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

Kevin Dillon[1], Jane Caffrey[2], Ruth H. Carmichael[3,4], Kim Cressman[5], Mark Woodrey[45,6]
[1]Department of Coastal Sciences, University of Southern Mississippi, Gulf Coast Research Lab, Ocean Springs, MS
[2]Center for Environmental Diagnostics and Bioremediation and Department of Biology, University of West Florida, Pensacola, FL
[3]Dauphin Island Sea Lab, Dauphin Island, AL
[4]University of South Alabama, Mobile, AL
[5]Grand Bay National Estuarine Research Reserve, Moss Point, MS
[6]Coastal Research and Extension Center, Mississippi State University, Biloxi, MS

Abstract: Bangs Lake, an estuarine water body in the Grand Bay NERR, has been the site of three industrial phosphate spills from a nearby fertilizer plant since 2005. Due to restricted tidal exchange in Bangs Lake, these events have had long lasting effects on water column phosphate concentrations which may stimulate biological activity and alter the biogeochemical cycling of essential elements within the water column and the sediments. To determine the fate of excess phosphate from the industrial spills, researchers measured soluble reactive phosphate concentrations in sediment pore water and total particulate phosphate concentrations from sediment cores (0-25 cm depth) from four locations: North Bangs Lake (closest to spill locations), Bangs Lake, and two low impact reference sites (Bayou Cumbest and Bayou Heron). Researchers also conducted phosphate adsorption experiments and measured benthic chlorophyll concentrations with sediments from these sites to determine if the excess PO_4 was fertilizing benthic microalgae to determine the fate of this excess PO_4. Pore water phosphate concentrations were highest (21 uM) from 10 to 20 cm depths in North Bangs Lake cores however pore water from the surface sections of these cores had much lower phosphate concentrations (<0.5 uM). Pore water from the Bangs Lake cores consistently had elevated phosphate concentrations (2 to 5 uM) throughout the core length while pore water phosphate concentrations from one reference site were much lower (<0.7 uM), likely reflecting background levels. Phosphate adsorption experiments show that surface sediments from North Bangs Lake and Bayou Cumbest rapidly stripped phosphate from solution to final concentrations of <3 uM while surface sediments from Bangs Lake had greatly reduced phosphate adsorption capacity with much higher final concentrations (24 to 32 uM) indicating these sediments are nearing saturation. Sediment chlorophyll *a* concentrations were higher in Bangs Lake compared to the reference site. Sediment chlorophyll *a* was significantly correlated with extractable phosphate concentration in

sediments (r = 0.88). In addition, grow out experiments with amendments of phosphorus to water and sediment samples stimulated the growth of cyanobacteria capable of fixing nitrogen.

Introduction

Two large phosphate spills which led to large fish kills have occurred from Mississippi Phosphate Corporation (a fertilizer production facility) to the Grand Bay National Estuarine Research Reserve's (GBNERR) Bangs Lake since 2005 (Fig. 1). Following these spills, pH dropped dramatically from an average of ~7.5 to near 3.7 in Bangs Lake and phosphate concentrations following spills rose from near zero to 4.3 mg L^{-1} in 2005 and 7 mg L^{-1} in 2012 (SWMP, Darrow et al, in prep) and took six months to return to background levels of 0.01 mg L^{-1} (Fig. 2). Other nearby locations within the NERR showed smaller increases of 2.6 mg L^{-1} (Point Aux Chenes) and 0.30 mg L^{-1} (Bayou Cumbest, Darrow et al., in prep). These data demonstrate that recurrent phosphate spills can have relatively long-lasting water quality impacts across the Reserve. Further, there is some evidence of potential continuous input of phosphate to Bangs Lake from smaller ongoing spills or dry deposition. These events and the obvious biological impacts to the waters of a protected NERR warrant further investigation. While regular monitoring of water quality parameters and nutrient concentrations by the GBNERR's System Wide Monitoring Program (SWMP) provide 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 or flushed out of GBNERR waters by tidal action. 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 (Fig.2). Phosphorus is not typically measured in atmospheric monitoring programs; however, it is relatively simple and inexpensive to quantify (Williams et al., 1992).

Understanding the fate of excess phosphate inputs to Bangs Lake and nearby waters is essential to defining biological responses of the ecosystem. Phosphate can bind rapidly to sediments within the estuary and adjacent Mississippi Sound due to adsorption of phosphate to aluminum and iron rich minerals (Gomez et al., 1999, Dillon, in prep). Subsequent desorption may release phosphate back to the water column at a later time. Desorption experiments in Mississippi Sound showed increases in dissolved phosphate concentrations to 1 - 2 µM are possible (Dillon in prep.). Similar phosphorus adsorption/desorption reactions have been reported for a variety of estuarine sediments (Gomez et al., 1999, Dillon et al., 2003). Importantly, changes in sediment resuspension, pH, redox potential and ionic strength, or water column salinity that might occur during a phosphate spill or severe storm events can all alter phosphate adsorption/desorption processes (Froelich, 1988), potentially remobilizing previously stored phosphate from the sediments to the water column and affecting ecosystem processes such as nutrient cycling and food web dynamics.

In marine ecosystems, nitrogen availability often limits growth of phytoplankton and benthic microalgae. Amacker (2013) found that phosphorus additions to some sites in Grand Bay did not increase phytoplankton. Accordingly, increased water column algae growth (phytoplankton; estimated by measuring chlorophyll *a*) has not been detected in Bangs Lake following the documented phosphate spills (Caffrey et al. 2013, Cressman, unpublished data). Significantly higher benthic (bottom) microalgae growth, however, has been found closer to the fertilizer plant (Modestini and Caffrey, unpublished data) and phytoplankton concentrations have not been measured with sufficient temporal and spatial detail to dismiss possible water column effects. Because the sediments contain greater amounts of nitrogen than the water column, it is possible that phosphate spills have a greater influence on benthic algae compared to water column phytoplankton. Additionally, elevated phosphorus concentrations in freshwater dominated systems often result in blooms of toxin-producing cyanobacteria that can be harmful to animals and people (Paerl et al. 2001). Although Grand Bay is strongly influenced by freshwater inputs, no studies have tested for harmful algal blooms following the phosphate spills into Bangs Lake.

The former GBNERR Site Manager (David Ruple, now retired) and Research Coordinator (Dr. Mark Woodrey) have 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 research and addressing environmental management issues within the GBNERR. This one year research project addresses four basic questions developed by the PWG to assess the water quality impacts of repeated phosphate spills on an otherwise relatively undisturbed estuarine ecosystem. (1) What is the fate of phosphorus after a spill (Where does it go)? (2) Is there a detectable preserved sedimentary record of past phosphorus spills? (3) Is there a biological 'fertilizer' effect on microalgal production? (4) Is dry deposition of gypsum particles from the fertilizer plant a source of phosphorus to the Reserve? This research project addresses the Mississippi Water Resources Research Institute's Water Quality research priority area.

This project had a large student training component: we recruited six undergraduate interns from three regional institutions to collect data to better define the fate and biological effects of recurrent phosphate spills into Bangs Lake within the GBNERR. To determine whether phosphate is adsorbed to and preserved in sediments through time, we collected sediment cores from Bangs Lake, which has been altered by direct spilling of phosphate from the Mississippi Phosphates Corporation, and 2 control sites which we believe were historically less impacted (Bayou Cumbest and Bayou Heron). We measured phosphate concentrations down-core in the sediments and are combining phosphate data with radiometric dating using Lead-210 to define dates of historical spills, including spills prior to the GBNERR's monitoring program. To define the potential for phosphate adsorption to sediments, we conducted adsorption experiments using sediments from each site. To determine if there is a biological 'fertilizer' effect on microalgal production, we measured water column and pore water nutrients and chlorophyll a concentrations in the water column (phytoplankton) and at the sediment surface (benthic microalgae) at the phosphate enriched site (Bangs Lake) and at the control site (Bayou Cumbest). We also tested the potential for dry deposition of gypsum particles to contribute phosphate to the GBNERR by measuring phosphorus dryfall and compared the results to a reference site located near the Mississippi Sandhill Crane Refuge in western Jackson County.

Sampling and Analytical Methods

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. Phosphate was analyzed as described by Aspila et al. (1976). Radiometric analysis and dating will be conducted by the Geotop Lab at the University of Montreal Quebec using a ^{210}Pb model.

Phosphate adsorption experiments – Separate sediment cores were collected from Bangs Lake and Bayou Cumbest. One 5 cm section of the surficial sediments from each core was dried and 10g of each sediment sample were placed in an acid-washed flask with 75 mls of artificial seawater with a phosphate concentration of 50uM (1.5 mg L^{-1}) then capped and placed on a shaker table. Phosphate concentrations in each flask was sampled at approximately 2, 4, 8, 15, and 30 minutes then again at 1, 2 and 4 hours. Phosphate samples were syringe filtered with a Whatman glass fiber filter and then frozen until analysis. Phosphate concentrations were determined colormetrically (Strickland and Parsons, 1972).

Benthic microalgae activity - Surface sediment samples from the top 0.5 cm layer were be collected from the marsh and subtidal sediments for analysis of chlorophyll a and the pigments associated with cyanobacteria as in Neveux et al. (2011). Samples were also collected for measurement of nitrogen fixation at the same sites as the chlorophyll analyses. We used the acetylene reduction method which has been a standard technique for measuring nitrogen fixation since the 1970s (McCarthy and Bronk 2008). During nitrogen fixation, acetylene is reduced to ethylene by the nitrogenase enzyme. Samples were incubated in an air tight flask; headspace was replaced with 10% acetylene. Headspace samples were collected at 30 minute intervals over a 3 hour time course with syringes. These gas samples were injected into a GC with an FID detector for analysis of ethylene. If necessary, the time course were lengthened if rates were low or shortened if rates were high.

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) will be digested with peroxide to remove organic matter. Samples will be 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 will be sampled from a graduated cylinder using fall velocity tables to determine the removal time.

Particulate phosphate dry deposition

Airborne particles for phosphate analysis were collected on 47mm glass fiber filters with a 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 35 LPM. 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 analyzed. 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 60 RPM) for 2 days to extract the phosphorus from the filters. The resultant liquid sample was then transferred to a clean vial and analyzed for phosphate colormetrically (Strickland and Parsons, 1972) after the samples with neutralized with 10N sodium hydroxide.

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 20-28 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.

Results

Sediment cores phosphate inventory & ^{210}Pb dating

Sediment cores from Bangs Lake showed elevated particulate organic phosphorus (POP) concentrations at shallower core depths (Figure 3) with decreasing POP concentrations with increasing depth. One core from the southeast corner of Bangs Lake showed two distinct peaks at core depths of 4 and 14 cm. Based on preliminary results of the lead-210 analysis the peak at 4 cm depth corresponds to the documented 2005 spill from the Mississippi Phosphate Corporation. At this time, the lead-210 analysis has been completed however the final model results to assign dates to each core section are still being processed. Final results will be included in the Year 2 study funded by the Mississippi Water Resources Research Institute that is currently underway.

Phosphate adsorption experiments

Phosphate adsorption experiments at the Bayou Cumbest reference site showed that phosphate was rapidly adsorbed onto surficial sediments (Figure 4). Within 2 hours of exposure, the phosphate concentrations in the experimental incubations had decreased from 50uM to less than 3 uM. Concentrations continued to decrease until the last sampling at 48 hours. Pore waters from this site had low phosphate concentrations indicating that sediments had not been exposed to phosphorus from the spills. In contrast, surficial sediments from Bangs Lake had elevated pore water phosphate concentrations and sediments from this site had a reduced capacity to adsorb phosphorus out of solution (Figure 4). Phosphate concentrations in these incubations dropped from 50uM to 28uM over a 48 hour period. This shows that these sediments have been exposed to high phosphorus concentrations and are nearing their saturation point for phosphorus.

Benthic microalgae activity

Benthic chlorophyll represents microalgae living on the sediment surface. We hypothesized that fertilizer plant inputs of phosphorus would stimulate the production of benthic microalgae and potentially nitrogen fixation. Benthic chlorophyll a was measured at three locations near the fertilizer plant (Bangs Creek, Bangs North and Bangs Lake) and one location distant to the plant (Bayou Heron). Benthic chlorophyll a concentrations were highest in Bangs Lake and were higher at sites with high extractable P (Figure 5). Preliminary experiments suggested that phosphorus inputs can stimulate nitrogen fixation and growth of cyanobacteria.

Grain size analysis

Percent silt-clay was lowest at Bayou Heron west and Bangs Lake northwest and increased with increasing core depth at eastern Bangs Lake (Figure 6). Sediment cores from Bayou Heron showed evidence of previous mixing.

Particulate phosphate dry deposition

Airborne particles collected from the Grand Bay and reference site had similar baseline rates of collection (0.5 to 0.6 ug P day^{-1}) however the Grand Bay collector showed occasional increases above this baseline level to values as high as 1.2 ug P d^{-1}. The bucket collector in Grand Bay showed that rates of dry deposition at Grand Bay can range dramatically from 2 to 64 ug P day^{-1} m^{-2}. During the year 2 of this project we are developing more accurate wind rose diagrams that take wind speed and duration into account. At this time it is unclear if this dry deposited phosphorus is coming from the nearby gypsum stacks at the Mississippi Phosphates Corporation.

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

Joshua Allen	MS Student USM	Coastal Sciences
Chris Griffin	senior USM	Biology
Sarah Holcomb	junior USM	Geology
Jason Hall	senior DISL	Biology
Pavel Dimens	senior DISL	Biology
Kaleb Price	junior UWF	Marine Biology
Tashane Jones	junior UWF	Biology

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. Another major finding is that sediments in Bangs Lake had a reduced capacity to adsorb phosphorus indicating that the sediments in Bangs Lake are approaching saturation. Once saturation is reached, excess phosphorus will not be adsorbed and will only be affected by tidal advection or biological uptake. 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.

Future Research:

<u>In Year-2 we will refine and expand on our Year-1 research in three ways</u>, including addition of: 1) an artificial tracer (fluorescein) study to directly visualize and 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. Ongoing work continued from Year-1 will include sampling of sediment grain size, organic carbon and nitrogen content, phytoplankton and benthic microalgae concentrations, pore water and water column nutrient analyses, which will be needed to support the newly proposed analyses and integrate the results of Year-2 with Year-1 data.

Information Transfer and Outreach:

Results from this research to date have been presented as three student posters at the Bays and Bayous Symposium 2014 (Mobile AL), a poster by PI Caffrey at ASLO's 2014 Ocean Science

Meeting (Honolulu, HI), and an oral presentation by Dillon at the 2015 Mississippi Water Resources Conference (Jackson, MS).

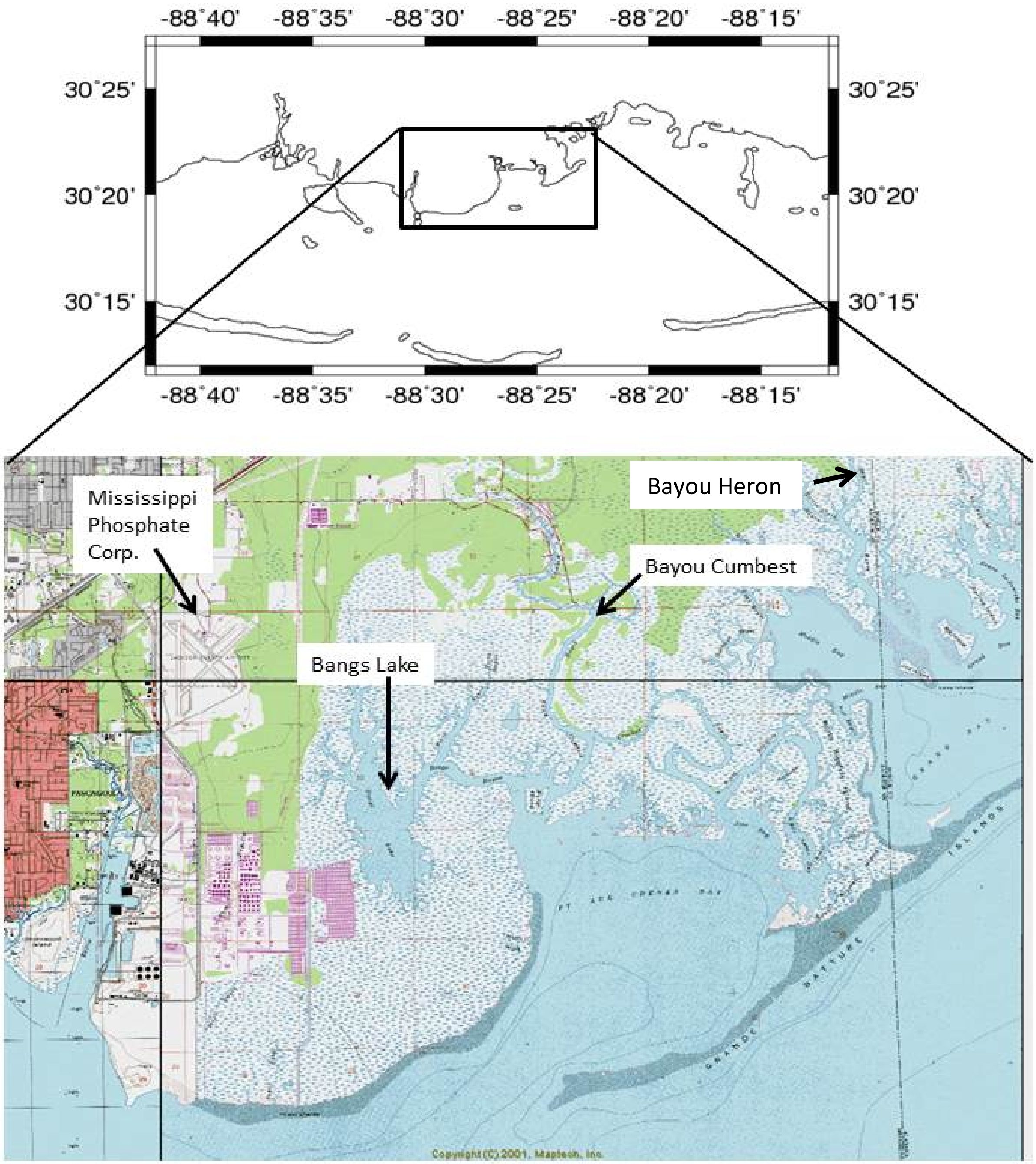


Figure 1. Map of the study sites (Bangs Lake, Bayou Cumbest, and Bayou Heron. The location of nearby gypsum stacks at Mississippi Phosphates Corporation are shown for reference.

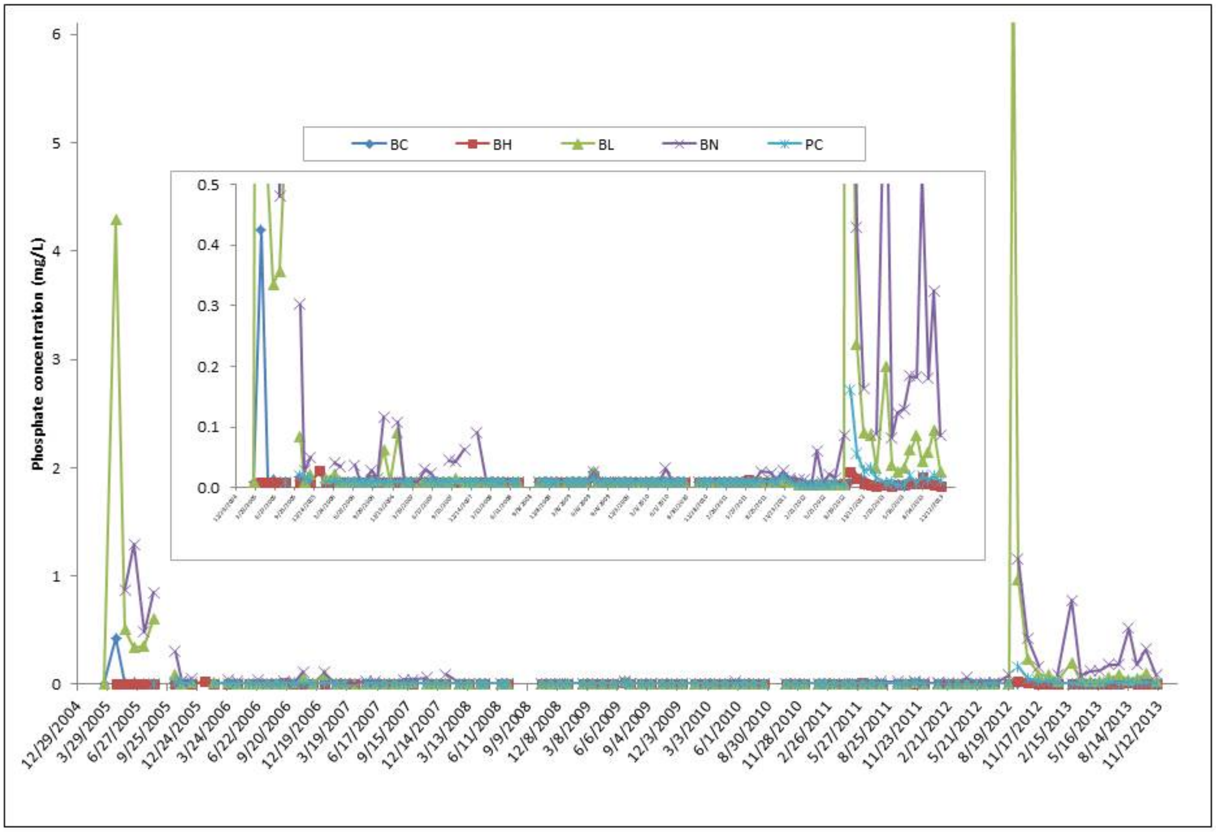


Figure 2. Water column phosphate concentration at monthly sampled stations within the GBNERR. BC = Bayou Cumbest; BH = Bayou Heron; BL = Bangs Lake; BN = Bangs Lake Nort; PC = Point aux Chenes. Inset is the same data on a smaller scale to better show smaller, more frequent changes in phosphate concentrations.

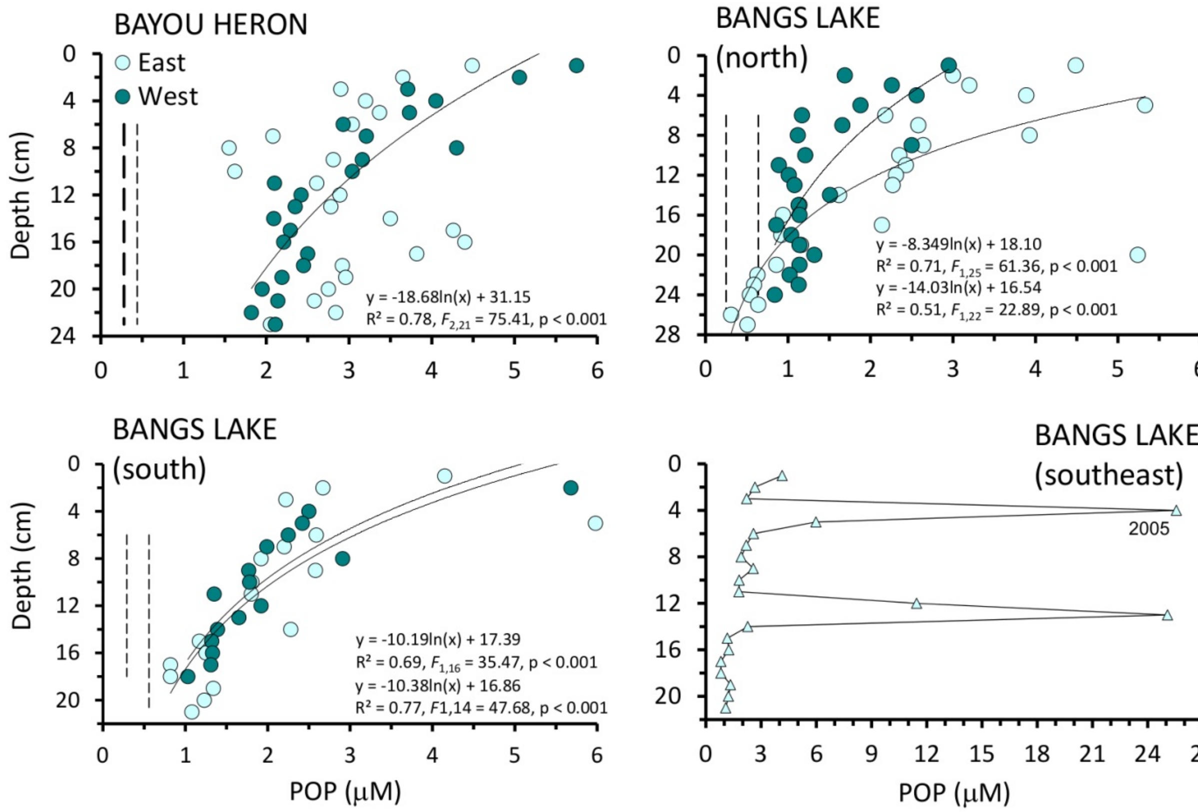


Figure 3. Particulate organic phosphorus (POP) concentrations in sediment cores from four stations in Bangs Lake. Dotted lines show background P concentrations in deeper core section.

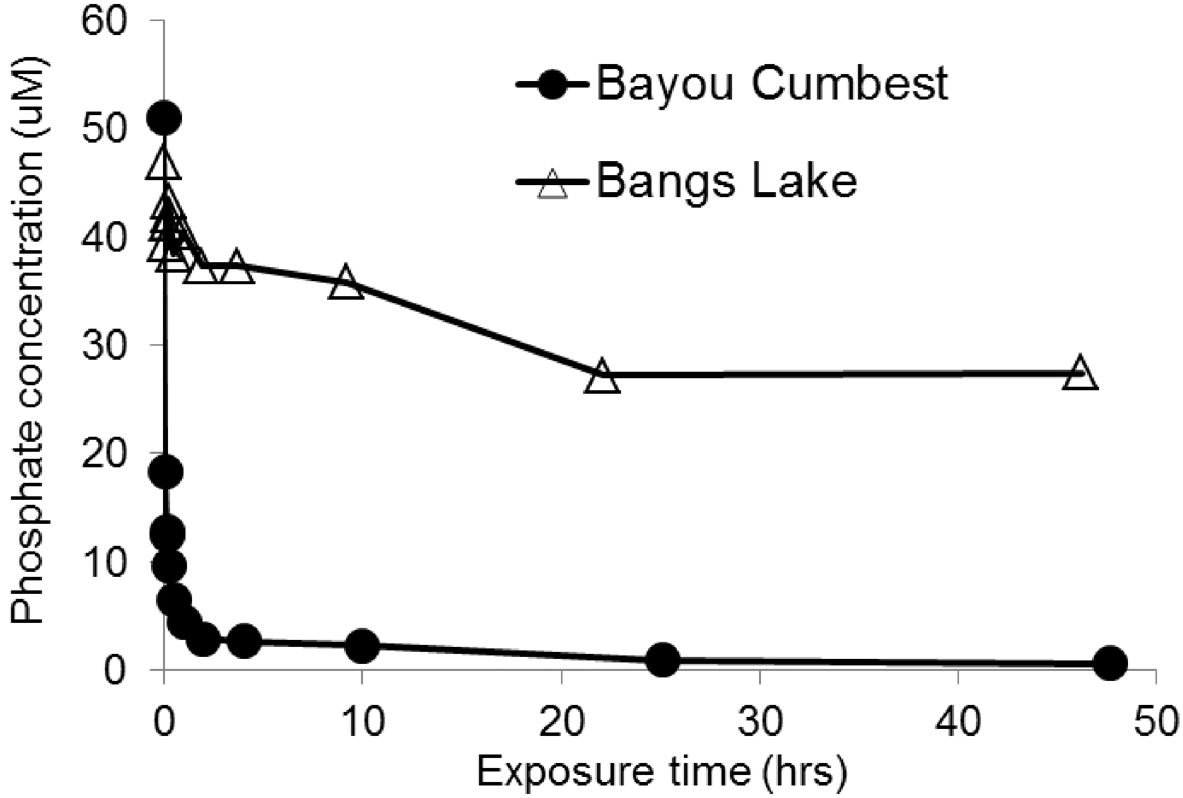


Figure 4. Results of the phosphate adsorption experiments. Phosphate concentration over 48 hours at Bangs Lake (triangle) and Bayou Cumbest (circle).

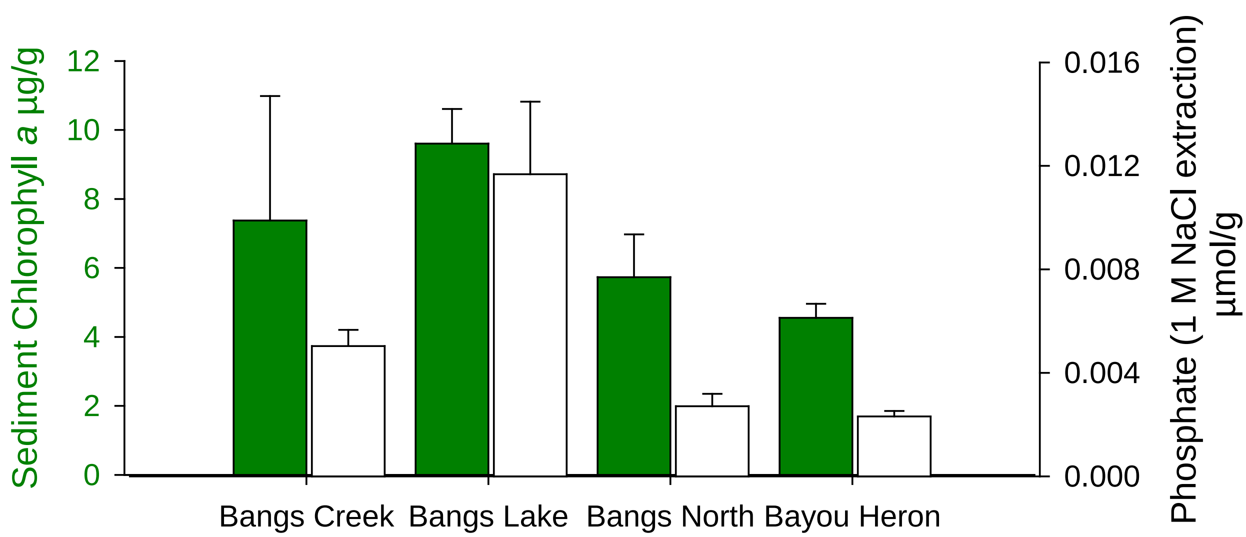


Figure 5. Sites closest to fertilizer plant had higher benthic chlorophyll a (green bars) and extractable phosphate concentrations (white bars) than site furthest away (Bayou Heron)

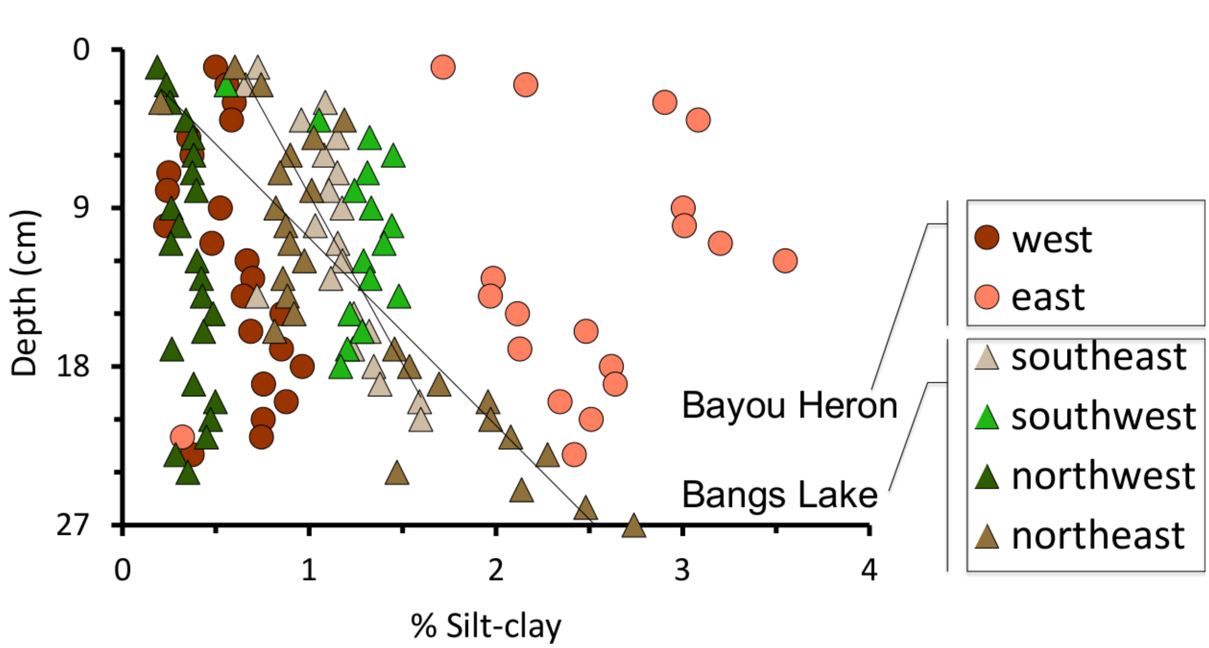
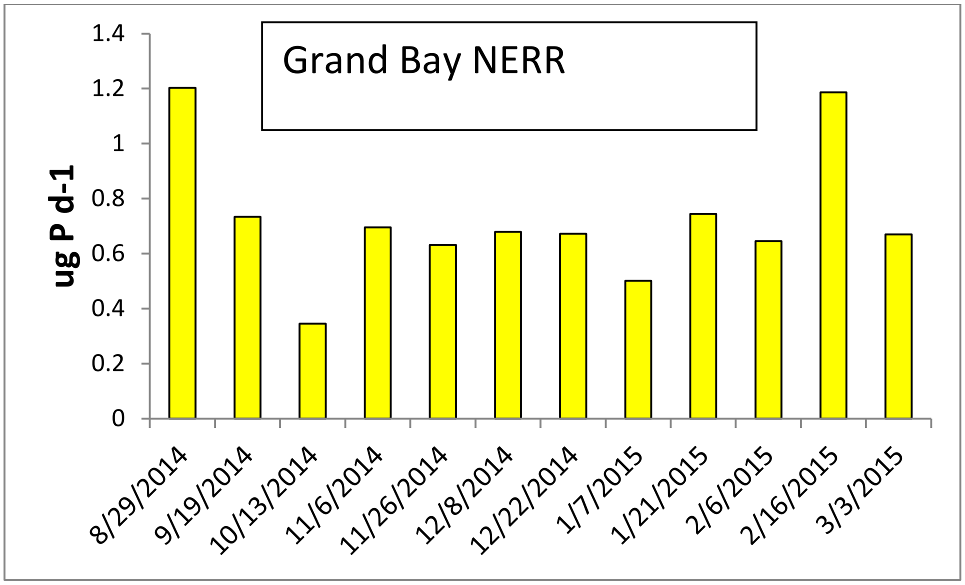


Figure 6. Results of grain size analysis for sediment samples collected in Bayou Heron and Bangs Lake.



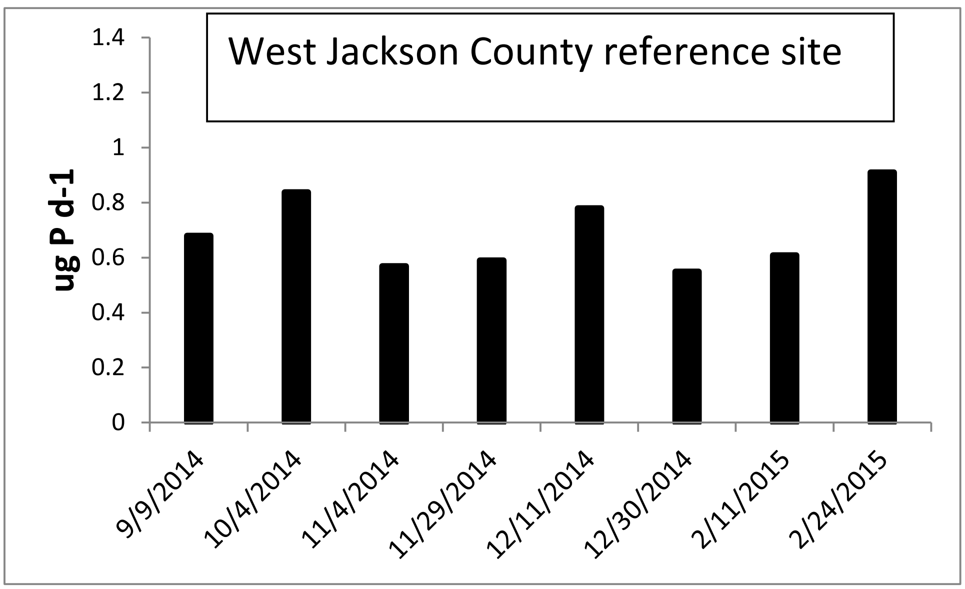


Figure 7. Average phosphate amounts collected daily on airborne particulate filters at the Grand Bay NERR and the reference site located in West Jackson County, Mississippi from August 2014 until March 2015.

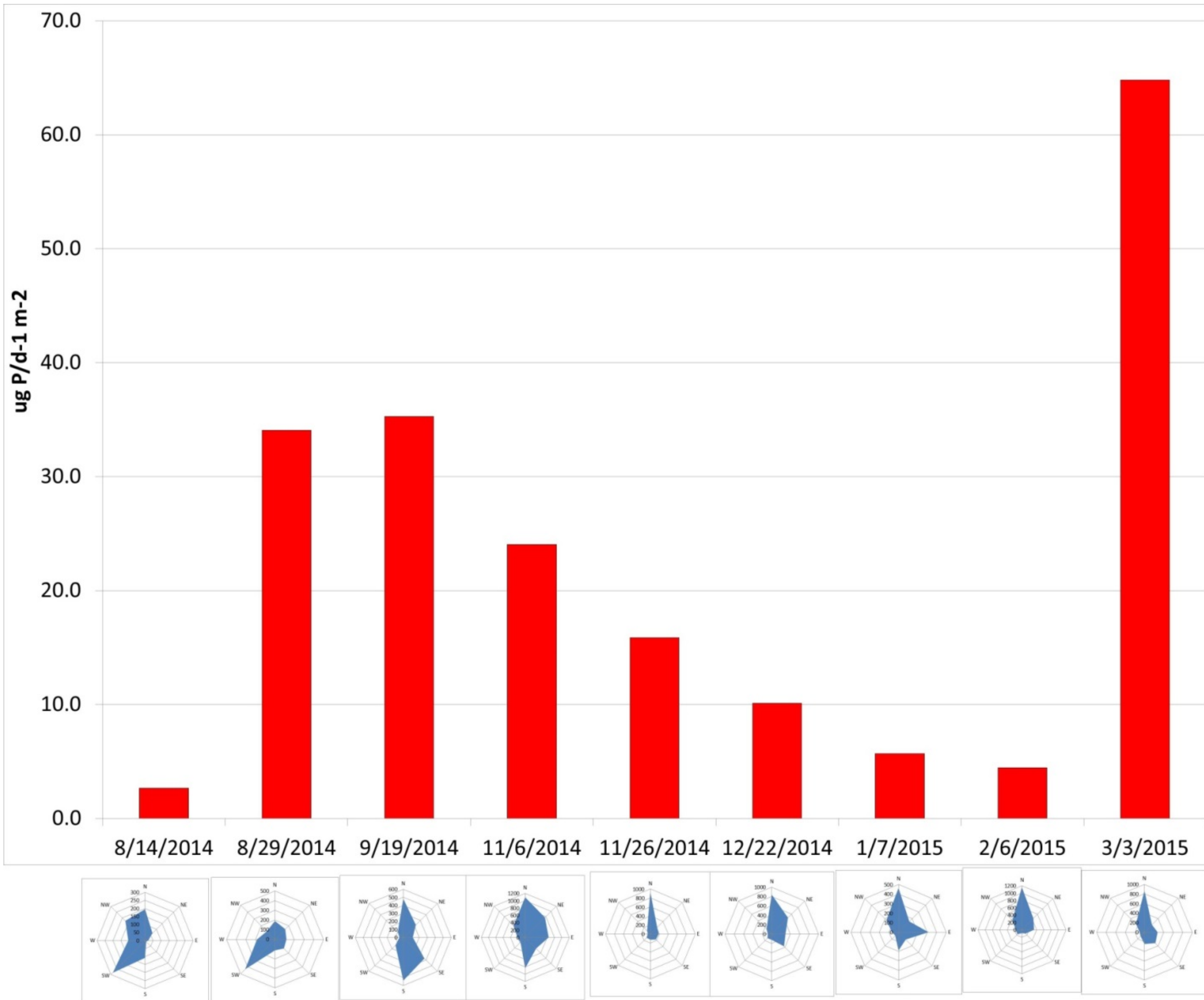


Figure 8. Settling rates of phosphorus from dry deposition collected from August 2014 to March 2015. Wind rose plots at the bottom of the graph show wind direction for the time period that the dry deposition bucket was deployed.

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