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# WATER QUALITY TRENDS FOLLOWING ANOMALOUS PHOSPHORUS INPUTS TO GRAND BAY, MISSISSIPPI, USA

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**Abstract:** Grand Bay National Estuarine Research Reserve (GBNERR) is a 7500 ha protected area in Jackson County, MS. In 2005, a levee breach at a fertilizer manufacturing facility released highly acidic and phosphate—rich wastewater into the reserve. A second spill occurred in September 2012 following Hurricane Isaac. We used orthophosphate ($PO_4^{3-}$) concentrations to categorize the 2 events, post—events, and non—impact periods between the 2 spills. We examined spatial and temporal patterns in nutrients, chlorophyll, pH, and other parameters within and between monitoring stations. After the first event, pH at the Bangs Lake water quality station decreased to 3.7 and $PO_4^{3-}$ increased to over 4 mg P/l. Orthophosphate returned to background concentrations near the detection limit after approximately one year. Sampling 3 weeks after Hurricane Isaac showed $PO_4^{3-}$ concentrations over 1 mg P/l in Bangs Lake. Elevated $PO_4^{3-}$ levels were detected at other monitoring locations for 3—5 months, depending on distance from the fertilizer facility. Multiple comparison tests of trends within stations showed that both events had statistically similar $PO_4^{3-}$ concentrations, although the magnitudes and the time to return to baseline concentrations differed between stations. Temporal patterns of other nutrients had apparent long—term trends, particularly chlorophyll a, which showed an increase from 18—56% depending on station. This study provides a rare description of decadal water quality trends in a shallow, temperate estuary in response to discrete spill events. The results provide new information on the effects of phosphorus inputs to nitrogen—limited systems, having management implications for Gulf Coast estuaries.

**Key words:** estuary, monitoring, orthophosphate, phosphogypsum, spills

## Introduction

Grand Bay National Estuarine Research Reserve (GBNERR) is nitrogen—limited (Blackburn 2000, Amacker 2013, Baine 2017) and adjacent to a phosphate fertilizer production facility (Mississippi Phosphates Corporation, MPC, Figure 1). The MPC produced diammonium phosphate (DAP) fertilizer from the 1960s until late 2014. Calcium sulfate, or phosphogypsum, a byproduct of this process, was stored in large stacks as waste. Phosphogypsum is rich in phosphorus, highly acidic (pH ~2.4), and contains several impurities such as radionuclides, heavy metals, fluoride, and sulfide (Rutherford et al. 1994, Tayibi et al. 2009, USEPA 2015, Garrard 2016). Phosphogypsum effluent may include a substantial amount of ammonium, where molar ratios of 6:1 have been estimated for orthophosphate and ammonium (Lee et al. 2004, Garrard 2016).

Waste products from fertilizer production have been observed in GBNERR. A significant storm event occurred in April 2005 when 43.2 cm of rainfall was recorded, of which 26 cm fell in less than 24 hours. A levee containing the phosphogypsum stacks breached on 14 April, causing a spill of over 66,000 $m^3$ of wastewater. Damage to marsh vegetation, fish, and oysters at the Bangs Lake station of GBNERR was estimated at over $2 million (Viskup 2005[1], State of Mississippi 2008[2]). A second storm event occurred from 28—30 Au-

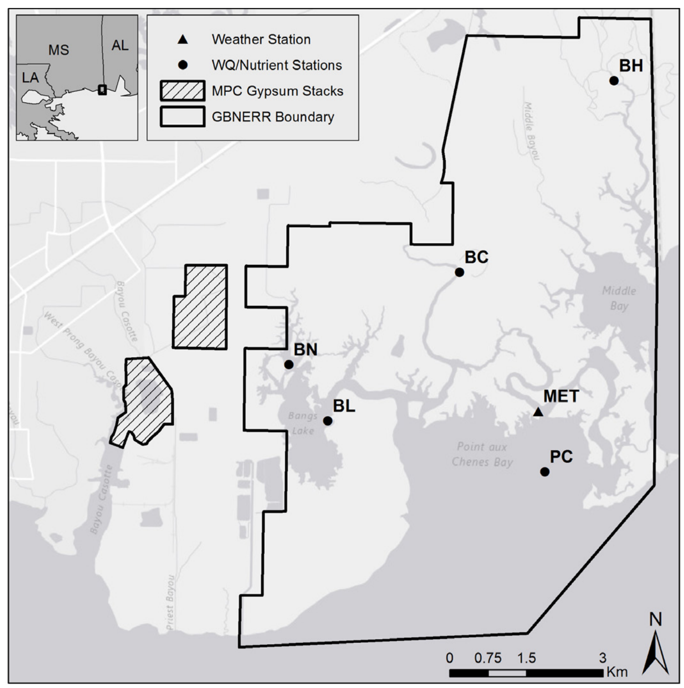


***FIGURE 1.*** *Station locations in the Grand Bay National Estuarine Research Reserve. BC, Bayou Cumbest; BH, Bayou Heron; BL, Bangs Lake; BN, Bangs North; PC, Points aux Chenes, MET, weather station. The two phosphogypsum stacks are shown to the left near Pascagoula, MS. Bayou Heron (no nutrient data) to the northeast is not shown.*

[1]Viskup, B. 2005. Memorandum Re: Monetary Damages due to spill at Mississippi Phosphates. Obtained from Mississippi Department of Environmental Quality via Public Records request, 10/28/2005.

[2]State of Mississippi. 2008. Mississippi Commission on Environmental Quality v. Mississippi Phosphates Corporation—Agreed Order No. 5357 08. 39pp. Obtained from Mississippi Department of Environmental Quality via Public Records Request, 7/28/2015.

gust 2012, when 76 cm of rainfall was recorded from Hurricane Isaac (MPC 2012a[3], b[4]). The MPC released 90,000,000 gallons of wastewater over 3 days into Bayou Casotte to the west, where a fish kill was subsequently observed (MDEQ 2015[5], 2017[6]). Elevated levels of orthophosphate were also observed in Bangs Lake to the east. The US Environmental Protection Agency (USEPA) currently maintains control of wastewater treatment operations at the site through the Superfund Removal Program (USEPA 2017a).

Anthropogenic nutrient inputs into natural water bodies have been well—described, and the ecological understanding of eutrophication continues to evolve with new information (e.g., Cloern 2001). Like Grand Bay, most estuaries are nitrogen (N)—limited (Howarth and Marino 2006, Conley et al. 2009), though many, including Pensacola Bay (Murrell et al. 2002, Juhl and Murrell 2008), the Louisiana shelf (Sylvan et al. 2006), and several North Carolina estuaries (Mallin 1994), can exhibit seasonal phosphorus (P)—limitation. The potential effects of sustained inputs of non—limiting nutrients have been less studied. There are few examples of long—term datasets that document the effects of phosphorus inputs to nitrogen—limited systems, especially regarding impacts of concentrated fertilizer waste loads. Very little is known regarding the long—term impacts of concentrated fertilizer waste inputs.

The few studies of the effects of phosphogypsum discharge have focused on relatively short periods of time or specific impacts related to discrete discharge events. For example, Tampa Bay is a large nitrogen—limited estuary on the Gulf coast of Florida that has historically received inputs from fertilizer manufacturing, processing, and accidental spills (Greening and Janicki 2006, Sherwood et al. 2015). Wastewater removal from phosphogypsum stacks was required following closure of a phosphate plant near southern Tampa Bay in 2001 (Garrett et al. 2011). The potential effects of partially treated effluent on the growth of harmful algal bloom (HAB) species was of concern, particularly for *Karenia brevis*. Although growth of *K. brevis* was not stimulated, other HAB species increased in abundance near the effluent, demonstrating differential species response to wastewater inputs (Garrett et al. 2011). In addition, acute effects to the nekton community were not reported, and long—term studies to understand chronic impacts to the ecosystem were not available (Switzer et al. 2004). An example in the Huelva estuary in Spain provided evidence suggesting phosphogypsum inputs contain additional impurities. Perez—Lopez et al. (2007, 2010) found that uranium and other heavy metals are present in higher concentrations in phosphogypsum than in raw phosphate ore and are readily mobilized in the environment.

In this analysis, the effects of 2 different discharge events of wastewater to GBNERR are quantitatively described using 10 years of continuous monitoring data. To our knowledge, this is the first study to use long—term water quality data to describe changes from phosphorus inputs in a shallow, nitrogen—limited estuary, particularly regarding byproducts of fertilizer production. We hypothesized that phosphogypsum spills would lead to significant differences in water quality parameters (salinity, pH), dissolved nutrients (nitrite+nitrate, ammonium and phosphate), and chlorophyll *a*. However, the effects were expected to vary based on distance from the source, time following inputs, and the nature of each spill (short—term vs long—term). Long—term monitoring programs often have goals of detecting and describing change, and results from these programs can be used to guide management decisions. As such, the results presented herein demonstrate the utility of a long—term dataset in studying the effects of phosphorus inputs in the estuary, with relevance for coastal systems in the Gulf of Mexico (GOM).

## Materials and Methods

### Study Area

The GBNERR was established in 1999 as the 24[th] of 29 reserves (at present) in the National Estuarine Research Reserve (NERR) System (http://oceanservice.noaa.gov/ecosystems/nerrs/). The reserve contains about 18,400 acres of coastal habitat including extensive shallow waters with a mean depth of 0.9 m (Figure 1; Dillon and Walters 2007, Woodrey 2007, GBNERR 2013). The surrounding watershed contains a mixture of forested land and wetlands with minimal anthropogenic development. The soils are primarily sandy and low in nutrients, similar to other estuarine systems on the northern GOM. Tides are diurnal and microtidal with a mean range of 0.6 m (GBNERR 2013). Salinity ranges from 0—30, with a long—term median of 22 (GBNERR 2013). The reserve is a retrograding deltaic system and does not have significant freshwater inflows. The Escatawpa River is located about 5 km north of the reserve and minor inputs into Grand Bay may occur during flood events through small channels. The GBNERR also has extensive bayou systems where water originates from localized

[3]Mississippi Phosphates Corporation (MPC). 2012a. Attachment I to August, 2012 Outfall 002 DMR. Daily Rainfall Received, Inches. Obtained from Mississippi Department of Environmental Quality via Public Records Request, 7/27/2015.

[4]Mississippi Phosphates Corporation (MPC). 2012b. Attachment II to August, 2012 Outfall 002 DMR. Report of circumstances necessitating treatment and discharge of water from outfall 002. Obtained from Mississippi Department of Environmental Quality via Public Records Request, 7/27/2015.

[5]Mississippi Department of Environmental Quality (MDEQ). 2015. Mississippi Phosphates Corporation Release – Bypass History. Obtained via Public Records Request, 11/12/2015.

[6]Mississippi Department of Environmental Quality (MDEQ). 2017. Mississippi Phosphates Corporation Release – Bypass History. Obtained via Public Records Request, 12/13/2017.

runoff and groundwater (GBNERR 2013). The watershed of GBNERR is generally undeveloped (GBNERR 2013) and nutrients are low compared to similar systems on the northern GOM. However, failing septic systems in the watershed have likely contributed to elevated levels of fecal coliform (LaSalle 1997, MSU—CREC 2000). The NOAA 30—year climate normal (1981—2010) for total annual precipitation in the area (Pascagoula, MS) is 166 cm (Arguez et al. 2012).

**Monitoring Data**

Monitoring stations at GBNERR were installed in 2004 as part of the System Wide Monitoring Program (SWMP, Wenner et al. 2004). The current network includes 5 continuous stations: 4 that measure physiochemical water quality (Bayou Heron, BH; Bayou Cumbest, BC; Bangs Lake, BL; and Point aux Chenes, PC), and one that records meteorological data (MET, Figure 1). Monthly nutrient sampling at the water quality stations began in March 2005 and a nutrient—only station (Bangs North, BN; Figure 1) was added in May 2005 after the first phosphate spill. For this analysis, we did not include BH data because station—specific characteristics prevented meaningful comparisons with the remaining stations (i.e., frequent stratification, regular freshwater dominance, sustained summer hypoxia, and groundwater influence). The PC station was established in August 2005 with removal of an existing station. All data from GBNERR are publicly available (www.nerrsdata.org, NOAA NERRS 2015).

Water quality parameters logged every 15 minutes by YSI dataloggers were water temperature (°C), specific conductance (mS/cm), salinity, dissolved oxygen (mg/l), pH, turbidity (NTU), and depth (m). Dataloggers were deployed 0.5 m above the bottom before August 2005 and 0.25 m thereafter. Meteorological data were logged using a Campbell Scientific datalogger and included air temperature (°C), relative humidity (%), barometric pressure (mb), wind speed (m/s) and direction, photosynthetically active radiation (PAR, mmol/$m^2$), and precipitation (mm/day) every 15 minutes. The weather station was destroyed by Hurricane Katrina on 29 August 2005, and replaced on 21 June 2006. Missing weather data were supplemented with data from the Pascagoula, MS airport (station code KPQL; 4/1—5/12 2005; 8/29/05 – 6/21/06; and 9/14—9/28 2012), which is about 15 km from Grand Bay. All monitoring data were previously verified by NERR staff and manually checked by the authors. For water quality and weather data, only data points that passed quality checks were analyzed.

Duplicate nutrient and chlorophyll *a* grab samples were collected monthly during low tide at each water quality monitoring station. Diel samples were also collected monthly using an ISCO automated water sampler programmed to sample for 5 min every 2 h over a complete tidal cycle. Monthly diel sampling was only conducted at one station within a calendar year. During this study, diel samples were obtained from BL from 2005—2007 and 2014—2015; PC in 2008; and BC from 2010—2012. All nutrient samples (grab and diel) were placed on ice and filtered through glass fiber filters in the lab (NERRS 2012). Samples were analyzed for ammonium ($NH_4^+$), nitrite+nitrate ($NO_2^-/NO_3^-$), orthophosphate ($PO_4^{3-}$), and chlorophyll *a*. Ammonium, $NO_2^-/NO_3^-$, and $PO_4^{3-}$ were analyzed colorimetrically (American Public Health Association 1998). Chlorophyll *a* was analyzed using the spectrophotometric acidification method through April 2007 (American Public Health Association 1998) and using the Welschmeyer (1994) fluorometric method with a Turner Trilogy starting in May 2007. Only fluorometric chlorophyll data starting in 2007 were used for analysis because of improved sensitivity. Minimum detection limits (MDLs) at GBNERR have changed over time. All nutrient values below the highest MDL of 0.01 mg/l were changed to 0.01 for this analysis. As described below, statistical analyses of the nutrient data accounted for left—censored (below detection limit) observations.

**Time Periods**

The dataset was divided into 6 time periods based on $PO_4^{3-}$ concentrations at the BL and BN stations and occurrence of the spill events in 2005 and 2012 (Table 1). Each of the two major events were divided into ‘acute' and ‘chronic' periods, where acute was the initial stage immediately following each event with extremely high $PO_4^{3-}$, and chronic was the period where $PO_4^{3-}$ was higher than baseline concentrations but lower than the acute period. Two non—impact (NI) periods were identified as baseline conditions: NI1 between the 2 major events and NI2 after fertilizer production stopped in December 2014. The *a priori* identification of time periods was primarily based on visual interpretation of nutrient parameters at each station and the authors' knowledge of deviations from background conditions in GBNERR. This approach was preferred over more formal statistical approaches to identify breaks in the data (e.g., changepoint analysis) to prevent identification of spurious changes that likely differed between parameters and stations. The analysis below provided a thorough evaluation of between—group comparisons using additional statistical approaches.

***TABLE 1.*** *Time periods evaluated for water quality changes at monitoring stations. See Figure 2 for a graphical depiction..*

| Identifier | Time period | Approximate dates |
|---|---|---|
| E1A | Event 1 Acute | Apr 2005 – Jun 2006 |
| E1C | Event 1 Chronic | Jul 2006 – Jan 2008 |
| NI1 | Non-Impact 1 | Feb 2008 – Aug 2012 |
| E2A | Event 2 Acute | Sep 2012 – Dec 2013 |
| E2C | Event 2 Chronic | Jan 2014 – Nov 2014 |
| NI2 | Non-Impact 2 | Dec 2014 – Aug 2015 |

### Statistical Analyses

Nutrient samples (2005—2015) and water quality parameters (2004—2015) were evaluated using descriptive statistics to interpret changes over time in relation to each event. Water quality data in the time series plots were evaluated using local polynomial regression (loess, smoothing span = 0.1) to emphasize the seasonal and long-term trends independent from daily mean observations (Cleveland et al. 1992). In addition to time series plots for each variable, differences in $PO_4^{3-}$ concentrations between stations were evaluated using boxplot summaries to examine distributions within the time periods. These plots were used to visually assess the extent and magnitude of changes in $PO_4^{3-}$ concentrations from acute to non—impact years following each event. Based on our hypotheses, we expected the relative magnitudes between stations and each event period to differ. Stations closest to the initial spill and suspected spill locations (BN, BL) were expected to have elevated nutrient concentrations that persisted longer than stations that were farther or more hydrologically distinct from those near the spill locations (BC, PC).

Non—parametric statistical tests were used to further evaluate differences in $PO_4^{3-}$ concentrations between time periods and within each station. A non—parametric or rank—based approach was required because numerous observations were at or below the minimum detection limit, particularly for the non—impact years. Further, nutrient time series were filtered using a seasonal decomposition to reduce autocorrelation among model residuals. All nutrient time series were evaluated after filtering the seasonal component using the decomp_cj function of the SWMPr package for R (Beck 2016). For each station, overall differences between time periods were evaluated using a Kruskal—Wallis one—way analysis of variance (ANOVA) followed by multiple comparisons using 2—sided Mann—Whitney U tests (Hollander and Wolfe 1999). Probability values were adjusted using the sequential Bonferroni method described in Holm (1979) to account for the increased probability of Type I error rates with multiple comparisons. An adjusted p—value < 5% ($\alpha$ = 0.05) was considered a significant difference between time periods or stations. Finally, we examined long term trends in nutrient and chlorophyll *a* data using the non—parametric Seasonal Kendall Tau (Jassby and Powell 1990, Tian and Fernandez 1999, Helsel and Hirsch 2002). Trends were evaluated using pooled data for the acute and chronic events of each period to meet sample size requirements of the tests. The second non—impact period (NI2) was not evaluated because of insufficient observations. Trend tests were not used to evaluate $NO_2^-/NO_3^-$ because more than 50% of the data were below detection.

## Results

### Station characteristics

Data from the GBNERR monitoring stations are summarized in Table 2. PC was the most marine—influenced station, with a median salinity of 24.3 and pH of 8.1. BC was the most freshwater—influenced station, particularly after rainfall events, with a lower median salinity of 18 and pH of 7.3. Dissolved oxygen was generally high at all

***TABLE 2.*** *. Station summaries of water quality (15 min) and nutrient (monthly) observations from 2005 to 2015. Nutrient summaries are based on maximum likelihood estimates and summary values for left-censored data less than the detection limit (0.01 mg/l) are estimated accordingly. Station codes: BC, Bayou Cumbest; BL, Bangs Lake; BN, Bangs North (no water quality data); PC, Point aux Chenes. Chl-a, Chlorophyll a; Dosat; dissolved oxygen saturation.*

| Stations | Mean | Median | St. Dev. | Min | Max |
|---|---|---|---|---|---|
| **Chl-*a* (µg/l)** | | | | | |
| BN | 7.9 | 5.0 | 9.8 | 0.6 | 36.7 |
| BL | 8.3 | 5.4 | 9.4 | 0.5 | 42.0 |
| PC | 8.0 | 5.2 | 9.4 | 0.5 | 34.0 |
| BC | 10.8 | 6.7 | 13.8 | 0.7 | 47.7 |
| **Dosat (%)** | | | | | |
| BL | 92.1 | 93.1 | 16.3 | 8.6 | 297.7 |
| PC | 97.1 | 97.9 | 15.5 | 8.4 | 221.9 |
| BC | 80.1 | 80.9 | 19.1 | 1.8 | 221.9 |
| **$NH_4^+$ (mg N/l)** | | | | | |
| BN | 0.03 | 0.01 | 0.07 | 0.01 | 0.16 |
| BL | 0.02 | 0.01 | 0.06 | 0.01 | 0.18 |
| PC | 0.02 | 0.01 | 0.06 | 0.01 | 0.42 |
| BC | 0.04 | 0.01 | 0.08 | 0.01 | 0.21 |
| **$NO_2^-/NO_3^-$ (mg N/l)** | | | | | |
| BN | 0.01 | 0 | 0.02 | 0.01 | 0.10 |
| BL | 0.01 | 0 | 0.03 | 0.01 | 0.09 |
| PC | 0.01 | 0 | 0.04 | 0.01 | 0.10 |
| BC | 0.01 | 0.01 | 0.02 | 0.01 | 0.09 |
| **pH** | | | | | |
| BL | 7.8 | 7.7 | 0.4 | 3.7 | 9.6 |
| PC | 8.1 | 8.1 | 0.2 | 7.0 | 9.0 |
| BC | 7.3 | 7.3 | 0.5 | 5.1 | 9.0 |
| **$PO_4^{3-}$(mg P/l)** | | | | | |
| BN | 0.12 | 0.02 | 0.90 | 0.01 | 1.29 |
| BL | 0.09 | 0 | 2.13 | 0.01 | 4.29 |
| PC | 0.01 | 0 | 0.02 | 0.01 | 0.16 |
| BC | 0 | 0 | 0.03 | 0.01 | 0.43 |
| **Salinity** | | | | | |
| BL | 22.0 | 22.4 | 5.5 | 1.5 | 32.1 |
| PC | 23.3 | 24.3 | 5.4 | 4.3 | 33.2 |
| BC | 17.2 | 18.0 | 7.9 | 0 | 33.5 |

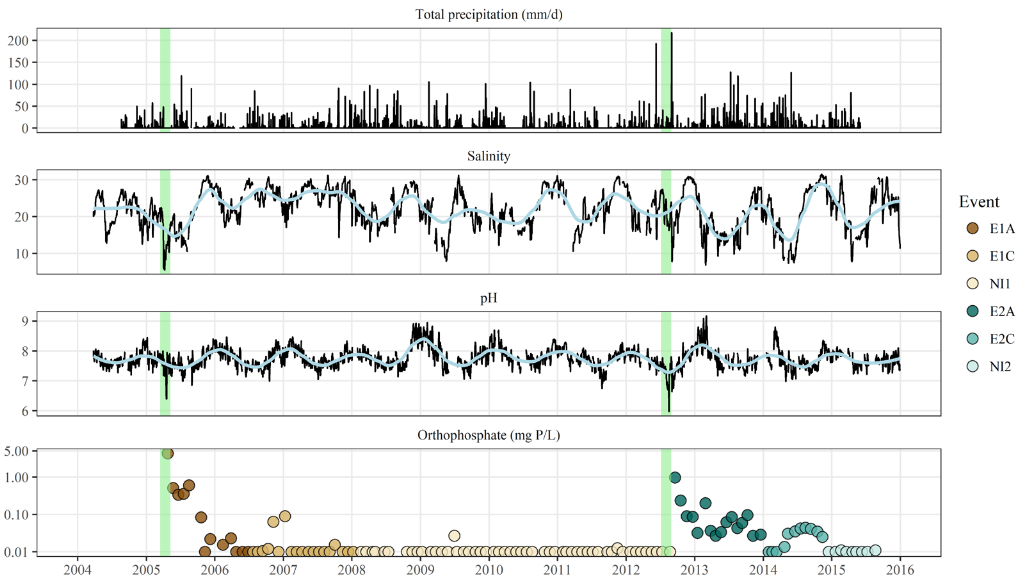


***FIGURE 2.*** *Time series of total precipitation, salinity, pH, and orthophosphate ($PO_4^{3-}$) for Bangs Lake, within the Grand Bay National Estuarine Research Reserve. All observations are daily means, excluding $PO_4^{3-}$ which was sampled monthly. Vertical green bars indicate a levee breech on 14 April 2005 from a heavy rain event and Hurricane Isaac in August 2012. Salinity and pH include a loess-smoothed regression to emphasize the seasonal and long-term trends. Orthophosphate is shown in log-space and colored by event categories (Table 1) in relation to the vertical green bars. E1A, event 1 acute; E1C, event 1 chronic; NI1, non-impact 1; E2A, event 2 acute; E2C, event 2 chronic; NI2, non-impact 2.*

stations. Median saturation values above 90% were observed at BL and PC; BC had a lower median saturation of 80.9%. Orthophosphate concentrations were highest at BL and BN. Chlorophyll *a* median values ranged from 5.0—6.7 µg/l between stations, with the highest concentration observed at BC (max Chlorophyll *a* 47.7 µg/l). All stations had low concentrations of $NO_2^-/NO_3^-$ and $NH_4^+$, usually below detection.

Annual precipitation in 2012 and 2013 was in the upper 80th percentile, with annual totals of 164 and 196 cm, while 2006 and 2011 were dry years, in the lower 20th percentile of annual totals for the period of record (75 and 79 cm, respectively). Seasonally, July and August were the wettest months within each year. Seasonal patterns were also observed for salinity and pH (Figure 2). For example, salinity at BL was generally lowest from April to June and highest in November, similar to pH, which was lowest from May to July.

**Event 1**

Precipitation began on 27 March 2005 and was heaviest from 31 March to 1 April, producing a total of 43.2 cm of rainfall. Prior to the storm, salinity at BL was 20—21, then fell during the event and reached its minimum of 2.8 on 2 April, one day after the storm ended (Figure 3). Salinity thereafter started increasing, which included some spikes during the first week of recovery. The levee at MPC was breached on 14 April, 2 weeks post—storm. Salinity ranged from about 7 to 12 during the breach and the days immediately following as it continued an upward trend. Turbidity at BL was normally < 10 NTUs before the storm, but surged to about 100 NTU just prior to the

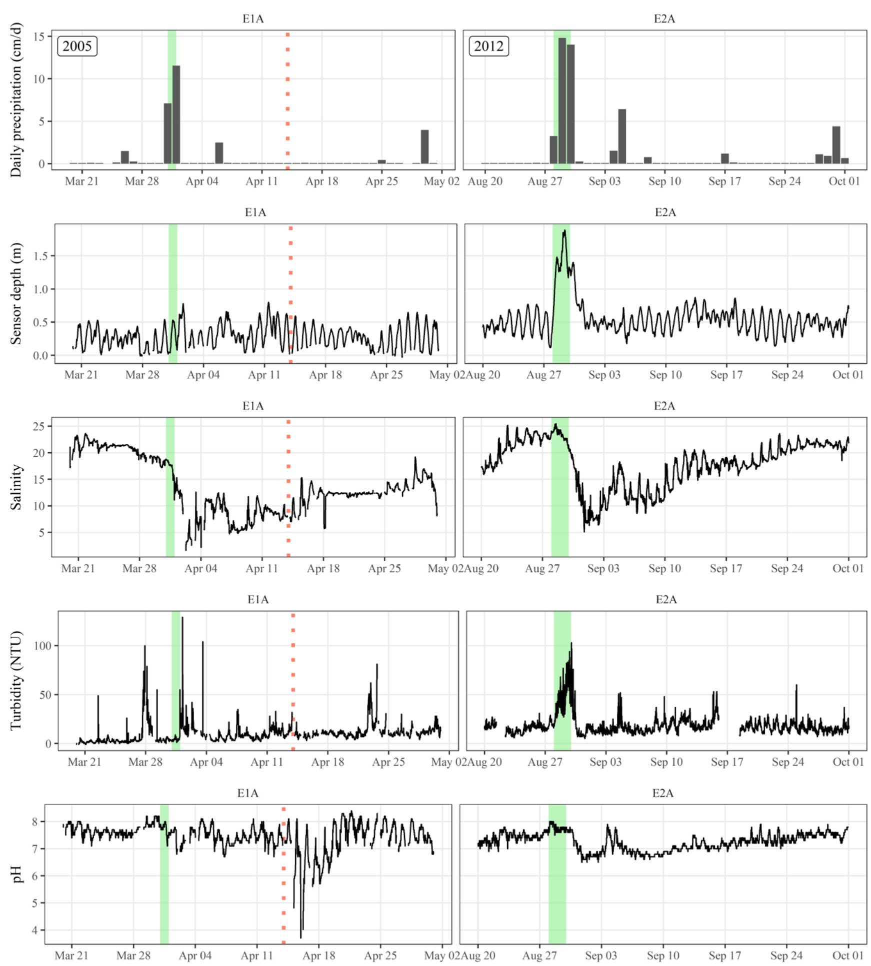


***FIGURE 3.*** *Time series of daily precipitation, sensor depth, salinity, turbidity, and pH for Bangs Lake, Grand Bay National Estuarine Research Reserve. Precipitation data are daily totals from the Pascagoula International Airport. All other data were collected at 15 min time steps. Green shading indicates periods of high precipitation for a heavy rain event in 2005 (left, centered on 1 April, precipitation began on 27 March) and hurricane Isaac in 2012 (right, 28-30 August). The dotted red line for the first event indicates the date of the documented spill. E1A, event 1 acute; E2A, event 2 acute.*

storm, fell to normal concentrations during the rain event, then spiked to 129 NTU immediately following the storm. However, despite some reoccurring spikes, turbidity quickly declined over the next several days, after which it usually remained < 20 NTU. Like salinity, turbidity seemed to be unaffected by the breach (Figure 3).

Unlike salinity and turbidity, pH changed significantly following the breach. The BL water quality station is sufficiently shallow such that the water drops below the sensors for a short time during extremely low tides. Observed pH was 7.2 before the tide dropped below the sensors on 14 April 2005 at 21:00 CST. The observed pH was 4.8 when the sensor was again submerged at 03:30 on 15 April. Over the following tidal cycle, pH increased to 8.1 at high tide then decreased to a minimum pH of 3.7 at 22:30 as water level decreased. This minimum was the lowest for the event and for all values in the 10 year dataset. The pH increased slightly to 4.4 before the water level decreased again below the sensor at 23:00. Observed pH values remained above 6.0 after the sensor was immersed again on 18 April at 06:30. On April 19, pH values returned to similar levels prior to the spill, 5 days following the first event.

Like pH, $PO_4^{3-}$ was highly impacted by the breach. Only one nutrient observation was available prior to the rain event, which measured $PO_4^{3-}$ below detection. At BL on 25 April, 11 days after the levee breach, $PO_4^{3-}$ averaged 4.29 mg P/l (Figure 4). Orthophosphate decreased gradually to 0.60 mg P/l on 16 August 2005, the last sample before Hurricane Katrina. The first samples after Katrina were taken 19 October, with a mean concentration of 0.084 mg P/l. Orthophosphate concentrations at BL were between 0.01 and 0.025 mg P/l until April 2006, when concentrations were consistently below 0.01 mg P/l. Orthophosphate spiked again in November 2006 and January 2007, to 0.064 and 0.090 mg P/l respectively, but was otherwise below or close to the detection limit of 0.01 mg P/l (Figure 4). Similarly, $PO_4^{3-}$ at BN remained elevated throughout the E1A time period through June 2006. Concentrations decreased below detection for a short time, then spiked repeatedly (up to 0.118 mg P/l) through January 2008 (Figure 4). Elevated $PO_4^{3-}$ was also observed at BC to the north, with a concentration of 0.426 mg P/l during the April 2005 sampling (Figure 4). For the trend tests, the reductions per year in $PO_4^{3-}$ during the first event were a decrease of about 236% at BL and 80% at BN (Table 3, percent change based on slope per year divided by median).

**Event 2**

A substantial amount of rain and about 1.5 m of storm surge was produced by Hurricane Isaac on 28—30 August, 2012 (Figure 3). Prior to the storm, observed pH at BL ranged from 7.2—7.7 and salinity ranged from 22—25. The initial storm surge on 28 August increased the pH slightly to 7.6—8.0, whereas salinity was not affected. A steady increase in turbidity from ~23 NTU to over 100 NTUs was observed with the storm surge. As the surge receded on 31 August, the observed pH and salinity decreased to a minimum of 6.5 and 5.6 at 18:30, respectively. After the storm passed, pH remained low, varying between 6.5 and 7.0 from 31 August to 3 September, with occasional increases to 7.8. After 13 September, pH observations stayed above 7.0 and by 30 September, one month after the initial storm surge, pH had nearly attained its pre—storm level (Figure 3). Salinity began to steadily increase after reaching its post—surge low, with daily tidal variations that exceeded 5. Like pH, salinity also had nearly fully recovered one month after the initial storm surge. Turbidity rapidly decreased after the storm (< 10 NTU) and was at pre—storm conditions one day after the surge.

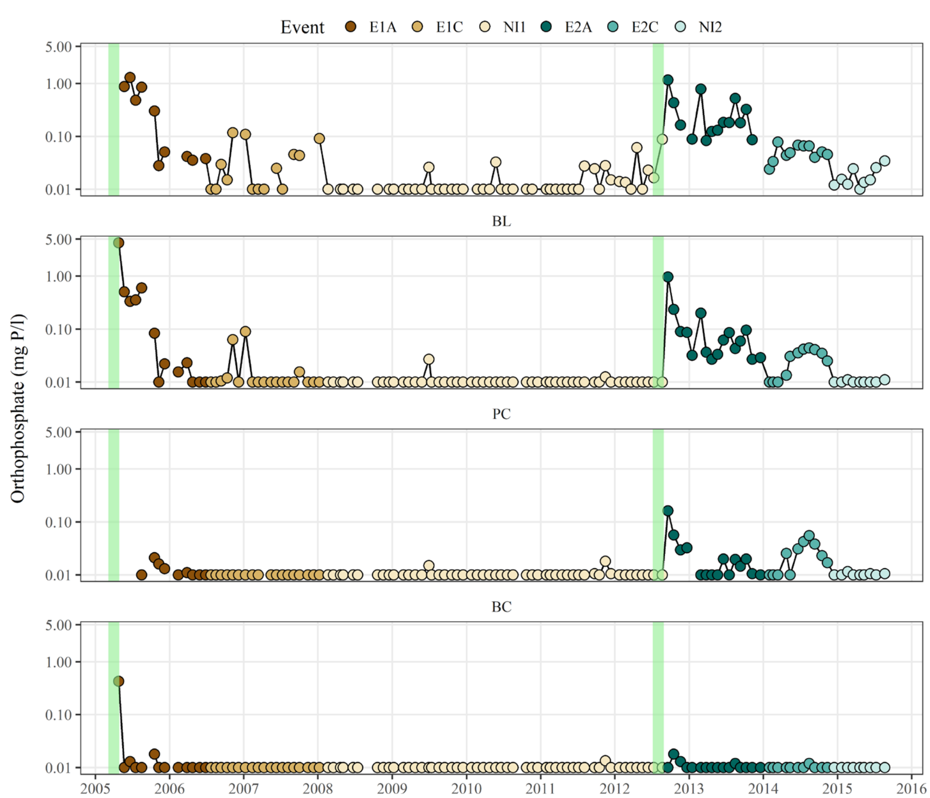


***FIGURE 4.*** *Monthly log-orthophosphate time series at Bangs North (BN), Bangs Lake (BL), Point aux Chenes (PC), and Bayou Cumbest (BC) stations at Grand Bay National Estuarine Research Reserve. Distance of stations from spill increases from top to bottom panels. Vertical green bars indicate a levee breech on 14 April 2005 from a heavy rain event and Hurricane Isaac in August 2012. E1A, event 1 acute; E1C, event 1 chronic; NI1, non-impact 1; E2A, event 2 acute; E2C, event 2 chronic; NI2, non-impact 2.*

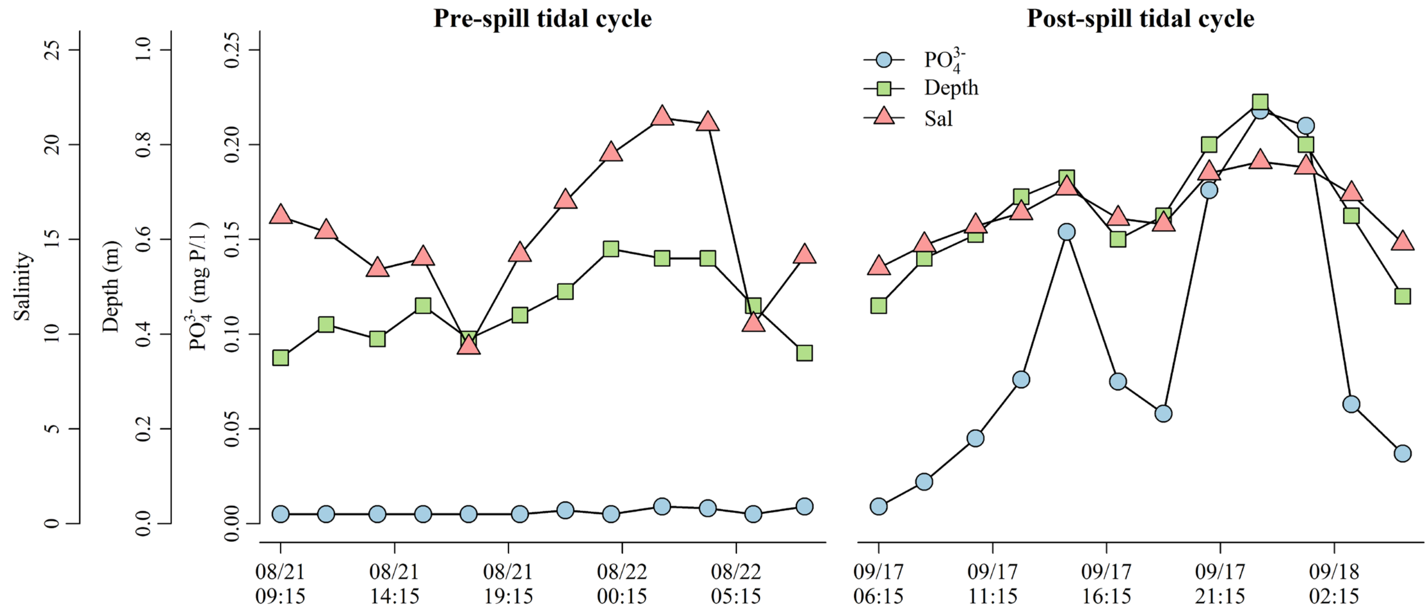


***FIGURE 5.*** *Diel orthophosphate ($PO_4^{3-}$) and salinity data before and after Hurricane Isaac during the second spill event on 28 August, 2012 (times in PST). Bayou Cumbest is about 7 km from the spill site and elevated $PO_4^{3-}$ is observed with tidal influx (depth) following the event. Diel patterns in $PO_4^{3-}$ were correlated with sensor depth after the spill.*

Three weeks after Hurricane Isaac, $PO_4^{3-}$ concentrations were elevated in monthly grab samples, with the highest concentrations at BN (1.16 mg P/l), BL (0.97 mg P/l) and PC (0.16 mg P/l) (Figure 4). Concentrations from monthly grab samples declined at all 3 stations over about 5 months to < 0.089 mg P/l. In February 2013, concentrations at BN and BL increased to 0.78 mg P/l and 0.2 mg P/l, respectively. At BL during this time period, pH was also high, with peaks of 9.5 on 16 February and 9.6 on 2 March.

In contrast to the other stations, changes in monthly $PO_4^{3-}$ concentrations at BC were small and did not persist (Figure 4). However, a more defined temporal analysis of ISCO diel samples collected at BC in 2012 shows a more dynamic range of $PO_4^{3-}$ before and after the storm (Figure 5). Orthophosphate concentrations showed little change in the 24—hour sampling period prior to the storm, when concentrations were near detection at low tide, but increased to 0.2 mg P/l at high tide 3 weeks following the storm (Figure 5). Diel patterns in $PO_4^{3-}$ after the spill were correlated with sensor depth on the YSI logger. Salinity and pH also had a strong tidal signal with higher values at high tide. Although the duration of the 2 events were similar, they differed in the amount of $PO_4^{3-}$ recovery toward pre—event conditions. The reduction in $PO_4^{3-}$ from the beginning to the end of the second event, based on the Kendall Tau tests (Table 3), was a decrease of 105% at BL and 135% at BN (slopes divided by medians).

**TABLE 3.** *Summary of $PO_4^{3-}$ (mg P/l) trends for time periods with sufficient data. Trends are based on seasonal Kendall Tau tests, where τ is the direction and strength of the trend, slope is the change per year, median is the median of the time period, and percent change is the slope divided by the median. Stations are Bangs Lake (BL), Bangs North (BN), Point aux Chenes (PC), and Bayou Cumbest (BC). Time periods are event 1 acute (E1A), event 1 chronic (E1C), non-impact 1 (NI1), event 2 acute (E2A), and event 2 chronic (E2C). *p < 0.05; **p < 0.005*

| Time Periods<br>Stations | τ | slope | median | %<br>change |
|---|---|---|---|---|
| **E1A, E1C** | | | | |
| BN | -0.48 | -0.03 | 0.04 | -79.25 |
| BL | -0.66** | -0.02 | 0.01 | -236.25 |
| PC | -0.31* | 0 | 0.01 | 0 |
| BC | -0.19 | 0 | 0.01 | 0 |
| **NI1** | | | | |
| BN | 0.37** | 0 | 0.01 | 0 |
| BL | 0.02 | 0 | 0.01 | 0 |
| PC | 0.1 | 0 | 0.01 | 0 |
| BC | 0.04 | 0 | 0.01 | 0 |
| **E2A, E2C** | | | | |
| BN | -1.00** | -0.12 | 0.09 | -134.88 |
| BL | -0.85** | -0.04 | 0.04 | -104.79 |
| PC | 0.12 | 0 | 0.02 | 0 |
| BC | -0.15 | 0 | 0.01 | 0 |

### Differences between stations and time periods

Within stations, BN consistently had the highest $PO_4^{3-}$ concentrations given its location near the MPC fertilizer plant (Figure 6A, Table 1). BL had the second highest concentrations followed by PC and BC, with the latter having the lowest median concentrations among all stations. Multiple comparisons of time periods within each station indicated that $PO_4^{3-}$ concentrations for both acute events (E1A, E2A) were not statistically different. Comparisons within stations

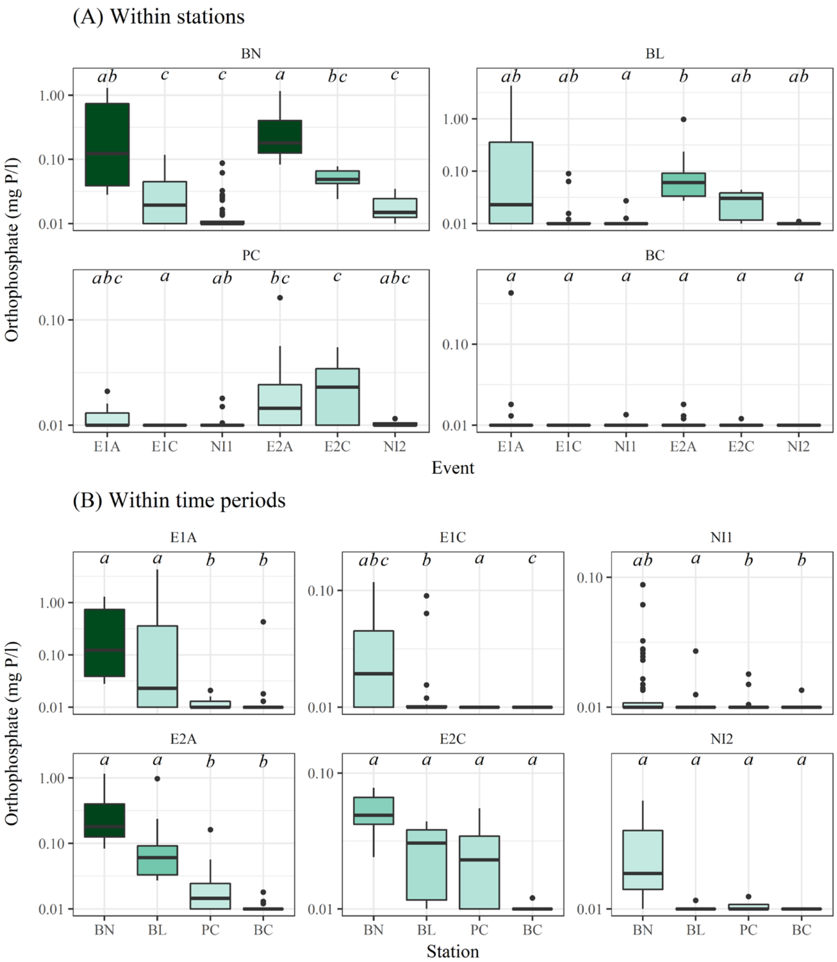


**Figure 6.** *Boxplot summaries of monthly orthophosphate ($PO_4^{3-}$) data (log-scale) for (A) time periods grouped by station and (B) stations grouped by time period. Boxes depict median and middle quartiles of the values, and whiskers depict 1.5 times the interquartile range. Outliers are represented as points. Boxplots within each panel that do not share a letter have significantly different concentrations determined using multiple comparisons with Mann–Whitney U tests. Boxes are shaded by relative magnitudes of the median. Stations are Bangs Lake (BL), Bangs North (BN), Point aux Chenes (PC), and Bayou Cumbest (BC). Time periods are event 1 acute (E1A), event 1 chronic (E1C), non-impact 1 (NI1), event 2 acute (E2A), event 2 chronic (E2C), and non-impact 2 (NI2).*

between the acute and chronic periods following each spill showed that concentrations were significantly lower in the chronic periods for BN (E1A—E1C, Mann—Whitney U = 121, $p = 0.03$; E2A—E2C, U = 147, $p = 0.002$). The highest $PO_4^{3-}$ concentration for BC occurred in E1A. None of the time periods were significantly different from the others at this station (Figure 6A). At PC, there were no obvious trends based on time period, although median $PO_4^{3-}$ was highest in the E2C time period. Comparisons within time periods showed substantial spatial variation between stations in $PO_4^{3-}$ concentrations (Figure 6B). Concentrations at BL and BN were statistically similar during both acute periods of each spill event (E1A, E2A), and significantly different from the remaining stations for these same periods (during E1A, BN—PC, U = 81, $p = 0.01$; BN—BC, U = 17, $p = 0.01$; BL–PC, U = 106, $p = 0.01$; BL—BC, U = 24, $p = 0.01$; during E2A, BN—PC, U = 204, $p < 0.001$ ; BN—BC, U = 0, $p < 0.001$ ; BL–PC, U = 200, $p = 0.005$; BL—BC, U = 32, $p = 0.001$). Similarly, concentrations at the PC and BC station were statistically similar during both acute periods. Concentrations among stations during the chronic and non—impact periods for the first event were dissimilar, particularly for the BL station which was significantly different from the PC (during E1C, U = 276, $p = 0.009$; during NI1, U = 2130, $p < 0.001$) and BC (during E1C, U = 75, $p = 0.01$; during NI1, U = 599, $p < 0.001$) stations. Concentrations for the chronic and non—impact periods of the second event were not significantly different among stations. Seasonal Kendall Tau tests indicated that concentrations at each station were generally decreasing within each time period (Table 3).

Within time periods, there were no significant differences between stations in $NO_2^-/NO_3^-$ (Figure 7), nor were there significant differences between time periods (Figure 8). For $NH_4^+$, there were no differences between stations during time periods, except BC had greater concentrations than PC (U = 1659, $p = 0.007$) and BL (U = 1587, $p = 0.03$), and BN had greater concentrations than PC (U = 1457, $p = 0.03$) during the first non—impact period (Figure 7). Seasonal Kendall Tau trend tests for $NH_4^+$ during sampling within time periods indicated reductions within stations, although none of these changes were significant (Table 4). For chlorophyll *a*, there were no significant differences between stations for any time period (Figure 7). However, an increasing trend was indicated at most stations during advancing time periods (Figure 8), with significant trends at BN (NI1—E2C, U = 134, $p = 0.04$) and BL (NI1—E2C, U = 127, $p = 0.02$). The seasonal Kendall Tau tests of samples within time periods showed a significant ($p < 0.005$ for all) positive change at all stations during NI1, ranging from 32% to 56% (Table 5).

## Discussion

Elevated $PO_4^{3-}$ concentrations were the only observed similarities between the events. The first event was characterized by extremes in $PO_4^{3-}$ concentrations and both low salinity (< 3) and pH (<5). Although we did not have sufficient nutrient observations prior to the first levee breech, these water quality changes are likely a direct cause of a spill rather than freshwater inputs from the rain event. Salinity decreased with precipitation, whereas dramatic pH changes did not occur until 14 April when high concentrations of $PO_4^{3-}$ were also observed. The reduction of $PO_4^{3-}$ concentrations to levels near or below detection limit during the

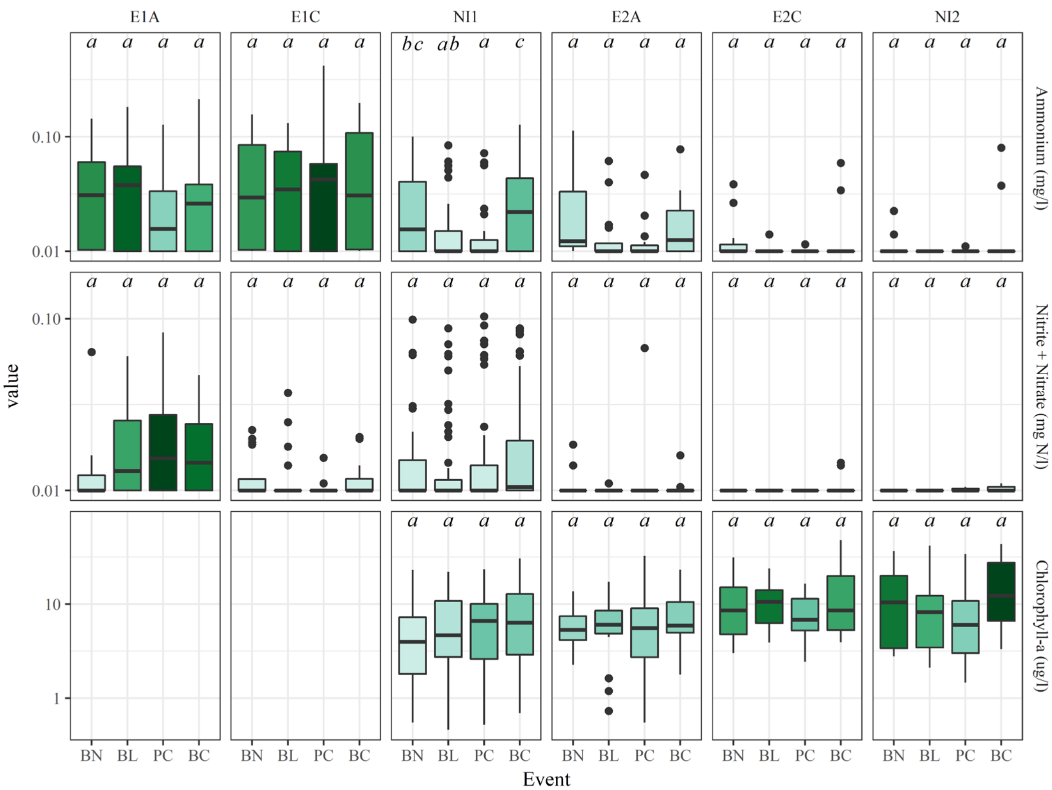


***FIGURE 7.*** *Boxplot summaries of nitrogen and chlorophyll a (log-scale) for stations grouped by time periods. Boxes depict median and middle quartiles of the values, and whiskers depict 1.5 times the interquartile range. Outliers are represented as points. Boxplots within each panel that do not share a letter have significantly different concentrations determined using multiple comparisons with Mann-Whitney U tests. Boxes are shaded by relative magnitudes of the median. Insufficient chlorophyll data were removed for E1A and E1C. Stations are Bangs Lake (BL), Bangs North (BN), Point aux Chenes (PC), and Bayou Cumbest (BC). Time periods are event 1 acute (E1A), event 1 chronic (E1C), non-impact 1 (NI1), event 2 acute (E2A), event 2 chronic (E2C), and non-impact 2 (NI2).*

non—impact years suggests background concentrations prior to the first event were at similarly low levels. Similar patterns in salinity and pH following Hurricane Isaac were not observed during the second event. Moreover, spatial and temporal patterns of $PO_4^{3-}$ concentrations also differed between events despite similar concentrations. The second event was characterized by longer persistence of elevated concentrations, including higher concentrations at stations other than BN and BL. Water quality changes associated with the second event were more characteristic of chronic inputs relative to the discrete changes observed with the first event, suggesting different causes for each. These different causes are important from a resource management perspective in that they lead to potentially different environmental effects.

The potentially negative impact of excess phosphorus on ecosystem condition depends on station—specific characteristics. Nationally, criteria from the U.S. EPA used in the National Coastal Condition assessment ranks waters with < 0.01 mg/l of dissolved inorganic phosphorus in good condition, between 0.01—0.05 mg/l as fair, and > 0.05 mg/l poor (USEPA 2006). Based on these criteria, BL and BN had poor conditions during both the E1A and E2A periods and generally fair conditions during E1C and E2C. Correll (1998) suggested that total phosphorus > 0.02 mg/l could be sufficient for excessive primary production in many systems. Although our observations included only inorganic phosphorus, concentrations at both BL and BN were well above 0.02 mg/l. Additional sources of $PO_4^{3-}$ from the watershed that could have caused the observed concentrations are unlikely given that most of the area is forested. More detailed and focused analyses beyond the routine monitoring data

***TABLE 4.*** *Summary of $NH_4$+ (mg N/l) trends for time periods with sufficient data. Trends are based on seasonal Kendall Tau tests, where τ is the direction and strength of the trend, slope is the change per year, median is the median in the time period, and percent change is the slope divided by the median. Stations are Bangs Lake (BL), Bangs North (BN), Point aux Chenes (PC), and Bayou Cumbest (BC). Time periods are event 1 acute (E1A), event 1 chronic (E1C), non-impact 1 (NI1), event 2 acute (E2A), and event 2 chronic (E2C). *p < 0.05; **p < 0.005*

| Time Periods<br>Stations | τ | slope | median | %<br>change |
|---|---|---|---|---|
| **E1A, E1C** | | | | |
| BN | -0.12 | -0.01 | 0.03 | -26.03 |
| BL | -0.20 | -0.01 | 0.03 | -41.73 |
| PC | -0.17 | -0.01 | 0.03 | -18.46 |
| BC | -0.07 | 0 | 0.03 | -5.13 |
| **NI1** | | | | |
| BN | 0.13 | 0 | 0.02 | 19.35 |
| BL | -0.19 | 0 | 0.01 | 0 |
| PC | -0.18 | 0 | 0.01 | 0 |
| BC | 0 | 0 | 0.02 | 0 |
| **E2A, E2C** | | | | |
| BN | -0.32 | 0 | 0.01 | -4.55 |
| BL | -0.04 | 0 | 0.01 | 0 |
| PC | -0.22 | 0 | 0.01 | 0 |
| BC | -0.3 | 0 | 0.01 | -11.25 |

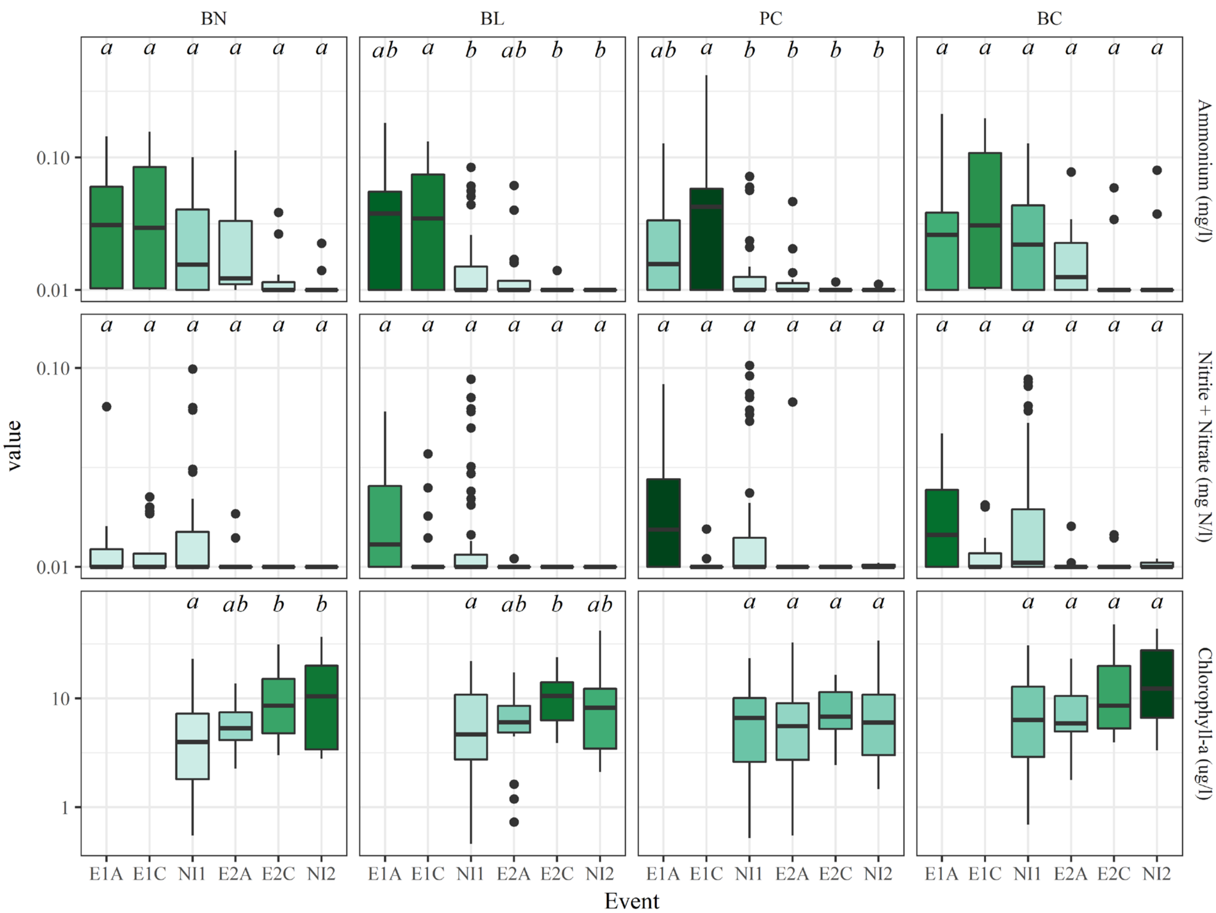


**Figure 8.** *Boxplot summaries of nitrogen and chlorophyll a (log-scale) for time periods grouped by station. Boxes depict median and middle quartiles of the values, and whiskers depict 1.5 times the interquartile range. Outliers are represented as points. Boxplots within each panel that do not share a letter have significantly different concentrations determined using multiple comparisons with Mann-Whitney U tests. Boxes are shaded by relative magnitudes of the median. Insufficient chlorophyll data were removed for E1A and E1C. Stations are Bangs Lake (BL), Bangs North (BN), Point aux Chenes (PC), and Bayou Cumbest (BC). Time periods are event 1 acute (E1A), event 1 chronic (E1C), non-impact 1 (NI1), event 2 acute (E2A), event 2 chronic (E2C), and non-impact 2 (NI2).*

could identify further effects of each spill event, both in past observations and potential changes in water quality.

Effects of each spill on water quality were expected to be detected in other SWMP parameters, particularly $NH_4^+$, which is a known constituent of phosphogypsum waste (Rutherford et al. 1994, Tayibi et al. 2009). High $PO_4^{3-}$ and dissolved inorganic nitrogen (DIN, $NH_4^+$ and $NO_2^-/NO_3^-$) concentrations have been observed in other systems with phosphogypsum inputs. For example, salt ponds in Sfax, Tunisia had mean $PO_4^{3-}$ concentrations of 4.5 mg P/l before restoration and 0.6 mg P/l after removal of contaminated sediments (Kobbi–Rebai et al. 2012). Similarly, mean DIN in the salt ponds declined from 1.2 to 0.17 mg N/l after restoration. Effects were also observed in nearby coastal waters which had $PO_4^{3-}$ concentrations of 1.2 mg P/l and DIN concentrations of 0.14 mg N/l (Rekik et al. 2012). A similar study showed that water quality stations near a fertilizer plant in the Kavala Gulf, Greece had N:P ratios (2.5) that were comparable to fertilizer used in the region (3.2, Sylaios et al. 2005). These studies are similar to the results of GBNERR, such that elevated nitrogen ($NH_4^+$ and $NO_2^-/NO_3^-$) was also observed with elevated $PO_4^{3-}$ concentrations. These results were supported by significant within–station differences between time periods for each analyte. Because of the large proportion of $PO_4^{3-}$ and nitrogen observations at GBNERR that were below detection during this study, we were not able to calculate N:P ratios for comparison to other systems. Detection limits have been lowered in recent years and comparisons may be possible in the future.

Orthophosphate concentrations were not correlated with chlorophyll *a* concentrations, despite an increase in chlorophyll *a* over time. Biological monitoring data were not available to evaluate the potential of increased macroalgae or benthic production as a result of the spills, although water column blooms were observed after both events (unpublished GBNERR photographs 2005; Condon 2015). Previous analyses have found positive correlations between total phosphorous and chlorophyll *a* in Bayou Casotte,

***TABLE 5.*** *Summary of chlorophyll-a (μg/l) trends for time periods with sufficient data. Trends are based on seasonal Kendall Tau tests, where τ is the direction and strength of the trend, slope is the change per year, median is the median in the time period, and percent change is the slope divided by the median. Stations are Bangs Lake (BL), Bangs North (BN), Point aux Chenes (PC), and Bayou Cumbest (BC). Time periods are non-impact 1 (NI1), event 2 acute (E2A), and event 2 chronic (E2C). *p < 0.05; **p < 0.005*

| Time Periods Stations | τ | slope | median | % change |
|---|---|---|---|---|
| **NI1** | | | | |
| BN | 0.61** | 2.24 | 3.98 | 56.36 |
| BL | 0.67** | 2.14 | 4.66 | 45.98 |
| PC | 0.59** | 2.12 | 6.63 | 31.90 |
| BC | 0.39** | 2.17 | 6.34 | 34.29 |
| **E2A, E2C** | | | | |
| BN | 0.36 | 1.21 | 6.12 | 19.69 |
| BL | 0.56 | 1.25 | 6.86 | 18.23 |
| PC | -0.04 | 0.01 | 5.96 | 0.13 |
| BC | 0.26 | 1.42 | 6.92 | 20.52 |

where MPC effluent was discharged during the study period (Blackburn 2000). However, Bayou Casotte receives direct effluent from the plant's outfall, which is a more direct mode of entry for nitrogen and phosphorus than either of our recorded events. Further, Blackburn (2000) evaluated total phosphorus, whereas the data herein included only $PO_4^{3-}$. Effluent may also include nitrate and ammonium as by—products of phosphogypsum production (Lee et al. 2004, Polaris and Lewis 2005). Nutrient bioassay experiments showed that phytoplankton growth in GBNERR is stimulated by nitrogen rather than phosphorus, both before the 2012 spill (Amacker 2013) and in recent experiments (Baine 2017). Phytoplankton production was also shown to be equally stimulated by nitrate or ammonium (Baine 2017). In the Peace River and Charlotte Harbor estuary, phytoplankton uptake of nitrate and phosphate from fertilizer production resulted in peak chlorophyl—*a* concentrations of 52 ug/l, followed by a reduction in nitrate from 0.7 to 0.03 mg N/l and phosphate from 2.8 to 0.8 mg P/l (Froelich et al. 1985). Excess phosphorus was exported from the system after the nitrogen was removed by primary production. A similar export process to the open marine system could occur at BL and the remainder of Grand Bay. However, the relative hydrological isolation of BL (only one narrow channel connects it to open water) suggests export may be limited and effluent constituents could remain in the system. Recent studies suggest that sequestration of excess phosphate in sediments is occurring (K. Dillon and R. Carmichael, pers. comm., University of Southern Mississippi and University of South Alabama).

**Management implications**

Acute impacts of large events, like the 2005 catastrophic levee breach, are clear and quantifiable. The pH decreased to levels that severely damaged vegetation and induced significant mortality in fish, crabs, and other biota (Viskup 2005[1], State of Mississippi 2008[2]). Observed pH was well below established criteria for designated aquatic life uses (pH < 6.5, USEPA 2017b). These impacts are disastrous, but short—lived. Since the 2005 spill, pH at Bangs Lake is closely monitored with telemetered systems during storm events. A large reduction in pH would suggest occurrence of a spill, warranting action to mitigate acute impacts. However, as shown by the 2012 event and the lack of a large drop during Hurricane Isaac, pH is not the only indicator of inputs. This distinction is critical for understanding different signals of spill events to mitigate or prevent future impacts.

Chronic effects are less clear, but important. The challenge of addressing potential chronic impacts stems from an incomplete understanding of linkages between production, limiting nutrients, and physical drivers. Experimental work has demonstrated some of these relationships, particularly between algal production and nutrients (Amacker 2013, Baine 2017). However, nutrient fate and transport in Grand Bay is not well understood and remains a research priority for more effective management. Although we observed elevated concentrations of nutrients following each spill event, concentrations returned to baseline conditions in the non—impact periods. The amount of nutrients and other contaminants buried in sediment should be quantified to identify the role of sediments as a sink and the potential as a source during resuspension events. Physical transport of nutrients by tidal advection was also observed, and removal by flushing to the GOM is another potential explanation for the long—term reduction in phosphorus concentrations, although chlorophyll concentrations in the bay have steadily increased. As such, management priorities for GBNERR and similar systems on the Gulf Coast could differ depending on relative rates of export as compared to sediment burial. Recent research has focused on evaluating profiles of sediment cores (R. Carmichael, pers. comm., University of South Alabama) and a working group has also been established with the objective of better describing the fate and transport of phosphorus and other components of phosphogypsum in GBNERR. Despite incomplete knowledge of nutrient cycling in GBNERR, the existing long—term monitoring data establishes a foundation for additional research. The continued provenance of these data at GBNERR, in addition to the larger NERRS monitoring network, is critical for tracking environmental changes and assessing the effectiveness of management activities.

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