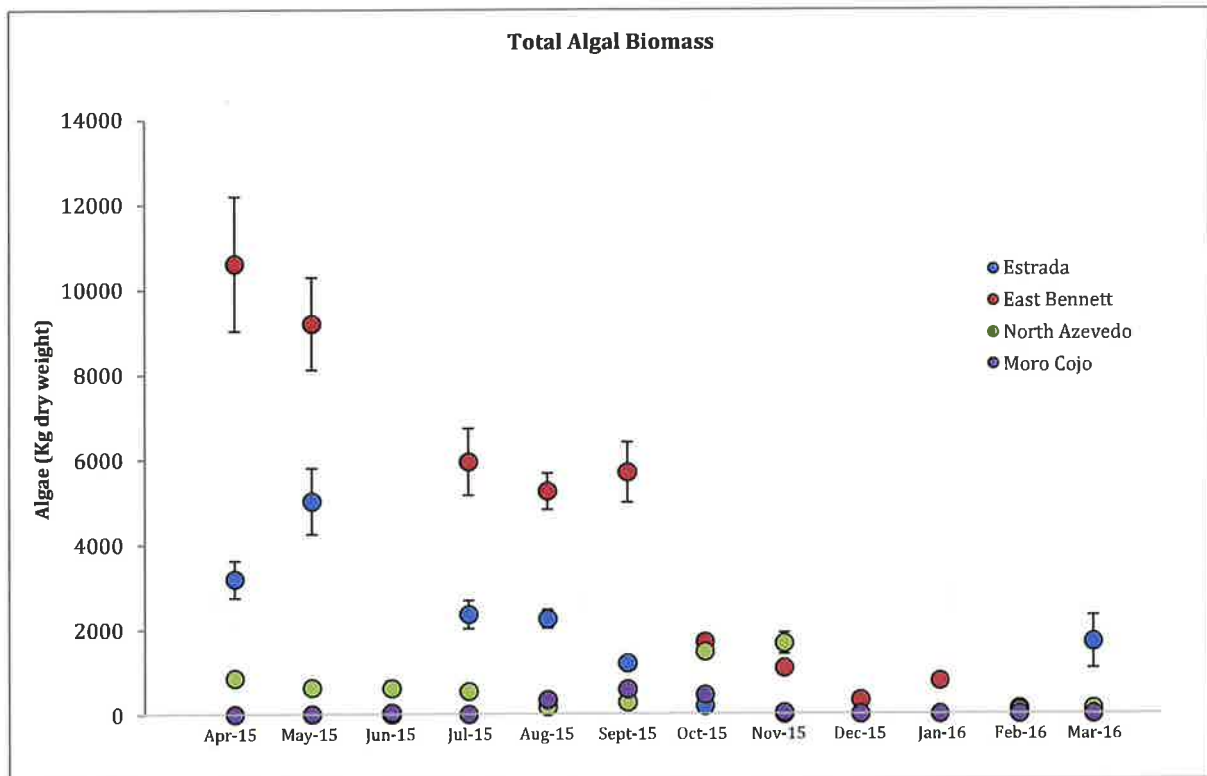


Figure 16. Monthly Total Algae (kg Dry Weight). Bars Are Standard Deviation.

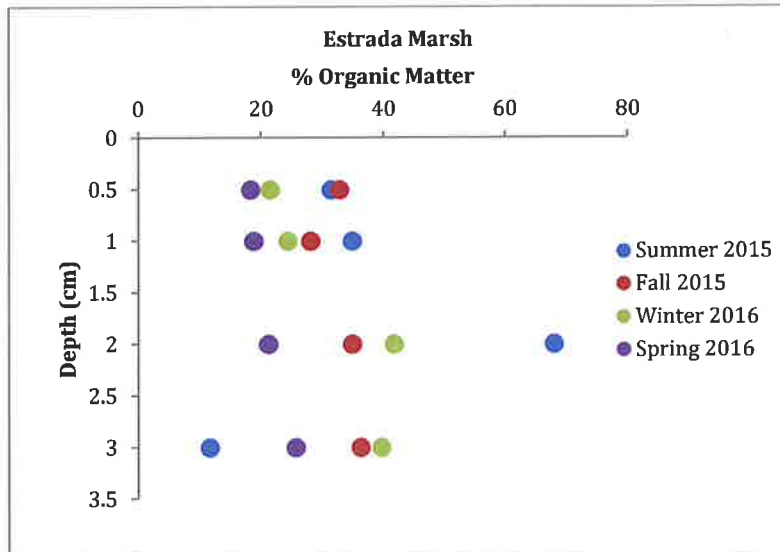


Fig. 17a. Estrada Marsh Sediment Organic Matter

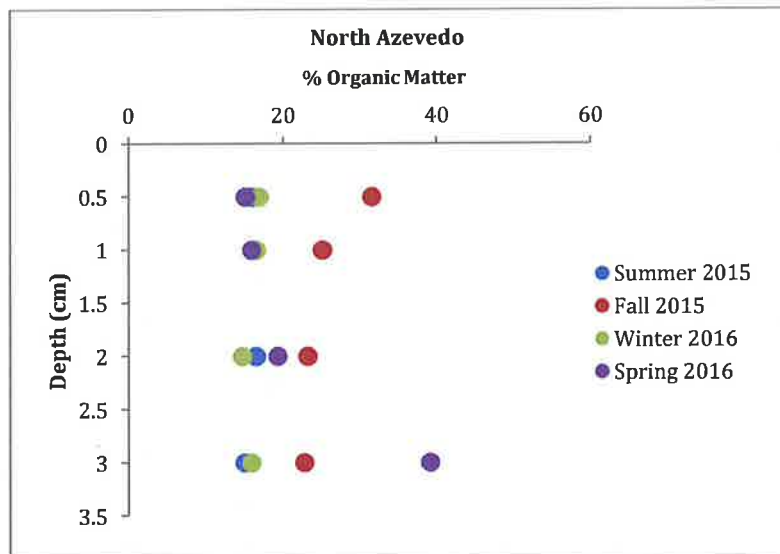


Fig. 17b. North Azevedo Sediment Organic Matter (%)

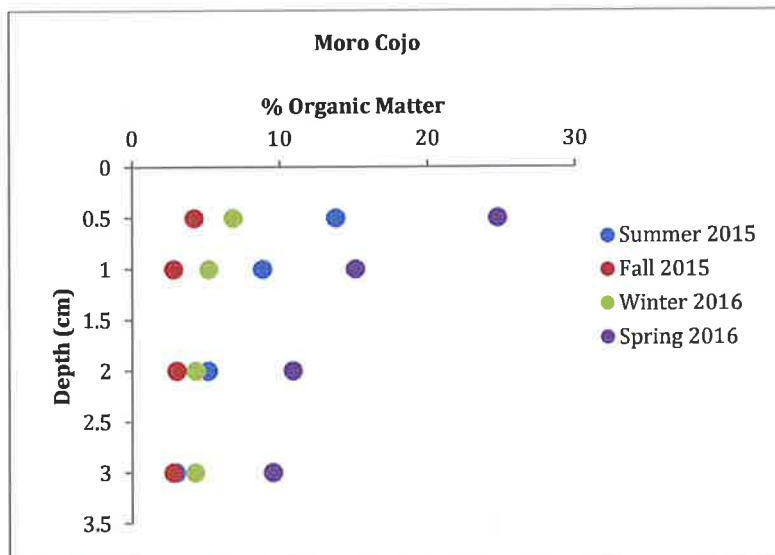


Fig. 17c. Moro Cojo Sediment Organic Matter (%).

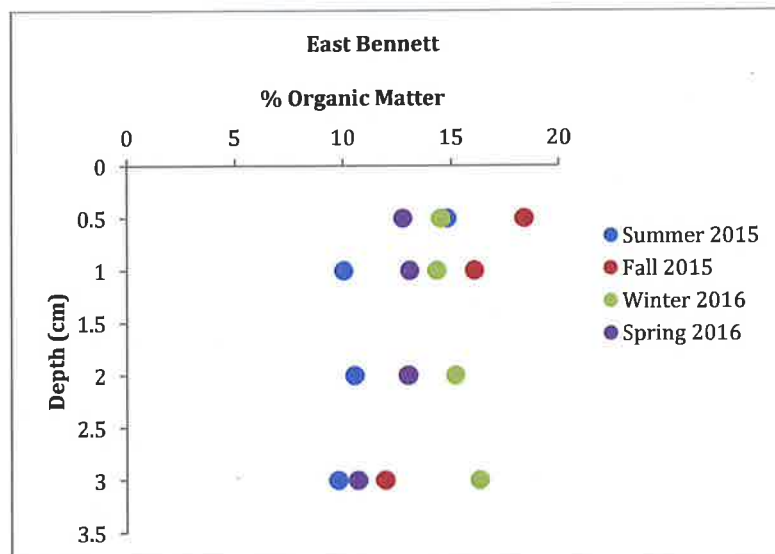


Fig. 17d. Estrada Marsh Sediment Organic Matter

Fig. 17(a.-d): Sediment Organic Matter Cores. Depth of Core Increases from Top To Bottom.

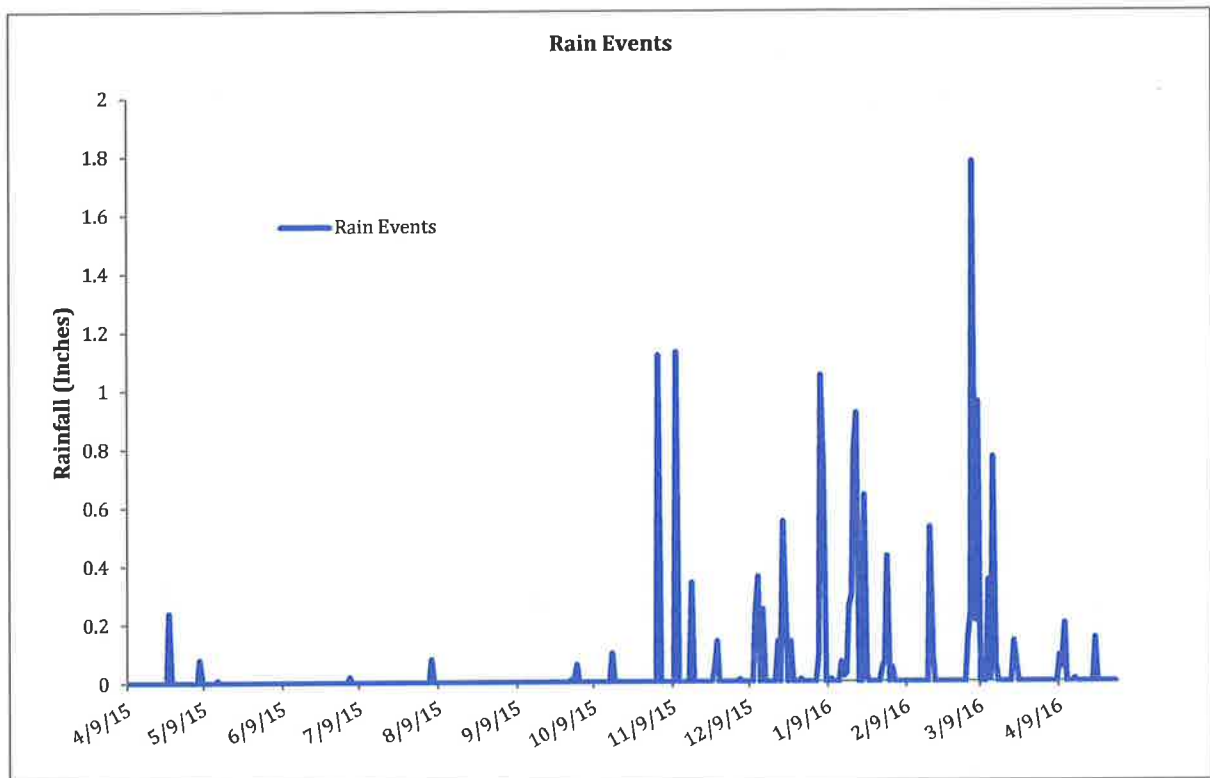


Fig. 18: Rain Events During Sampling Season.
Pubdata.mlml.calstate.edu

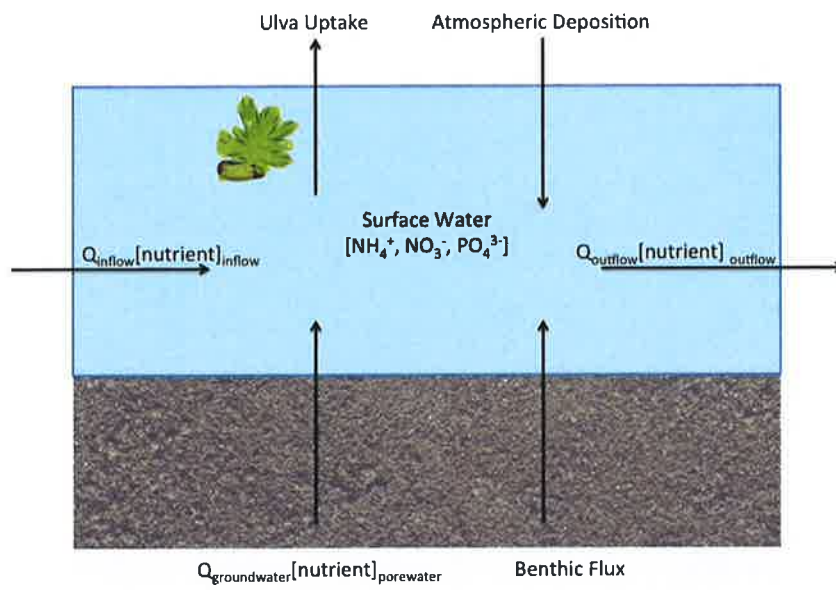


Fig. 19. Box Model – Water Column Processes, Sources and Sinks

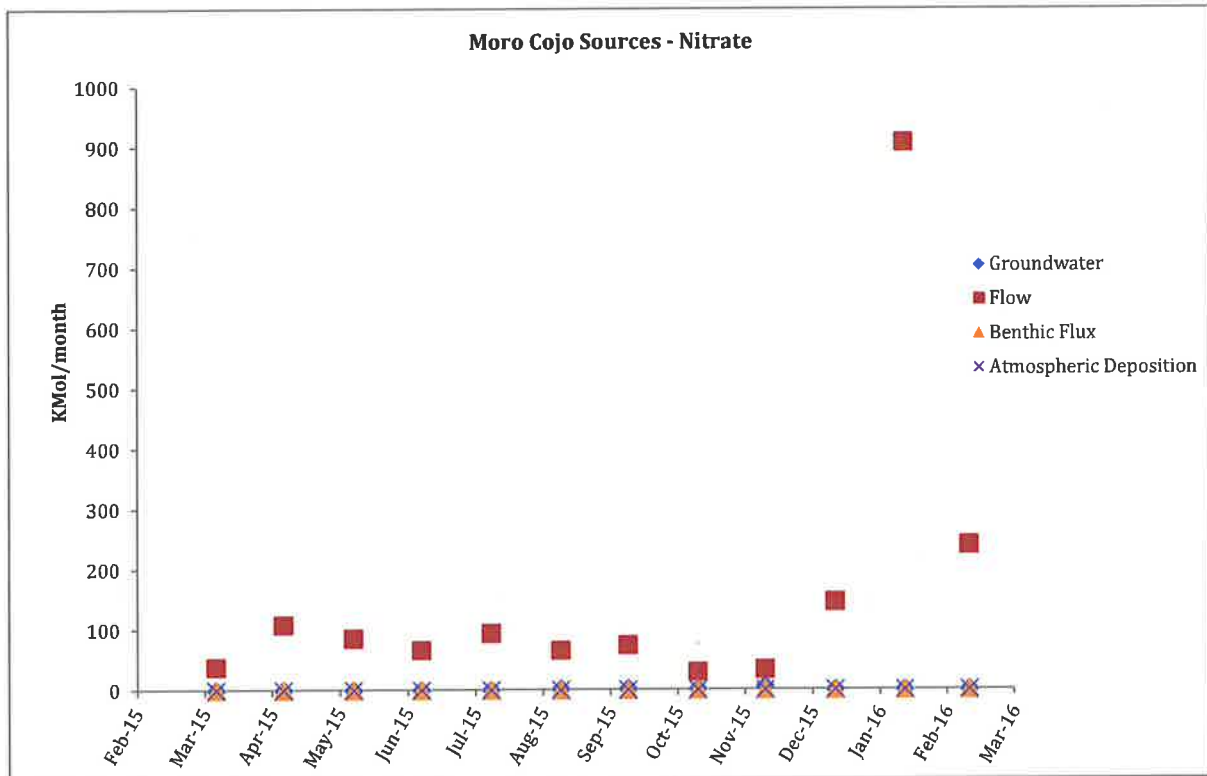


Fig. 20: Box Model Nitrate Sources – Moro Cojo Slough. Values Represent the Amount (KMols) of Nitrate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

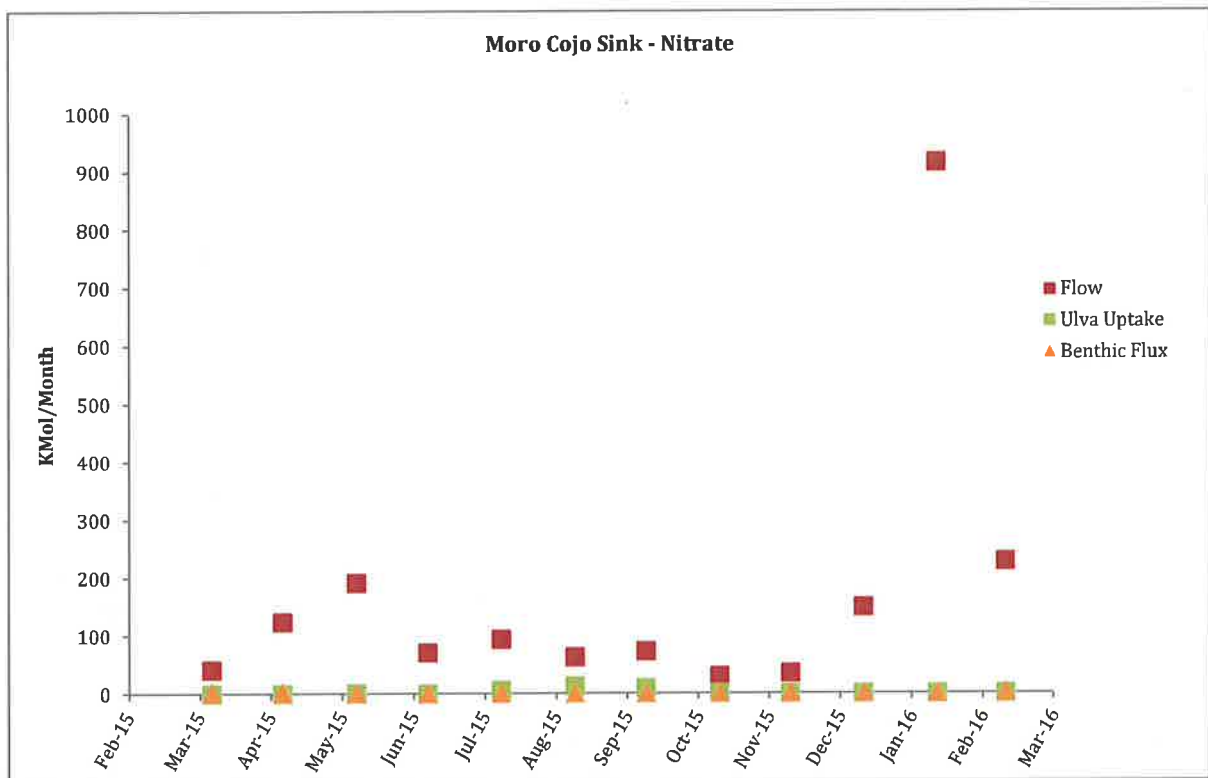


Fig. 21: Box Model Nitrate Sinks – Moro Cojo Slough. Values Represent the Amount (KMols) of Nitrate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

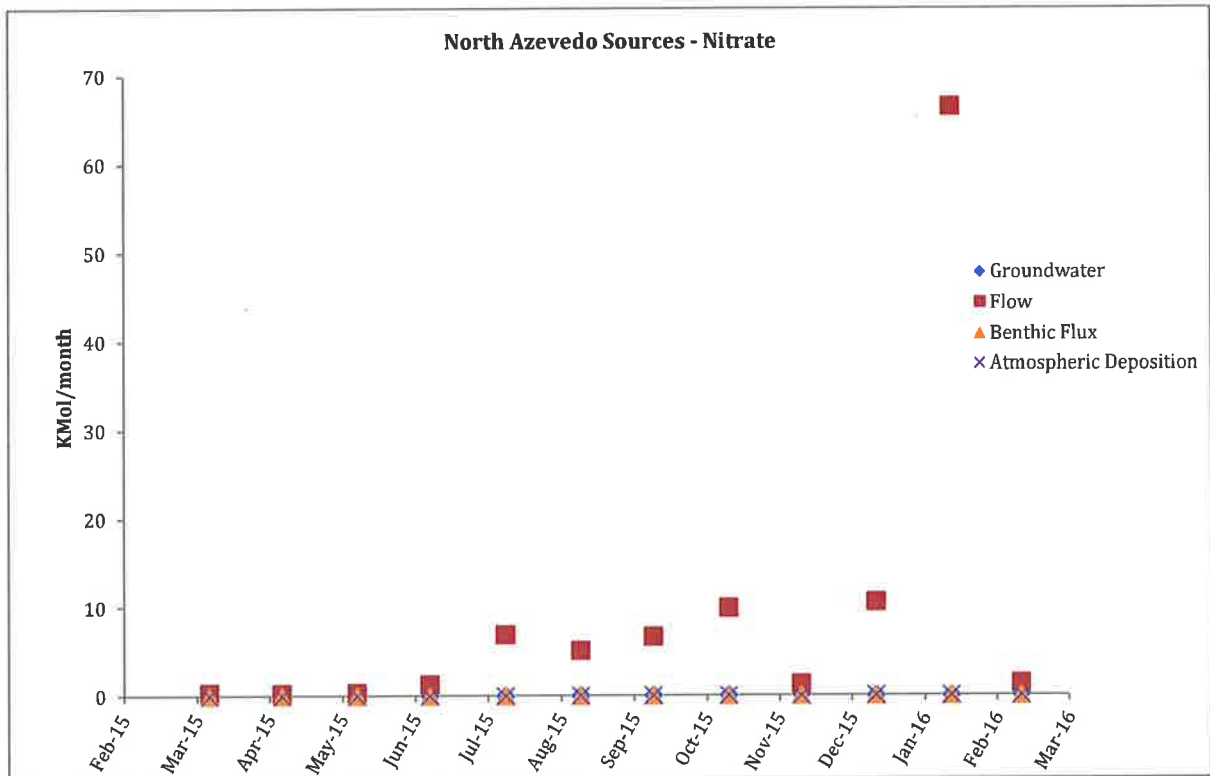


Fig. 22: Box Model Nitrate Sources –North Azevedo Pond. Values Represent the Amount (KMols) of Nitrate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

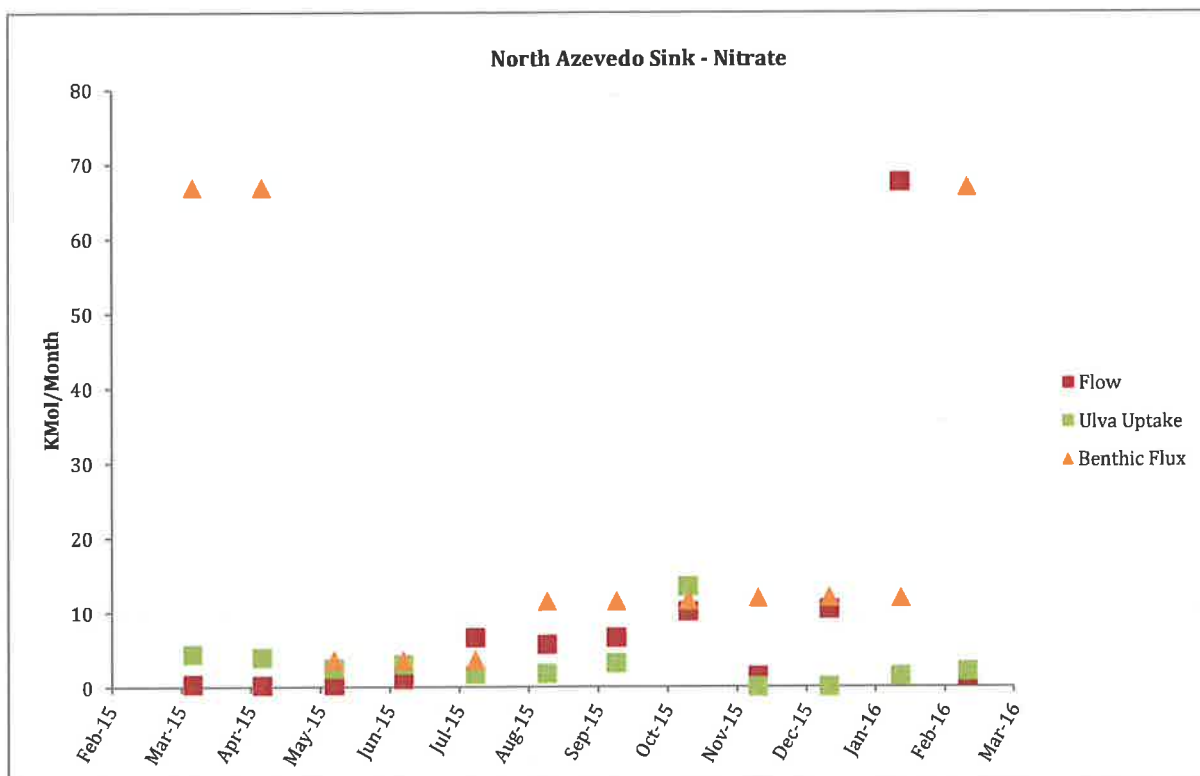


Fig. 23: Box Model Nitrate Sinks – North Azevedo Pond. Values Represent the Amount (KMols) of Nitrate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

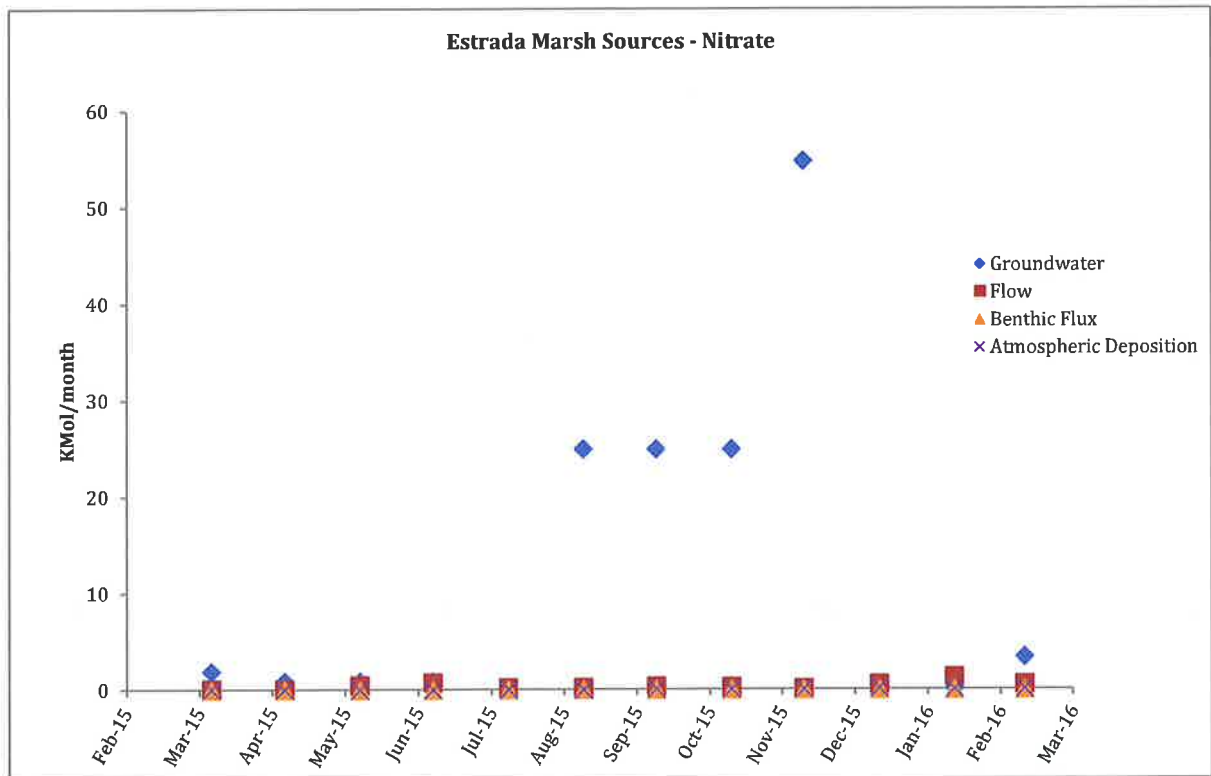


Fig. 24: Box Model Nitrate Sources – Estrada Marsh. Values Represent the Amount (KMols) of Nitrate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

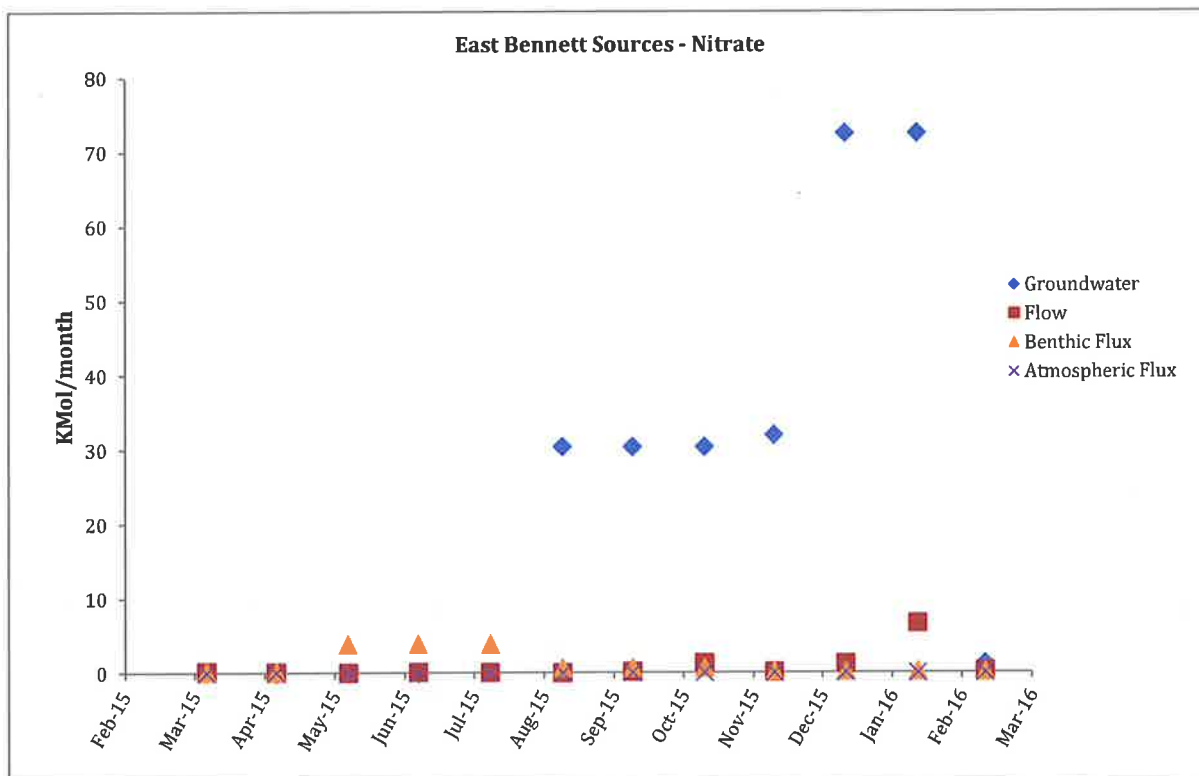


Fig. 25: Box Model Nitrate Sources – East Bennett Slough. Values Represent the Amount (KMols) of Nitrate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

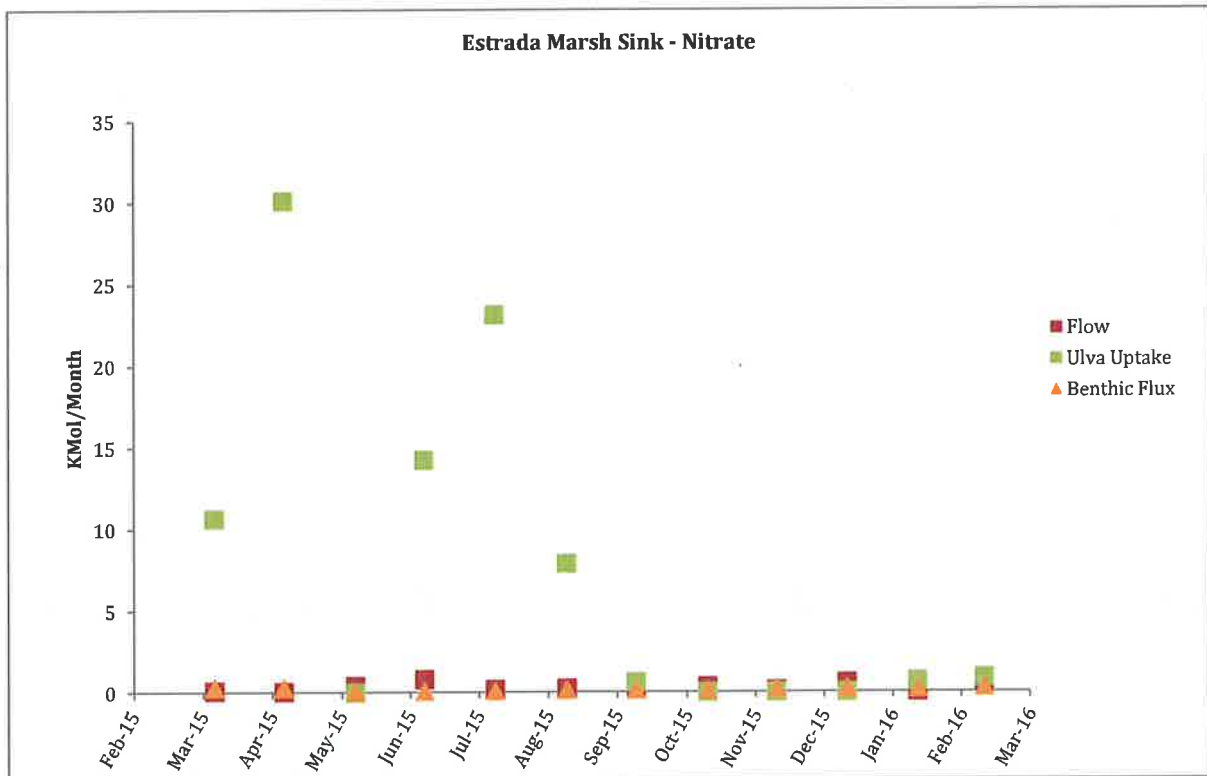


Fig. 26: Box Model Nitrate Sinks – Estrada Marsh. Values Represent the Amount (KMols) of Nitrate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

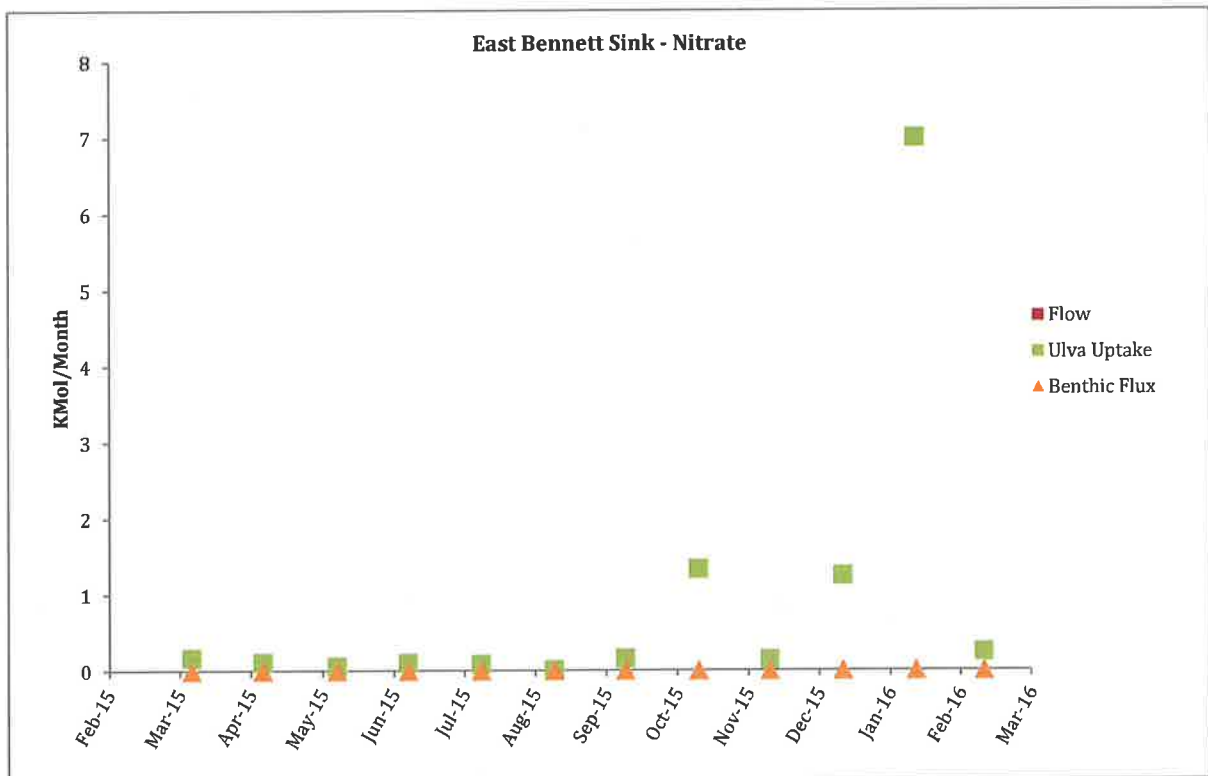


Fig. 27: Box Model Nitrate Sinks – East Bennett Slough. Values Represent the Amount (KMols) of Nitrate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

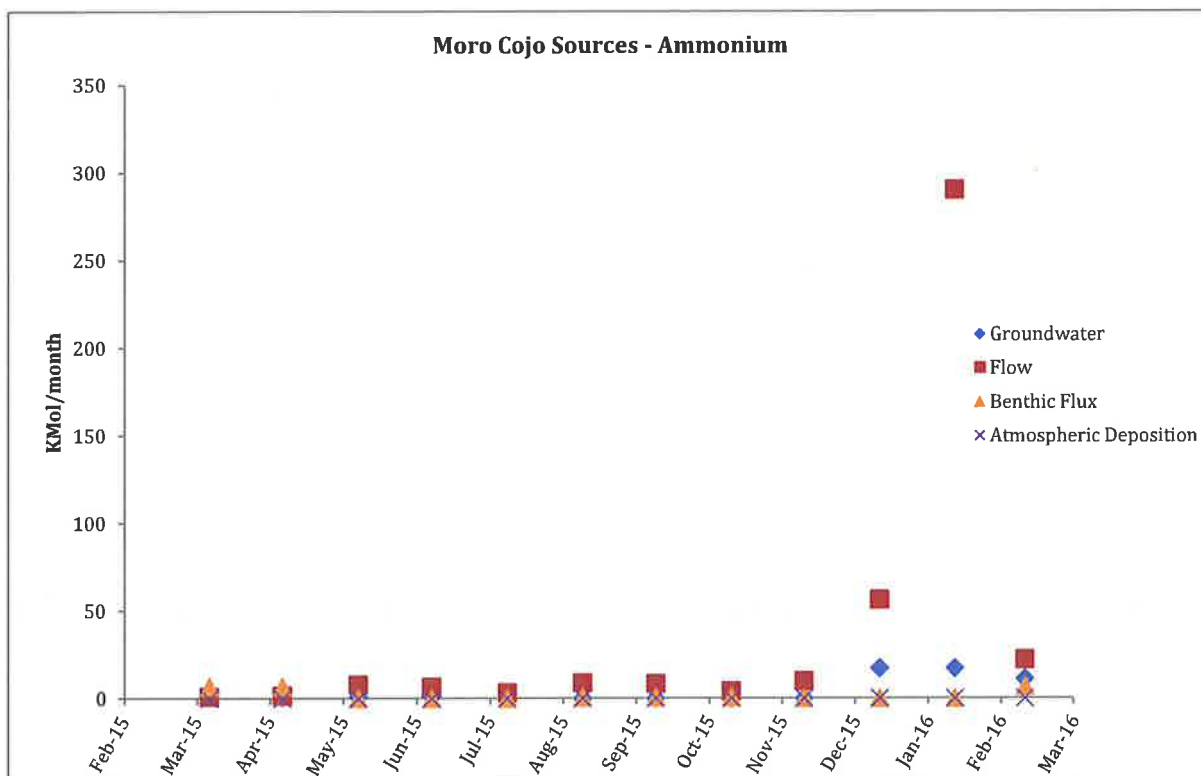


Fig. 28: Box Model Ammonium Sources – Moro Cojo Slough. Values Represent the Amount (KMols) of Ammonium Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

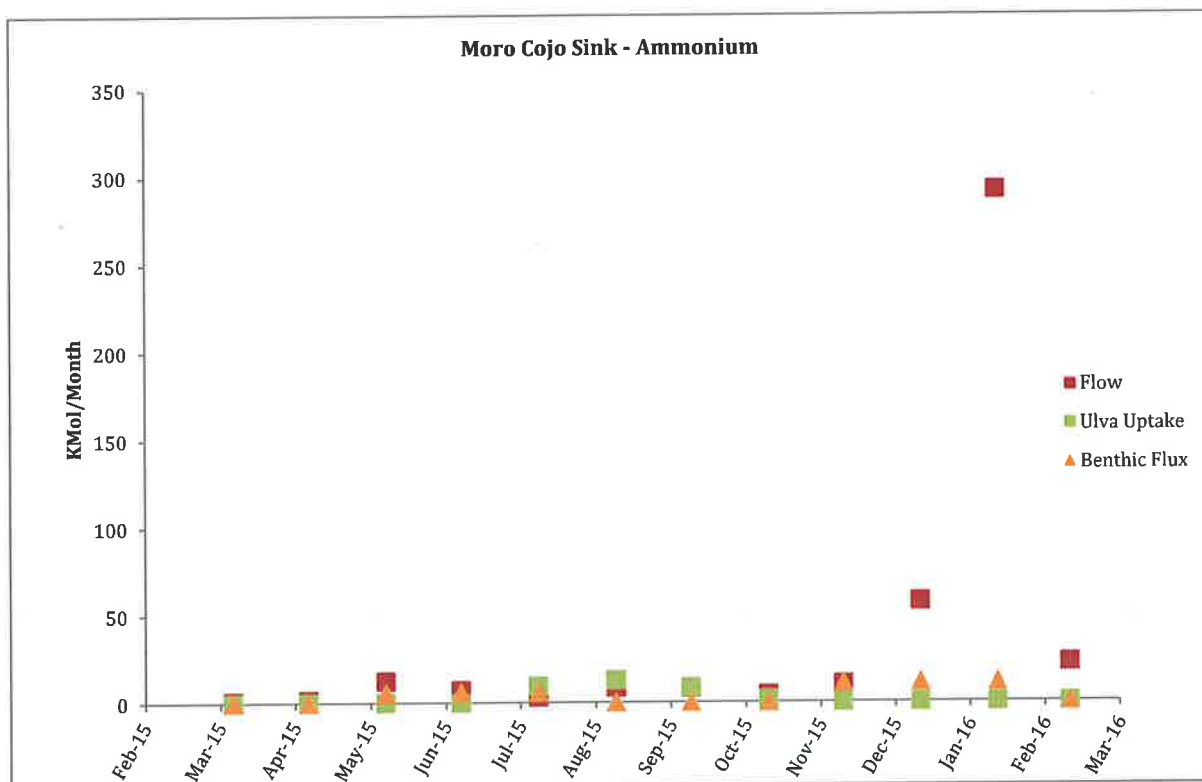


Fig. 29: Box Model Ammonium Sink – Moro Cojo Slough. Values Represent the Amount (KMols) of Ammonium Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

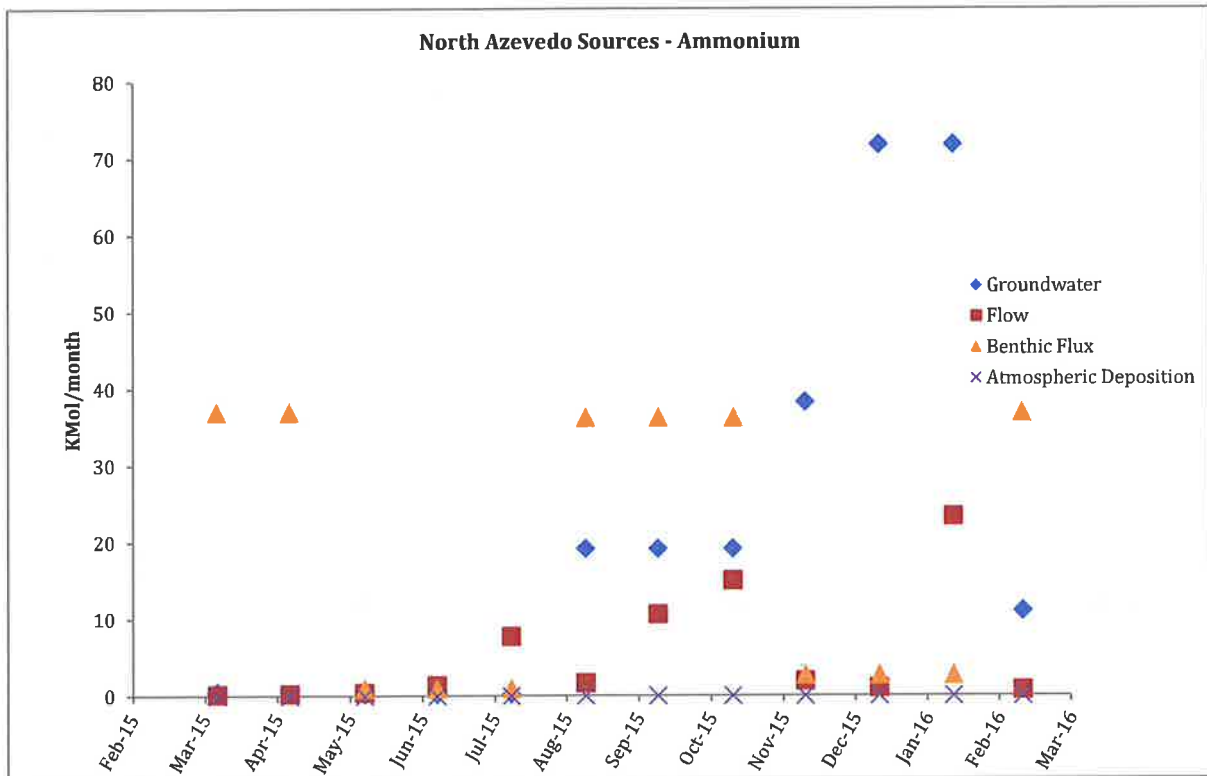


Fig. 30: Box Model Ammonium Sources – North Azevedo Pond. Values Represent the Amount (KMols) of Ammonium Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

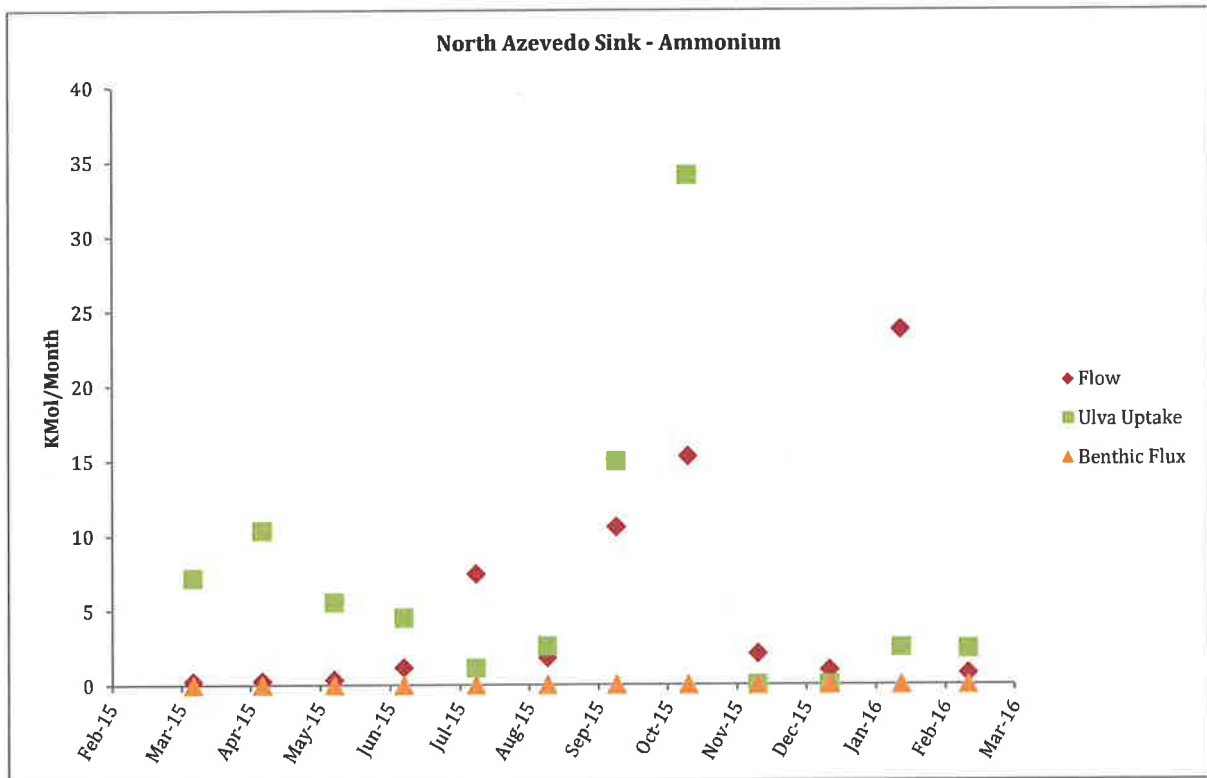


Fig. 31: Box Model Ammonium Sink – North Azevedo Pond. Values Represent the Amount (KMols) of Ammonium Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

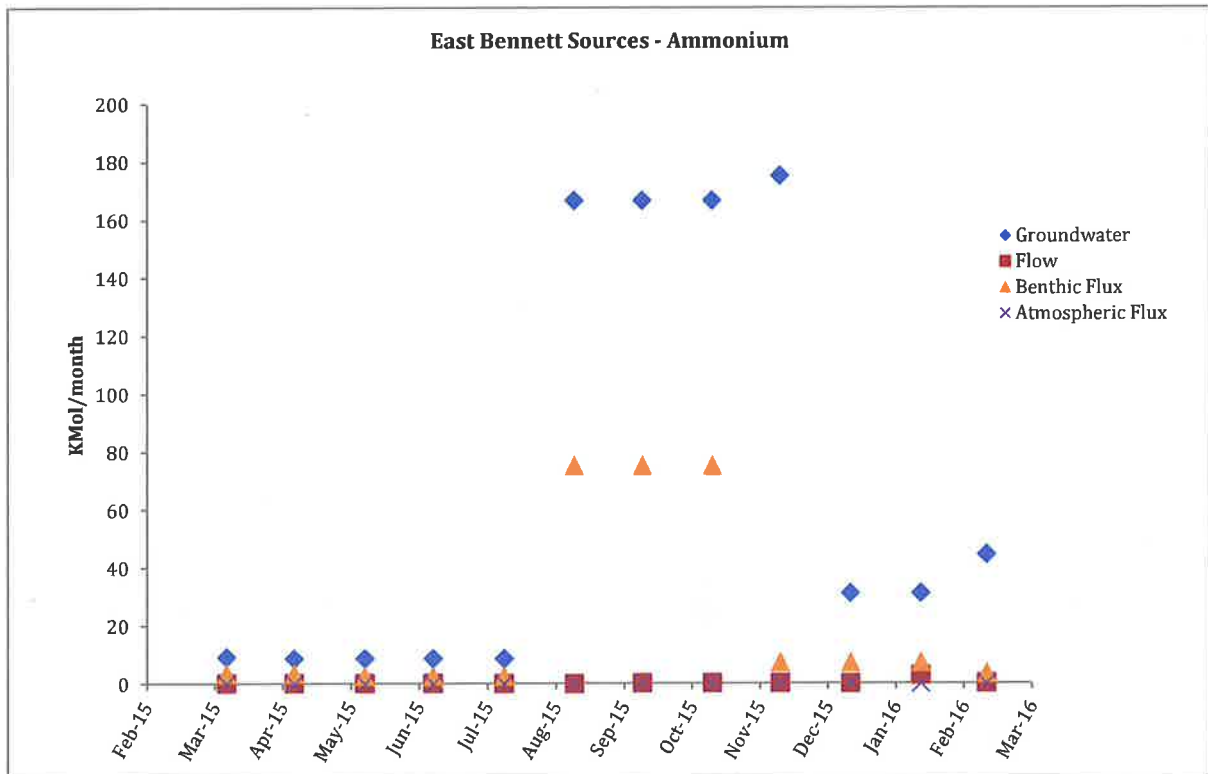


Fig. 32: Box Model Ammonium Sources – East Bennett Slough. Values Represent the Amount (KMols) of Ammonium Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

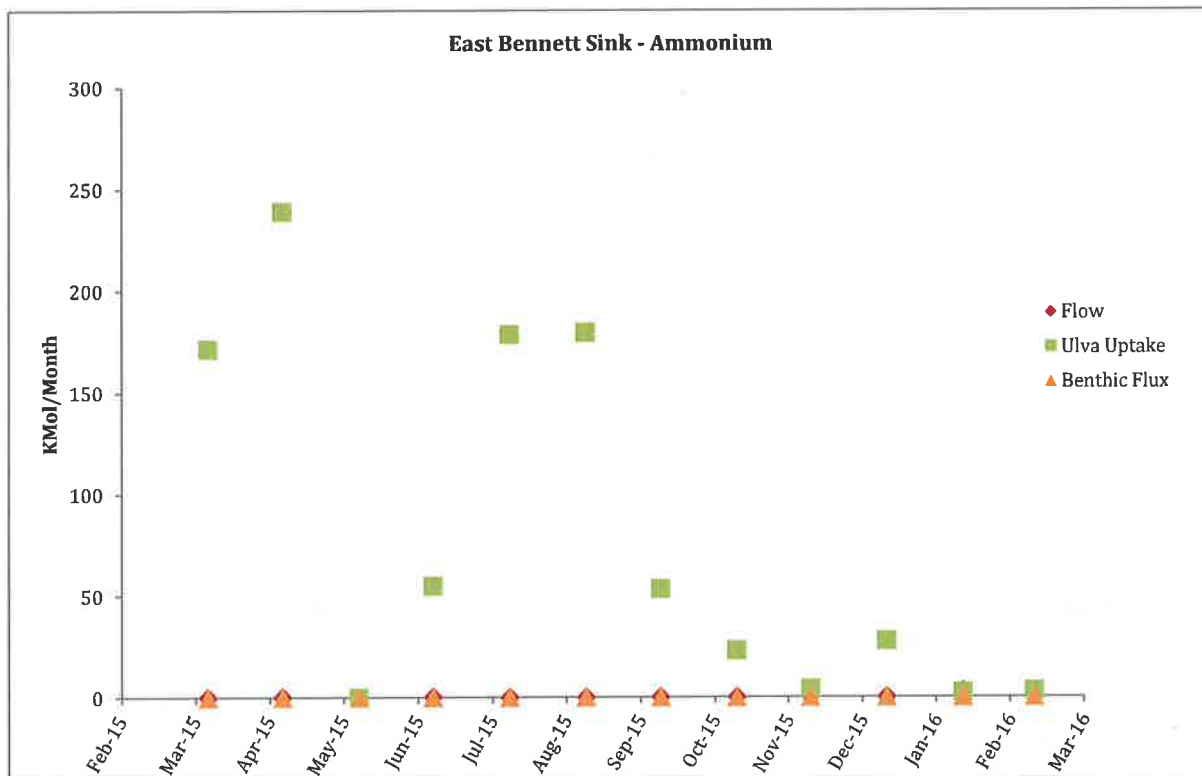


Fig. 33: Box Model Ammonium Sink – East Bennett Slough. Values Represent the Amount (KMols) of Ammonium Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

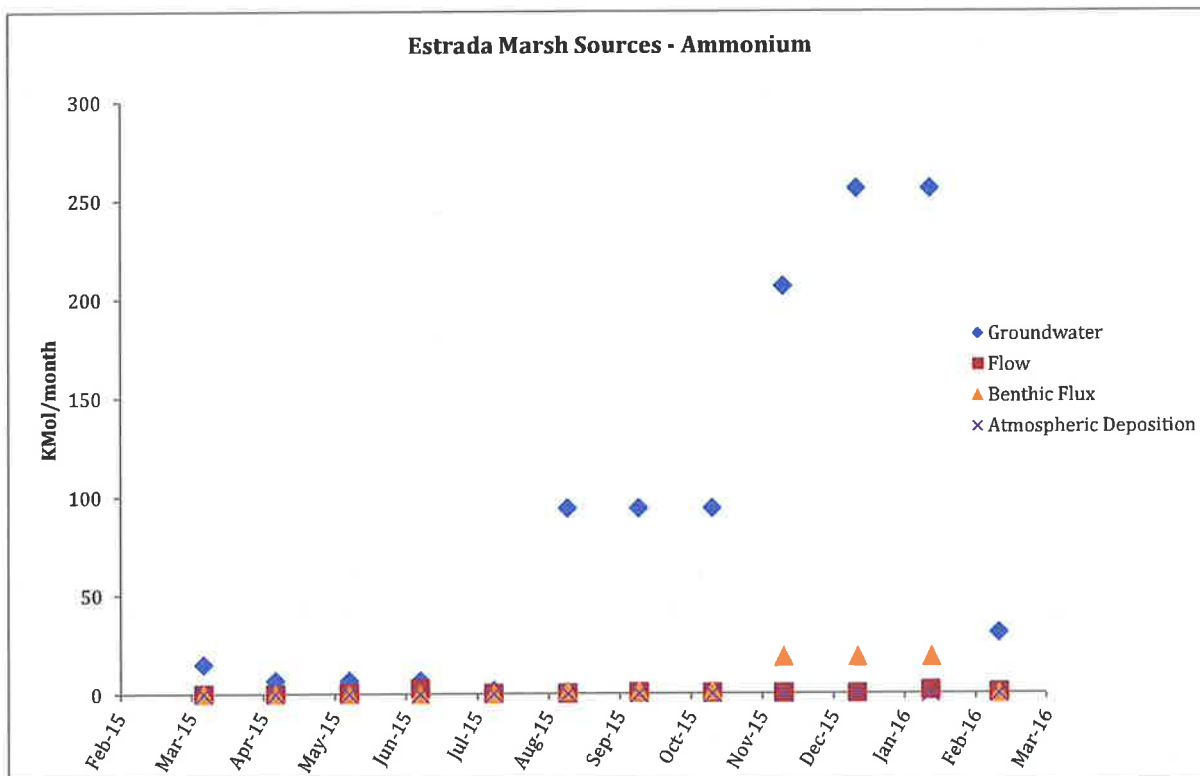


Fig. 34: Box Model Ammonium Sources – Estrada Marsh. Values Represent the Amount (KMols) of Ammonium Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

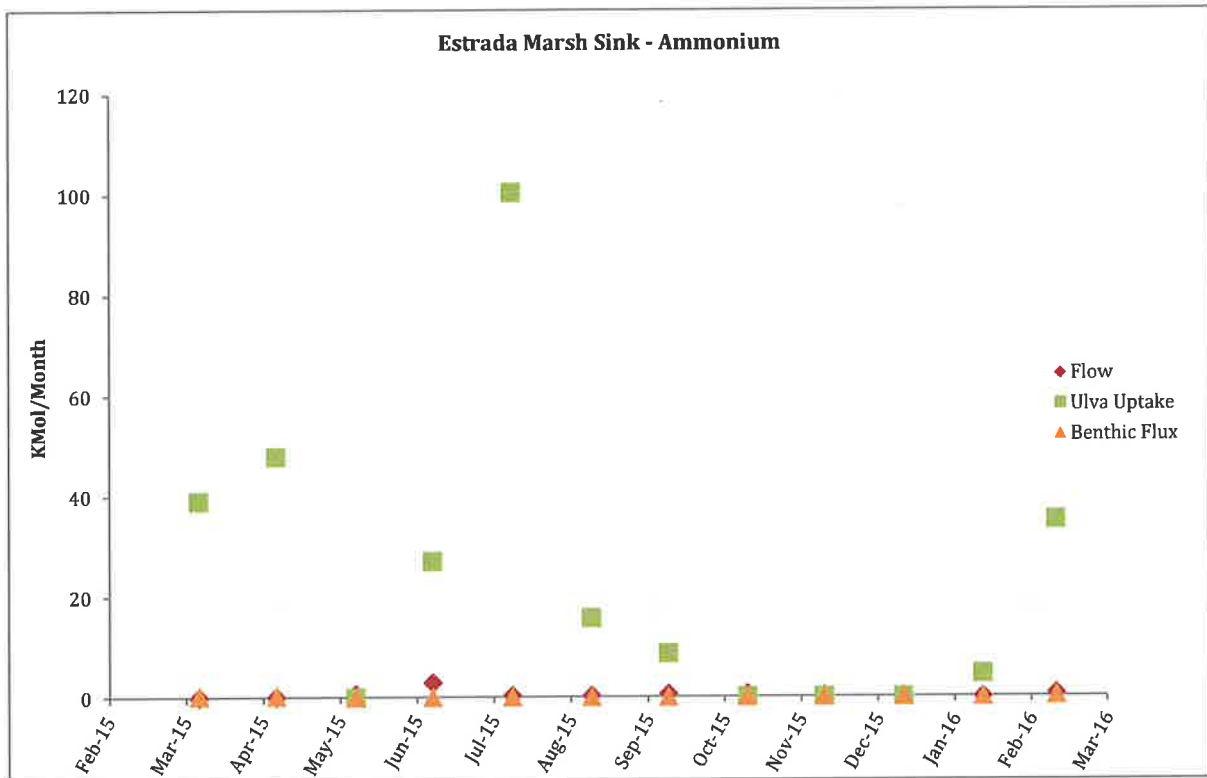


Fig. 35: Box Model Ammonium Sink – Estrada Marsh. Values Represent the Amount (KMols) of Ammonium Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

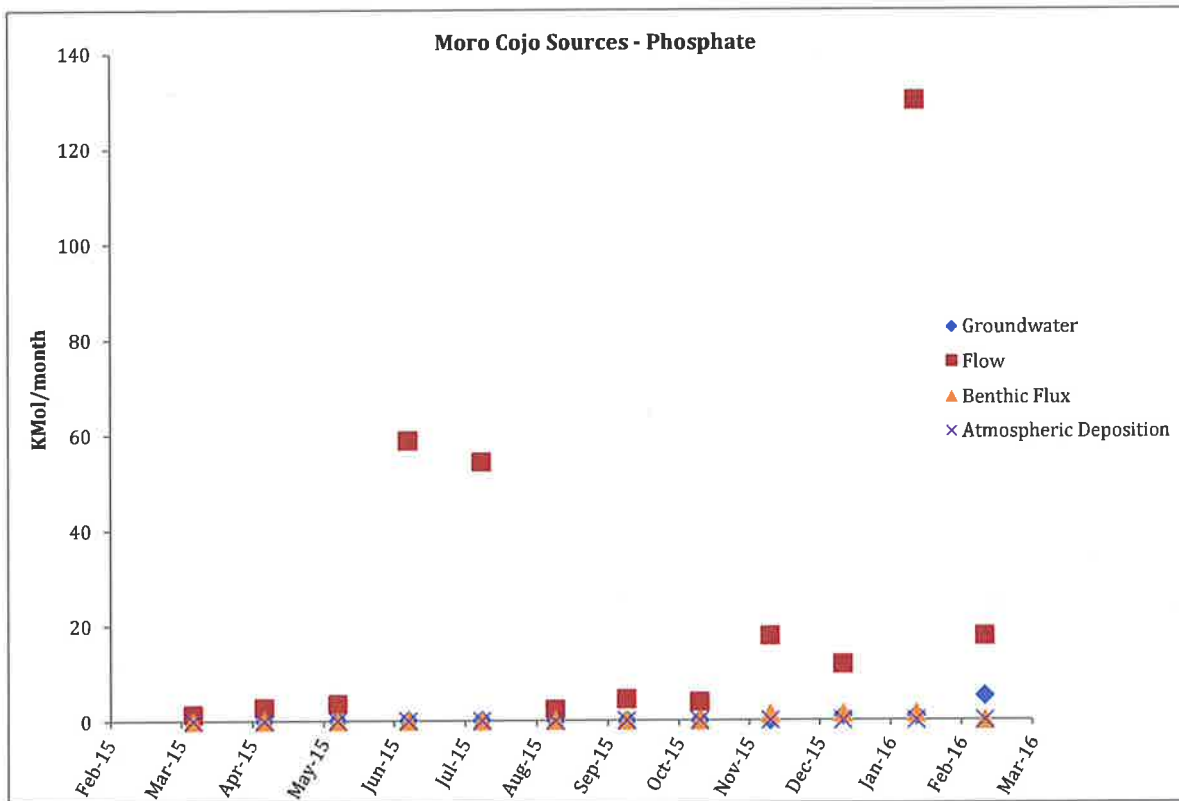


Fig. 36: Box Model Phosphate Sources – Moro Cojo Slough. Values Represent the Amount (KMols) of Phosphate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

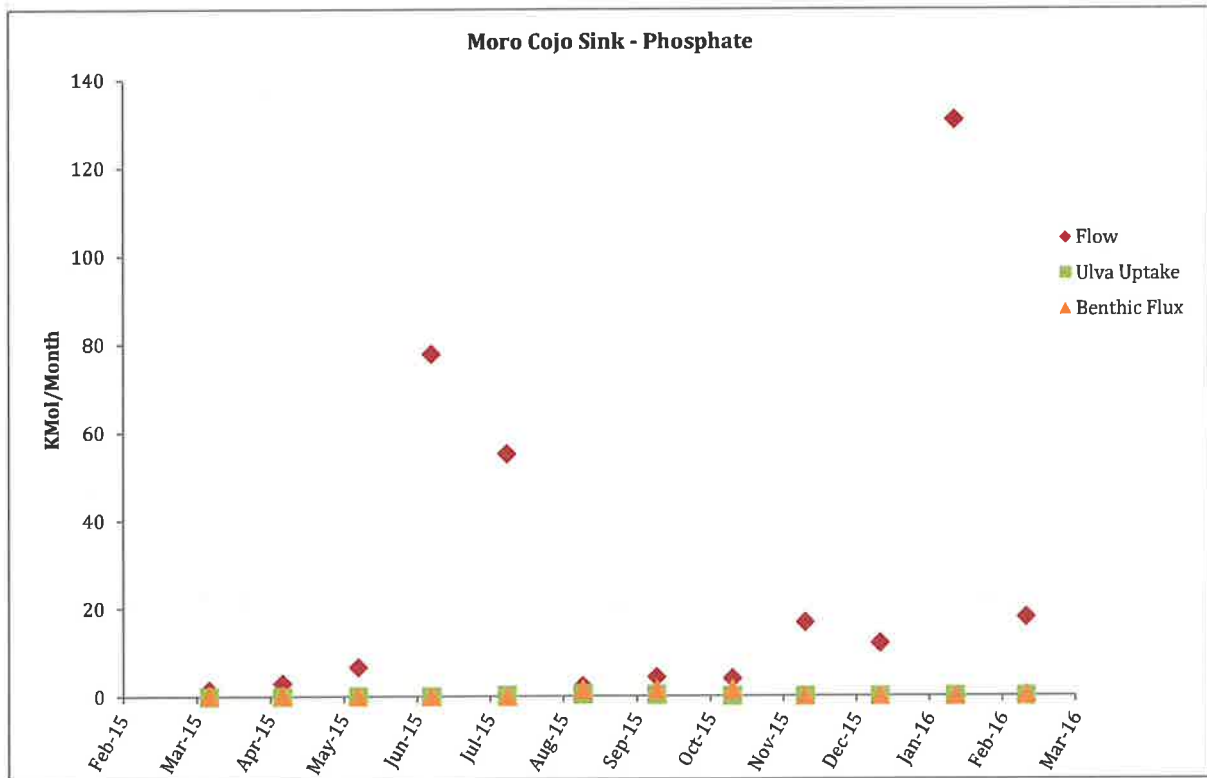


Fig. 37: Box Model Phosphate Sink – Moro Cojo Slough. Values Represent the Amount (KMols) of Phosphate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

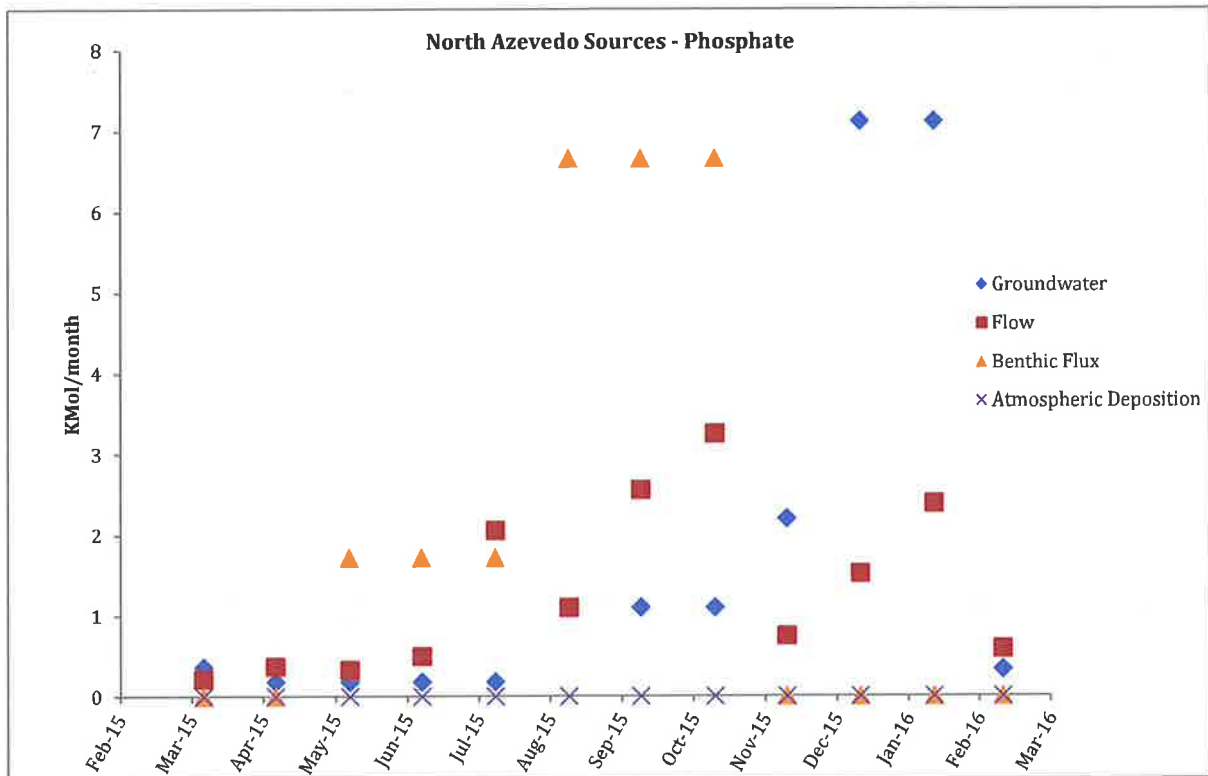


Fig. 38: Box Model Phosphate Sources – North Azevedo Pond. Values Represent the Amount (KMols) of Phosphate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

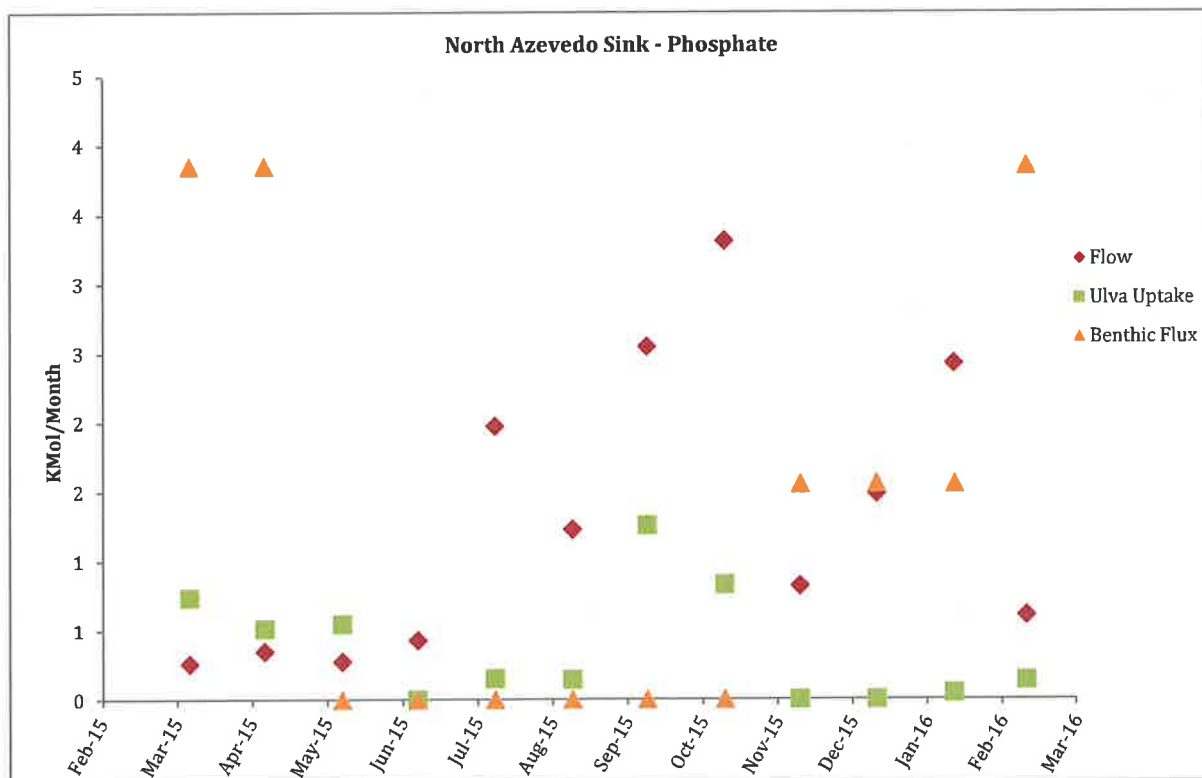


Fig. 39: Box Model Phosphate Sink – North Azevedo Pond. Values Represent the Amount (KMols) of Phosphate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

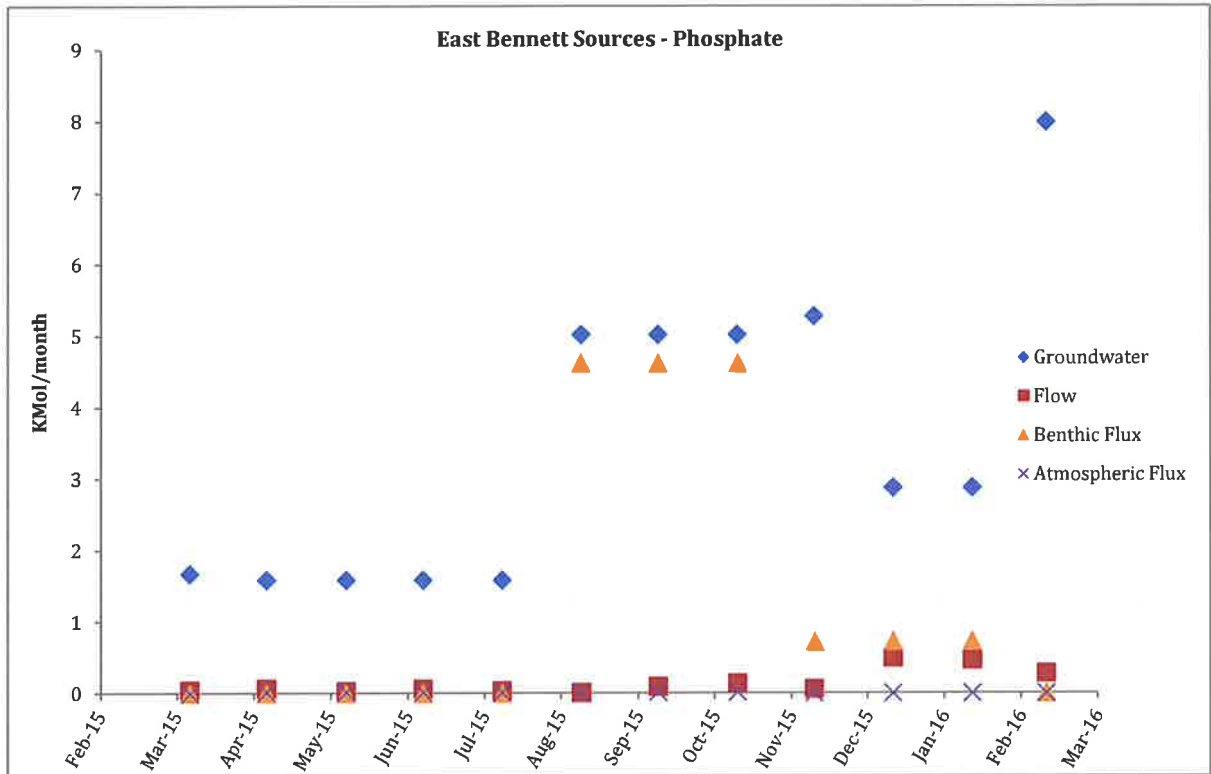


Fig. 40: Box Model Phosphate Sources – East Bennett Slough. Values Represent the Amount (KMols) of Phosphate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

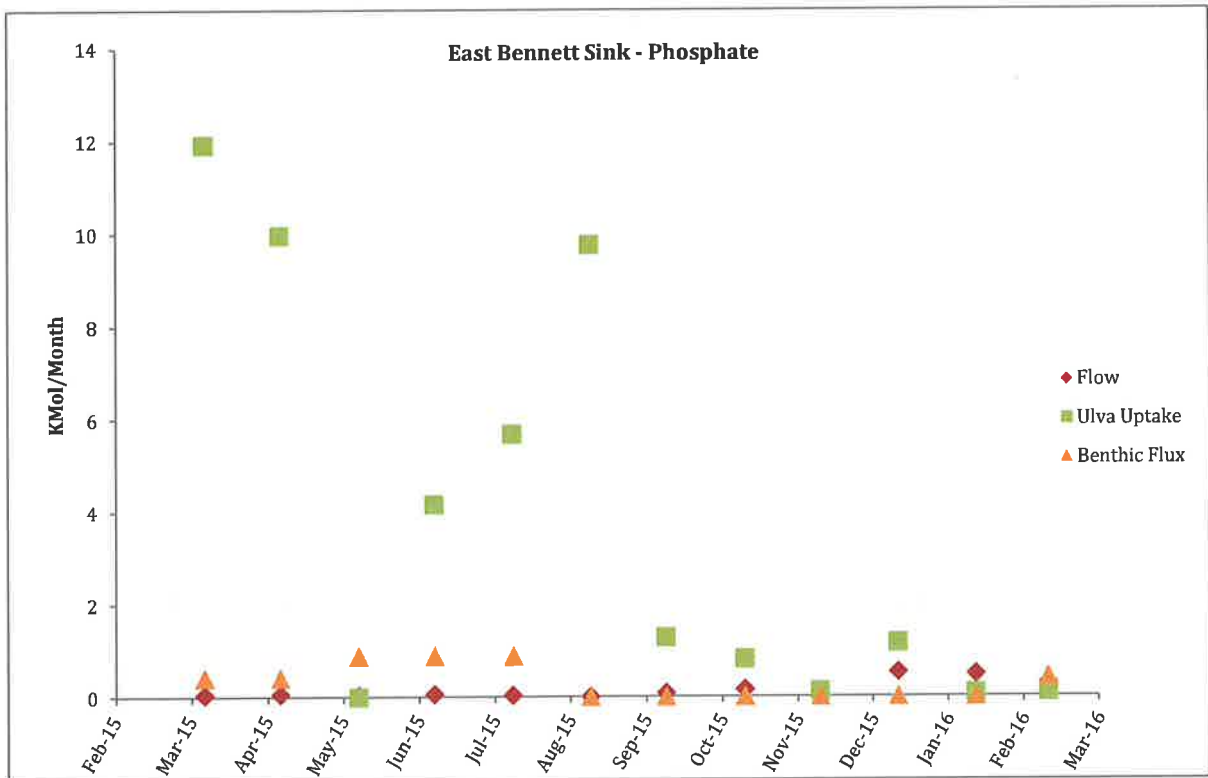


Fig. 41: Box Model Phosphate Sink – East Bennett Slough. Values Represent the Amount (KMols) of Phosphate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

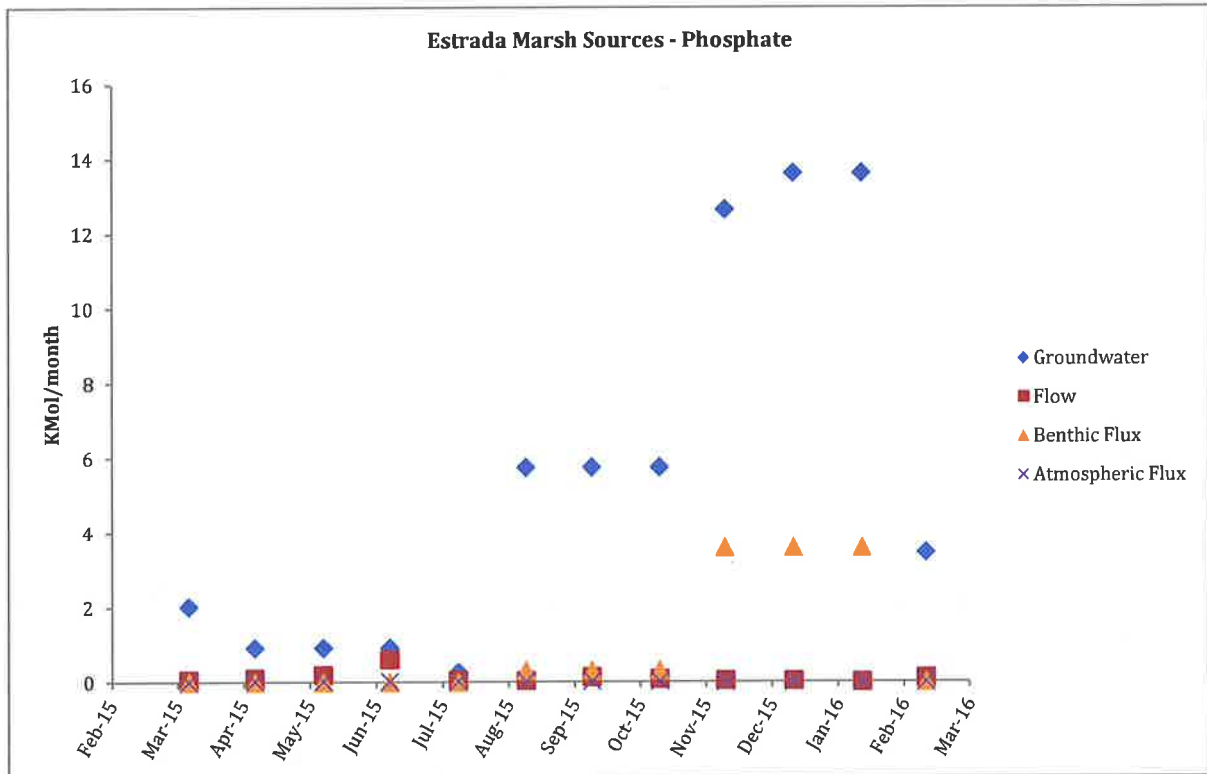


Fig. 42: Box Model Phosphate Sources – Estrada Marsh. Values Represent the Amount (KMols) of Phosphate Entering the System Each Month via Groundwater, Surface Water Flow, Benthic Flux and Atmospheric Flux.

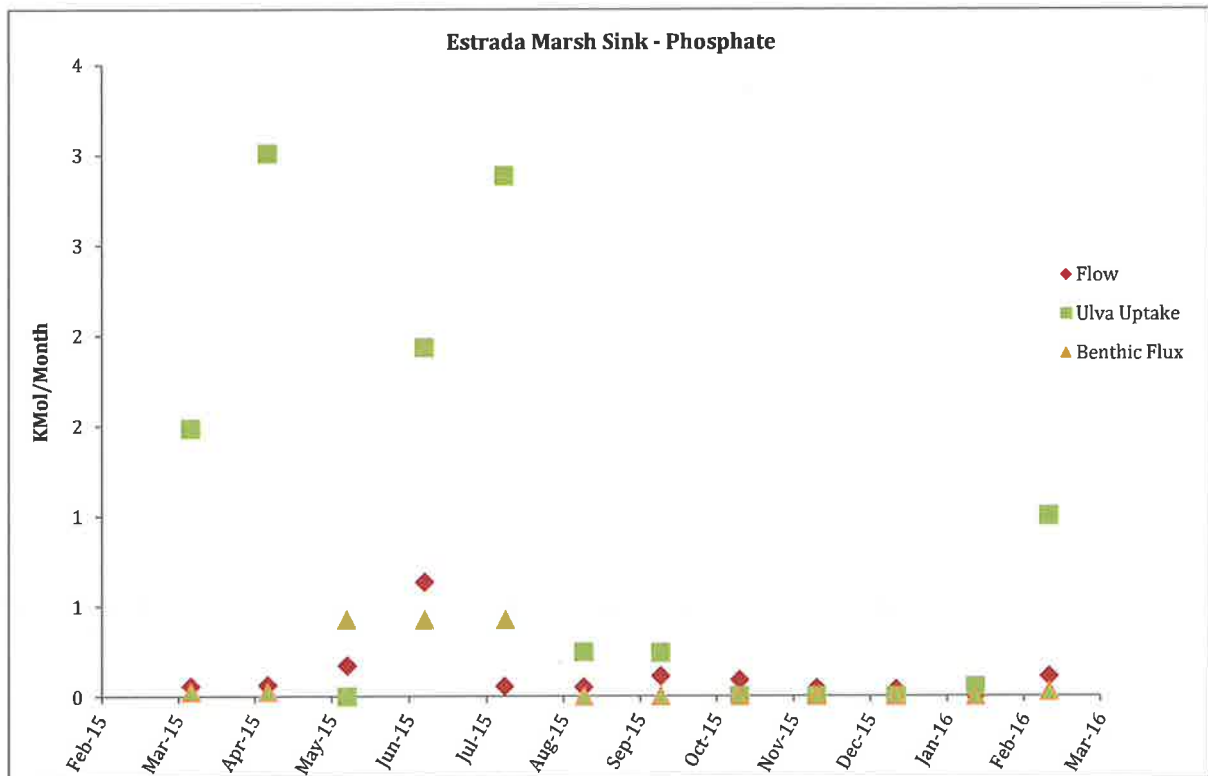


Fig. 43: Box Model Phosphate Sink – Estrada Marsh. Values Represent the Amount (KMols) of Phosphate Removed from the System Each Month via Surface Water Flow, *Ulva* Uptake and Benthic Flux.

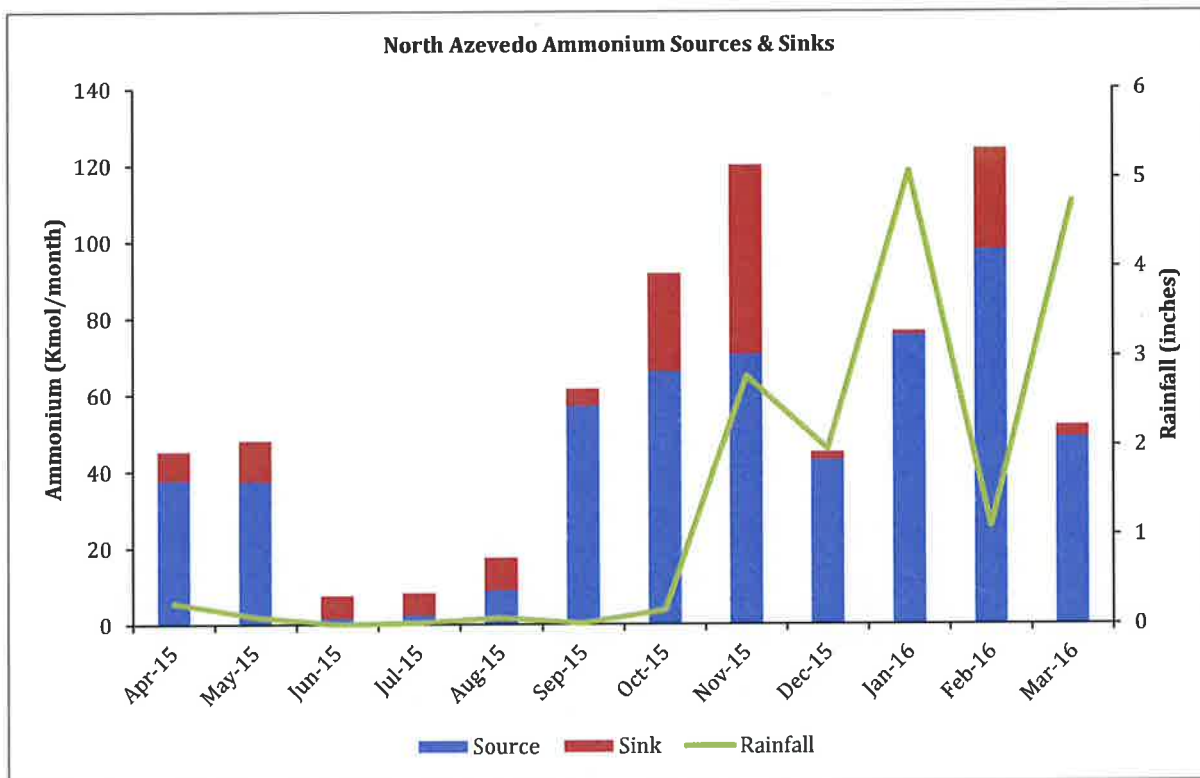


Fig. 44: North Azevedo Pond Ammonium Total Sources and Sinks. Stacked Bars Represent Sources and Sinks. Green Line Represents Rainfall Each Month.

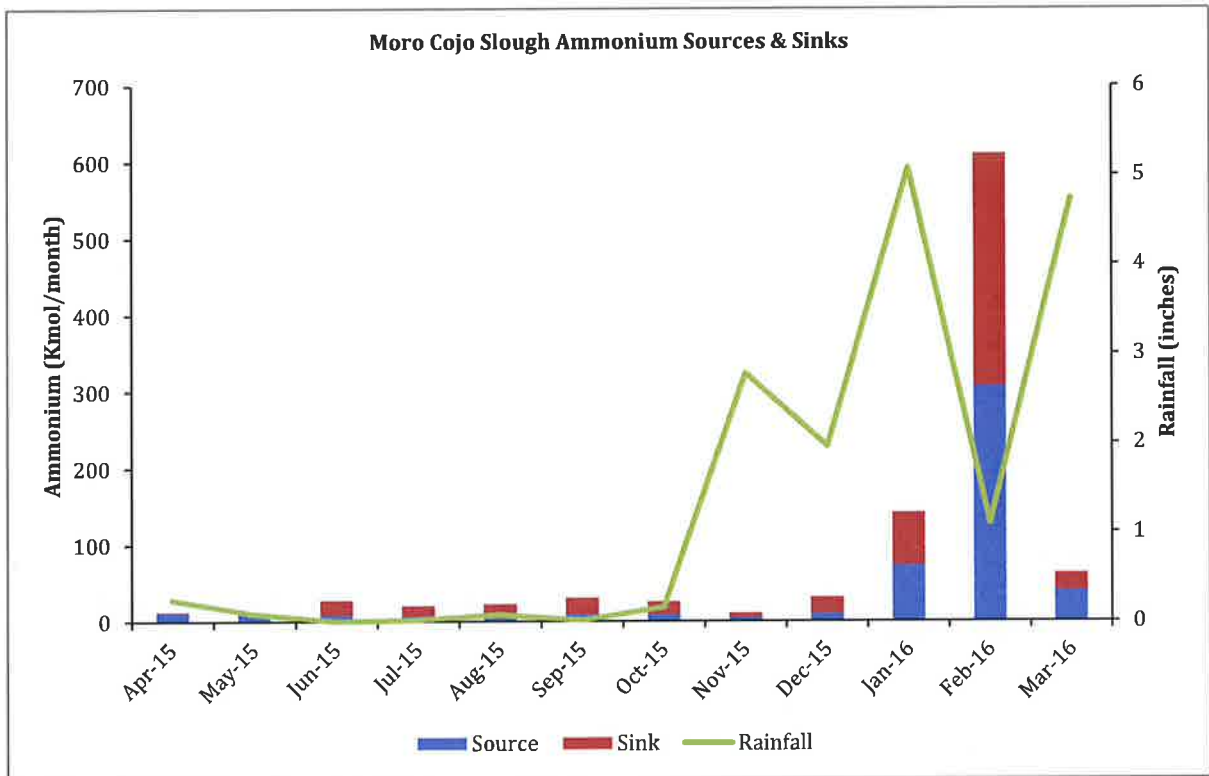


Fig. 45: Moro Cojo Slough Ammonium Total Sources and Sinks. Stacked Bars Represent Sources and Sinks. Green Line Represents Rainfall Each Month.

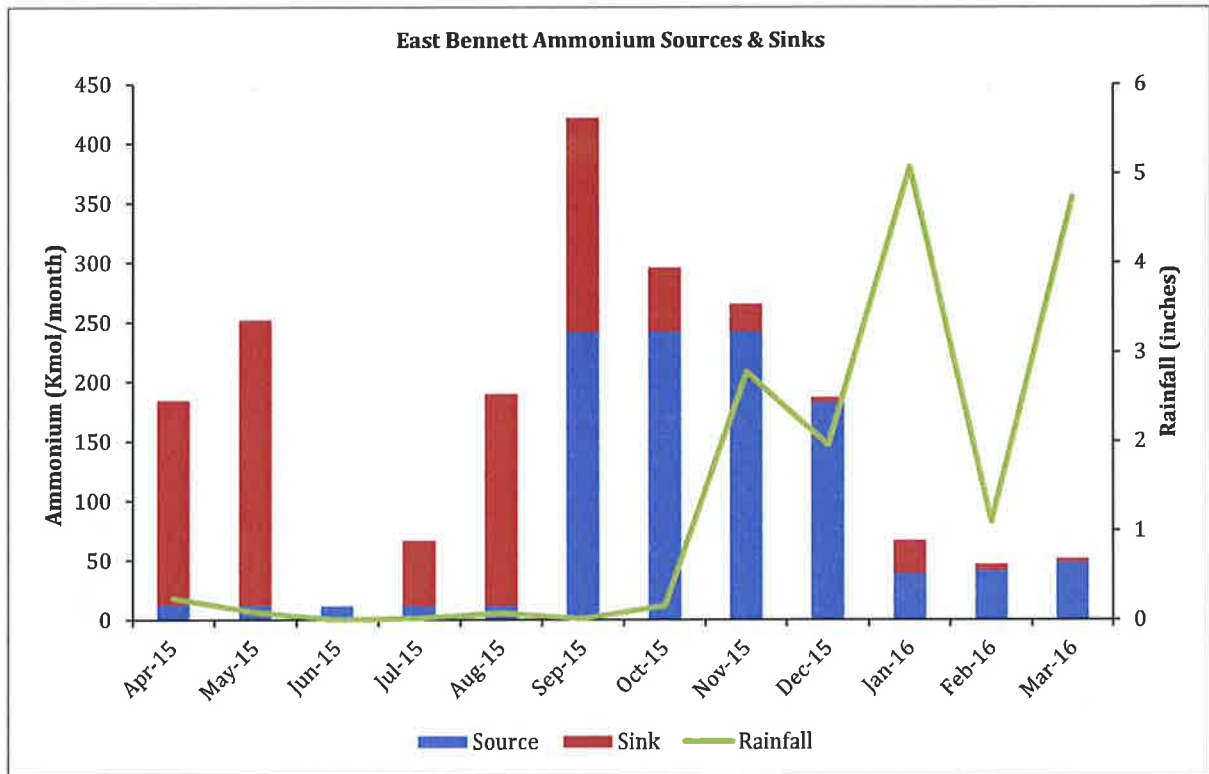


Fig. 46: East Bennett Slough Ammonium Total Sources and Sinks. Stacked Bars Represent Sources and Sinks. Green Line Represents Rainfall Each Month.

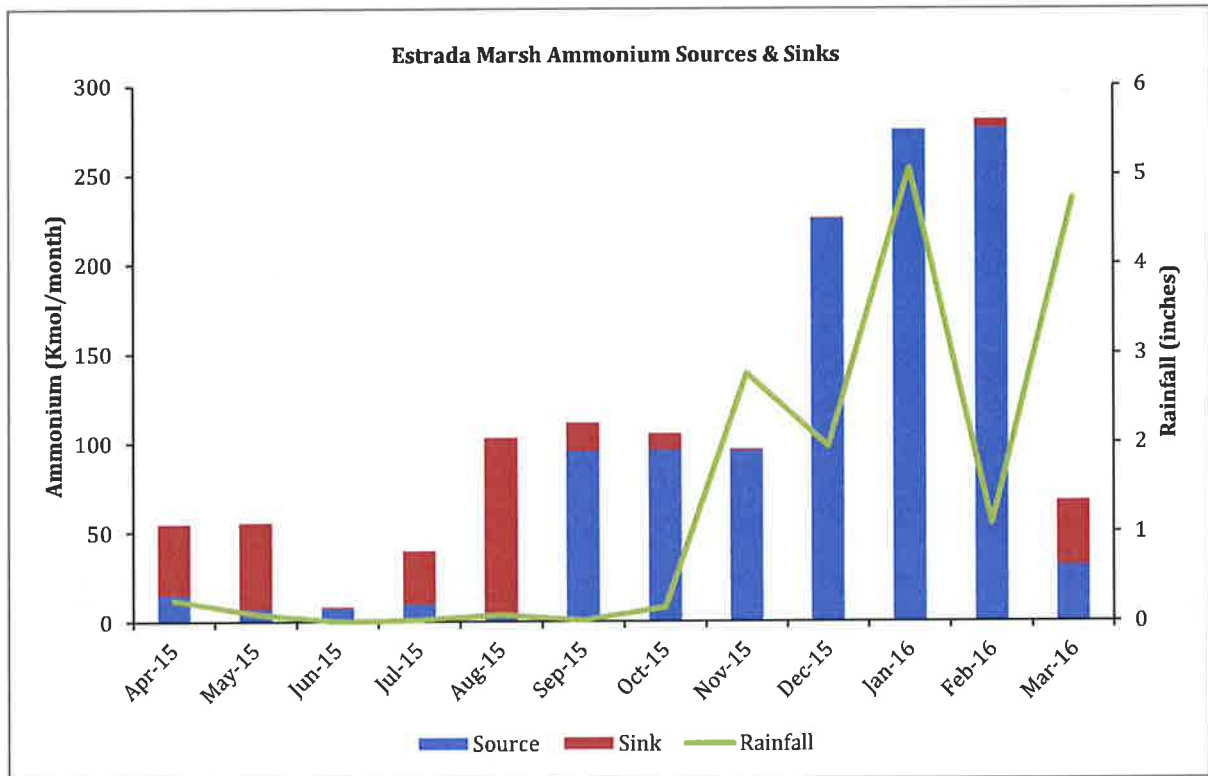
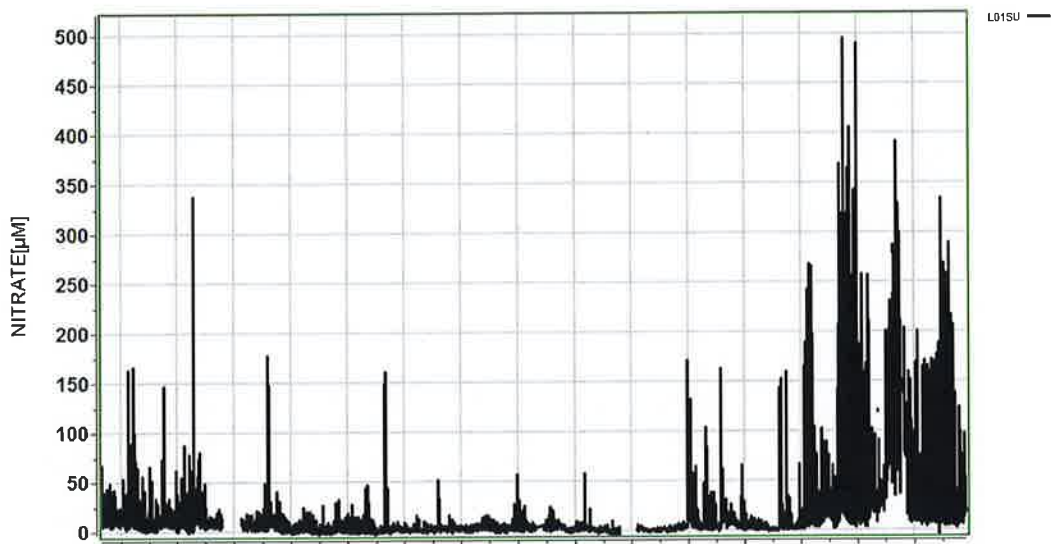
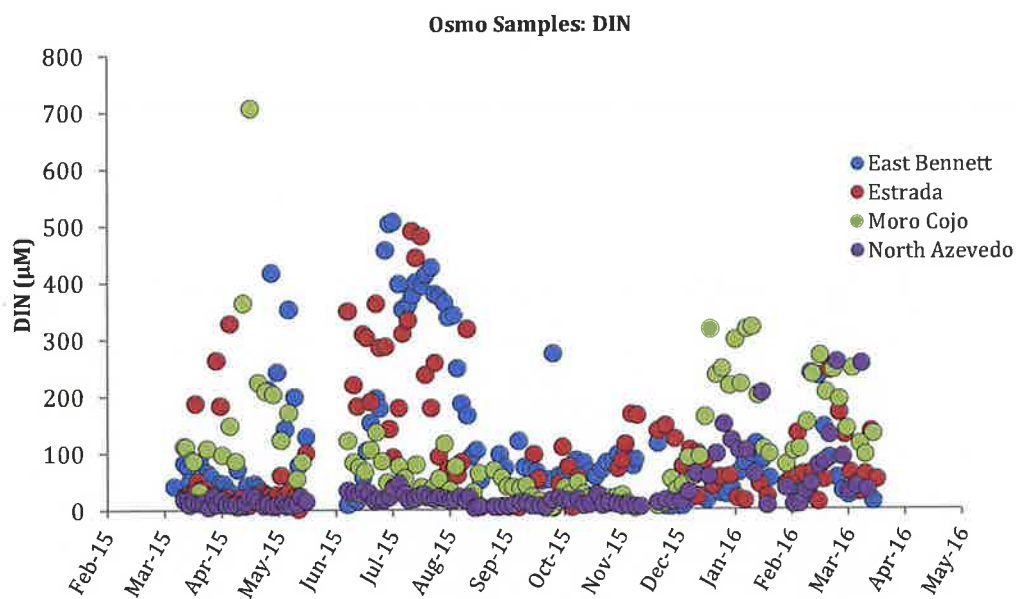


Fig. 47: Estrada Marsh Ammonium Total Sources and Sinks. Stacked Bars Represent Sources and Sinks. Green Line Represents Rainfall Each Month.



48a.



48b.

Fig. 48(a,b): Land/Ocean Biogeochemical Observation Buoy (LOBO) Nitrate Data (a.) Compared to OsmoSampler DIN Data (b.) During Same Time Scale (x-axis), With Different Nutrient Scales (y-axis).

Table 1. Average Seasonal Temperature, pH, Salinity and Dissolved Oxygen at Each Site.

Season	Site	°C	pH	Salinity (PSU)	DO (µM)
Spring	Estrada	19.36	8.74	43.84	257.55
Summer	Estrada	24.20	8.78	48.10	196.14
Fall	Estrada	20.76	7.88	40.79	167.44
Winter	Estrada	14.37	8.01	29.35	291.10
Spring	Moro Cojo	16.77	8.88	32.3	376.21
Summer	Moro Cojo	20.66	8.07	33.94	321.96
Fall	Moro Cojo	20.14	8.25	31.71	311.65
Winter	Moro Cojo	15.81	8.41	16.77	398.15
Spring	North Azevedo	18.04	8.11	36.94	280.30
Summer	North Azevedo	19.44	8.02	36.65	152.55
Fall	North Azevedo	22.1	7.97	35.97	248.31
Winter	North Azevedo	15.26	8.01	29.47	330.13
Spring	East Bennett	18.04	8.80	33.64	270.40
Summer	East Bennett	22.51	8.36	41.77	162.15
Fall	East Bennett	21.7	7.92	45.72	178.06
Winter	East Bennett	14.58	8.44	21.41	391.8

Table 2. Average Flow Rates and Hydraulic Residence Time.

<u>Site</u>	<u>Average Flow (m/s)</u>	<u>In or Out</u>	<u>Source</u>	<u>Area of culvert (m²)</u>	<u>Discharge (m³/second)</u>	<u>Discharge (m³/day)</u>	<u>Residence Time (days)</u>
East Bennett	0.05	In	North Harbor	0.3	0.02	648	19.5
East Bennett	0.04	In	Struve Pond	0.3	0.01	518.4	
East Bennett	0.19	Out	North Harbor	0.3	0.06	2462.4	
East Bennett	0.03	Out	Struve Pond	0.3	0.01	388.8	
Estrada	0.04	In	North Marsh	1.9	0.08	3283.2	4.13
Estrada	0.04	Out	North Marsh	1.9	0.08	3283.2	
Moro Cojo	0.13	In	Upper M.C.	4.68	0.61	26282.9	0.3
Moro Cojo	0.07	In	South Harbor	6.8	0.48	20563.2	
Moro Cojo	0	Out	Upper M.C.	4.68	0.00	0	
Moro Cojo	0.15	Out	South Harbor	6.8	1.02	44064	
North Azevedo	0.27	In	Kirby Park	1.7	0.46	19828.8	0.3
North Azevedo	0.1	Out	Kirby Park	1.7	0.17	7344	

Table 3. OsmoSampler Dissolved Inorganic Nitrogen Ranges and Averages for Each Site for Sampling Year (2015-2016).

Continuous (Osmosampler) DIN		
	DIN (uM) Range	DIN (uM) Average
Moro Cojo Slough	2.53 - 707.13	106.96 ± 10.63
North Azevedo Pond	2.81 - 258.46	31.42 ± 4.37
Estrada Marsh	1.67 - 490.32	95.95 ± 9.87
East Bennett Slough	4.85 - 506.98	124.62 ± 11.93

Table 4. Discrete Grab Sample Nitrate, Ammonium and Phosphate Ranges and Averages for Each Site for Sampling Year (2015-2016).

Discrete (Grab) Sample Nitrate, Ammonium, Phosphate						
	Nitrate (uM) Range	Nitrate (uM) Average	Ammonium (uM) Range	Ammonium (uM) Average	Phosphate (uM) Range	Phosphate (uM) Average
Moro Cojo Slough	0- 355.5	18.4 ± 10.27	0.5-107.1	18.6 ± 4.31	0.8-17.1	7.6 ± 1.08
North Azevedo Pond	0-130	10.9 ± 3.21	1.4-77.9	8.7 ± 1.79	0.8-10.6	3 ± 0.36
Estrada Marsh	0.3-19	4 ± 0.59	1.8-199.3	29.6 ± 6.88	0-62	5.3 ± 2.01
East Bennett Slough	0.4-272.7	26.6 ± 7.26	1.7-69	12.4 ± 1.78	1.1-22.8	6 ± 0.94

Table 5. East Bennett Monthly Grab Sample Nutrient Averages
 Errors represent an average nutrient concentration based on 3-4 individual weekly grab samples taken throughout the month.

Month	Nitrate (uM)	Ammonium (uM)	Phosphate (uM)
Apr-15	51.4 ± 30.07	6.31 ± 1.76	6.25 ± 3.00
May-15	129.94 ± 43.01	11.53 ± 2.23	4.73 ± 1.45
Jun-15	7.88 ± 2.89	5.17 ± 1.70	1.94 ± 0.29
Jul-15	3.95 ± 0.87	3.32 ± 1.31	3.05 ± 1.00
Aug-15	9.68 ± 0.25	16.96 ± 5.39	5.84 ± 0.68
Sep-15	5.12 ± 0.10	15.14 ± 2.85	15.26 ± 5.89
Oct-15	14.64 ± 6.99	15.01 ± 3.37	3.38 ± 0.45
Nov-15	14.36 ± 6.93	8.79 ± 3.07	3.33 ± 0.33
Dec-15	4.24 ± 3.45	4.51 ± 1.73	1.28
Jan-16	17.21 ± 3.48	18.04 ± 3.25	10.65 ± 3.30
Feb-16	17.4 ± 7.70	22.77 ± 8.58	9.72 ± 2.64
Mar-16	10.15 ± 9.43	37.43 ± 31.57	12.3 ± 4.23

Table 6. Moro Cojo Monthly Grab Sample Nutrient Averages

Errors represent an average nutrient concentration based on 3-4 individual weekly grab samples taken throughout the month.

Month	Nitrate (uM)	Ammonium (uM)	Phosphate (uM)
Apr-15	87.70 ± 18.18	2.36 ± 0.14	11.14 ± 4.04
May-15	160.72 ± 50.51	6.81 ± 1.88	6.9 ± 1.76
Jun-15	122.20 ± 32.08	3.61 ± 1.03	1.94 ± 1.23
Jul-15	105.51 ± 8.81	5.58 ± 1.08	8.68 ± 2.08
Aug-15	29.96 ± 0.61	12.57 ± 1.36	2.5 ± 0.44
Sep-15	47.98 ± 2.54	8.88 ± 0.40	3.33
Oct-15	44.17 ± 23.30	7.65 ± 2.46	3.02 ± 0.89
Nov-15	25.51 ± 9.11	24.05 ± 7.91	10.81 ± 3.02
Dec-15	5.53 ± 0.85	27.93 ± 10.86	1.28 ± 0.95
Jan-16	45.02 ± 27.54	84.76 ± 8.41	14.82 ± 0.79
Feb-16	59.72 ± 30.40	41.72 ± 19.56	14 ± 0.79
Mar-16	65.00	30.00	13.82

Table 7. North Azevedo Monthly Grab Sample Nutrient Averages

Errors represent an average nutrient concentration based on 3-4 individual weekly grab samples taken throughout the month.

Month	Nitrate (uM)	Ammonium (uM)	Phosphate (uM)
Apr-15	3.64 ± 2.04	3.01 ± 0.63	4.15 ± 0.80
May-15	4.60 ± 1.38	6.38 ± 2.04	3.75 ± 0.94
Jun-15	2.70 ± 1.75	3.2 ± 0.52	3.36 ± 0.88
Jul-15	4.00 ± 0.93	2.97 ± 1.29	3.84 ± 0.25
Aug-15	8.68 ± 0.11	2.30 ± 0.44	4.26 ± 0.39
Sep-15	4.82 ± 0.40	3.33 ± 0.07	1.93 ± 1.10
Oct-15	1.34 ± 0.46	3.68 ± 0.68	4.65 ± 2.97
Nov-15	6.52 ± 3.79	8.41 ± 2.84	1.97 ± 0.24
Dec-15	1.56 ± 0.42	6.84 ± 2.14	1.51 ± 0.40
Jan-16	24.17 ± 6.69	39.45 ± 19.33	2.58 ± 0.26
Feb-16	33.83 ± 24.22	15.11 ± 4.75	1.82 ± 0.19
Mar-16	19.36 ± 10.89	6.97 ± 1.19	6.72 ± 1.46

Table 8. Estrada Marsh Monthly Grab Sample Nutrient Average

Errors represent an average nutrient concentration based on 3-4 individual weekly grab samples taken throughout the month.

Month	Nitrate (uM)	Ammonium (uM)	Phosphate (uM)
Apr-15	2.17 ± 1.34	4.56 ± 1.97	1.83 ± 0.13
May-15	4.37 ± 1.65	3.44 ± 0.61	2.49 ± 0.82
Jun-15	4.05 ± 1.56	2.4 ± 0.28	2.19 ± 1.05
Jul-15	4.43 ± 1.20	4.25 ± 0.48	3.82 ± 0.81
Aug-15	9.36 ± 0.21	26.82 ± 13.04	7.94 ± 6.75
Sep-15	4.91 ± 0.14	4.92 ± 1.08	0.71 ± 0.71
Oct-15	2 ± 0.40	26.29 ± 9.66	7.39 ± 3.35
Nov-15	2.14 ± 0.58	97 ± 24.45	20.32 ± 17.97
Dec-15	1.86 ± 0.55	132.36 ± 41.51	13.24
Jan-16	8.38 ± 5.31	58.17 ± 25.87	4.68
Feb-16	3.44 ± 0.99	16.14 ± 3.64	0.98 ± 0.13
Mar-16	0.3 ± 0.01	8.54 ± 0.39	2.43 ± 1.57

Table 9. Porewater Diffusional Flux. *Negative values indicate a loss of nutrients from the water column (sink).*

		Phosphate $\mu\text{mol}/\text{m}^2/\text{day}$	Nitrate $\mu\text{mol}/\text{m}^2/\text{day}$	Ammonium $\mu\text{mol}/\text{m}^2/\text{day}$
East Bennett	Winter 2016	6.05	234.02	92.51
	Fall 2015	16.81	107.31	590.52
	Spring 2016	22.35	0.50	142.83
	Summer 2015	3.57	3.72	33.40
Estrada Marsh	Winter 2016	34.10	-0.59	646.15
	Fall 2015	31.66	138.97	523.17
	Spring 2016	51.15	-73.91	81.81
	Summer 2015	-1.17	-78.66	45.20
Moro Cojo	Winter 2016	2.95	-37.66	99.90
	Fall 2015	-0.49	76.50	420.98
	Spring 2016	0.25	-18.72	63.48
	Summer 2015	3.27	-0.85	21.58
North Azevedo	Winter 2016	18.71	-2.15	188.55
	Fall 2015	4.63	0.14	101.78
	Spring 2016	2.32	0.40	20.16
	Summer 2015	0.47	-0.18	1.21

Table 10. Seasonal Groundwater Flux

Groundwater Flux		
	September 2015 – Dry Season	March 2016 – Wet Season
Moro Cojo Slough	398.64 m ³ /day	1304.64 m ³ /day
East Bennett Slough	4500.76 m ³ /day	4670.6 m ³ /day
Estrada Marsh	3730.14 m ³ /day	6775.52 m ³ /day
North Azevedo Pond	880.6 m ³ /day	1610.24 m ³ /day

Table 11. Moro Cojo Slough Box Model Source and Sink Balance. Negative Values Indicate A Sink Value Greater Than A Source In The System – A Time With High Nutrient Removal

Month	Source (Kmol)	Sink (Kmol)	Nutrient	Sum (Sources - Sinks)	Yearly Sum Kmols/year (April – March)
Apr-15	11.89	1.09	Ammonium	10.80	-16.84
May-15	9.58	2.00	Ammonium	7.58	
Jun-15	8.92	18.98	Ammonium	-10.06	
Jul-15	7.55	13.29	Ammonium	-5.75	
Aug-15	4.30	18.69	Ammonium	-14.38	
Sep-15	9.53	21.18	Ammonium	-11.65	
Oct-15	9.13	16.94	Ammonium	-7.81	
Nov-15	4.82	5.69	Ammonium	-0.87	
Dec-15	9.88	21.41	Ammonium	-11.53	
Jan-16	73.56	68.63	Ammonium	4.93	
Feb-16	307.59	303.36	Ammonium	4.23	
Mar-16	40.14	22.47	Ammonium	17.68	
Apr-15	37.99	43.96	Nitrate	-5.97	-163.14
May-15	108.39	127.31	Nitrate	-18.92	
Jun-15	85.51	192.94	Nitrate	-107.43	
Jul-15	66.00	71.44	Nitrate	-5.44	
Aug-15	94.09	100.68	Nitrate	-6.60	
Sep-15	67.11	76.35	Nitrate	-9.24	
Oct-15	75.43	83.04	Nitrate	-7.61	
Nov-15	30.78	31.31	Nitrate	-0.53	
Dec-15	38.80	35.70	Nitrate	3.10	
Jan-16	145.70	150.26	Nitrate	-4.56	
Feb-16	907.97	917.49	Nitrate	-9.52	
Mar-16	240.11	230.54	Nitrate	9.58	
Apr-15	1.81	1.81	Phosphate	0.00	-18.41
May-15	2.91	3.41	Phosphate	-0.50	
Jun-15	3.75	6.89	Phosphate	-3.14	
Jul-15	59.04	77.96	Phosphate	-18.92	
Aug-15	54.56	55.46	Phosphate	-0.90	
Sep-15	2.43	4.36	Phosphate	-1.93	
Oct-15	4.47	6.30	Phosphate	-1.82	
Nov-15	3.96	5.67	Phosphate	-1.72	
Dec-15	19.17	16.83	Phosphate	2.34	
Jan-16	14.13	12.05	Phosphate	2.08	
Feb-16	132.52	130.93	Phosphate	1.60	
Mar-16	22.76	18.26	Phosphate	4.51	

Table 12. North Azevedo Pond Box Model Source and Sink Balance. Negative Values Indicate A Sink Value Greater Than A Source In The System – A Time With High Nutrient Removal.

Month	Source (Kmol)	Sink (Kmol)	Nutrient	Sum (Sources-Sinks)	Yearly Sum Kmols/year (April – March)
Apr-15	37.79	7.43	Ammonium	30.36	397.57
May-15	37.58	10.62	Ammonium	26.97	
Jun-15	1.64	5.92	Ammonium	-4.28	
Jul-15	2.57	5.70	Ammonium	-3.13	
Aug-15	8.96	8.58	Ammonium	0.37	
Sep-15	57.15	4.44	Ammonium	52.71	
Oct-15	66.14	25.55	Ammonium	40.59	
Nov-15	70.56	49.44	Ammonium	21.12	
Dec-15	42.93	2.09	Ammonium	40.84	
Jan-16	75.61	0.99	Ammonium	74.62	
Feb-16	97.98	26.28	Ammonium	71.70	
Mar-16	48.85	3.15	Ammonium	45.70	
Apr-15	0.36	71.76	Nitrate	-71.40	-321.06
May-15	0.28	71.14	Nitrate	-70.86	
Jun-15	0.34	6.41	Nitrate	-6.08	
Jul-15	1.28	7.76	Nitrate	-6.48	
Aug-15	6.91	11.96	Nitrate	-5.05	
Sep-15	5.17	19.13	Nitrate	-13.96	
Oct-15	6.73	21.43	Nitrate	-14.70	
Nov-15	9.99	35.20	Nitrate	-25.21	
Dec-15	1.40	13.43	Nitrate	-12.03	
Jan-16	10.63	22.39	Nitrate	-11.76	
Feb-16	66.53	81.11	Nitrate	-14.59	
Mar-16	1.44	70.40	Nitrate	-68.95	
Apr-15	0.59	4.86	Phosphate	-4.27	25.63
May-15	0.56	4.72	Phosphate	-4.16	
Jun-15	2.24	0.83	Phosphate	1.42	
Jul-15	2.41	0.43	Phosphate	1.98	
Aug-15	3.97	2.13	Phosphate	1.84	
Sep-15	8.86	1.37	Phosphate	7.49	
Oct-15	10.32	3.81	Phosphate	6.51	
Nov-15	11.02	4.14	Phosphate	6.87	
Dec-15	2.95	2.38	Phosphate	0.57	
Jan-16	8.64	3.05	Phosphate	5.59	
Feb-16	9.51	4.04	Phosphate	5.47	
Mar-16	0.92	4.60	Phosphate	-3.68	

Table 13. Estrada Marsh Box Model Source and Sink Balance. Negative Values Indicate A Sink Value Greater Than A Source In The System – A Time With High Nutrient Removal

Month	Source (Kmol)	Sink (Kmol)	Nutrient	Sum (Sources-Sinks)	Yearly Sum Kmols/year (April – March)
Apr-15	15.22	39.54	Ammonium	-24.32	851.65
May-15	7.05	48.38	Ammonium	-41.33	
Jun-15	7.72	0.73	Ammonium	7.00	
Jul-15	9.71	30.03	Ammonium	-20.32	
Aug-15	2.28	100.75	Ammonium	-98.47	
Sep-15	95.53	15.99	Ammonium	79.54	
Oct-15	96.07	9.27	Ammonium	86.80	
Nov-15	95.82	0.57	Ammonium	95.25	
Dec-15	225.69	0.26	Ammonium	225.43	
Jan-16	274.98	0.17	Ammonium	274.81	
Feb-16	276.45	4.55	Ammonium	271.90	
Mar-16	31.55	36.19	Ammonium	-4.64	
Apr-15	2.03	11.04	Nitrate	-9.01	49.15
May-15	1.01	30.50	Nitrate	-29.49	
Jun-15	1.33	0.50	Nitrate	0.83	
Jul-15	1.63	15.13	Nitrate	-13.50	
Aug-15	0.43	23.42	Nitrate	-22.99	
Sep-15	25.17	8.50	Nitrate	16.67	
Oct-15	25.39	1.06	Nitrate	24.33	
Nov-15	25.31	0.47	Nitrate	24.84	
Dec-15	54.97	0.32	Nitrate	54.65	
Jan-16	0.79	0.79	Nitrate	-0.01	
Feb-16	1.47	0.90	Nitrate	0.57	
Mar-16	3.96	1.71	Nitrate	2.25	
Apr-15	2.09	1.57	Phosphate	0.52	65.47
May-15	1.05	3.10	Phosphate	-2.05	
Jun-15	1.14	0.60	Phosphate	0.54	
Jul-15	1.56	3.00	Phosphate	-1.44	
Aug-15	0.35	3.37	Phosphate	-3.03	
Sep-15	6.14	0.30	Phosphate	5.84	
Oct-15	6.23	0.35	Phosphate	5.87	
Nov-15	6.18	0.09	Phosphate	6.09	
Dec-15	16.30	0.04	Phosphate	16.26	
Jan-16	17.27	0.04	Phosphate	17.23	
Feb-16	17.24	0.05	Phosphate	17.18	
Mar-16	3.58	1.14	Phosphate	2.45	

Table 14. East Bennett Slough Box Model Source and Sink Balance. Negative Values Indicate A Sink Value Greater Than A Source In The System – A Time With High Nutrient Removal

Month	Sum of Sources (Kmol)	Sum of Sinks (Kmol)	Nutrient	Sum (Sources-Sinks)	Yearly Sum Kmols/year (April – March)
Apr-15	12.97	171.85	Ammonium	-158.88	155.75
May-15	12.54	239.50	Ammonium	-226.95	
Jun-15	11.46	0.14	Ammonium	11.32	
Jul-15	11.55	55.21	Ammonium	-43.66	
Aug-15	11.42	178.71	Ammonium	-167.29	
Sep-15	242.23	179.66	Ammonium	62.57	
Oct-15	242.37	53.59	Ammonium	188.78	
Nov-15	242.39	23.25	Ammonium	219.15	
Dec-15	182.89	4.25	Ammonium	178.64	
Jan-16	38.72	27.91	Ammonium	10.81	
Feb-16	41.47	5.36	Ammonium	36.10	
Mar-16	48.38	3.22	Ammonium	45.16	
Apr-15	0.35	225.16	Nitrate	-224.80	-347.22
May-15	0.31	227.72	Nitrate	-227.41	
Jun-15	3.92	0.06	Nitrate	3.86	
Jul-15	3.96	33.06	Nitrate	-29.10	
Aug-15	3.94	55.36	Nitrate	-51.42	
Sep-15	31.10	38.63	Nitrate	-7.52	
Oct-15	31.31	22.89	Nitrate	8.42	
Nov-15	32.42	15.73	Nitrate	16.69	
Dec-15	32.33	2.11	Nitrate	30.21	
Jan-16	74.04	12.60	Nitrate	61.44	
Feb-16	79.42	7.85	Nitrate	71.57	
Mar-16	1.71	0.87	Nitrate	0.84	
Apr-15	1.72	12.40	Phosphate	-10.68	9.18
May-15	1.68	10.46	Phosphate	-8.78	
Jun-15	1.64	0.92	Phosphate	0.72	
Jul-15	1.67	5.12	Phosphate	-3.45	
Aug-15	1.64	6.61	Phosphate	-4.97	
Sep-15	9.66	9.77	Phosphate	-0.12	
Oct-15	9.74	1.37	Phosphate	8.37	
Nov-15	9.79	0.97	Phosphate	8.82	
Dec-15	6.07	0.19	Phosphate	5.88	
Jan-16	4.10	1.69	Phosphate	2.41	
Feb-16	4.07	0.56	Phosphate	3.51	
Mar-16	8.27	0.80	Phosphate	7.48	

Table 15. T-Test P-Values. Yellow Boxes Indicate a Significant Difference in Nutrient Loading Between Wet and Dry Seasons.

Site	Ammonium	Nitrate	Phosphate
East Bennett Slough	0.4632	0.077	0.2693
Estrada Marsh	0.0325	0.3002	0.0241
Moro Cojo Slough	0.1114	0.1639	0.3215
North Azevedo Pond	0.0261	0.1598	0.3663