

Internal loading of phosphorus from sediments of Lake Pontchartrain (Louisiana, USA) with implications for eutrophication

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Abstract Diffusive flux of bioavailable soluble reactive phosphorus (SRP) across the sediment–water interface is one mechanism by which sediments can be a source of phosphorus to the water column in aquatic systems and contribute to primary productivity. This process is dependent on sediment biogeochemistry and SRP concentration gradients at the sediment–water interface. In systems subjected to episodic external pulses of nutrient-rich water, SRP concentration gradients can have potential implications for diffusive flux. In this study, we sought to investigate two hypotheses: (1) diffusive flux of SRP from sediments is a significant source of SRP in the annual budget for the oligohaline Lake Pontchartrain estuary and (2) under SRP-depleted water column conditions

following large episodic, external pulses of nitrogen-rich Mississippi River water to the estuary, internal SRP loading by diffusive flux can regenerate SRP in the water column to previously observed levels rapidly. Our specific objectives were to: (i) determine sediment, water column, and phytoplankton characteristics at multiple locations in the estuary, (ii) measure rates of SRP diffusive flux from sediments using intact cores under aerobic and anaerobic incubations, (iii) estimate the potential for water column SRP regeneration by diffusive flux under SRP-depleted conditions using a simple model, and (iv) estimate the annual load of SRP from the sediments by diffusive flux. Results indicate that diffusive flux of SRP from Lake Pontchartrain sediments likely contributes ~30–44% of the annual SRP load to the estuary. Further, internal SRP loading by diffusion has the potential to regenerate SRP in SRP-depleted waters to previously observed concentrations in <60 days. Our findings suggest that a sequence of events is feasible where external pulses of nitrogen-rich water produce phosphorus-limited conditions, followed by an internal pulse of SRP from sediments to restore nitrogen-limited conditions. This internal SRP load may be an important contributor in promoting blooms of nitrogen-fixing harmful algae under summertime low-nutrient conditions.

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Introduction

Eutrophication has been defined as “an increase in the rate of supply of organic matter to an ecosystem” (Nixon, 1995). While several factors can contribute to eutrophication, the enrichment of aquatic systems with phosphorus (P), and nitrogen (N) is the most common (Nixon, 1995; Cloern, 2001). Eutrophication can lead to harmful algal blooms (HABs), oxygen depletion, and fish kills, all of which negatively impact humans in terms of reduced environmental quality and increased management costs (Wetzel, 2001; Wilson & Carpenter, 1999). Coastal Louisiana is particularly vulnerable to eutrophication because it receives a large input of nutrients from upstream agricultural activities and wastewater inputs delivered via the Mississippi River (Rabalais et al., 2002). Watershed nonpoint source P and N pollution has long been identified as the major cause of eutrophication in the United States (Carpenter et al., 1998). However, internal loading of P from sediments can also significantly impact the nutrient budgets of estuarine and freshwater ecosystems (Malecki et al., 2004; Reddy et al., 2007) and have important implications for management efforts aimed at alleviating eutrophication. For example, the eutrophication of some freshwater lakes has proven to be irreversible regardless of severe reductions in external P loading due to previous P accumulation in sediments and the continuing release of this P to the water column after management action has been taken (Carpenter et al., 1999).

Expressions of eutrophication, including HABs, have been documented in Lake Pontchartrain, LA, particularly in the northwest quadrant of the lake (Dortch & Achee, 1998; McCorquodale et al., 2009; Mize & Demcheck, 2009; Bargu et al., 2011). External nutrient loading to the oligohaline Lake Pontchartrain estuary is associated with nonpoint source and point source pollution in the watershed delivered by the fresher Lake Maurepas and several small rivers, urban runoff pumped from the New Orleans area, and leakage of Mississippi River water through the Bonnet Carré Spillway in the southwest corner of the lake (Penland et al., 2002; Turner et al., 2002). Freshwater diversions of nutrient-laden Mississippi River water through the Bonnet Carré Spillway when the Lower Mississippi River flood stage threatens New Orleans may cause the receiving waters in Lake Pontchartrain to become more eutrophic. For example, HABs were

reported following the 1997 spillway opening (Dortch & Achee, 1998; Turner et al., 2004). On the other hand, recent observations indicate that the large nutrient influx from the 2008 spillway opening first produced a diatom bloom that stripped the water column of nutrients, after which N-fixing HAB species became dominant in the summer (Bargu et al., 2011). This pattern suggests limited direct plume influence on the summer HAB in 2008. The majority of the toxic cyanobacteria species observed in Lake Pontchartrain after the 2008 Spillway diversion event competed well at low-nutrient levels relative to diatoms, most likely because of their ability to fix atmospheric N and/or store P (Thompson et al., 1994; Dignum et al., 2005; Bargu et al., 2011). It is therefore important to investigate P dynamics within the lake that may play a critical role in promoting HABs under certain environmental conditions.

One source of P to phytoplankton in Lake Pontchartrain is internal loading from sediments by both diffusion driven by concentration gradients and advection caused by wind-waves. Physical resuspension by wind-waves can dominate the upward transport of P in some shallow lakes (Havens et al., 2007). Sediments in Lake Pontchartrain are predominantly silt and clay with several isolated areas where sand content is greater than 50% (Flocks et al., 2009). Lake Pontchartrain is a wind-dominated system and the currents associated with storm-generated waves frequently resuspend surface sediments (Flocks et al., 2009). Effects of this resuspension include increased sediment oxygen demand, increased biological oxygen demand, restricted sequestration of contaminated material that enters the lake, and potential release of sediment-bound nutrients into the water column (Malecki et al., 2004; Flocks et al., 2009).

External nutrient loading, over time, increases the concentration of nutrients in the sediment that can be released back into the overlying water column (Reddy et al., 1998). After receiving elevated external inputs of P for decades, some wetland systems including the Florida Everglades are now greatly impacted by internal P flux, a phenomenon referred to as “phosphorus legacy” (Bostic et al., 2010; Reddy et al., 2011). In other aquatic systems, external nutrient loading remains the primary factor directly influencing ecological response. Before managers can devise successful nutrient reduction strategies in any watershed, knowledge of the size and mobility of the internal P

loading is required to better assess external load reduction needs. The sedimentary P cycle is characterized by burial of inorganic P, degradation of organic P, and interaction of phosphate with metal oxides in the sediment. Inorganic P in sediments is found in combination with amorphous and crystalline forms of iron, magnesium, aluminum, and calcium (Malecki-Brown et al., 2007). Depending on carbonate availability, inorganic P can also be more permanently immobilized in the form of authigenic P minerals (e.g., carbonate fluorapatite) (Ruttenberg & Berner, 1993; Rozan et al., 2002). Microbial processes mediating fluxes of P bound to metal oxides are largely dependent on environmental factors that vary with time (Thayer, 1971). Changes in sediment redox conditions caused by changes in oxygen concentrations in the overlying water column can result in the benthic regeneration of metal oxides and associated phosphate (Sundby et al., 1986; Kemp, 1989). The release of bioavailable soluble reactive P (SRP, i.e., the dissolved inorganic form of P readily available for phytoplankton uptake) to the water column can contribute to eutrophication.

Primary production in Lake Pontchartrain is typically N-limited (Turner et al., 2004), but due to the massive amounts of inorganic N loaded to Lake Pontchartrain during Bonnet Carré Spillway openings ($\sim 10,000$ t of $\text{NO}_3\text{-N}$ in 2008, molar N:P = 58.9, White et al., 2009), the region of the estuary impacted by the Mississippi River can switch from N- to P-limited (Mize & Demcheck, 2009). The depletion of water column SRP in the presence of bioavailable N increases the SRP concentration gradient between the sediment pore water and water column, thereby increasing rates of diffusive flux. Initial field evidence of this process of high-N loading, followed by P-depletion, and eventual P regeneration is reported for the 2008 Bonnet Carré Spillway event by Bargu et al. (2011) for Lake Pontchartrain waters along a fixed transect in the western portion of the estuary with salinity between 1 and 2 PSU (this range was chosen to minimize dilution impacts). Following the closure of the Spillway, SRP concentrations first decreased from ~ 0.05 to <0.01 mg SRP-P l^{-1} from May 5th to 30th, after which a rebound to ~ 0.04 mg SRP-P l^{-1} was observed on June 17th. Internal loading of P from sediments is a potential source for this P regeneration.

This study addressed diffusion of SRP from Lake Pontchartrain sediments as a source of P regeneration to the water column. There are several methods available

to measure SRP flux across the sediment–water interface by diffusion including (1) simple one-dimensional diagenetic models employing Fick's first law of diffusion based upon pore water concentration gradients (Kemp, 1989) and (2) measuring changes in water column nutrient concentrations over time from intact sediment cores (Fisher & Reddy, 2001; Malecki et al., 2004). The specific objectives of this study were to: (i) determine sediment, water column, and phytoplankton characteristics at multiple locations in the estuary, (ii) determine mean and maximum rates of SRP diffusive flux from sediments using intact cores under aerobic and anaerobic incubations, (iii) use measured maximum rates of diffusive flux and a simple model to estimate the potential for water column SRP regeneration in Lake Pontchartrain under SRP-depleted conditions that have been observed following large pulses of N, and (iv) estimate the annual internal load of SRP from the sediment to the overlying water column by diffusion. Taken together, these objectives were used to test two hypotheses: (1) diffusive flux of SRP from sediments is a significant source of SRP in the annual SRP budget for Lake Pontchartrain and (2) under SRP-depleted water column conditions following large external pulses of bioavailable N, internal SRP loading by diffusive flux can regenerate SRP to previously observed levels rapidly (<2 months). Further, the possible implications of internal SRP loading for the growth of potentially toxic cyanobacteria under low-nutrient conditions are discussed.

Materials and methods

Study site

Lake Pontchartrain is a shallow (mean depth = 3.7 m), estuary with a surface area of 1637 km² and a volume of ~ 6 km³ located just north of New Orleans, LA (Turner et al., 2002). External loading of SRP to Lake Pontchartrain occurs primarily through seasonal runoff via several tributaries on the northern shore and episodic high-loading events in those years that the Bonnet Carré Spillway is opened to alleviate Lower Mississippi River flooding concerns. There is some evidence that tributary SRP loading is increasing due to urbanization on the estuary's north shore. Silcio et al. (2010) report a 3.4-fold increase in the loading of SRP to Lake Maurepas since 2003 and suggest that it is

linked to erosion caused by new construction, fertilization of new lawns, and stress to existing wastewater treatment facilities. Under typical conditions, estuarine water exchanges with the saline Gulf of Mexico via three restricted outlets to the east/southeast, one of which has been permanently closed in 2010 (Turner et al., 2002). Salinity in the estuary depends on freshwater discharges and wind conditions, and ranges from 2 to 9 PSU (practical salinity units) under normal conditions (Li et al., 2008). Available measurements of bottom water dissolved oxygen in Lake Pontchartrain indicate aerobic conditions (dissolved oxygen $>>2$ ppm) in spring and summer during both normal conditions and spillway diversion events (McCorquodale et al., 2002; Brammer et al., 2007; White et al., 2009). It has been suggested that episodic events of hypoxia may go undetected (Brammer et al., 2007).

Sediment sampling

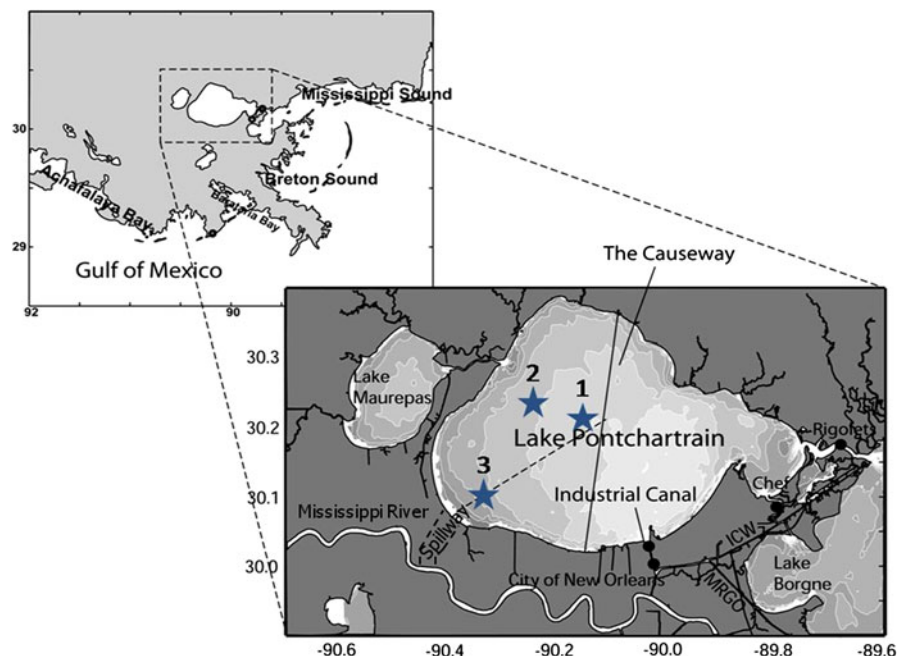
Three sampling locations were selected to represent different regions of Lake Pontchartrain (Fig. 1). One of the stations was proximal to the Bonnet Carré Spillway inflow (SWI), one was in the lake center (LC), and one was in the northwest quadrant (NWQ) where HABs have been repeatedly observed. Sediments at the

spillway inflow are predominantly sand and clay, while those in the lake's center and the northwest quadrant are composed mainly of silt and clay (DeLaune et al., 2008). Intact sediment core samples were collected on June 16, 2010 by driving a 7 cm diameter piston-core sampler into the sediment. At each station, 9 cores were collected in total: 3 cores for sediment characterization, 3 cores for anaerobic laboratory incubations, and 3 cores for aerobic laboratory incubations. Sediment cores were 20–30 cm in length and no compaction occurred during either retrieval or transportation. Characterization cores were immediately sectioned at 5 cm intervals in the field and stored on ice until return to the lab where they were stored at 4°C until analyzed.

Sediment characterization

Upon return to the laboratory, samples for sediment characterization were analyzed for total P, extractable SRP, organic matter, moisture content, and bulk density. Solid-phase total P analysis involved combustion of oven-dried subsamples at 550°C for 4 h in a muffle furnace and subsequent dissolution of the ash in 6 M HCl on a hot plate (Anderson, 1976) and concentrations were determined using a Seal Analytical AQ2

Fig. 1 Location of the three stations in Lake Pontchartrain used in this study: 1 Lake Center (LC), 2 Northwest Quadrant (NWQ), and 3 Spillway Inflow (SWI). Map courtesy of Dr. Chunyan Li



discrete analyzer (Method 365.1; USEPA, 1993). Extractable SRP ($\text{PO}_4\text{-P}$) was determined by shaking triplicate soil samples with 25 ml of 1 M KCl at a ratio of approximately 1:50 (g dry soil:extractant) on a longitudinal shaker for 1 h. Samples were centrifuged for 10 min and vacuum-filtered through Whatman #42 filter paper, after which the supernatant was analyzed for SRP (Method 365.1; USEPA, 1993). Organic matter content was determined as loss on ignition (LOI) using ash weight divided by sediment weight (White & Reddy, 1999). Moisture content was determined by placing homogenized wet sediment into a drying oven at 70°C until constant weight. Bulk density was calculated for the sediment intervals on a dry weight basis.

Metals analyses

Water column and sediment metals concentrations were measured using methods described by Malecki-Brown & White (2009). Water samples (100 ml) were filtered through a 0.45 μm membrane filters, acidified with concentrated trace metal grade nitric acid to pH <2 and analyzed for dissolved metals. For total metals, sediments were dried for 24 h at 105°C and then ground. Approximately 1 g of dry ground sediment was placed in a ~75 ml glass digestion tube and digested with 3 ml of concentrated trace metal grade nitric acid at ~120°C for 8 h. The digests were brought to 50 ml total volume with deionized water, shaken, and allowed to settle for ~6 h before centrifuging. Metal determinations for both dissolved and total metals were performed using a Varian model MPX ICP-OES.

Chlorophyll *a* (chl *a*) and microscopy analyses

Triplicate 1 l surface water samples were collected at each sample station in clean polypropylene bottles and stored in the dark on ice for biological analyses. Upon return to the lab, chl *a* was determined as a measure of phytoplankton biomass. Fifty millimeter sub-samples of surface water were filtered through 25 mm GF/F filters. Filters were then extracted for 24 h in 90% aqueous acetone at -20°C and subsequently analyzed for chl *a* using a Turner fluorometer (Model 10-AU) (Parsons et al., 1984). Subsamples were preserved with 2% glutaraldehyde and kept in the dark at room temperature and analyzed for species composition of

the phytoplankton community using an inverted microscope (Axiovert 135, Zeiss).

Intact sediment core experiments

The remaining intact sediment cores underwent anaerobic (three per station) and aerobic (three per station) incubation. The water column for each core was drained and then re-filled with water from its respective lake station that was filtered through no. 4 Whatman (Maidstone, UK) filter paper (20- μm), resulting in a 20 cm water column. Re-flooding was done slowly by trickle to minimize sediment disruption. Salinities for stations SWI and LC were 1.78 and 1.90 PSU, respectively. For anaerobic incubations, O_2 -free nitrogen gas was bubbled into the water column to purge all oxygen in the core for 24 h initially and then 2 h per day thereafter. Anaerobic cores were sealed with rubber stoppers to prevent the entrance of O_2 . For the aerobic incubation, room air was bubbled continuously into the water columns for the duration of the experiment to maintain fully aerobic conditions. All cores were placed in a water bath to maintain temperature (25°C) and incubations were carried out in the dark. Dissolved oxygen and pH were monitored throughout the course of the experiment.

The SRP flux from sediments to the water column was quantified by measuring changes in water column SRP concentrations over time (Fisher & Reddy, 2001; Malecki et al., 2004). At designated intervals, 9 ml of water was collected from the water column using a syringe and filtered through a 0.45 membrane syringe filter. After sampling, an equal amount of filtered station water was added back to the core to maintain the water column volume. The total incubation time was 15 days with a total of 13 discrete sampling events. Water samples were characterized for SRP using a Seal Analytical AQ2 discrete analyzer (Method 365.1; USEPA, 1993).

Data analysis

Mean SRP flux rates were calculated from the slope of the best-fit line from SRP concentration versus time curves for the first 8 days of the experiment. Maximum SRP flux rates for anaerobic cores were calculated using the steepest portion of each individual SRP concentration versus time curve including at least

three data points. Data normality was determined using the Kolmogorov–Smirnov test ($\alpha = 0.01$). Data was log-transformed to fit a normal distribution if necessary. *T* tests were performed to determine significant differences ($P < 0.05$) in sediment characteristics, water column SRP concentrations, SRP flux rates, trace metal concentrations, and solid-phase metal concentrations among sample stations and between oxygen conditions.

Model of SRP flux from sediments under P-depleted conditions

To estimate the feasible rate of water column SRP concentration increase in Lake Pontchartrain due to diffusive flux from sediments under SRP-depleted conditions, an algorithm was developed based on the maximum rates of SRP flux by diffusion determined here. The sediment surface area of SRP regeneration (*A*) was assumed to be equal to the maximum area of the high N:P ratio Mississippi River plume in Lake Pontchartrain during the Bonnet Carré Spillway opening of 2008 as determined by satellite imagery ($6.13 \times 10^8 \text{ m}^2$; White et al., 2009). Water column depth (*d*) was assumed to be equal to the mean depth of Lake Pontchartrain (3.7 m; Turner et al., 2002). The water column was assumed to be well-mixed and water column SRP concentration at time *t* (*C*, mg SRP-P l^{-1}) was determined as:

$$C(t) = \frac{M(t-1) + A \times F_{\max}}{A \times d \times 1000} \quad (1)$$

where $M(t-1)$ is the total mass of SRP in water volume (mg) at time $t-1$ and F_{\max} is the maximum SRP flux rate by diffusion ($\text{mg SRP-P m}^{-2} \text{ d}^{-1}$). At $t = 0$, *M* was set equal to zero to represent P-depletion. This simple model was run for 60 days at a one day time-step using maximum SRP flux rates by diffusion determined here for each station.

Table 1 Sediment characteristics for cores sectioned during field collection

Data are mean values ($n = 3$) \pm 1 standard deviation
LOI loss on ignition (organic matter content)

Station	Interval (cm)	Total P (mg kg^{-1})	LOI (%)	Moisture (%)	Bulk density (g cm^{-3})
Lake center	0–5	510 \pm 32	7.84 \pm 1.47	74.2 \pm 2.7	0.29 \pm 0.03
	5–10	455 \pm 11	6.16 \pm 1.02	69.5 \pm 0.8	0.38 \pm 0.03
Northwest quadrant	0–5	461 \pm 11	8.79 \pm 0.16	74.9 \pm 0.8	0.32 \pm 0.01
	5–10	499 \pm 29	5.53 \pm 0.3	61.7 \pm 1.6	0.48 \pm 0.06
Spillway inflow	0–5	390 \pm 4.3	3.20 \pm 0.84	37.5 \pm 1.0	1.05 \pm 0.06
	5–10	414 \pm 30	3.27 \pm 0.66	32.4 \pm 1.3	1.23 \pm 0.05

Results

Sediment characterization

Sediment characteristics measured, including total phosphorus (TP), organic matter content (LOI), moisture, and bulk density, were not significantly different between the lake center and northwest quadrant stations for both the 0–5 cm and 5–10 cm intervals (Table 1, $P > 0.05$ in all cases except moisture at 5–10 cm). In general, sediments from the spillway inflow were characterized by less TP, LOI, and moisture content, and greater bulk density in comparison to the lake center and northwest quadrant stations ($P < 0.05$ in all cases except TP at 5–10 cm for spillway inflow versus lake center). Sediments from the spillway inflow are composed of sand and clay, as opposed to the fine silts and clays found at the lake center (DeLaune et al., 2008).

Sediment from the lake center and the northwest quadrant stations exhibited similar concentrations of aluminum, iron, magnesium, and calcium in the 0–5 cm sediment layer (Table 2). In comparison, the spillway inflow sediments had significantly ($P < 0.05$) lower concentrations of aluminum, iron, and magnesium, corresponding to lower values of TP. The spatial differences in sediment parameters are likely due to the influence of periodic influxes of Mississippi river water and associated sediment via the Bonnet Carré Spillway.

Extractable SRP and oxygen conditions

During the laboratory experiment, dissolved oxygen concentrations in aerobic cores were consistently between 5.0 and 7.0 mg l^{-1} . These oxygen concentrations corresponded well to field measurements of surface water on June 16, 2010 at the three sample stations (dissolved $\text{O}_2 = 6.8\text{--}7.3 \text{ mg l}^{-1}$). Dissolved

Table 2 Sediment concentrations (mg kg^{-1}) of aluminum, iron, magnesium, and calcium in characterization cores sectioned during field collection

Station	Interval (cm)	Al (mg kg^{-1})	Fe (mg kg^{-1})	Mg (mg kg^{-1})	Ca (mg kg^{-1})
Lake center	0–5	1111 \pm 24	945 \pm 19	263 \pm 8	62 \pm 5
	5–10	1080 \pm 19	949 \pm 8	262 \pm 3	131 \pm 68
Northwest quadrant	0–5	1072 \pm 34	919 \pm 16	252 \pm 5	83 \pm 12
	5–10	857 \pm 31	812 \pm 21	222 \pm 14	555 \pm 405
Spillway inflow	0–5	286 \pm 23	319 \pm 32	93 \pm 11	402 \pm 200
	5–10	353 \pm 43	399 \pm 44	131 \pm 11	223 \pm 56

Data are mean values ($n = 3$) \pm 1 standard deviation

Table 3 Mean extractable SRP values (mg kg^{-1}) \pm 1 standard deviation of Lake Pontchartrain sediments for characterization cores sectioned in the field upon collection and intact experiment cores incubated in the laboratory

Station	Interval (cm)	Extractable SRP (mg kg^{-1})		
		Field characterization	Anaerobic lab experiment	Aerobic lab experiment
Lake center	0–5	0.96 \pm 0.37 ^a	0.80 \pm 0.24 ^a	0.05 \pm 0.08 ^b
	5–10	0.96 \pm 0.25 ^a	1.08 \pm 0.15 ^a	0.52 \pm 0.07 ^b
Northwest quadrant	0–5	0.73 \pm 0.29 ^a	0.82 \pm 0.34 ^a	0.05 \pm 0.08 ^b
	5–10	0.76 \pm 0.11 ^a	0.58 \pm 0.07 ^a	0.11 \pm 0.16 ^b
Spillway inflow	0–5	0.45 \pm 0.11 ^a	0.35 \pm 0.02 ^a	0.07 \pm 0.03 ^b
	5–10	0.33 \pm 0.09 ^a	0.25 \pm 0.02 ^a	0.00 \pm 0.00 ^b

Letters indicate statistically significant differences ($P < 0.05$) among treatments for a given station and sediment interval

oxygen measurements of the water column verified that the anaerobic cores were in fact anaerobic (mean dissolved $\text{O}_2 \pm 1$ standard error = $0.39 \pm 0.04 \text{ mg l}^{-1}$) and was confirmed by the significant flux of manganese from the sediment under anaerobic conditions (data not shown). Sediment extractable SRP data (Table 3) indicate that characterization cores sectioned in the field had similar concentrations of extractable SRP to experimental cores for which anaerobic conditions were imposed. To the contrary, experimental cores exposed to continuous aerobic water column conditions had significantly ($P < 0.05$) lower extractable SRP concentrations, indicating that the oxygenation of the sediments during the aerobic laboratory experiment led to soluble P binding with abundant metal oxides in the sediment.

Phytoplankton biomass and species composition

In general, lake phytoplankton biomass and diversity were low at the time of sampling in June 2010. The chl *a* concentrations (± 1 standard error) in the lake center and the northwest quadrant stations were similar, averaging $3.59 \pm 0.38 \mu\text{g l}^{-1}$ ($n = 6$), while the

concentration of chl *a* was significantly lower at $2.14 \pm 0.08 \mu\text{g l}^{-1}$ ($n = 3$) for the spillway inflow station ($P < 0.05$). The phytoplankton community at the lake center station was composed of the diatom *Skeletonema* and potentially toxin-producing cyanobacteria *Anabaena* and *Microcystis*. The potentially toxic *Anabaena* was more abundant than the other two groups at the northwest quadrant station which is consistent with findings from previous samplings (Turner et al., 1999; S. Bargu, unpublished data). The spillway inflow station contained potentially toxic *Microcystis* at lower presence.

SRP flux across the sediment–water interface during laboratory incubations

SRP concentrations at the onset of the flux experiment correspond to those occurring in the field during the time of sampling. Mean initial SRP concentrations were 0.03, 0.03, and $0.04 \text{ mg SRP-P l}^{-1}$ for the lake center, northwest quadrant, and spillway inflow stations, respectively (Fig. 2). Based on observations shown in Fig. 2, calculated mean rates of SRP flux across the

sediment–water interface (averaged for each station) ranged from 0.30 to 1.06 mg SRP-P m⁻² d⁻¹ (Table 4). There were no significant differences between stations for mean SRP fluxes during either the aerobic or anaerobic incubations. Anaerobic mean SRP flux rates were significantly ($P < 0.05$) higher than the aerobic mean flux rates for the lake center and spillway inflow stations, as well as for the overall mean rate. Anaerobic and aerobic mean SRP flux rates for the northwest quadrant station were not significantly different. Calculated maximum rates of SRP flux by diffusion (averaged for each station) for anaerobic incubations ranged from 2.89 to 4.21 mg SRP-P m⁻² d⁻¹ with no significant differences among stations (Table 4). Maximum flux rates for aerobic incubations (averaged for each station) ranged from 1.82 to 3.16 mg SRP-P m⁻² d⁻¹, with the overall mean significantly ($P < 0.05$) less than for anaerobic incubations. However, on a station basis, the trend of significantly greater maximum flux rates for anaerobic incubations was significant only at the spillway inflow.

No significant ($P < 0.05$) difference in final water column dissolved Fe was observed between anaerobic and aerobic incubations at the spillway inflow station, despite significantly greater SRP flux rates in anaerobic cores (Fig. 3). For sediment from the lake center, final water column dissolved Fe was significantly ($P < 0.05$) greater during anaerobic incubations. However, in this case no significant difference was observed for SRP flux rate between anoxic and oxic cores. No correlation between the fluxes of Fe and SRP across the sediment–water interface was observed.

SRP flux from sediments by diffusion under SRP-depletion

Using Eq. 1 and calculated maximum rates of SRP flux by diffusion in anaerobic incubations (Table 4), water column SRP regeneration following SRP-depletion is shown for each station in Fig. 4. These results indicate that an internal pulse of SRP following SRP-depletion could increase water column concentrations from below detection to the levels loaded via the Mississippi river (~ 0.05 mg SRP-P l⁻¹) in less than 60 days. The magnitude of this episodic internal SRP load will depend on the areal extent of SRP-depletion in Lake Pontchartrain influenced by the Bonnet Carré Spillway plume. For example, if the sediment surface area

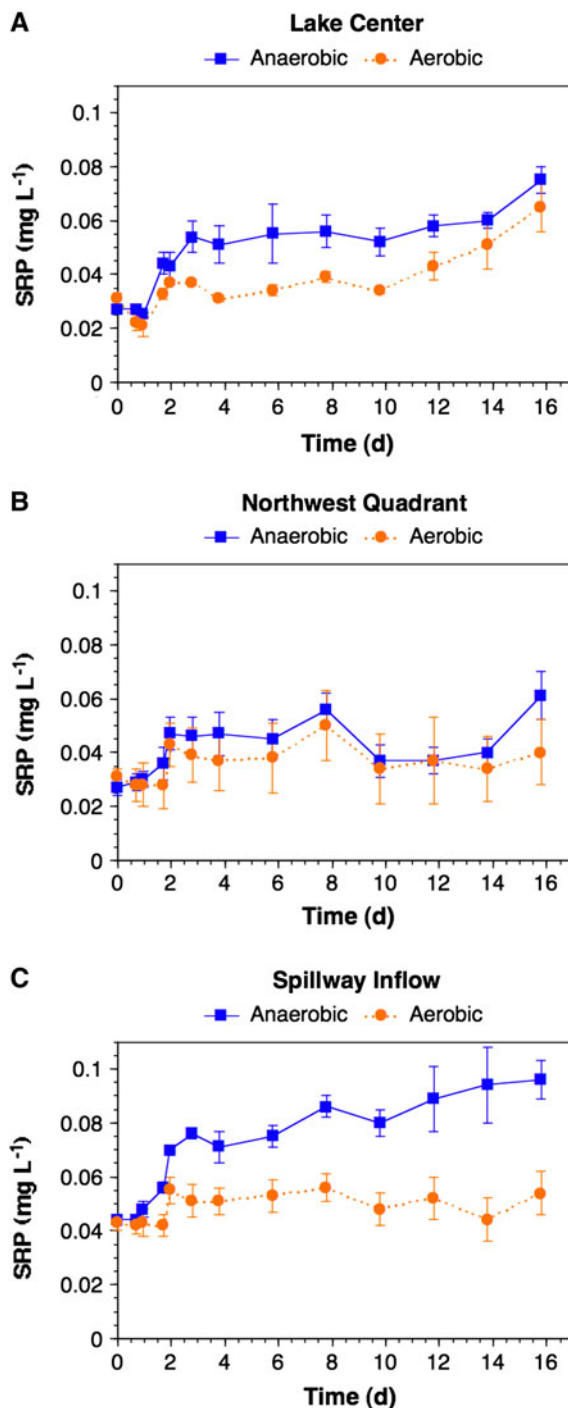


Fig. 2 Changes in mean soluble reactive phosphorus concentration ± 1 standard error of the water column under anaerobic and aerobic laboratory incubations for intact sediment cores from the lake center (A), northwest quadrant (B), and Bonnet Carré Spillway inflow (C) in Lake Pontchartrain ($n = 3$ per O₂ condition)

Table 4 Mean and maximum soluble reactive phosphorus flux rates ($\text{mg SRP-P m}^{-2} \text{d}^{-1}$) from Lake Pontchartrain sediments to the water column by diffusion under anaerobic and aerobic laboratory incubations

Station	Mean SRP flux by diffusion		Max SRP flux by diffusion	
	Anaerobic $\text{mg SRP-P m}^{-2} \text{d}^{-1}$	Aerobic	Anaerobic $\text{mg SRP-P m}^{-2} \text{d}^{-1}$	Aerobic
Lake center	$^{1}0.84 \pm 0.39^{\text{a}}$	$^{1}0.30 \pm 0.08^{\text{b}}$	$^{1}4.21 \pm 1.19^{\text{a}}$	$^{1}3.16 \pm 0.80^{\text{a}}$
Northwest quadrant	$^{1}0.69 \pm 0.20^{\text{a}}$	$^{1}0.48 \pm 0.52^{\text{a}}$	$^{1}2.89 \pm 1.44^{\text{a}}$	$^{1,2}1.83 \pm 0.34^{\text{a}}$
Spillway inflow	$^{1}1.06 \pm 0.15^{\text{a}}$	$^{1}0.37 \pm 0.22^{\text{b}}$	$^{1}3.86 \pm 0.58^{\text{a}}$	$^{2}1.82 \pm 0.11^{\text{b}}$
Overall mean	$0.87 \pm 0.19^{\text{a}}$	$0.38 \pm 0.09^{\text{b}}$	$3.66 \pm 0.68^{\text{a}}$	$2.27 \pm 0.77^{\text{b}}$

Numbers and letters indicate statistically significant differences ($P < 0.05$) among stations and oxygen conditions, respectively. All data are mean values ($n = 3$) ± 1 standard deviation

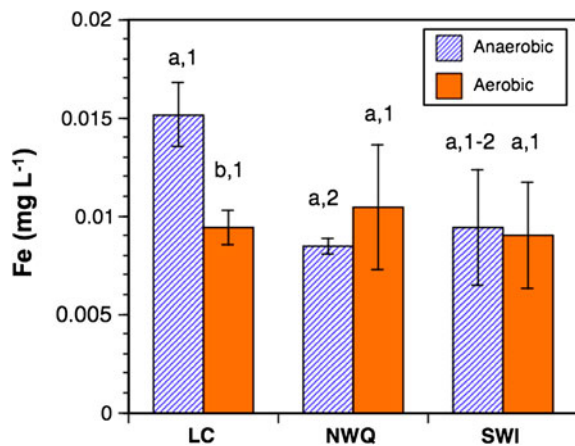


Fig. 3 Final water column mean dissolved iron concentrations ± 1 standard error for anaerobic and aerobic water columns at the LC lake center, NWQ northwest quadrant, and SWI spillway inflow stations in Lake Pontchartrain. Significant differences ($P < 0.05$) between anaerobic and aerobic incubations at each station are indicated by different letters. Significant differences ($P < 0.05$) among stations for either anaerobic or aerobic water columns are indicated by different numbers

exposed to a SRP-depleted water column is equal to the maximum N-rich freshwater plume area in 2008 (613 km^2), the internal load by diffusion could amount to $106\text{--}142 \text{ t SRP-P}$ over 60 days in the plume region.

Discussion

SRP flux across the sediment–water interface

Release of P from sediments under anoxic conditions in aquatic systems is attributed to iron reduction due to

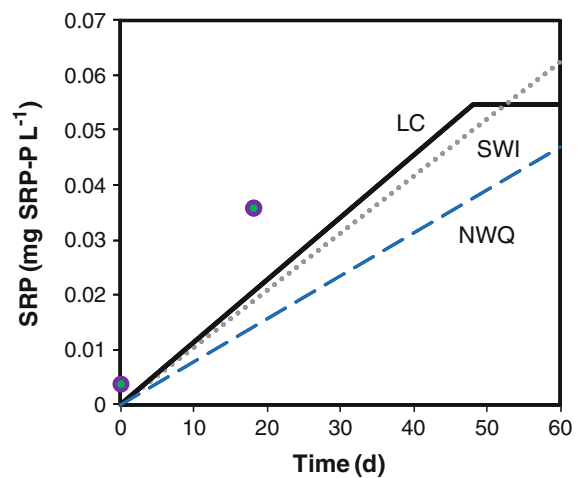


Fig. 4 Potential regeneration of soluble reactive phosphorus (SRP) to the water column in Lake Pontchartrain under phosphorus-depleted conditions by diffusive flux from sediments over 60 days. The model is based on measured maximum rates of diffusive flux for the LC lake center, NWQ northwest quadrant, and SWI spillway inflow stations. In the case of LC, the maximum concentration used to determine the maximum flux rate ($0.055 \text{ mg SRP-P l}^{-1}$) is achieved in <60 days. The depression of regenerated SRP by phytoplankton assimilation is neglected for all cases. Circles show mean SRP concentrations measured by Bargu et al. (2011) for Lake Pontchartrain water along a fixed transect in the western portion of the estuary with salinity between 1 and 2 PSU on May 30, 2008 ($t = 0$, $n = 8$) and June 17, 2008 ($t = 18$, $n = 3$)

lower redox conditions in the sediment (Mortimer, 1941). Phosphorus that is removed from the water column by binding with ferric iron (Fe^{3+}) in the sediment under oxic conditions can be subsequently liberated from the sediments under anoxic conditions as Fe^{3+} is reduced to soluble ferrous iron (Fe^{2+}). The P is

then released into the water column by diffusion driven by concentration gradients in sediment pore water and the water column (Upchurch et al., 1974; Shaffer, 1986). Field water column SRP concentrations reported here ($0.03\text{--}0.04\text{ mg SRP-P l}^{-1}$) fall within the range observed by White et al. (2009) and Barga et al. (2011) in Lake Pontchartrain during the spring and summer of 2008 for both more typical estuarine water and freshwater loaded via the Bonnet Carré Spillway ($0.00\text{--}0.07\text{ mg SRP-P l}^{-1}$). The impacts of water column SRP concentration on SRP diffusive flux from sediments are discussed in detail below.

In freshwater lakes, increases in water column dissolved iron concentrations are typically observed concurrently with the release of SRP from sediments (e.g., Moore & Reddy, 1994) and the molar ratio between dissolved Fe and dissolved PO_4 (i.e., the Fe/P release ratio) under anoxic conditions is typically ≥ 2 (Mortimer, 1941; Gunners & Blomqvist, 1997). To the contrary, the Fe/P ratio is much lower in estuarine and marine systems (≤ 1), presumably due to the greater supply of sulfide, which binds a larger fraction of soluble Fe as iron sulfides than in freshwater environments (Capone & Kiene, 1988; Morse et al., 1987; Gunners & Blomqvist, 1997). The Fe/P release ratios ranged from 0.1 to 0.9 for Lake Pontchartrain sediments, falling within the range of ratios reported by Gunners & Blomqvist (1997) for estuarine and marine systems. The lack of correlation between water soluble Fe and P observed here was likely due to the binding of iron by sulfides. For Fe/P release ratios less than ~ 2 , there is insufficient iron to bind all dissolved phosphate and therefore the scavenging of P by precipitating ferric iron in an oligohaline system like Lake Pontchartrain is likely less effective than in freshwater systems (Gunners & Blomqvist, 1997). This may increase the bioavailability of P in the estuary.

Oxygen conditions in Lake Pontchartrain sediments

Results from this study indicate that the magnitude of the internal SRP load in Lake Pontchartrain is dependent in some areas upon whether surface sediments are primarily aerobic or anaerobic (Table 4). Available data indicate that the water column in Lake Pontchartrain is generally aerobic (McCorquodale et al., 2002; Brammer et al., 2007; White et al.,

2009, this study) with the potential for undetected episodic occurrences of hypoxia (Brammer et al., 2007). Turner et al. (2004) assume implicitly that surface sediments in Lake Pontchartrain are aerobic due to an aerobic overlying water column, limiting anaerobic sedimentary biogeochemical processes. However, results from this study indicate that both control cores sectioned in the field and cores subjected to anaerobic conditions had significantly greater concentrations of extractable SRP at both the 0–5 cm and 5–10 cm layers in comparison to the aerobic cores (Table 3). The lower concentrations of SRP in the aerobic cores were likely a result of the binding of soluble P in the sediments to metal oxides caused by the introduction of oxygen into the sediments by vigorously bubbling room air. These results therefore suggest that sediments in Lake Pontchartrain were anaerobic in the field during the time of collection, despite the aerobic water column. It appears that even under an oxygenated water column subjected to repeated wind mixing, the fine-grained sediments in Lake Pontchartrain largely limit the diffusion of oxygen. This finding has implications for nutrient cycling at the sediment–water interface, including the rate of SRP flux from sediments by diffusion.

Annual internal phosphorus loads from diffusion

The annual internal load of SRP to Lake Pontchartrain was calculated using the overall mean SRP flux rates (Table 4). A shortcoming of the annual internal load calculation, as with all such studies, is that the lake-wide load estimate is based on limited stations, three in this case, sampled at one point in time and may not capture the full range of spatio-temporal heterogeneity for SRP flux in Lake Pontchartrain. The calculated annual mean internal load of SRP to Lake Pontchartrain from sediments ranged from 227 t y^{-1} under 100% aerobic conditions to 517 t y^{-1} under the assumption that the bulk of the surface sediments are anaerobic 100% of the time. Our data suggest that the latter is more likely the case and that is the rate used to calculate the annual SRP load below. The contribution of the internal total P load may be even more significant than reported here given that the loads calculated in this study consists only of the SRP fraction of the internal P load. The total internal P load to Lake Pontchartrain contains dissolved inorganic P (SRP), particulate P, as well as dissolved organic P.

McCorquodale et al. (2009) provide a phosphorus budget for the upper estuary in terms of total P and state that the ratio of SRP:TP is ~ 0.5 during “normal open water conditions” and ~ 0.2 in the plume of the Bonnet Carré Spillway. The SRP:TP fraction is likely dynamic in reality and further research is needed to verify this assumption. In order to gauge the relative contribution of the annual internal SRP load from sediments, TP loads under normal conditions and spillway plume conditions presented by McCorquodale et al. (2009) were multiplied by 0.5 and 0.2, respectively, and used to construct an annual SRP budget for the Upper Pontchartrain estuary (Fig. 5).

Despite the uncertainty of the SRP:TP fraction, it is apparent that internal flux of SRP from the sediments to the water column by diffusion ($517 \text{ t SRP-P year}^{-1}$) is a significant source of bioavailable P to the Lake Pontchartrain ecosystem (30–33% of total loading in spillway years, 44% in non-spillway years), potentially greater than or equal to the total annual SRP load delivered by tributaries to Lakes Maurepas and Pontchartrain ($444 \text{ t SRP-P year}^{-1}$). In

addition, wind-induced sediment resuspension could significantly increase the transport of sediment P to the water column. In Florida’s Lake Okeechobee, a system with a similar surface area to mean depth ratio to that of Lake Pontchartrain, wind-induced sediment resuspension has been estimated to transport 6–18 times more P to the water column than flux via diffusion (Moore & Reddy, 1994). However, sediment resuspension may be a source, sink, or have no net impact on water column SRP that may limit primary production and harmful algal blooms depending on sediment geochemistry (Havens et al., 2007). Further research is needed to determine the impact of sediment resuspension by wind on P cycling in Lake Pontchartrain.

During the Bonnet Carré Spillway diversion events in 1997 and 2008, the SRP budget of the lake was dramatically altered increasing the total annual SRP load by 400–526 t, an increase of 34–45% (Fig. 5). The episodic loading of nutrients via the spillway over a relatively brief period of time has received attention in the context of eutrophication and harmful algal blooms in Lake Pontchartrain (Turner et al., 2004;

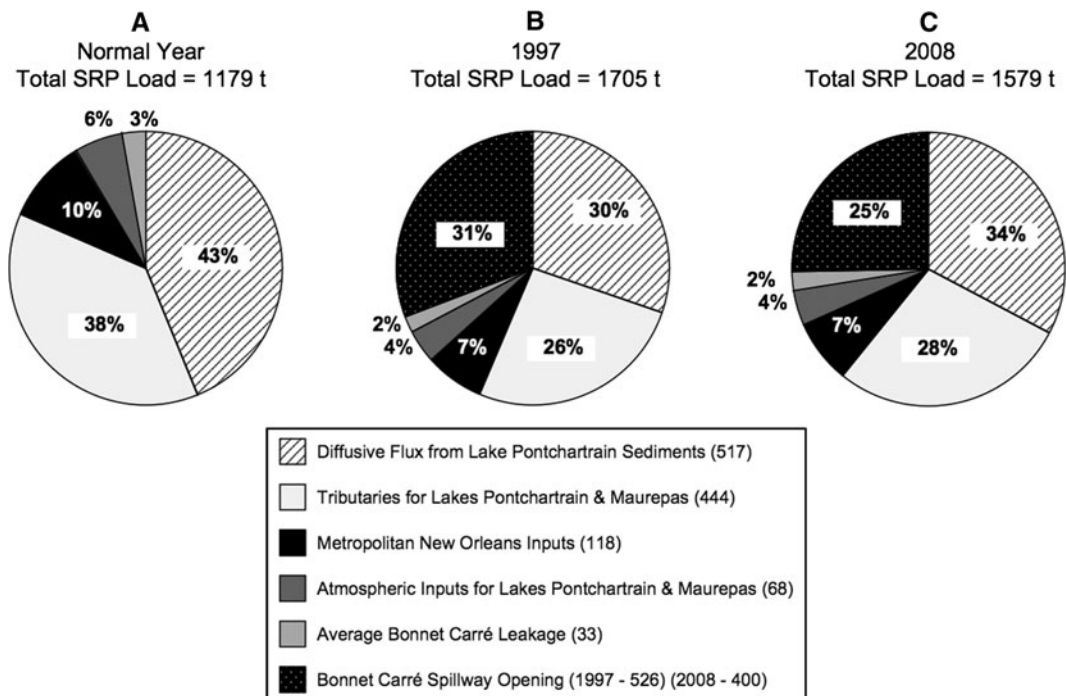


Fig. 5 Annual soluble reactive phosphorus (SRP) loads to the Upper Pontchartrain Estuary for normal years (A) and 2 years during which the Bonnet Carré Spillway was opened, 1997 (B), and 2008 (C). Individual loads (t) are shown in *parentheses*

within the legend. Load estimates are based on values provided by McCorquodale et al. (2009) except for diffusive flux from sediments (this study) and the 2008 Bonnet Carré Spillway opening (White et al., 2009)

Bargu et al., 2011). Results from this study indicate that the slower release of SRP from sediments by diffusive flux over the course of an entire year may provide as much SRP to Lake Pontchartrain as these relatively short-term (month long) diversion events.

Potential for episodic pulses of SRP from Lake Pontchartrain sediments by diffusion

Our results here illustrate that internal loading of SRP by diffusion may not always act as a slow P feedback in cases when SRP becomes depleted. During the laboratory incubations, SRP concentrations increased in a logarithmic fashion (Fig. 2), having maximum rates of SRP flux at lower water column SRP concentrations that were much greater than the mean rates used to construct the lake-wide annual SRP budget (Table 4). Based on these maximum flux rates for anaerobic incubations and a simple model of SRP regeneration from the sediments to the water column in Lake Pontchartrain under SRP-depleted conditions, it appears that a large internal pulse of SRP following an initial external N pulse from the spillway is feasible (Fig. 4). Without additional external loading of N, such an internal SRP pulse could result in a return to N-limited conditions over a relatively short period of time. Also plotted on Fig. 4 are two points showing water column concentrations of SRP in Lake Pontchartrain waters with salinity between 1 and 2 PSU on May 30, 2008 ($t = 0$) and June 17, 2008 ($t = 18$) based on data from Bargu et al. (2011). This observed increase in SRP concentration occurred at a greater rate than that based on maximum rates of SRP diffusive flux from sediments measured here. This increased rate of SRP regeneration is possibly due to advective flux of P from sediments. Further field work is needed to verify SRP regeneration from sediments and determine the relative importance of both diffusion and advection processes.

Potential effects of internal P loading on the Lake Pontchartrain ecosystem

Chl *a* concentrations measured in this study (2.14–3.81 $\mu\text{g l}^{-1}$) were at the low end of the range observed by Bargu et al. (2011) in Lake Pontchartrain during the spring and summer of 2008 for both more typical estuarine water and freshwater loaded via the Bonnet Carré Spillway (2.76–54.65 $\mu\text{g l}^{-1}$). Potentially toxic

cyanobacteria species were observed at all stations in this study. Previous research in Lake Pontchartrain indicates that toxic cyanobacteria are most abundant when water temperature is high, waters are calm, and nutrient concentrations are low (Bargu et al., 2011). Under summertime low-nutrient conditions, cyanobacteria can out-compete diatoms due to efficient nutrient uptake related to their surface area, N-fixation and P-storage capabilities, and reduced grazing pressure enabled by toxicity (Thompson et al., 1994; Dignum et al., 2005). However, cyanobacteria biomass under these conditions will ultimately remain low due to nutrient limitation unless an additional source of nutrients becomes available. By late July of 2008 following the collapse of nutrients loaded via the Bonnet Carré Spillway, N-fixing cyanobacteria dominated the phytoplankton community while dissolved inorganic nitrogen remained below detection (Bargu et al., 2011). Under these conditions, internal loading of P from sediments may play a critical role in stimulating growth of toxic cyanobacteria and possibly even bloom formation, especially species that are capable of N-fixation. To better understand algal bloom formation in the lake, increased monitoring of nutrient biogeochemistry and phytoplankton parameters is needed during both normal years and those during which the spillway is opened. Harmful algal blooms are patchy and therefore this scenario may differ across space depending on local environmental conditions and sediment biogeochemistry.

The results from this study have significant implications for the management of eutrophication in Lake Pontchartrain, including blooms of toxic cyanobacteria. Continual internal loading of SRP from sediments may limit the effectiveness of modest reductions in external P loading from the watershed designed to mitigate eutrophication, as well as increase the sensitivity of the estuary to any increases in external nutrient loading (Reed-Andersen et al., 2000). The latter is of particular concern in the Upper Pontchartrain Estuary where significant human population growth has occurred in the watershed following migration out of New Orleans after Hurricane Katrina in 2005, potentially increasing external loading of SRP (Silcio et al., 2010). Such an increase in external SRP loading coupled with the internal SRP loading reported here may exacerbate eutrophication and harmful algal blooms in portions of the estuary. Clearly, any plan to reduce eutrophication requires

taking into account internal loading of P from sediments when determining restoration strategies.

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