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Water Quality in Bangs Lake: effects of recurrent phosphate spills to a coastal estuary: Year 2

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Abstract:

Grand Bay National Estuarine Research Reserve (GBNERR) is located in a relatively pristine estuary in the northern Gulf of Mexico, with ambient nutrient concentrations often below detection. However, since 2005, periodic breaches in a containment levee from a phosphogypsum stack have led to high phosphate levels (over 200 μM) while pH dropped from 7.5 to near 4.5. GBNERR staff assembled a phosphate working group to investigate scientific questions related to these phosphate loadings. This working group includes members from GBNERR, regional universities, marine labs, and Mississippi Department of Environmental Quality. They identified four essential questions needed to assess the impacts of repeated phosphate spills on water quality in an otherwise pristine ecosystem. (1) What is the fate of phosphorus after a spill? (2) Is there a preserved sedimentary record of past phosphorus spills? (3) Is there a biological fertilizer effect on benthic microalgae in this shallow photic system? (4) Is dry deposition of gypsum particles from the adjacent fertilizer plant a smaller but constant source of phosphorus to GBNERR? Research results will provide information critical for management of the Reserve.

Introduction

Two large phosphate spills have occurred from Mississippi Phosphate Corporation (a fertilizer production facility) to the Grand Bay National Estuarine Research Reserve's (GBNERR) Bangs Lake (Fig. 1) since 2005. Following these spills, phosphate concentrations in Bangs Lake surface waters rose from near zero to extremely high concentrations (as high as 7mg L^{-1} or $225\ \mu\text{M}$) and pH dropped dramatically from an average of ~ 7.5 to 3.7. Less dramatic changes in phosphate concentrations and pH were measured at other regularly sampled stations nearby, and large fish kills also occurred throughout the Reserve. In addition to delivery of phosphorus itself to coastal waters, other contaminants including trace elements and heavy metals that are hazardous to local

biota are conveyed in spill material (Salomons 1989). Further, there is some evidence of potential continuous input of phosphate to Bangs Lake from smaller sources (i.e. ongoing spills, dry deposition, and/or groundwater seepage). These events and the obvious biological impacts to the waters of a protected NERR warranted further investigation. While regular monitoring of water quality parameters and nutrient concentrations by the GBNERR's System Wide Monitoring Program (SWMP) provides basic information to detect these spills, the fate and persistence of the externally loaded phosphate within the system are poorly understood. For example, we know that phosphate concentrations remained elevated in surface waters for up to six months after a spill before returning to background concentrations, but we do not understand if phosphate is adsorbed and persists in sediments, flushed out of NERR waters by tidal action, or some combination of these two fates. We also do not know if there is a nutrient enrichment or 'fertilizer' effect on the ecosystem that could stimulate growth of phytoplankton, benthic microalgae, or species responsible for harmful algal blooms (Caffrey et al. 2013). In addition to acute phosphorus spills, dry deposition of phosphate-rich gypsum particles from large phosphorus stacks on the chemical plant site may be a smaller but consistent phosphate source to the GBNERR which may be responsible for frequently observed smaller phosphorus increases. Phosphorus is not typically measured in atmospheric monitoring programs, however, it is relatively simple and inexpensive to quantify (Williams et al., 1992).

The GBNERR assembled a Phosphate Working Group (PWG) to investigate scientific questions related to these anthropogenic phosphate loadings. This working group includes members from the GBNERR, regional universities and marine labs (University of Southern Mississippi/ Gulf Coast Research Lab, University of West Florida, and Dauphin Island Sea Lab/ University of South Alabama), and the Mississippi Department of Environmental Quality (DEQ) who are currently conducting MWRRI funded research that addresses the following scientific questions developed by the PWG to assess the water quality impacts of repeated phosphate spills on an otherwise relatively undisturbed estuarine ecosystem. In year 1, we conducted experiments to characterize phosphate adsorption by sediments in Bangs Lake and less impacted reference sites within the GBNERR (Bayou Cumbest, Bayou Heron). We found that sediments from Bangs Lake had a reduced capacity for phosphate adsorption due to previous phosphate exposure while sediments from the less impacted site had a much higher capacity for phosphate adsorption. Sediment core results also showed spikes in particulate phosphorus concentrations at depth consistent with historical phosphate spills preserved within the sedimentary record. We also observed increased benthic chlorophyll concentrations at the Bangs Lake site relative to nearby Bangs Creek and Bayou Heron, suggesting that benthic microalgae production in Bangs Lake is stimulated by periodic phosphorous spills and/or chronic atmospheric deposition of phosphorus. This was a consistent pattern throughout the summer months.

In Year 2 we completed radiometric dating analysis for sediment cores from Year 1 and expanded on our research in three ways, including addition of: 1) an artificial tracer (fluorescein) study to simulate a phosphorus spill which will allow direct visualization of a contaminated

plume and will allow us to track water movement in Bangs Lake to define likely areas of phosphate accumulation, 2) Iron and trace element analyses to spatially and temporally trace phosphate spills through detection of the chemical signature of other contaminants in spill materials, and 3) continuation of work from Year-1 at new sampling stations chosen based on outcomes of the tracer study and results of Year-1 to better define locations of effects. More than 99% of trace metals are bound to and retained in sediments, serving as an archive of historical changes in environmental conditions including contaminant exposure (Salomons 1998). Phosphate mineral fertilizers and the by-products from their production have distinct and traceable element profiles that can function like a fingerprint to indicate the types of pollution or contaminant entering a system. Ongoing work continued from Year-1 included sampling of sediment grain size, organic carbon and nitrogen content, phytoplankton and benthic microalgae concentrations, porewater and water column nutrient analyses, and airborne particulate phosphorous concentrations which will all be needed to support the newly proposed analyses and integrate the results of Year-2 with Year-1 data.

Sampling and Analytical Methods

Fluorescent dye tracer experiment to track water movement from spill area –

A fluorescent dye (fluorescein) was used as a surface water tracer to characterize movement of a parcel of tracer-laden fresh water that was released in north Bangs Lake. 1.5 kg of dye was added to a large tank filled with 750L fresh water and transported to the release site with MS DMR's oil skimmer pontoon boat. After release, surface water samples were collected at selected sites from small boats, canoes and kayaks into plastic sample bottles. We followed the colored water mass to collect samples based on visual observation of the dye after release. The position (latitude and longitude) of each sample location was determined with GPS units on each boat. In addition, ISCO automated water samplers were deployed to collect surface water samples at 15-60 minute intervals at two SWMP sampling locations (North Bangs Lake and Bangs Lake). Water samples were analyzed for fluorescein concentrations with a Turner field fluorometer that was calibrated with known fluorescein concentrations.

Grain size analysis

Sediment samples from the phosphorus inventory cores were used for grain size analysis using the pipette method (Folk 1974). Samples (ca. 20 g) were digested with peroxide to remove organic matter. Samples were sieved through 64 μm screen to retain the sand. After addition of 10 mL of dispersant (Calgon), the silt and clay fractions made up to 1 L was sampled from a graduated cylinder using fall velocity tables to determine the removal time.

Sediment cores phosphate inventory & ^{210}Pb dating - Eight sediment cores were collected from undisturbed locations in Bangs Lake and 2 cores were collected from less impacted reference sites (Bayou Cumbest and Bangs Lake) in at least 1.0 m of water using a 12.0 cm diameter x 30 cm long opaque PVC corer. We sectioned the sediment cores using clean methods in 1 cm

increments Each core was sectioned and processed within 24 hours of collection. To avoid cross contamination by sediments pressed along the wall of the corer, sediment sections were subsampled from the center using an acid-washed modified syringe corer. Subsamples were homogenized and divided into three portions to be analyzed for sediment phosphate concentrations, Lead-210 (^{210}Pb) activity, Cesium-137 (^{137}Cs) activity and Thorium-228:Thorium-232 ratios ($^{228}\text{Th}/^{232}\text{Th}$). Phosphate was analyzed as described by Aspila et al. (1976). Radiometric analysis and dating was conducted by the Geotop Lab at the University of Montreal Quebec using CRCS and CRS ^{210}Pb models.

Biological response to inputs from phospho-gypsum stack

Four sampling stations (BCr, BCr2013, BN, and BL; Figure 3) were selected to assess spatial variability associated with benthic microalgae and sediment characteristics near the phosphogypsum spill and contrast that with a control site far from the spill (BH). Two sites at an intermediate distance (BC and PC) were also sampled periodically. We collected sediment samples in summer and early fall from June through September in 2014 and June through October 2015. These results from 2014 and 2015 are compared with prior sampling from December 2012 and June 2013. Sediment nutrient bioassay experiments were conducted in June and August 2015 from Bangs Lake. In May 2015, Gary Baine began collecting monthly water samples from Bangs Lake to evaluate the response of phytoplankton to nutrient additions and the role of microzooplankton grazing on phytoplankton growth. This study provides a point of comparison to an earlier study on phytoplankton response to nutrient additions conducted in 2011 (Amacker 2013) before the inputs from the phosphogypsum stack began entering the Reserve.

Surface water samples were collected and later filtered through GF/F filters for chlorophyll a, nitrate+nitrite, ammonium and dissolved inorganic phosphate (DIP). Water quality parameters measured included temperature, salinity, dissolved oxygen concentration and pH. We calculated light attenuation using Beers Law from light profiles with a Licor 4 Pi sensor.

Sediment cores were collected using a push corer. Analyses were made in triplicate unless otherwise noted. Approximately 0.5 g from the top 0.5 cm layer was collected for analysis of chlorophyll a. The remaining top 0-1 cm surface layer was split into analyses for water content, sediment phosphorus and extractable P and NH_4^+ concentrations. For extractable nutrients, approximately 10 g of sediment was extracted with 10 mL of 1M NaCl for 15 minutes. Extracts were filtered through GF/F filters and later analyzed for DIP and NH_4^+ . Water content was determined by weight after drying at 60 °C for a week. In 2014, dry sediments were ashed at 500 °C for 1 hour to determine organic content. Water column and sediment chlorophyll samples were extracted in 6 mL of 90% acetone, sonicated and read after 24 h on a Turner Designs™ fluorometer (Welshmeyer 1994). Ammonium concentration was measured fluorometrically using an o-phthaldialdehyde and borate buffer reagent (Holmes et al. 1999). Nitrate + nitrite concentrations were measured using cadmium reduction to nitrite with subsequent addition of

sulfanilamide and N-1 naphthyl ethylenediamine dihydrochloride (Jones 1984). Phosphate was measured as in Parsons et al. (1984). Sediment phosphorus was measured as in Aspilla et al. (1976) where inorganic P is measured in dry sediments, total P was in ashed sediments and organic P was calculated as the difference.

Two types of nutrient bioassay experiments were conducted in 2015 from Bangs Lake, one with water to examine the phytoplankton community response to nutrient additions and the other with sediments to examine the response of benthic microalgae to nutrient additions. Starting in May 2015, we collected 10 L of water, filtered it through 80 μm mesh to remove large grazers and dispensed into 21 acid-washed, 250 ml polycarbonate bottles. Triplicate bottles of each treatment of the bioassay experiment were: (1) no nutrient addition (control), (2) nitrate only (15 μM N), (3) ammonium only (15 μM N), (4) phosphorus only (1 μM P as PO_4^{3-}), (5) silicate only (15 μM Si), (6) all nutrients, nitrogen, phosphorus and silicate (15 μM N, 1 μM P, 15 μM Si) and (7) a 10% diluted treatment with all nutrients to examine the effect of microzooplankton grazing. Bottles were incubated for 48 hours in a temperature controlled room under fluorescent lights with PAR levels of approximately 250 $\mu\text{mol photons m}^{-2} \text{ s}^{-1}$. In vivo chlorophyll fluorescence was measured initially and daily thereafter. After 48 hours, 60 ml samples were filtered onto GF/F filters to analysis of extracted chlorophyll. We performed similar bioassays using surface sediments. The top 1 cm was slurried and dispensed into 20 mL vials along with 10 mL of GF/F filtered sample water. The treatments were (1) a no nutrient addition control, (2) ammonium only (60 μM NH_4^+), (3) phosphate only (4 μM P) or (4) both ammonium and phosphate. After 24 and 48 hrs in the controlled temperature and light incubator, approximately 1 g of sediment was removed for chlorophyll a analysis. Phytoplankton production alone was estimated using the Cole and Cloern (1987) BZI method, which uses chlorophyll concentrations, secchi disk depth and daily light data, all values currently collected by the Reserve.

Potential nitrification and nitrogen fixation experiments were also conducted using sediments. Nitrification is the microbial oxidation of ammonium to nitrate. It was measured in aerobic sediment slurries where approximately 1 g of surficial sediment was dispensed into 50 mL centrifuge tubes along with 50 mL of filtered site water (Henriksen et al. 1981). Tubes were amended to a final concentration of 500 μM NH_4^+ . Initial and final (24 hr) samples were collected for analysis of nitrite and nitrate + nitrite. These are considered potential measurements because the required substrates, NH_4^+ and oxygen are added in excess. Experiments were conducted in July and September 2014 from Bangs Lake, Bayou Heron and Bangs Creek and in September and October 2015 from Bangs Lake and Bayou Heron. Nitrogen fixation is the reduction of dinitrogen gas to ammonium. In freshwater, phosphorus inputs often stimulate nitrogen fixation by cyanobacteria, while in marine systems, nitrogen fixation rates are generally low. Nitrogen fixation was measured using the acetylene reduction method which has been a standard technique since the 1970s (McCarthy and Bronk 2008). If nitrogen fixation is occurring, acetylene will be reduced to ethylene by the nitrogenase enzyme. In 2014, the top 1 cm of sediment was incubated under aerobic conditions while in 2015, the top 10 cm were incubated

under anaerobic conditions. Samples were incubated in an air tight flask and the headspace was replaced with 10% acetylene. Headspace samples were collected at 30 minute intervals over a 3 hour time course in syringes and analyzed in a GC with an FID detector for analysis of ethylene. Preliminary nitrogen fixation experiments were conducted in June and July 2014. Additional experiments were conducted in September and October 2015.

Particulate phosphate dry deposition

An automated wet/dry deposition collector was also used to collect settled airborne particles using the dry deposition side of the collector. These samplers have a rain sensor that automatically covers a dry bucket side of the collector during rain events. Buckets were cleaned with Neutrad laboratory soap, rinsed with deionized water, rinsed with 1.2N HCl, then rinsed thrice with DI water and then dried in a 40°C oven. Clean buckets were stored in plastic bags and then deployed on the dry deposition side of the collector and allowed to sit in the field for 20-40 days before being collected. Collected sample buckets were covered with aluminum foil, labeled and stored in sealed plastic bags at room temperature until analysis. For analysis, 50 to 100 mls of 1.2 N HCl was poured into the sample bucket which was then swirled carefully to wet the sides of the bucket. The acid was allowed to soak for 30 minutes then the buckets were swirled again and then the acid sample was filtered into clean vials and analyzed as described above for filter samples.

Airborne particles for phosphate analysis were collected on 47mm glass fiber filters with HiQ VS-Series Air Sampling Systems to estimate dry deposition to the study area. Filters were placed into the filter holder and air was pumped thru the filter for 10 to 14 days at a flow rate of 20 to 35 LPM. Flow rates were recorded when each filter was deployed and retrieved. An additional sampler was installed and sampled for the same time interval at a reference site located 5 miles inland from Ocean Springs in west Jackson County (38 miles away). After samples were collected the filters were placed into a plastic petri dishes dried in a 60C oven and then stored in a desiccator until analysis. For analysis, the filters were put in a glass vial with 20 mls of 1.2N hydrochloric acid and then placed in an incubator shaker (40C at 75 RPM) for 3-4 days to begin to extract the phosphorus from the filters. Sequential extractions with 20 mls of 1.2 N HCl for 3-4 days were conducted until all phosphorus had been recovered. The resultant liquid samples for each extraction was transferred to clean vials, neutralized with 10N sodium hydroxide and analyzed for phosphate colorimetrically (Strickland and Parsons, 1972). Sodium phosphate standards were made with 1.2 N HCl, neutralized with 10N NaOH and analyzed in the same manner as the samples.

RESULTS

Fluorescent dye tracer experiment to track water movement from spill area –

The tracer experiment was conducted on June 30, 2015 during a falling tide. We were able to track the fluorescein plume for approximately 4 hours. The tracer slug was advected south from

the release site and flowed along the marsh edge in the northeast portion of Bang Lake before being transported into the Bangs Bayou channel by the falling tide. Sample fluorescein concentrations are shown for hours 1 to 4 in Figures 4 - 7. Once in this deeper channel fluorescein concentrations dropped below detection quickly due to vertical mixing processes that diluted the tracer (Figure 7).

Grain size analysis

Percent silt-clay was lowest at the Bangs 2 site and highest the Bangs 1 and Bayou Heron sites (Figure 8). Percent silt-clay increased with depth at the western Bangs Lake sites (Bangs 2 and 3). The northeastern Bangs site (Bangs 1) showed little variability in texture with depth while Bangs 4 and Bayou Heron cores showed a general increase in silt-clay content to 12.5 cm depth and then decreased deeper in the cores.

Sediment cores phosphate inventory, ²¹⁰Pb dating and Porewater Analysis

Particulate organic phosphorus in all sediments cores increased toward the surface (Figure 9). Particulate organic phosphorus concentrations in Bayou Heron sediment core sites differed between 2014 and 2015 are shown separately in Figure 9A. Core phosphate concentrations from western Bangs Lake (Bangs 2 and 3) showed little variation between the two years hence the values presented as means for both years. West sites in Bangs Lake (nearer MS Phosphates) were similar to control (Bayou Heron), while east sites further from the source site had similar patterns but higher values, with distinct peaks near 13 cm and 4 cm depth in the Bangs 1 core, ~corresponding to the years in the 1980s and mid to late 2000s, respectively (Figure 9B; Tables 1-4). When these high values are removed (Figure 10), the remaining data more clearly show that phosphorus values were higher at depths above 7 cm at these sites on the east side of Bangs Lake, suggesting continuously higher phosphorus inputs in recent years (~corresponding to years since 2010 at all sites; Tables 1-4).

During 2015, sites on the eastern side of Bangs Lake (sites 1 and 4; Figure 11) had significantly higher phosphate concentrations in sediment porewater than the control site (Bayou Heron). TDN concentrations were higher than Heron Bayou only at the northeast site (site 4; Figure 10).

Biological response to inputs from phospho-gypsum stack

Hydrographic conditions

Summer temperatures ranged from 28 to 30 °C and was similar in both years at the Bangs Lake SWMP station (Fig 12). Salinity is normally at a minimum in the spring and increases throughout the summer and into the fall. In 2014, the minimum summer salinity was 6.2 and the maximum was 28.7, while in 2015, minimum salinity was 10.1 and maximum was 29.9 (Fig 12).

Sediment characteristics

Except for Bangs Creek and mid Bayou Cumbest, sediments were predominantly fine sand, with a relatively low water content. The highest sediment phosphorus values, both inorganic and

organic were at the two Bangs Creek stations. Bangs North also had high inorganic phosphorus concentrations. Surprisingly, there was little difference between sediment phosphorus concentrations either inorganic or organic in Bangs Lake and sites further away (Table 1, Figure 13). There were declines in the inorganic P at Bangs Creek and Bangs North between 2013 and 2015, although variability between replicates was high. In contrast extractable P in surficial sediments was significantly higher at Bangs Lake than Bayou Heron (Table 1, Figure 14, t-test $p = 0.04$). A vertical profile of extractable P and NH_4^+ from September 2015 revealed that P concentrations in the top 0-4 cm was higher at Bangs Lake than Bayou Heron ($p=0.002$) while the concentrations in the 4-6 cm layer was similar (Figure 15). In contrast, while extractable NH_4^+ in surficial sediments was generally higher at sites near the phosphogypsum stacks (Table 1), there was variability over time (Figure 16) and surficial sediments from Bangs Lake were not significantly different from Bayou Heron (t-test $p = 0.71$). However, vertical profiles of extractable NH_4^+ from Bangs Lake in September 2015 were significantly higher than at Bayou Heron (Figure 16, $p<0.001$).

Primary Producers

The highest concentrations of benthic microalgae occurred at Bangs Creek 2013 in June 2013 prior to sampling funded by MWRRI (Figure 17). Benthic chlorophyll was often higher at Bangs Lake compared to other locations (Figure 17). It was significantly greater at Bangs Lake than Bayou Heron (t-test $p = 0.004$). Benthic microalgae showed little response to additions of NH_4^+ , P addition or both nutrients (Figure 18). There was no significant difference ($p>0.05$) between nutrient treatments and control samples in either June or August (Figure 18). On average, light levels on the bottom were above 5% of surface irradiance and often above 20% (Figure 19), levels potentially high enough to saturate photosynthesis by benthic microalgae (Gattuso et al. 2006)

Phytoplankton biomass as measured by water column chlorophyll a concentrations were generally highest in the summer (Figure 20). Concentrations across the NERR were higher in 2015 than 2014 (Figure 20, K. Cressman, pers. Comm.). Nutrient bioassays revealed that the greatest response to nutrient additions during late fall and winter (Figure 21). Positive growth rates only occurred in nitrogen addition treatments and there were no consistent differences between ammonium and nitrate. Phosphate or silicate did not stimulate phytoplankton growth, although nitrate plus silicate did (Figure 21). These results are similar to Amacker (2013) which found that phytoplankton growth was only stimulated by N additions and never by P additions. The diluted + nutrient treatment (all diluted) had significantly higher growth rates than the corresponding whole water + nutrient treatment (all) (Figure 22). This suggests that grazing by microzooplankton can affect phytoplankton growth rates and is likely responsible for the negative growth rates observed in the control, P and Si treatments during summer months. Phytoplankton production based on the Cole and Cloern (1987) BZI model was highest during the summer months when chlorophyll a concentrations were high and longer daylight occurred.

Productivity was generally higher at Bayou Cumbest and Point aux Chenes compared to Bangs Lake or Bangs North (Figure 23).

A principal component analysis was conducted with the June data from 2013-2015. The first three components could explain 71.5 % of the variance in the data (Table 2). The first principal component was dominated by water column chlorophyll, water column chlorophyll, sediment chlorophyll and extractable P with stations closer to the phosphogypsum stacks separating from the stations further away (Figure 24). The second principal component was dominated by salinity, temperature, percent surface irradiance and water column ammonium concentrations which led to the stations grouping by year (Figure 24). There was much less difference among the stations in 2015 than in 2013 (Figure 24).

Sediment nitrogen transformations

Potential nitrification rates were highest in July 2014 at Bangs Creek (Figure 25). Rates from Bangs Lake and Bayou Heron were similar to one another and during all three sampling periods (Figure 25). There was little difference between 2014 and 2015 sampling dates. Because nitrogen fixation measurements in 2014 only included the top 1 cm of sediment and were incubated aerobically, rates were much lower and not directly comparable to rates measured in 2015. In 2014, nitrogen fixation was correlated to concentrations of extractable P (Figure 26), with rates near the gypsum stacks being somewhat higher than rates at Bayou Heron. In September 2015, nitrogen fixation was significantly higher at Bayou Heron than Bangs Lake which was slightly negative (Figure 27). However by October, rates at Bayou Heron had declined and were similar to those at Bangs Lake (Figure 27).

Particulate phosphate dry deposition

Phosphate dry deposition rates ranged from 2.4 to 64.8 ug P m⁻²d⁻¹ and was highest on March 2, 2015 (Figure 28) while deposition rates at the West Jackson County reference site ranged from 3.8 to 28.0 ug P m⁻²d⁻¹. The amount of bucket deposition samples collected from the reference site are more sparse than the Grand Bay site due to mechanical problems with the rain/dust collector and frequent contamination from birds utilizing the sides of the bucket. It appears that the Grand Bay site typically had higher rates of phosphate deposition than the background site however the smaller number of samples collected from the reference site does make direct statistical comparisons impossible. The average dry deposition rate for the Grand Bay site was 23.3 ± 16.1 ug P m⁻²d⁻¹ while the average deposition rate for the reference site was 15.0 ± 10.4 ug P m⁻²d⁻¹

Relevant Findings:

This study has shown that much of the phosphate release during major industrial spills from Mississippi Phosphate Corporation is adsorbed by sediments and then sequestered in the benthos. It is still unclear however what proportions of this excess phosphorus is buried versus how much is flushed out of Bangs Lake due to tidal action. Sediment cores collected from Bangs Lake had higher particulate organic phosphorus concentrations and distinct peaks of phosphorus were

found in cores collected from the southeast portion of Bangs Lake. Benthic chlorophyll a concentrations were highest in Bangs Lake and were higher at sites with high extractable phosphorus. Preliminary experiments suggested that phosphorus inputs can stimulate nitrogen fixation and growth of cyanobacteria.

List of student by institution and Major that received training for this project:

<u>Name</u>	<u>Level</u>	<u>Major</u>
Sarah Holcomb (USM)	Junior	Geology
Tiffany Berry (USM)	Junior	Geology
Jenna Sleek (UWF)	Senior	Biology
Rachel Capps (UWF)	Junior	Biology
Yishen Li (DISL)	Junior	Biology
Joshua Millwood (DISL)	Junior	Biology

Table 1 – Characteristics of sediments in Grand Bay. Average concentrations of water content, inorganic and organic sediment phosphorus, extractable phosphorus and ammonium.

Station	Sand content	Silt content	Clay content	Water content	Inorganic P	Organic P	Extract P	Extract NH4
	%	%	%	%	μmol/gdw	μmol/gdw	nmol/cm ³	nmol/cm ³
Bangs Creek 2014	nd	nd	nd	50%	722	633	2.25	33.2
Bangs Creek 2013	15%	52%	33%	44%	1311	1304	2.79	51.8
Bangs North	76%	23%	1%	49%	1212	232	1.46	33.0
Bangs Lake	95%	3%	1%	50%	330	303	6.52	21.1
Bangs Bayou	96%	2%	2%	26%	nd	nd	2.34	34.2
mid Bayou Cumbest	38%	40%	22%	nd	nd	nd	0.37	79.3
Point aux Chenes	74%	22%	4%	42%	267	361	2.76	13.3
Bayou Cumbest	86%	10%	4%	55%	nd	nd	1.32	46.1
Bayou Heron	85%	10%	5%	47%	495	231	0.98	17.2

Table 2 – First three Eigenvectors from principal component analysis using data from June in 2013, 2014, 2015.

Variable	PC1	PC2	PC3
% variation	35.9	23.2	12.4
Salinity	0.184	-0.427	0.182
Temp	0.091	-0.51	-0.195
DO	0.281	-0.136	-0.316
Percent Surface Irradiance	0.188	0.494	0.071
Water Column chlorophyll	-0.44	0.129	0.037
Water Column NH ₄ ⁺	0.152	0.324	-0.244
Water Column DIP	-0.442	-0.01	-0.257
Percent Water	-0.062	0.151	-0.72
Sediment Chlorophyll	-0.365	-0.101	-0.217
Extractable P	-0.276	0.25	0.344
Extractable NH ₄ ⁺	-0.379	-0.127	-0.007
Distance from stacks	0.273	0.247	-0.115

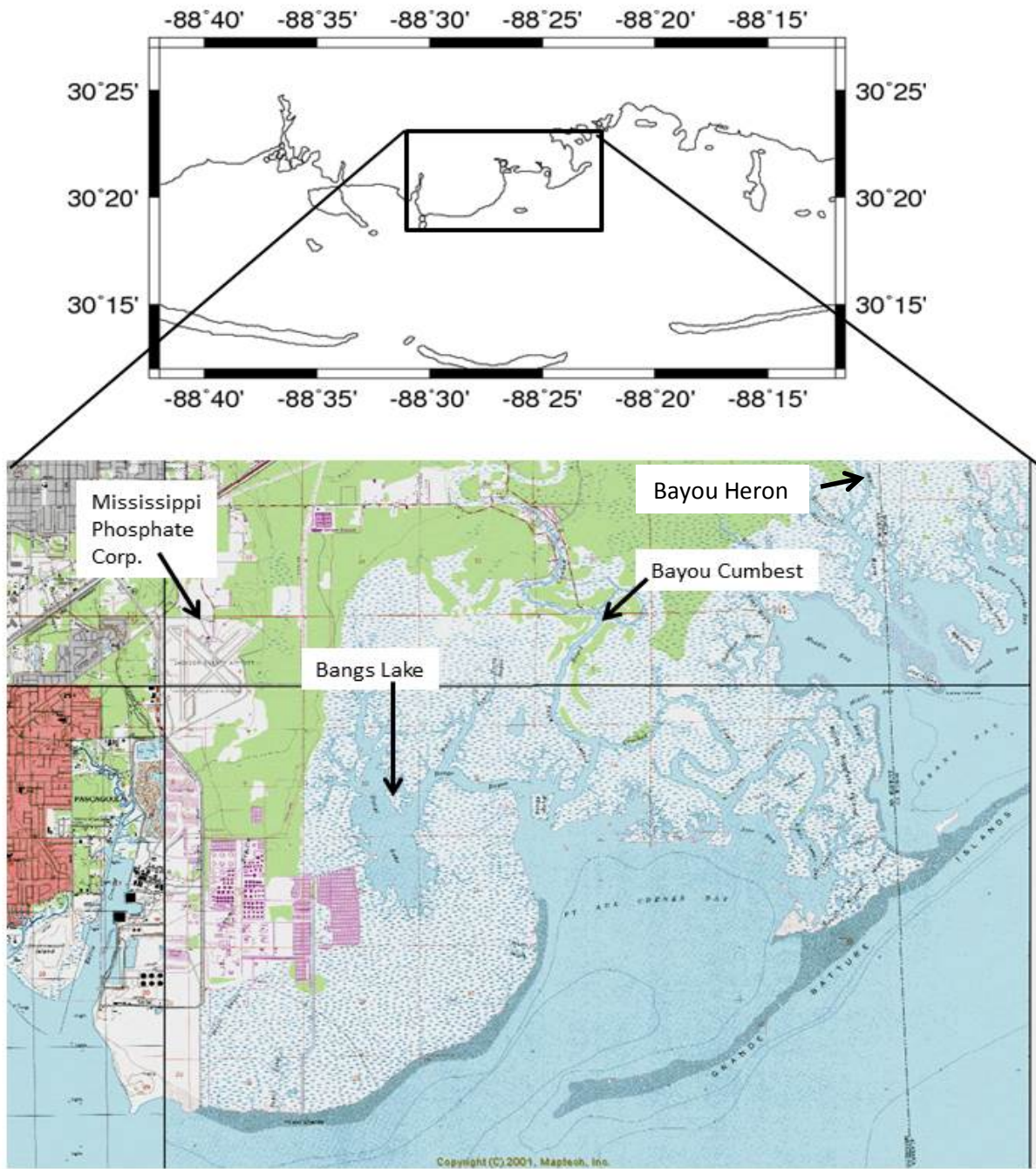


Figure 1. Map of the study sites (Bangs Lake, Bayou Cumbest, and Bayou Heron). The location of nearby gypsum stacks at Mississippi Phosphates Corporation are shown for reference.

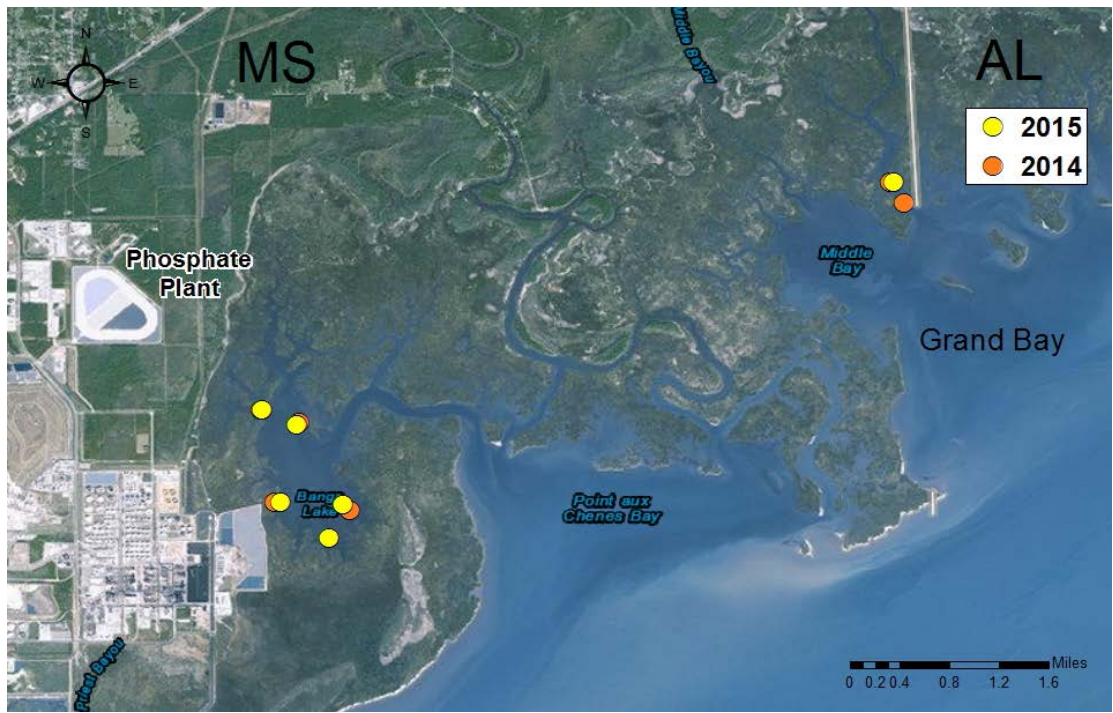


Figure 2. Map of Bangs Lake Bangs Lake sampling sites of sediment cores used for phosphate inventory and radiometric dating. Numbers denote core site numbers: 1 = Southeast (SE) 2 = Southwest (SW) 3 = Northwest (NW) 4 = Northeast (NE)



Figure 3. Location of benthic algae and sediment sampling stations in 2013-2015. BB and mid BC were only sampled in 2013.

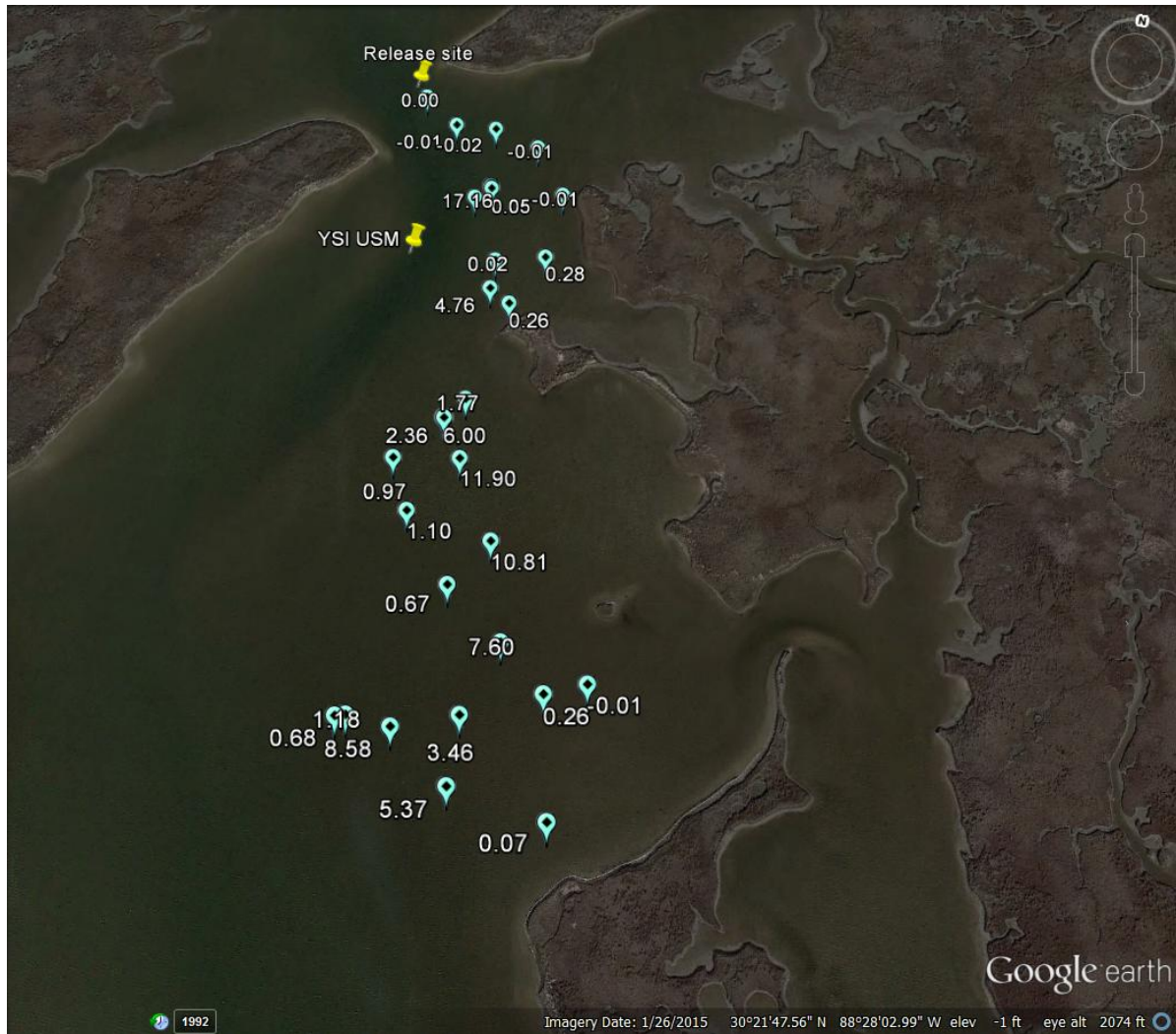


Figure 4. Fluorescein concentrations (ppm) collected in hour 1 of the tracer experiment.



Figure 5. Fluorescein concentrations (ppm) collected in hour 2 of the tracer experiment.



Figure 6. Fluorescein concentrations (ppm) collected in hour 3 of the tracer experiment.



Figure 7. Fluorescein concentrations (ppm) collected in hour 4 of the tracer experiment.

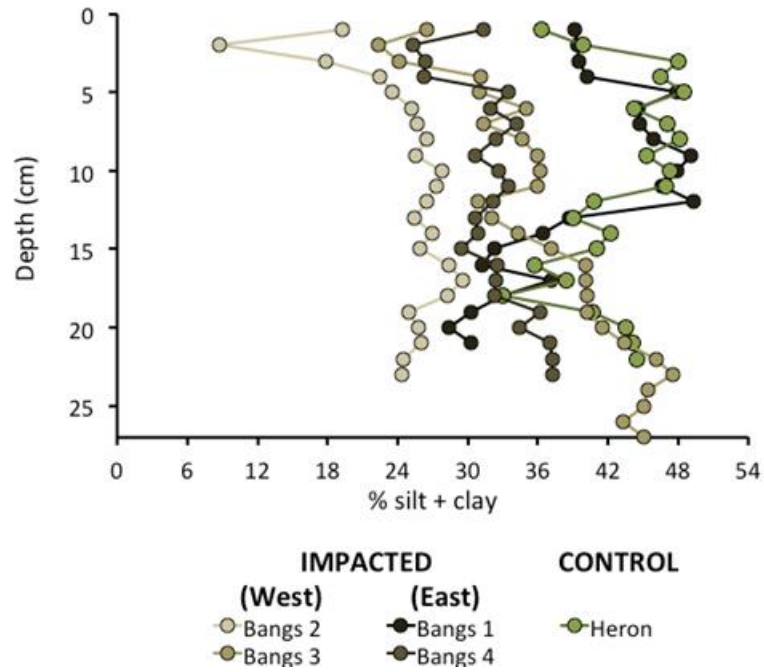


Figure 8. Results of grain size analysis for sediment samples collected in Bayou Heron and Bangs Lake.

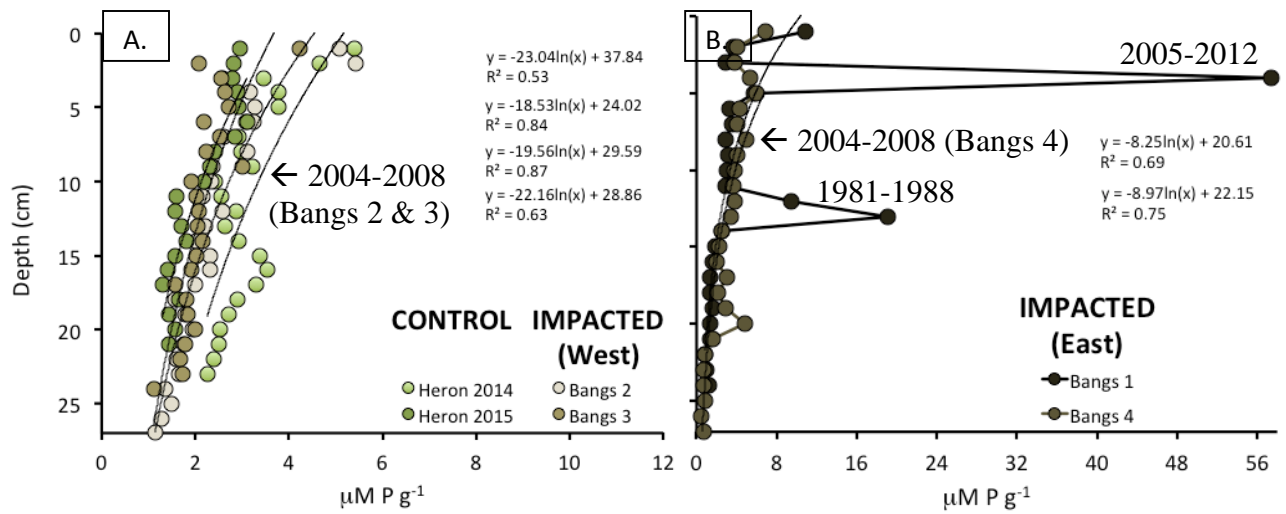


Figure 9. Concentrations of particulate organic phosphorus in sediments from Bayou Heron and 4 sites in Bangs Lake sampled during 2014 and 2015.

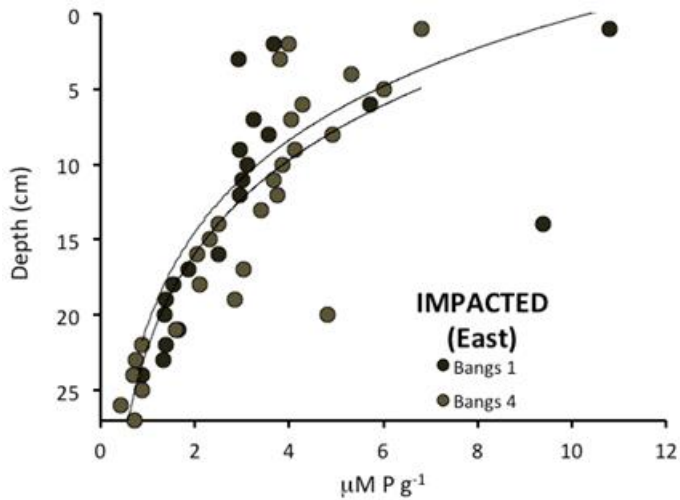


Figure 10. Concentrations of particulate organic phosphorus in sediments from Figure 9B with high concentrations removed from trendline.

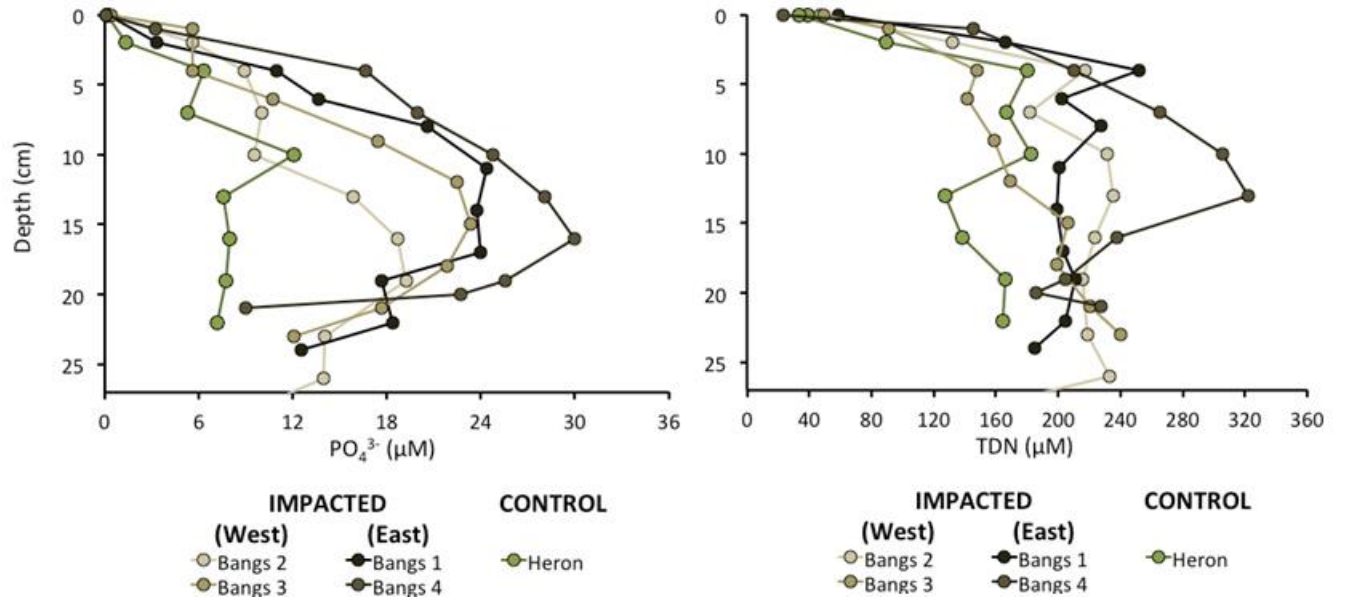


Figure 11. Porewater phosphate (left panel) and total dissolved nitrogen (right panel) concentrations from Bangs Lake and Bayou Heron coring sites.

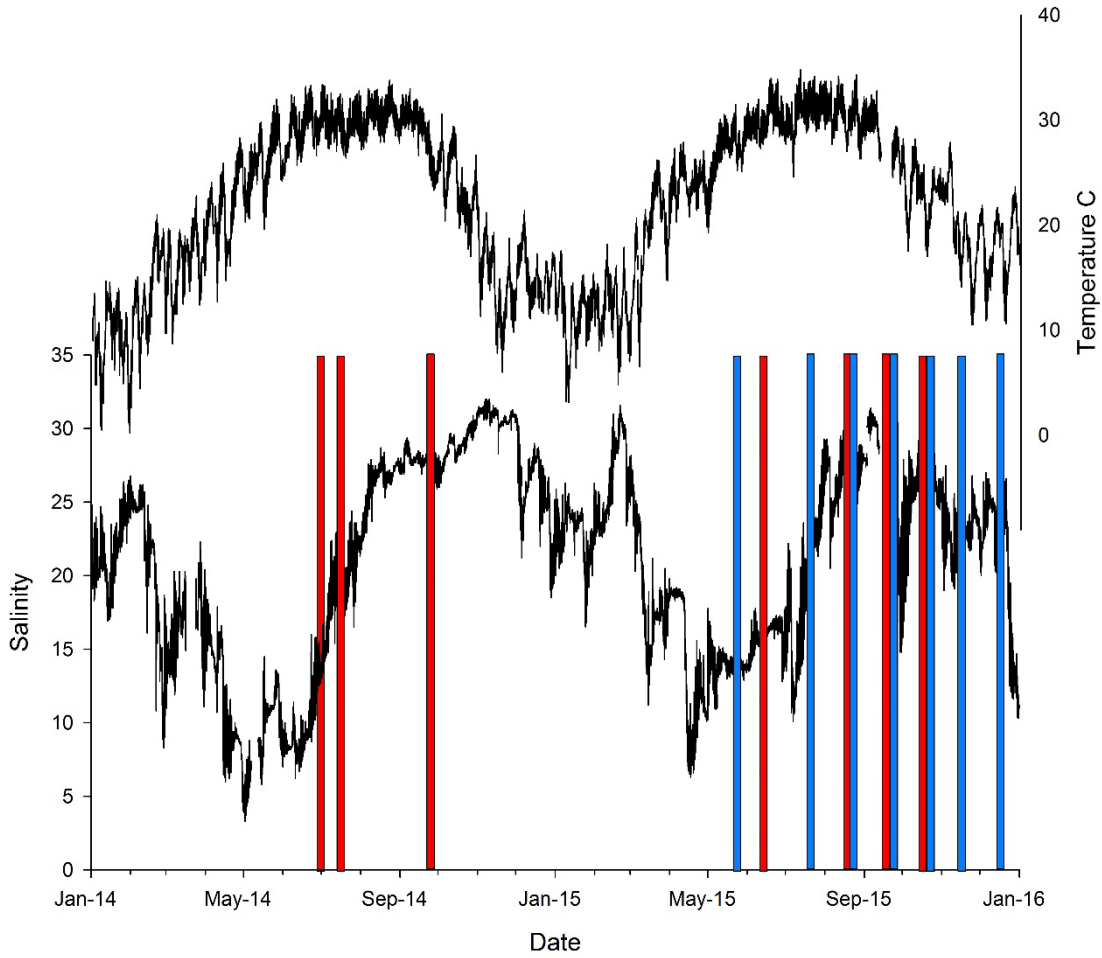


Figure 12. Temperature (°C) and Salinity between January 2014 and December 2015 from SWMP datasonde at Bangs Lake. Red bars represent sediment sampling dates. Blue bars represent water sampling for phytoplankton nutrient bioassays.

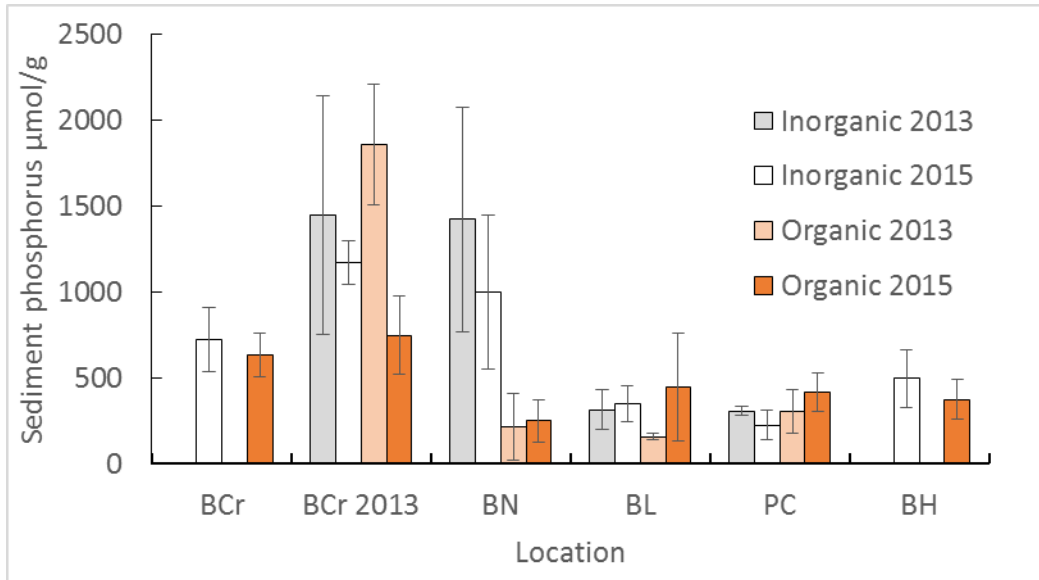


Figure 13. Surficial sediment phosphorus concentrations $\mu\text{mol/g}$ from June 2015 and June 2013 samples in Grand Bay. Mean \pm S.E.

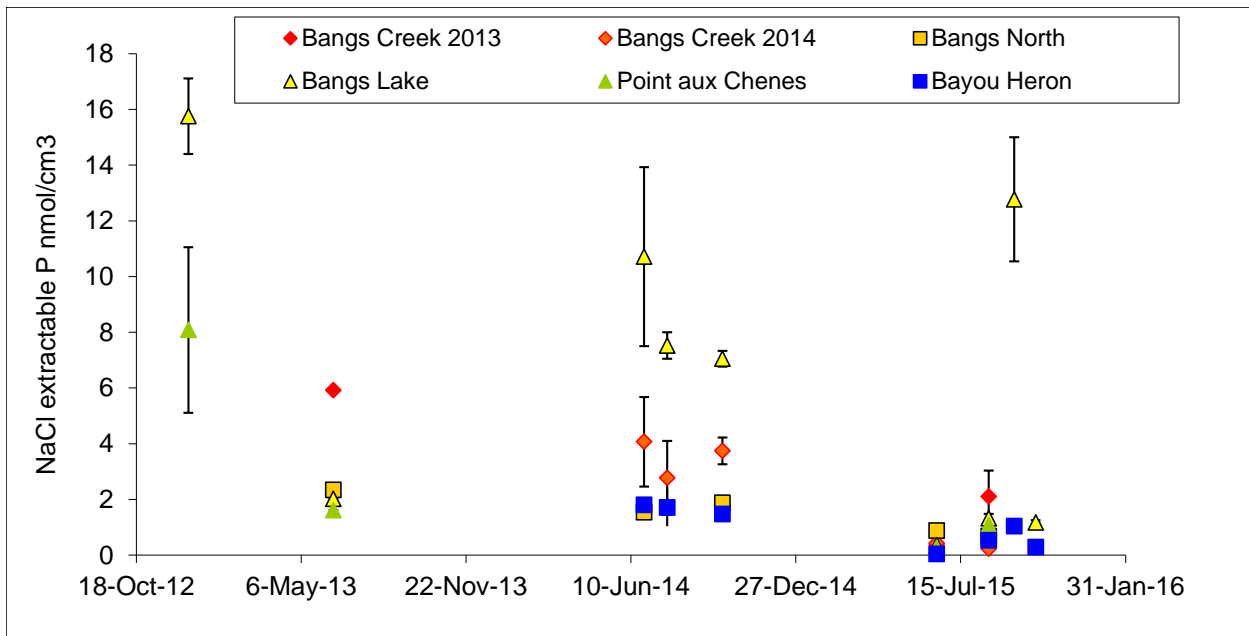


Figure 14. Extractable P (nmol/cm^3) in surficial sediments in Grand Bay. Mean \pm S.E.

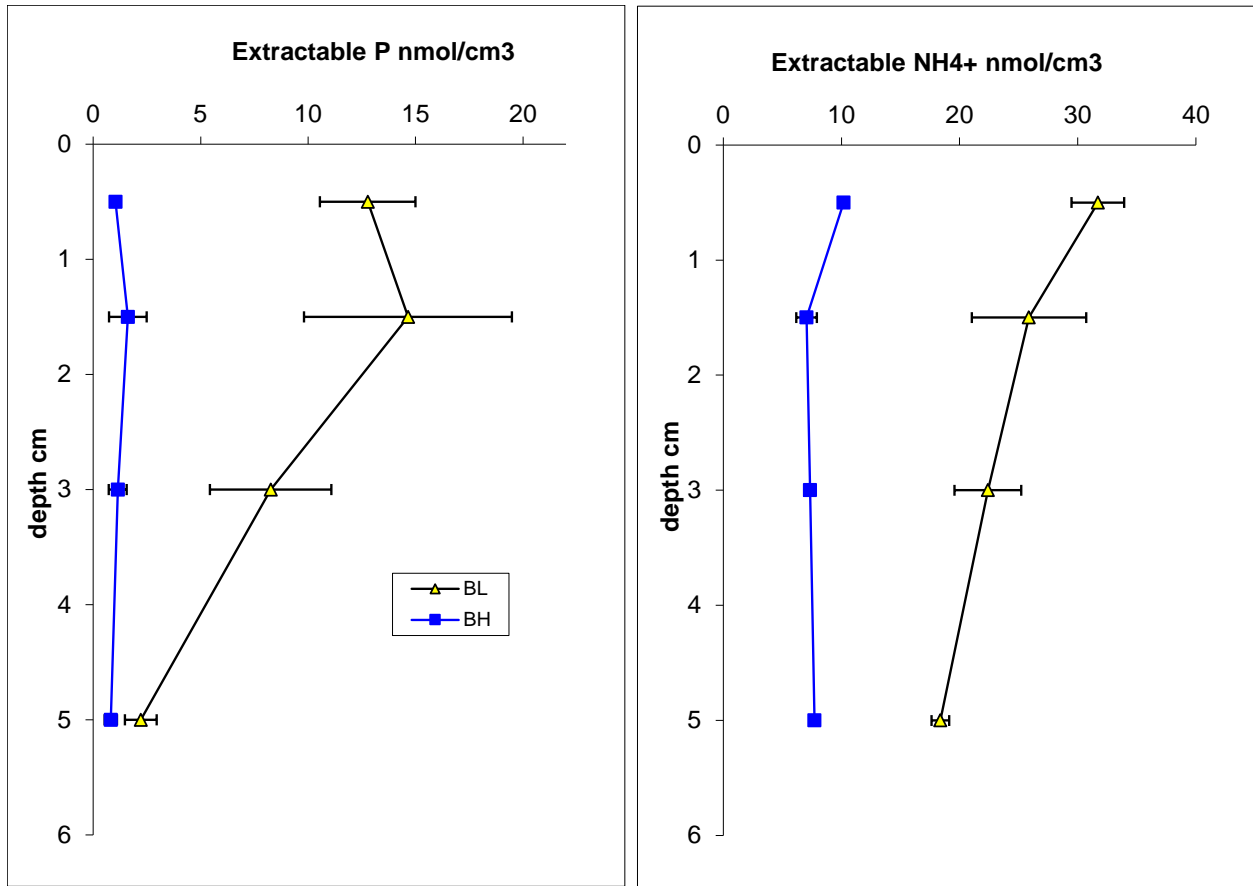


Figure 15. Vertical profile of extractable P (left panel) and NH₄⁺ (right panel) in Bangs Lake and Bayou Heron from September 2015. Mean \pm S.E.

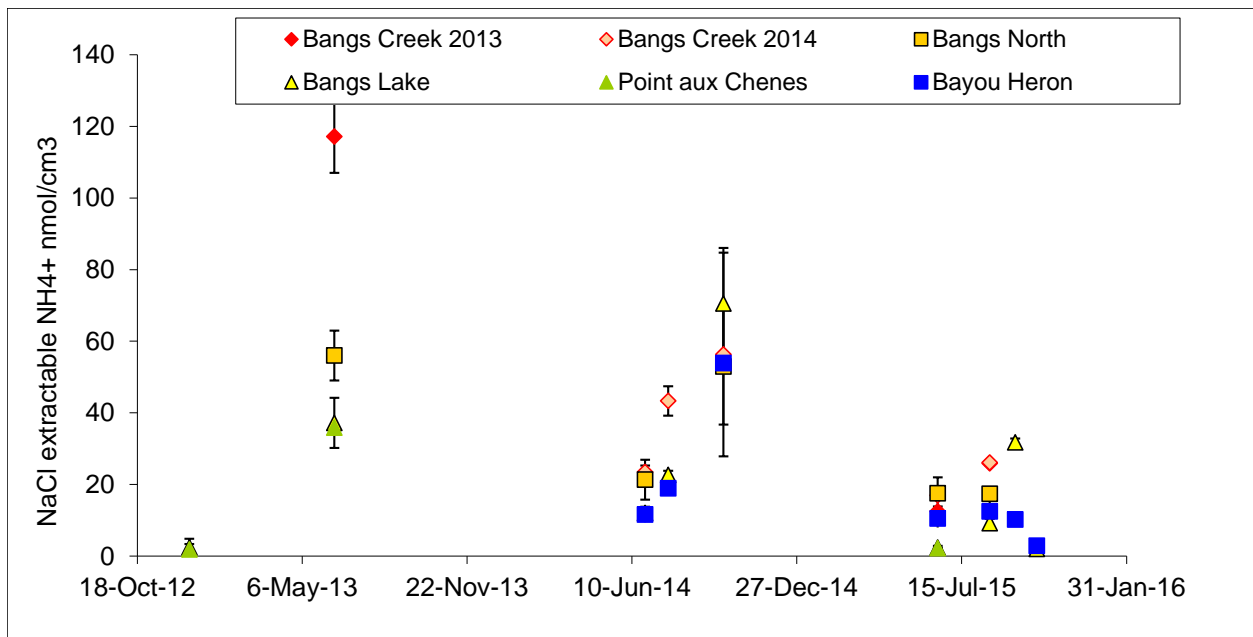


Figure 16. Extractable NH₄⁺ (nmol/cm³) in surficial sediments in Grand Bay. Mean \pm S.E.

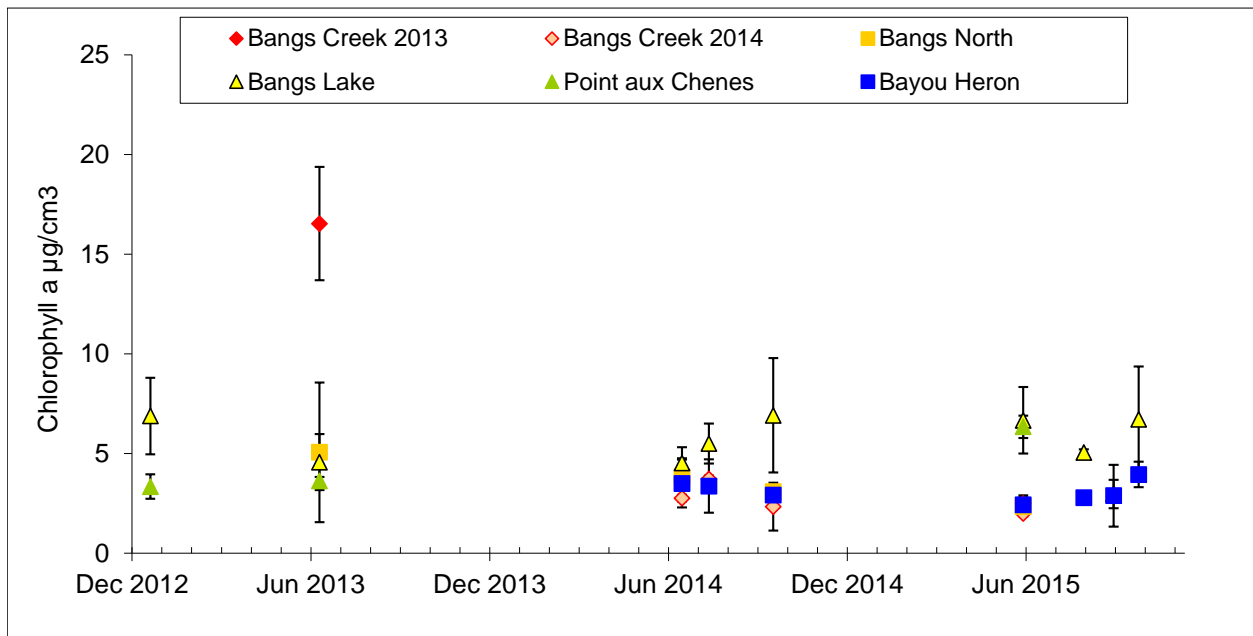


Figure 17. Sediment chlorophyll concentrations ($\mu\text{g chl a/cm}^3$) in surficial sediments from Grand Bay. Mean \pm S.E.

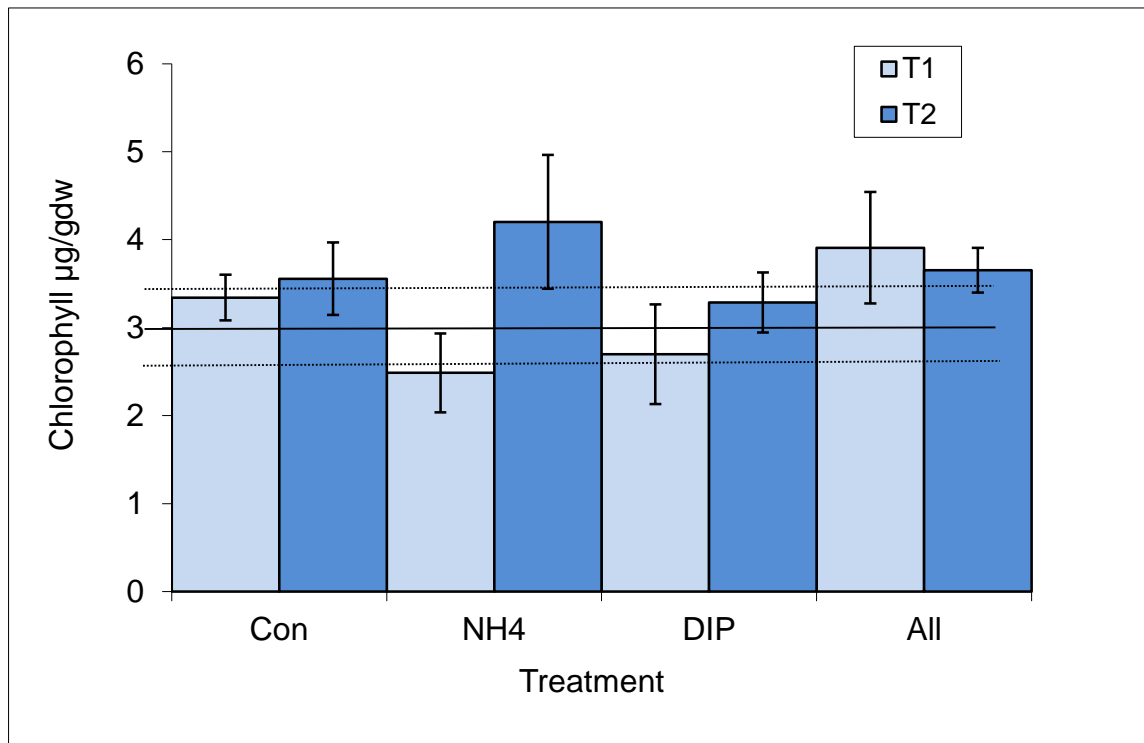
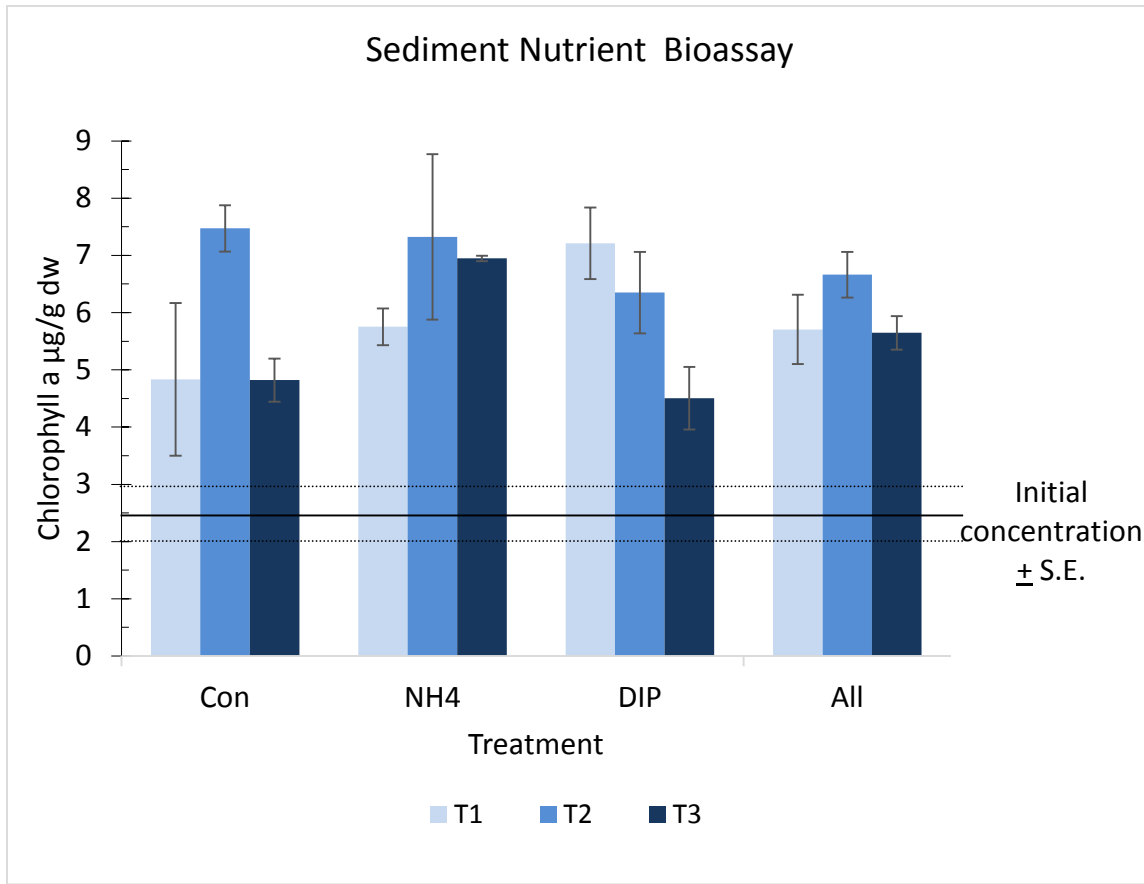


Figure 18. Nutrient bioassay experiment for benthic microalgae from Bangs Lake in June and August 2015. Solid line indicates initial concentration. Control treatments Mean \pm S.E.

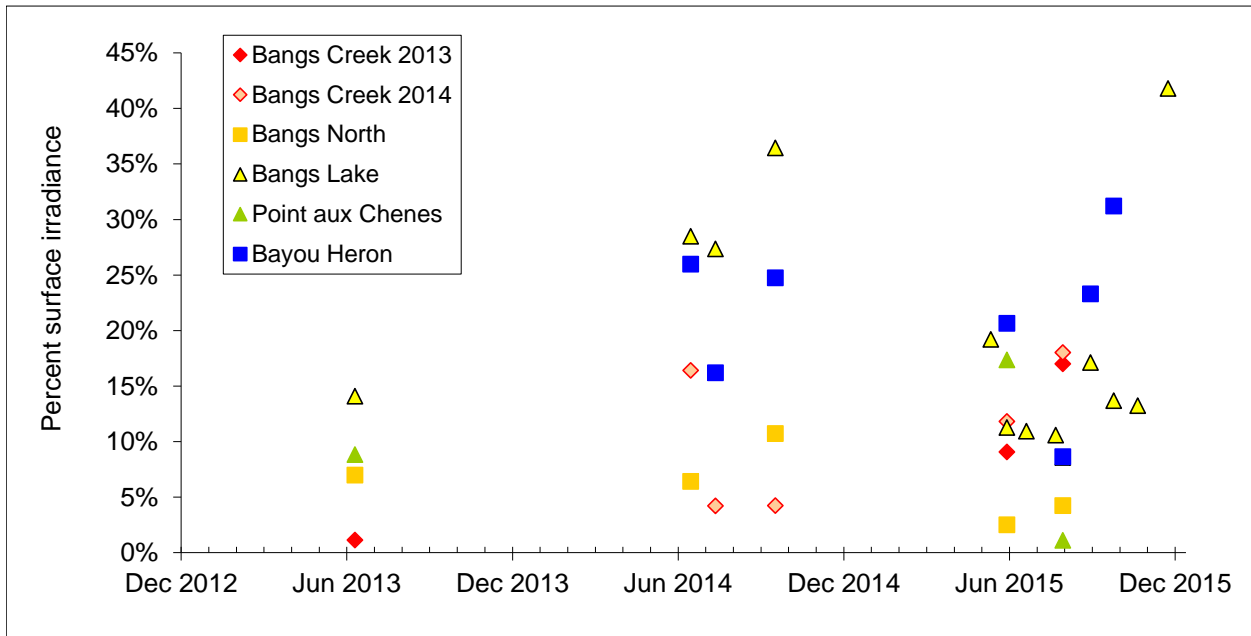


Figure 19. Percent of surface irradiance on bottom in Grand Bay. Values calculated based on k_d and water depth

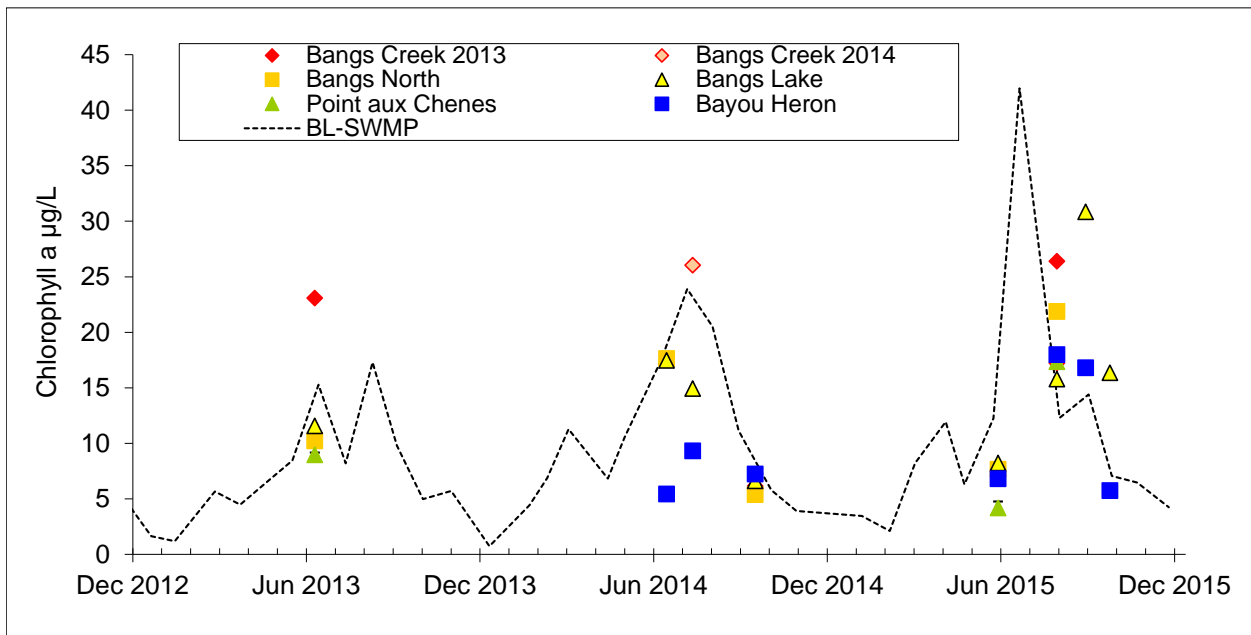


Figure 20. Water column chlorophyll a ($\mu\text{g chla/L}$) from Grand Bay. Dotted line represents monthly SWMP monitoring data from Bangs Lake (K. Cressman, pers. Comm.).

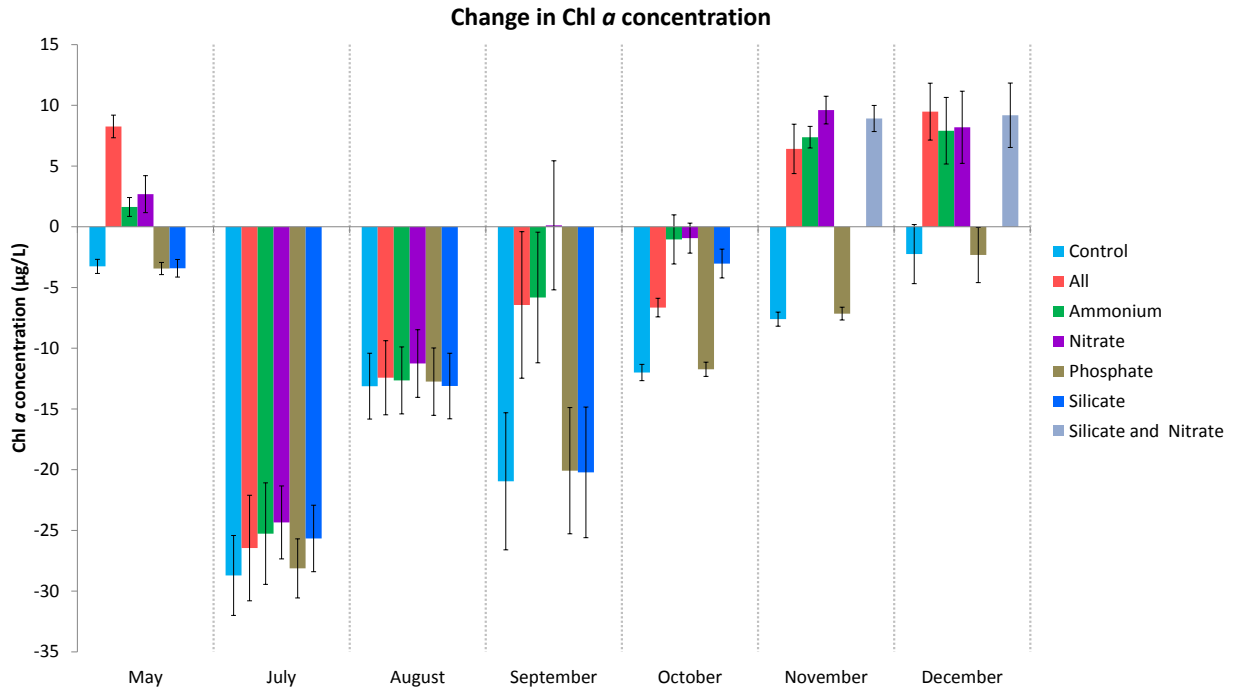


Figure 21. Phytoplankton nutrient bioassays from Bangs Lake between May 2015 and December 2015. Change in chlorophyll a concentration after 48 hrs relative to initial concentrations. Bars represent the change in chlorophyll a over 48 hours. Mean \pm SD.

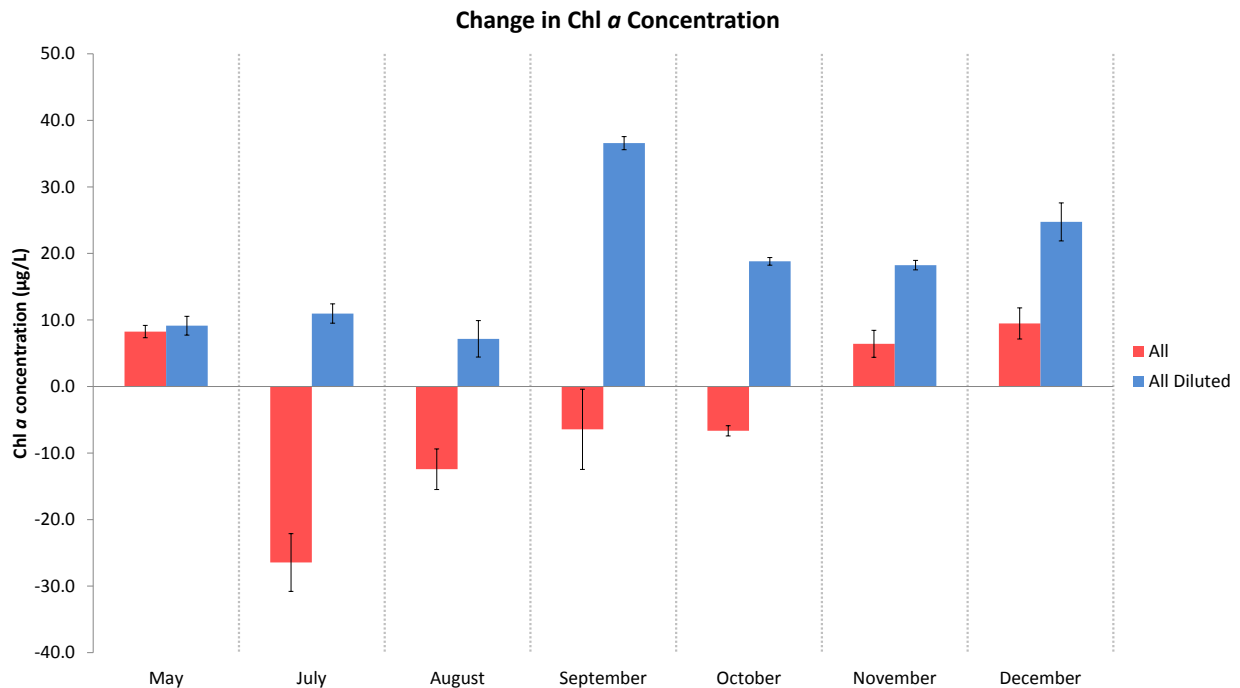


Figure 22. Effect of microzooplankton grazing on phytoplankton growth in Bangs Lake between May 2015 and December 2015. Change in chlorophyll a concentration after 48 hrs relative to initial concentrations. Whole water (all) or diluted (10% whole water & 90% GF/F filtered water) amended with nutrients (NH_4^+ , NO_3^- , DIP, Si). Mean \pm SD.

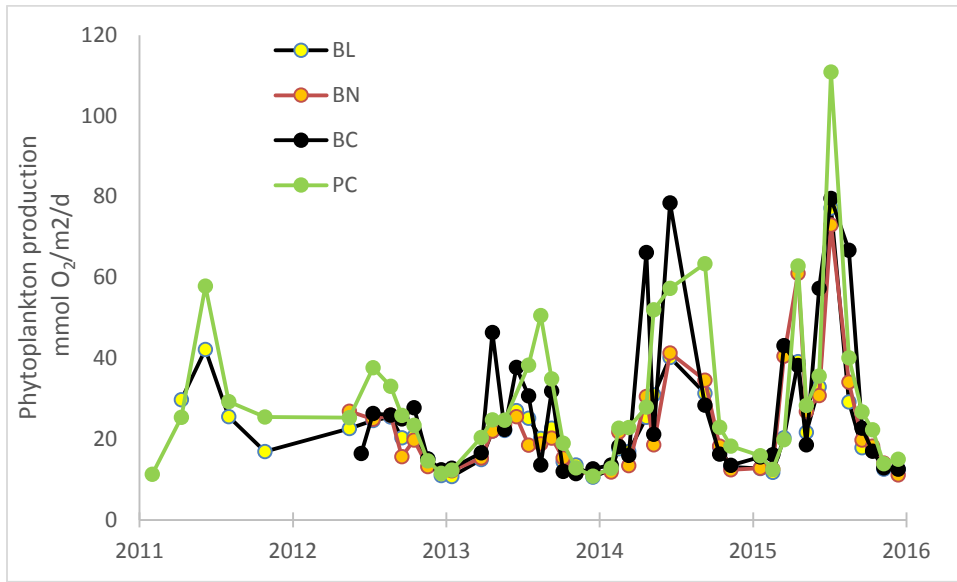


Figure 23. Phytoplankton production (mmol/m²/d) estimated using the Cole and Cloern (1984) BZI model using data from NERR SWMP monitoring program and this study.

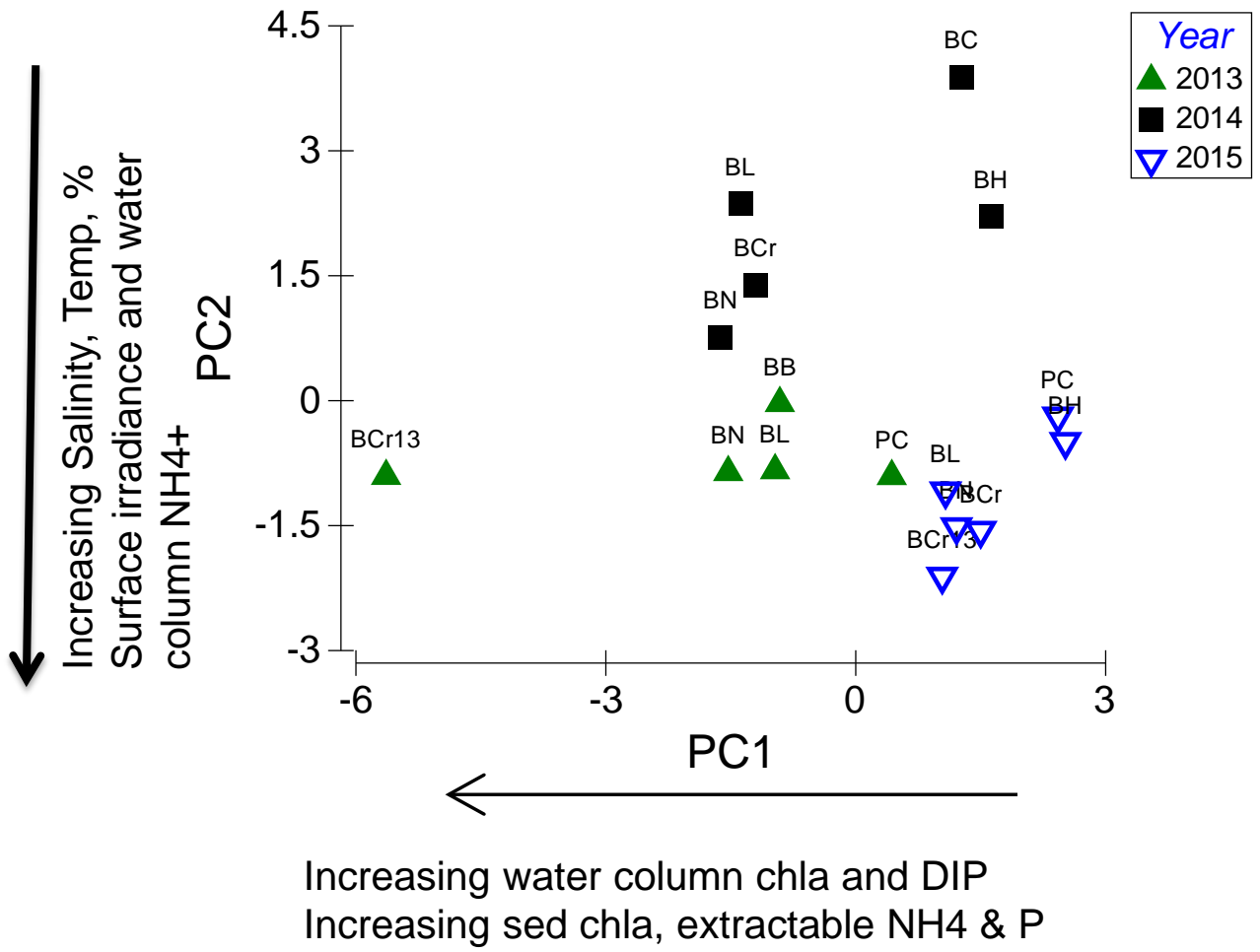


Figure 24. Principal component analysis of water column and sediment characteristics during June

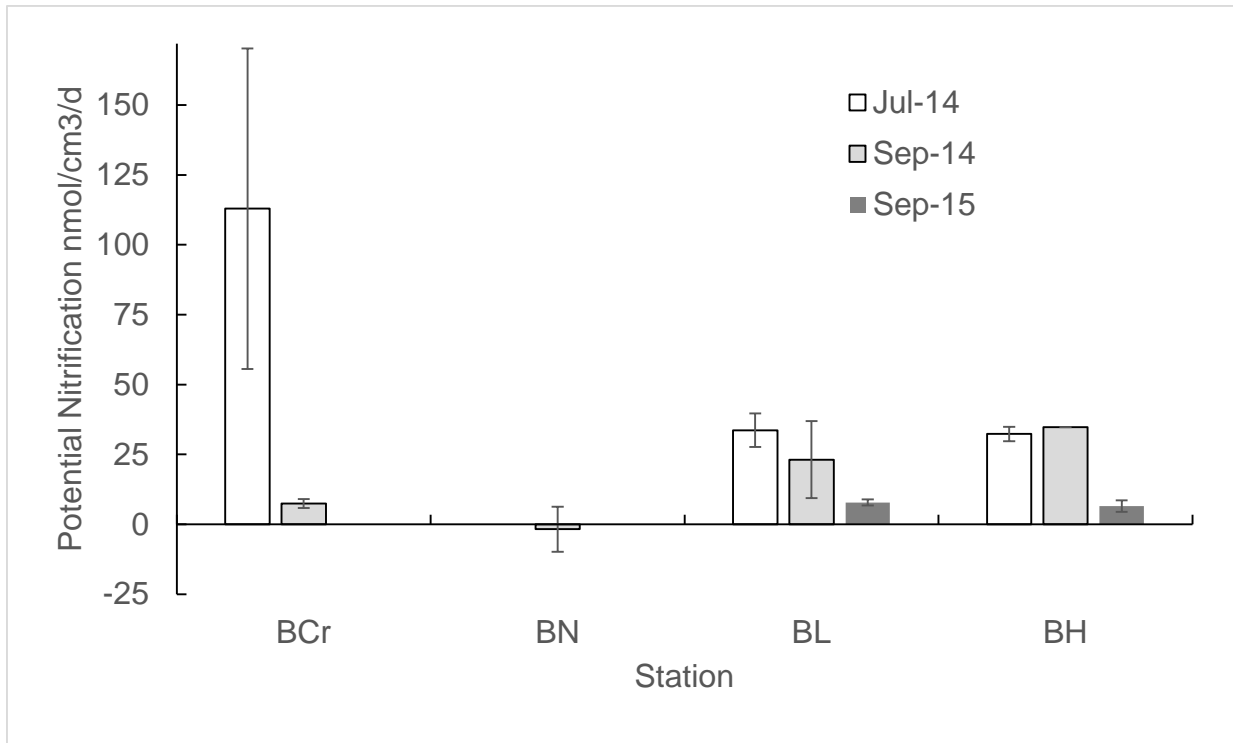


Figure 25. Potential nitrification rates (nmol/cm³/d) in Grand Bay on July 2014, September 2014, and September 2015. Mean \pm S.E.

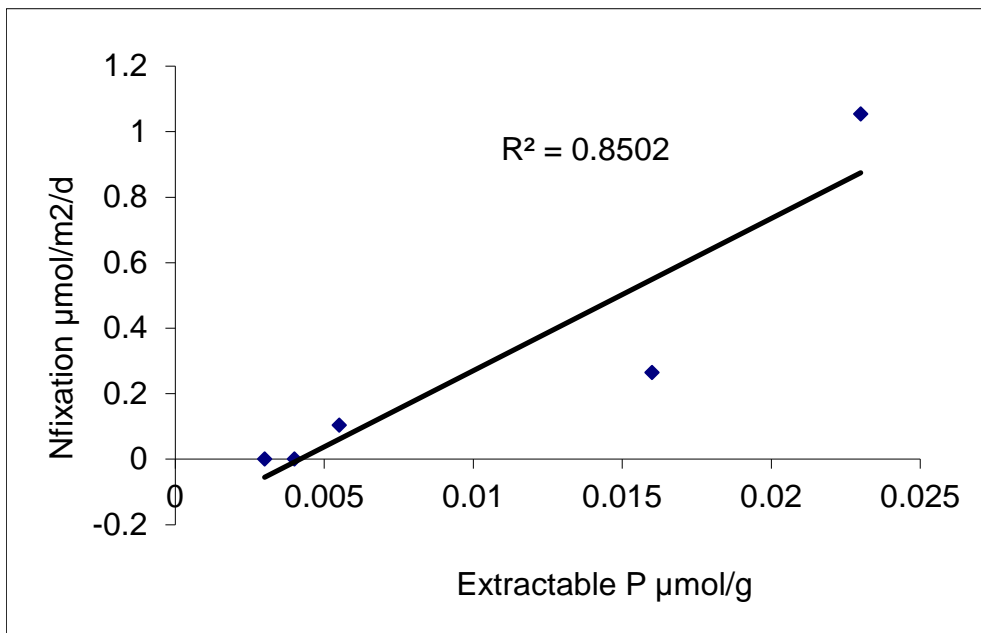


Figure 26. Nitrogen fixation ($\mu\text{mol}/\text{m}^2/\text{d}$) versus extractable P concentrations ($\mu\text{mol}/\text{g}$)

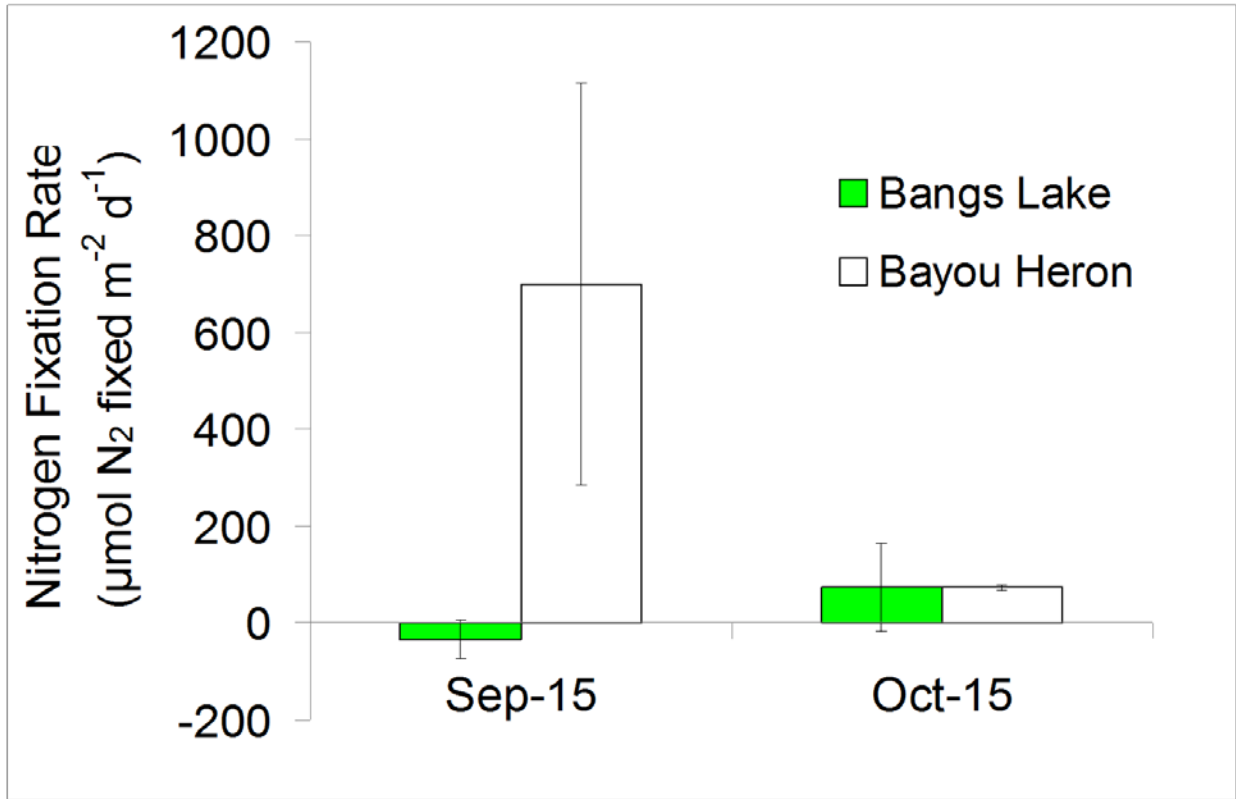


Figure 27. Nitrogen fixation rate ($\mu\text{mol}/\text{m}^2/\text{d}$) in September and October 2015 at Bangs Lake and Bayou Heron

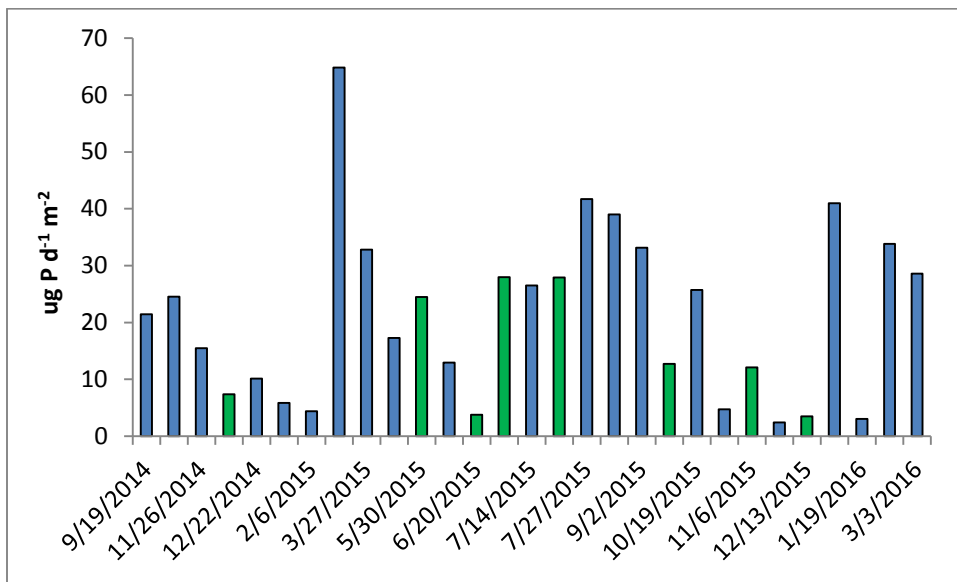


Figure 28. Phosphate dry deposition rates from dry bucket collectors. Blue bars denote GBNERR samples and green bars represent deposition rates from the reference site.

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