Microbial mediated sedimentary phosphorus mobilization in emerging and eroding wetlands of coastal Louisiana

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Abstract

The interactions between the microbial reduction of Fe (III) oxides and sediment geochemistry are poorly understood and mostly unknown for the Louisiana deltaic plain. This study evaluates the potential of P mobilization for this region during bacterially mediated redox reactions. Samples were collected from two wetland habitats (forested wetland ridge, and marsh) characterized by variations in vegetation structure and elevation in the currently prograding Wax Lake Delta (WLD) and two habitats (wetland marsh, and benthic channel) in degrading Barataria Bay in Lake Cataouatche (BLC). Our results show that PO_4^{3-} mobilization from WLD and BLC habitats were negligible under aerobic condition. Under anaerobic condition, there is a potential for significant release of PO_4^{3-} from sediment and wetland soils. PO_4^{3-} release in sediments spiked with Fe reducing bacteria *Shewanella putrefaciens* (Sp-CN32) were significantly higher in all cases with respect to a control treatment. In Wax Lake delta, PO_4^{3-} release from sediment spiked with Sp-CN32 increased significantly from 0.064±0.001 to 1.460±0.005 µmol/g in the ridge and from 0.079±0.007 to 2.407±0.001 µmol/g in the marsh substrates. In Barataria bay, PO_4^{3-} release increased from 0.103±0.006 µmol/g to 0.601±0.008 µmol/g in the channel and 0.050±0.000 to 0.618±0.026 µmol/g in marsh substrates. The PO_4^{3-} release from sediment slurries spiked with Sp-CN32 was higher in the WLD habitats (marsh 30-fold, ridge 22-fold) compared to the BLC habitats (marsh 12-fold, channel 6-fold). The increase in PO_4^{3-} release was significantly correlated with the Fe bound PO_4^{3-} in sediments from different habitats but not with their organic matter content. This study contributes to our understanding of the release mechanism of PO_4^{3-} during bacterial mediated redox reaction in wetland soils undergoing pulsing sediment deposition and loss.

Key words: Phosphorus mobilization, iron reduction, coastal Louisiana

1. Introduction

The availability of phosphorus (P) controls primary production rates in aquatic ecosystems including estuarine and wetland dominated environments. P has a low stoichiometric biological demand compared to other major nutrients (106C: 16N: 1P; Redfield, 1958). Thus, excessive P loading can promote growth of harmful algal blooms, exacerbate eutrophication, and lead to hypoxia (Schneider, 1997; Correll, 1998). In temperate latitudes, one of the most conspicuous eutrophic regions in the Gulf of Mexico (GOM) is coastal Louisiana. The northern Gulf of Mexico is mostly under the influence of the Mississippi River, which delivers the seventh largest discharge ($2.04x10^7$ million cubic-feet/yr) in the world. This discharge maintains a protracted increase in N and P loading in coastal waters since the 1950's as the nitrate (NO_3^{2-}) flux from the Mississippi River to GOM has tripled (Rabalais et al., 2002; Strauss et al., 2011; Goolsby et al., 2001).

Historically, nutrient excess in Louisiana water bodies have caused extensive and persistent toxic cyanobacterial blooms and fish kills, particularly across coastal regions that include the Atchafalaya and Mississippi River watershed basins (Dortch and Achee, 1998; Poirrier and King, 1998; Bargu et al., 2011; Day et al., 1998). Although specific plans to reduce, mitigate, and manage hypoxia in the northern GOM include the reduction of inorganic nutrients, most of the management actions are focused on NO_3^- reduction and not P (e.g., PO_4^{3-}, Soluble Reactive Phosphorus-SRP) (EPA, 2015). This approach seems prevalent despite the recognition of P as a key additional driver impacting regional eutrophication (Rabalais et al.,

2002; Justic et al., 2003; Scavia & Donnelly, 2007; Scavia et al., 2003). It is necessary to recognize the different roles and interactions played by NO_3^- and PO_4^{3-} as they undergo different biogeochemical transformations that are characterized by major differences in residence time in benthic sediments, wetland soils, and the water column. For instance, unlike NO_3^-, sedimentary release of P can maintain eutrophic conditions even after external loads are reduced or eliminated (Sylvan et al., 2006; Scavia & Donnelly, 2007). Although wetland restoration strategies have traditionally focused on the external loading of P (Rivera-Monroy et al., 2011), the internal release of P from sediments and soil has received little attention. This potentially large P input from sediment and soil (i.e., "legacy P"; Sharpley et al., 2013; McDowell et al., 2002) needs to be assessed in the context of long term wetland restoration projects (i.e., decades) to project future changes in eutrophication conditions and water quality in estuaries and wetland habitats (White & Reddy, 1999), lakes (Malecki et al., 2004; Reddy et al., 2007).

In the Mississippi and Atchafalaya River basins, P in the water column is characterized by relatively low SRP concentration (527 uM; White et al., 2009) while the suspended sediment can contain a large amount of total particulate P (9,645 uM; Zhang et al., 2012). A major portion of the particulate P associated within the sediment is eventually deposited in estuarine benthic substrates (McDowell et al., 2003; McDaniel et al., 2009) and wetland soils (Reddy and DeLaune, 2008), thereby ameliorating P loadings in coastal waters (Hoffman et al., 2009 ;Ekka et al., 2006; Wang et al., 2011). However, wetland soils are subjected to variable hydroperiod (i.e., flooding duration and frequency, depth) and long duration of inundation can trigger persistent soil reduction conditions promoting the release of P

(hereinafter referred to as P sedimentary release) from both wetland soils and in the receiving basin sediments (White et al., 2006; Zhang et al., 2012).

Sedimentary P release is regulated by the fluctuations in physiochemical variables including redox potential, pH, temperature (Kim et al., 2003; Upreti et al., 2015), salinity (Jordan et al., 2008; Upreti et al., 2015), and sediment microbial activity (Hupfer et al., 1995; Jaisi et al., 2008; Jaisi et al., 2011; Upreti et al., 2015). Although the role of bacteria is widely recognized in P cycling, our knowledge about the mechanisms regulating P release from anoxic substrates is lacking in comparison to other environmental drivers. Our current understanding about microbial community's role in P cycling include a) decomposition of organic P compounds (e.g. Khoshmanesh et al., 1999), b) removal of polyphosphate stored inside cells (e.g. Hupfer et al., 1995), and c) pore water dissolved oxygen (DO) consumption by bacteria in sediment/soils leading to a lower redox potential (<100 mv) and reduction of Fe (III) to Fe (II) causing subsequent release of iron oxide-bound P (Lovley & Phillips, 1988). This reductive dissolution of Fe (III) oxides under anoxic conditions by microbes and subsequent release of P is a key transformation that could lead to an increase in both pore water and water column SRP (Kemp et al., 2005). Such dissimilatory reduction of iron oxides in soils and sediments can be carried out by both bacteria and archaea that can perform anaerobic respiration utilizing metal as a terminal electron (Richter et al., 2012; Weber et al., 2006). Several studies have found facultative bacteria like *Shewanella sp.* and obligate anaerobes like *Geobacter sp, Dechloromonas sp*. in wetland sediments (Weber et al., 2006; Cooper et al., 2017; Pakingking et al., 2015). These microbes can carry out iron

reduction in sediments across a variety of environment including marine, brackish and freshwater (Weber et al., 2006).

The potential sediment release of P under anoxic conditions associated with flooding have been examined by few studies in coastal Louisiana (Stow et al., 1985; Roy et al., 2012; Zhang et al., 2012). However, none of these studies assess the specific interactions between the microbial reduction of Fe (III) oxides and sediment geochemistry. There is a general lack of information on the magnitude of P fluxes under oxic/anoxic conditions in wetland soils including the extent of microbial reduction of Fe (III) oxides. It is expected that an increase in air temperature, as a result of climate change, will translate into major changes in vegetation dominance in coastal Louisiana (Henry & Twilley, 2012; Ward et al., 2016), and therefore, on the availability of different organic carbon sources fueling microbial transformations; from N removal via denitrification to P release from soils and sediments with different mineral to organic content ratios. It is important to experimentally evaluate how P release varies as a function of seasonal changes and how microbial reduction of Fe (III) oxides mobilizes P under different organic and inorganic P and C availability. Louisiana naturally provides such a contrast for our current study in terms of organic matter and iron mineral content. It is among one of the few regions in the world where both newly formed prograding wetlands with low organic carbon to mineral ratio as well as mature degrading wetlands with high organic matter to mineral ratio are present, under similar climatic conditions (Day et al., 2000; Twilley and Rivera-Monroy, 2009). This setting allows us to test our main hypothesis that the interaction between organic matter and iron mineral content play an important role in microbial mediated release of P from wetland soils.

Thus, the main objective of this study is to experimentally quantify the potential magnitude of PO_4^{3-} and Fe (II) sedimentary release from benthic sediments and wetland soils commonly found in the Louisiana delta plain (LDP); these substrates have distinct physical properties and are subjected to a range of hydrological and sedimentary processes. As a result of major alterations in the delta cycle in the LDP caused by hydrological landscape-level alterations (Martin et al., 2002), there are distinct regions undergoing different rates of wetland loss (i.e., degrading Barataria Bay-BB) (Day et al., 1997) and gain (i.e., prograding: Wax Lake Delta-WLD) (Martin et al., 2002). Our specific objectives were to i) measure PO_4^{3-} fluxes in intact sediment, soil cores, and slurries obtained in prograding and degrading deltas characterized by similar type of habitats (i.e., marsh), and ii) evaluate the potential sedimentary PO_4^{3-} mobilization using *Shewanella putrefaciens* CN32. This is a facultative anaerobe commonly found in sediments and used as a model bacterium to study Fe (III) reduction (e.g. Upreti et al., 2015). We addressed three questions: 1) is there a significant difference in PO_4^{3-} fluxes between benthic sediments and wetland soils under similar seasonal conditions? 2) How do PO_4^{3-} fluxes and Fe (II) release vary among different substrates within each coastal basin? and 3) what is the relationship between potential PO_4^{3-} fluxes and Fe (II) release across different habitats?

2. Materials and Methods

2.1 Study area description and sample collection

Samples were collected during winter (December-February), spring (March-May), and summer (June-August) from two distinct habitats in Wax Lake Delta (WLD) and Barataria Bay-Lake Cataouatche (BLC) region. WLD is in coastal Louisiana about 20 miles southwest

of Morgan City (Figure 1B). This delta was recently formed as a result of sediment input through a man-made outlet (Wax Lake Outlet), which was dredged to divert water from Atchafalaya River to the Gulf of Mexico (Figure 1A,B) (Roberts & Sneider, 2003; Rosen & Xu, 2013). New land in the area emerged above the water line, after the extreme flood of 1973 by forming a sub aerial delta (Henry & Twilley, 2013). WLD is characterized by a diurnal micro tidal regime, which can be hampered as a result of wind-driven effects (Allen et al., 2012). The delta has a current extension of 65 km^2 and has increased at a rate of 1 km^2 $year^{-1}$ (1983-2010) promoting the establishment of distinct marsh and forested wetland vegetation across elevation gradients (Allen et al., 2012; Holm & Sasser, 2001).

BLC is an estuarine wetland system located between the Mississippi River and Bayou Lafourche and separated from the Gulf of Mexico by a chain of barrier islands (FitzGerald et al., 2004). In contrast to the WLD region, the Barataria Bay region represents an area of net wetland loss although new land and wetlands have been created upstream around the David pond diversion structure (Boesch, 2006; Boesch et al., 1994). It is estimated that this region had a net wetland loss of 1,177 ± 106 km^2 (31%) between 1932-2016 (Couvillion et al., 2017). It has been divided into four interconnected sub-basins (Figure 1C) with the northern region occupied by lakes while the southern region is tidally influenced (Li et al., 2011). The basin encompasses a total of approximately 6,000 km^2 of water bodies and wetlands.

Sediment cores were collected from two dominant habitats with different vegetation structure within each basin. In the WLD (Mike island, Figure 1), we sampled a forested wetland (herein referred to as ridge; dominant species: *Salix nigra*) and a marsh (dominant species:

196 *Sagittaria* spp, *Colocasia* spp, *Typha* spp) while in the Barataria Bay (north Lake Cataouatche, Figure 1) we sampled a marsh (dominant species: *Sagittaria* spp, *Typha* spp, 198 *Bidens* spp) and benthic sediments in a channel adjacent (~0.5 m) to the marsh site (Figure 1). All sampling sites represented freshwater /brackish wetlands with soil pore water salinity 200 ranging from 0.1 to 0.4 ppt and salinity in the channel water column from 0.1 to 0.3 ppt (Upreti, unpublished data). Sediment cores were collected at each site in triplicate using 202 acrylic tubes (length: 36 cm; internal diameter: 10.1 cm) to perform intact core incubations. One additional core was taken from each habitat in both sites to perform sediment slurry 204 incubation (see below) with and without soil bacterium *Shewanella putrefaciens* CN32 to estimate potential PO_4^{3-} release. Soil cores in the wetland habitats were collected by carefully 206 placing the acrylic core tubes on the soil surface and pushing them into the soil. Cores in the channel were collected using a core sampler operated from a boat (Hartzell et al., 2010). Site-208 specific water samples (6 L) for the laboratory incubation experiments were collected from the lake in BLC, whereas water in the WLD was sampled in a tidal channel adjacent (~0.3 m) 210 to the ridge site (Figure 1). Samples were collected in summer, winter and spring seasons (Figure 1B) during 2015-2016. We performed seasonal samplings to warrant actual *in situ* 212 substrate conditions (e.g., microbial biomass, diversity, inorganic nutrients) and the temperature regimes used in the laboratory incubations are similar to average water 214 temperature measured each sampling period (winter: 10 ^{o}C ; spring: 20 ^{o}C; summer: 30 ^{o}C). Water temperature at each site was recorded continuously using a HOBO temperature logger 216 (Onset-HOBO) deployed in the channel during the duration of the study. The average monthly water temperature during the winter, spring and summer times when samples were 218 collected were 11.2 °C, 22.2 °C and 28.1 °C, respectively for WLD; and 10.4 °C, 21.3 °C

and 28.9 °C for BLC, respectively. Thus, temperatures of 10 °C (winter), 20 °C (spring) and 30 °C (summer) were selected as treatments to represent each season. This allowed us to compare different sites across similar temperature regimes.

Sediment cores collected in the field were transported to the laboratory by partially draining the overlying water column to a water column height of ~3 cm above the sediment. This action prevented substrate resuspension during transportation and preserved soil *in situ* redox conditions. Cores were then stored in an ice cooler at ~ 5^{o}C to reduce bacterial activity during transport and brought to the laboratory within six hours of collection. Upon arrival to the laboratory, one set of cores (3 cores from each habitat) were prepared for intact core incubation and the remaining core from each habitat was sliced into 4 cm vertical depth intervals. The top 4 cm slice was then homogenized and used for slurry incubations spiked with a set volume of the soil bacterium *Shewanella putrefaciens* CN32. Water collected from each site was filtered (filtered size: 0.5 µm) to run incubation experiments.

2.2 Laboratory Incubation Experiments

2.2.1 Intact Core Incubations

Core incubations were conducted in triplicate until dissolved O_2 (DO) concentration reached approximately 50% of the initial value (~ 40 mg/ L in all core incubations) to evaluate PO_4^{3-} fluxes under aerobic conditions at different temperatures. Cores were carefully filled with *in situ* filtered water previously air-bubbled up to DO saturation. Each core was then tightly capped with custom-made PVC caps ensuring the absence of any headspace; caps were equipped with electrically controlled stirrers (18 rpm) to maintain a mix water column inside the cores. Two independent ports located on top of each lid allowed simultaneous water

sampling and replacement from a reservoir, also filled with *in situ* filtered water, during incubations. Cores were then immersed in an incubator (plastic sealed chamber 105.74 cm x 47.47 cm x 51.44 cm) filled with water (volume: 142 L) at temperatures corresponding to the season they were collected (i.e., winter: 10 ^{o}C; spring: 20 ^{o}C; summer: 30 ^{o}C). Cores were incubated for 2-3 hours prior to the start of the experiment for acclimation. DO concentrations inside the cores were monitored throughout the duration of the experiment by using an oxygen sensor (Unisense). Samples were collected every 1.5-3.0 hours depending on DO consumption rates. The incubation was terminated when oxygen concentration was found to be ~50% of the initial (t_0) DO saturation value. The total incubation periods lasted from 6-18 hours based on how fast DO concentrations changed; this reduction in DO was associated to differences in substrate (soil, sediment) organic matter content.

DO Samples and nutrient analyses consisted of 50 ml water samples withdraw at each sampling time after discarding the first 5-10 ml of tubing dead volume. Water was automatically replaced at each sampling period from the reservoir attached to the core lid and kept at a higher elevation to maintain constant overlying water depth inside the core. Volumetric corrections during flux calculations were performed for minor dilutions occurring at each sampling time step (Steingruber et al., 2001). Water samples were then filtered (GF/F syringe filter 0.45 µm) and stored in 20 ml plastic scintillation vials inside a freezer until analyses (usually within 2 weeks of collection) of PO_4^{3-} using auto analyzer (O.I. Analytical). The fluxes were calculated from the six-point linear regression of concentration (corrected for sample volume withdrawn) as a function of time as shown in Eq. 1 below.

$$F = (\frac{dc}{dt}xV)/A \qquad [Eq. 1]$$

where, F is the flux; $\frac{dc}{dt}$ is the change in concentrate over time derived from the linear regression; V is the volume of water incubated and A is the cross-section area of the sediment core.

Bulk Density and Organic Carbon analysis

Sediment cores were sliced at 4 cm depth- interval and oven dried at 60 ^{o}C to a constant weight. Bulk density (BD) was determined by dividing the total dry weight of the sediment by the soil volume (Buckman and Nyle, 1960). Previous to the analysis of % organic matter (OM), each sample was grinded using a Straub grinding mill and analyzed using Loss of Ignition (LOI) method at 550 ^{o}C (Heiri et al., 2001).

2.2.2 Sediment Slurry Incubation

A sediment slurry (1:50) was prepared (Upreti et al., 2015; Jaisi et al., 2007) from a homogenized mix of the top 4 cm sediment layer from cores collected from each habitat (see section *2.1 sample collection*). The slurries were placed in 125 ml serum bottles and incubated with and without facultative bacteria *Shewanella putrefaciens* CN32 (Sp-CN 32) capable of surviving in both oxic and anoxic conditions at 20±1 ^{o}C temperature and to evaluate the effect of biologically mediated redox reaction and PO_4^{3-} release from each habitat substrate.

Three treatments were used to estimate PO_4^{3-} release from each habitat substrate: a) bacteria spike (i.e, enhanced biological activity) mixed with the slurry, b) sediment with spike of dead microorganisms (dead cells: autoclaved at 121 ^{o}C for 15 minutes), c) control, slurry without

any bacteria spike. The treatment spiked with bacteria consisted of freshly grown CN32 cells at final concentration of 1.3×10^{8}–1.8×10^{8} cells/ml (Jaisi et al., 2005; Upreti et al., 2015). Sp-CN32 was grown in a minimal nutrient broth in lab as described in (Jaisi et al., 2005; Upreti et al., 2015). Twenty mM lactic acid (pH 7.0±0.2) was used as electron donor in all incubations. All incubations were performed inside the anaerobic chamber at a substrate: water ratio of 1:45 (i.e., 2 g in 90 mL) after 24 hours of substrate water suspension equilibrium (Upreti et al., 2015). Samples were taken from each incubation tube at selected sampling time points (0, 0.3, 1, 2, 4, 8, 12 days) for PO_4^{3-} and Fe (II) measurements. All slurry incubations were performed in triplicate per treatment combination.

PO_4^{3-} and Fe (II) Analysis

Water samples for Fe(II) measurement were acidified (0.5 mL sample with 0.5 mL 1 N HCl) inside an anaerobic chamber in order to avoid re-oxidation of Fe(II) to Fe(III). Samples collected for both PO_4^{3-} and Fe (II) were filtered through 0.45-micron syringe filters. Water PO_4^{3-} concentrations were measured using phosphomolybdate blue method (Murphy & Riley, 1962) while Fe (II) were determined using the Ferrozine assay method (Stookey, 1970) in a UV/VIS Spectrophotometer. Total fluxes were determined using triplicate measurement of the slope of a six-point linear regression of concentration as a function of time. Slurries from pre and post incubation were sequentially extracted to quantify the loosely bound and Fe bound PO_4^{3-} pools following the standard sequential extraction method SEDEX (Ruttenberg, 1992; Delaney and Anderson, 1997).

2.3 Statistical Analysis

2.3.1 Intact Core Incubations

Statistical analyses were performed using SAS and JMP statistical packages (SAS institute 2012; PROC MIXED). Since one of the objectives was to evaluate differences in marsh PO_4^{3-} across regions (BLC vs WLD) in three different temperatures (proxy for season: winter, spring, summer), we performed a three-factor factorial ANOVA (fix factors). In the case of the WLD region, we used a two-factor factorial ANOVA to evaluate differences between wetland type (marsh and forested wetland or Ridge) and season. Because we also sampled cores in a channel habitat in BLC, we evaluated the differences in fluxes between channel and the marsh habitats across seasons and their interactions using a two-factor factorial ANOVA.

2.3.2 Sediment Slurry Incubation

In the case of the slurry incubation experiment, we also used factorial ANOVAs (fix factors) to evaluate the role of bacteria in PO_4^{3-} and Fe (II) release from sediments following the same experimental design (region, habitat) as in the case of the intact cores within each region. The main difference in this case is that the incubations were performed at one incubation temperature representing the seasonal average value (21^{o}C). The third treatment in this experiment has three levels of bacterial additions (no cells or control, dead cells and spike).

All statistical analysis was evaluated at 0.05 levels. Test of normality for PO_4^{3-} and Fe (II) was performed using proc univariate. Additionally, a regressions analysis was used to determine the interaction between PO_4^{3-} and Fe (II) substrate release over time during slurry incubations.

3. Results

3.1 Field characteristics-study area

3.1.1 Soil properties

Organic matter content in WLD ridge and marsh soils ranged between 5.94-8.39% and 4.32-17.19% respectively for the upper 16 cm of the soil (Figure 2). In BLC, organic matter ranged between 24.31-48.76% in channel sediments and 27.57-80.13% in marsh soils. Overall the organic matter content did vary greatly with depth for any of the sites. Similarly, the bulk density was lower in habitats with higher organic matter content. In WLD habitats, bulk density ranged between 1.09-1.30 g cm^{-3} in the ridge soils, and 0.21-1.14 g cm^{-3} in the marsh soils (Figure 2). In BLC, bulk density ranged from 0.19-0.28 g cm^{-3} in channel sediments and 0.41-0.59 g cm^{-3} in marsh soils. Overall BLC marsh soil was found to have the highest organic matter content while WLD ridge had the lowest organic matter.

3.1.2 Surface and pore water chemistry

The dissolved PO_4^{3-} concentrations in the channel water that was used to carry out incubation varied between 1.51-2.5 µM at WLD and 1.9-4.9 µM at BLC (Table 1). The PO_4^{3-} concentrations in both the WLD and BLC channel were highest in the summer.

PO_4^{3-} concentrations in soil porewater for marsh ranged from 0.59 to 2.05 µM in the WLD while in the BLC the range was from 0.28 to 0.96 µM (Table 1). *In situ* DO measurements at the soil/water interface in WLD and BLC were low and ranged from 0.5-1.7 mg L^{-1}. Salinity in the WLD and BLC ranged between 0.1-0.4 ppt.

362 **3.2. Changes in dissolved O_2 and PO_4^{3-} concentrations during intact core incubations**

DO concentration in the water column reached 50% of the initial (t_0) concentration at
364 different times depending on incubation temperature and habitat. It ranged from 15-18 hours at 10 ^oC (winter), 12-15 hours at 20 ^oC (spring), and 6-7.5 hours at 30 ^oC (summer) (Figure
366 3a, c). The O_2 consumption rates were similar for all sites in winter while for spring both the sites from WLD had significantly higher O_2 consumption rates than the BLC sites. In
368 summer, BLC channel had the highest O_2 consumption among all the sites (Figure 3a, c, Table 2). PO_4^{3-} in intact cores remained similar even when DO was reduced by 50% (Figure
370 3b, d) indicating PO_4^{3-} fluxes were not significant irrespective of location and temperature (Figure 3d, Table 2). The only exception to this was the marsh site at BLC which had a net
372 flux of 90.05 μmol m^{-2} d^{-1} in summer.

374 **3.3 Bacterial enhanced PO_4^{3-} release in sediment slurry experiments**

3.3.1 PO_4^{3-} mobilization from sediment

376 PO_4^{3-} release was significantly higher when spiked with Sp-CN32 compared to control and "dead cells" treatment in all habitats within each region (Table 2, Figure 4a). In WLD, the
378 ridge (i.e., forested wetland) habitat showed a 22-fold increase in PO_4^{3-} concentration, from 0.064 to 1.460 μmol g^{-1} when spiked with Sp-CN-32. Although we also observed an increase
380 in the other treatments, the increase was smaller: from 0.0670 to 0.5396 μmol g^{-1} in the control (8-fold; control) and from 0.056 to 0.239 μmol g^{-1} (4-fold), in the dead cells
382 treatment (Figure 4a). A similar positive increase was observed in the marsh habitat, but comparatively this value was significantly higher than in the forested wetland; from 0.079 to
384 2.407 μmol g^{-1} (30-fold) when spiked with Sp-CN-32. The marsh control treatment showed a 10-fold increase from 0.0749 to 0.7595 μmol g^{-1} while the dead cell showed 4-fold increase,

386 from 0.068 to 0.266 μmol g^{-1} (Figure 4a). PO_4^{3-} flux in WLD ridge was 0.118 μmol g^{-1} d^{-1} and 0.180 μmol g^{-1} d^{-1} in marsh when spiked with Sp-CN32 (Figure 4c).

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In the BLC region, there was an increase in PO_4^{3-} concentration when spiked with Sp-CN32 390 across treatments and within habitats, yet this increase was significantly lower than in the case of the WLD core incubations. PO_4^{3-} concentrations in channel samples treated with 392 bacteria increased 6-fold from 0.103 to 0.601 μmol g^{-1} while in marsh increased from 0.050 to 0.618 μmol g^{-1} (12-fold) (Figure 4a). In contrast, control samples ranged between 0.036-394 0.185 μmol g^{-1} in channel and 0.032-0.214 μmol g^{-1} in marsh. The "dead cells" treatment responded with changes in PO_4^{3-} concentration from 0.037 to 0.134 μmol g^{-1} for channel and 396 from 0.033 to 0.160 μmol g^{-1} in the marsh habitat. PO_4^{3-} flux in BLC channel was 0.037 μmol g^{-1} d^{-1} and 0.043 μmol g^{-1} d^{-1} in the marsh when spiked with Sp-CN32 (Figure 4c).

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3.3.2 Fe (II) mobilization from sediment

400 Fe (II) concentrations in the sediment slurry experiment followed the same pattern observed in the case of soluble PO_4^{3-} across habitats and region treatments (Table 2, Figure 4b). In the 402 case of the WLD region, Fe (II) concentration increased significantly from 0.810 to 4.802 μmol g^{-1} (5-fold) in the ridge habitat and from 1.170 to 7.710 μmol g^{-1} (6-fold) in the marsh 404 when spiked with Sp-CN32. PO_4^{3-} concentration was highly correlated (linearly) with Fe (II) in samples from both habitats. We also observed an increase in Fe (II) concentration with 406 time in both control and dead cells treatments. Control samples showed an increase from 0.808 to 1.900 μmol g^{-1} in the ridge and from 1.154 to 3.333 μmol g^{-1} in the marsh habitats. 408 Fe (II) concentration in samples with the dead cells treatment ranged from 0.810 to 1.487

μmol g^{-1} in the ridge and from 1.163 to 2.420 μmol g^{-1} in marsh habitats. Fe (II) flux in WLD ridge was 0.378 μmol g^{-1} d^{-1} and 0.576 μmol g^{-1} d^{-1} in marsh when spiked with Sp-CN32 (Figure 4d).

The marsh and channel habitats in the BLC region showed similar trend in Fe (II) concentration over time (Figure 4b). Samples spiked with iron reducing bacteria responded with increasing Fe (II) concentrations from 0.138 to 0.575 μmol g^{-1} in the channel and from 0.137 to 0.642 μmol g^{-1} in the marsh habitats. Control treatments also showed an increase, although in much lower magnitude, from 0.136 to 0.279 μmol g^{-1} (channel) and 0.138 to 0.287 μmol g^{-1} (marsh). Concentrations in the dead cells treatment, increased from 0.137 to 0.176 μmol g^{-1} in channel and 0.139 to 0.213 μmol g^{-1} in the marsh. Fe (II) flux in BLC channel was 0.058 μmol g^{-1} d^{-1} and 0.059 μmol g^{-1} d^{-1} in the marsh when spiked with Sp-CN32 (Figure 4d).

3.3.3 Exchangeable and iron bound PO_4^{3-}-SEDEX phases

Sediment samples from the three replicates of each treatment were combined at the end of slurry experiment to provide enough material for carrying out sequential extraction of phosphorus. The first two steps of the SEDEX procedure was carried out to determine the loosely bound and iron bound PO_4^{3-} fractions; thus, the errors represent analytical uncertainties rather than standard error.

Exchangeable Loosely bound PO_4^{3-}: The sequential extraction of PO_4^{3-} from substrate slurries sampled in the WLD region showed similar concentration of loosely-bound PO_4^{3-} in

both the marsh and the forested wetland (i.e., ridge) habitats. Loosely-sorbed PO_4^{3-} pool were 0.232±0.01 μmol g^{-1} in ridge to 0.208±0.01 μmol g^{-1} in marsh. In the case of sediments extracted after incubation spiked with Sp-CN32, loosely bound PO_4^{3-} decreased from 0.232±0.01 to 0.181±0.01 μmol g^{-1} in the ridge and from 0.208±0.01 to 0.185±0.01 μmol g^{-1} in the marsh substrate. Similarly, in BLC, loosely bound PO_4^{3-} were similar in both habitats (Figure 5). Loosely bound PO_4^{3-} in the sediment did decrease post incubation similar to WLD habitats, particularly when spiked with bacterium Sp-CN32 in both habitats at BLC. In the case of Sp-CN32 spiked condition, loosely bound PO_4^{3-} decreased from 0.971±0.05 to 0.452±0.03 μmol g^{-1} in the channel and from 1.00±0.06 to 0.470±0.03 μmol g^{-1} in the marsh. Loosely bound PO_4^{3-} was found to be higher in both BLC habitats compared to the WLD habitats.

Fe bound PO_4^{3-}: In WLD, Fe bound PO_4^{3-} was about 1.5-fold higher in the marsh compared to the ridge habitat (Figure 5). Fe bound PO_4^{3-} varied from 0.309 μmol g^{-1} in the ridge to 0.518 μmol g^{-1} in the marsh habitat. Fe bound PO_4^{3-} in the sediment extracted after incubation with Sp-CN32 showed a significant decrease from 0.309 to 0.110 μmol g^{-1} in the ridge and from 0.518 to 0.141 μmol g^{-1} in marsh (Figure 5). In BLC, Fe bound PO_4^{3-} values were very similar in both habitats (Figure 5). Fe bound PO_4^{3-} in the sediment decreased post incubation as in the case of WLD habitats. However, the magnitude of Fe bound PO_4^{3-} was much lower compared to WLD. Fe bound PO_4^{3-} values decreased post incubation, particularly when spiked with bacterium Sp-CN32 in both habitats of BLC, but this reduction was not significant. In the case of Sp-CN32 spiked treatment, Fe bound PO_4^{3-} decreased from

454 0.281±.01 to 0.211±0.01 μmol g^{-1} in the channel and 0.252±0.01 to 0.208±0.01 μmol g^{-1} in the marsh.

456 **4. Discussion**

458 This study shows that there is no significant difference in PO_4^{3-} fluxes between benthic sediments and wetland soils under aerobic condition across different temperature 460 representing different seasons. However, PO_4^{3-} fluxes and Fe (II) release under anaerobic condition was found to vary significantly among different substrates within each coastal 462 basin.

464 **4.1 PO_4^{3-} mobilization during aerobic condition**

The sediment oxygen consumption rates during intact core incubations varied among seasons 466 and habitats due to differences in temperature and organic matter content (Figure 3a, c). Despite the large range in O_2 consumption rates, there were no significant release in PO_4^{3-} 468 with up to ~50% drop in dissolve oxygen (Figure 3b, d). PO_4^{3-} fluxes between benthic sediments and wetland soils under similar aerobic conditions did not show any significant 470 difference irrespective of location and temperature (Figure 3b, d). To the best of our knowledge, there is no previously reported study of PO_4^{3-} release from intact cores at either 472 of our study sites. However, similar results have been reported for sediment slurry experiments carried out in Big Mar Lake, Louisiana about ~35 miles East from Lake 474 Cataouatche (Zhang et al., 2012); this study reported no release in soluble reactive P (SRP) under aerobic conditions (0.063±0.013 μM) in contrast to a 32-fold (1.893±1293 μM) 476 increase in SRP under anaerobic conditions.

It is likely that PO_4^{3-} concentrations along with other reduced adsorbed species like Fe^{+2}/Mn^{+2} can be mobilized from sediments to pore water, depending on the redox conditions in the sediments. Mobilized PO_4^{3-} along with other dissolved species then diffuse up to the oxic/anoxic boundary and then are reprecipitated with Fe/Mn oxides/hydroxides formation in presence of oxygen (McManus et al., 1997). Our field observations suggest that the dissolved oxygen at or near sediment water interface were never completely anoxic but varied around 0.8±0.2 mg L^{-1} in both WLD and BLC marshes. Thus, PO_4^{3-} mobilization taking place under reducing conditions in sediments is probably driven by facultative bacteria capable of thriving in both aerobic and anaerobic conditions. These substrates have a PO_4^{3-} concentration as high as 2.40 μmol g^{-1} that can be mobilized from sediment by Sp-CN-32 or similar sediment bacteria (Upreti et al., 2015). Another possibility for this observed absence of net P flux from soil could be due to direct uptake of P by microbial community in the soil. Microorganisms effectively compete with plants for available orthophosphate in soil and can thus represent a significant pool of immobilized P (Richardson and Simon, 2011). Such microbial mediated capture of P can be significant at our study sites due to higher availability of C in the soil (Cheng, 2009).

4.2 PO_4^{3-} mobilization potential under anaerobic condition

4.2.1 Role of Fe reducer *Shewanella putrefaciens CN32* in PO_4^{3-} mobilization

In this study *shewanella putrefaciens* CN32 (Sp-CN 32) was used as the model bacterium to understand Fe (III) reduction. These bacteria were originally isolated from marine environment, brackish water, and sediments (Buller, 2014; Pakingking et al., 2015). Since then, it has been reported from different ecosystems, including freshwater environment

(Bowman, 2005, Kozińska and Pękala, 2004). In recent times, it has been widely isolated from various freshwater systems (Paździor, 2016). The optimum growth temperature for *S. putrefaciens* varies between 4 and 37ºC (Bowman, 2005, Kozińska and Pękala, 2004,). The major reason for selecting *Shewanella putrefaciens* as a model bacterium in our study is that it has an ability to switch from oxygen to Fe (III) as a terminal electron acceptor under low or no oxygen condition (Lovley & Phillips, 1988; Jaisi et al., 2005; Jaisi et al., 2008; Roden, 2006; Upreti et al., 2015).

The sediment slurry incubations were carried out in presence of *Shewanella putrefaciens* to specifically understand the potential of microbially mediated release of P under anaerobic conditions in these coastal habitats. Sediment bacterium such as *Shewanella putrefaciens* CN32 have been widely found to consume dissolved O_2 in the water column for respiration before inducing reductive dissolution of Fe (III) oxides (Lovely and Phillips, 1988) and subsequent release of Fe (III) bound PO_4^{3-} from the sediment (Jaisi et al., 2011; Upreti et al., 2015). In this study, the PO_4^{3-} release from the sediment spiked with *S. putrefaciencs* CN32 were significantly high ($p<0.05$) compared to non-spiked experiments for both benthic sediments and wetland soils in WLD and BLC regions (Figure 4a, c). Sediments amended with bacteria resulted in 3-fold increase in the release rate of PO_4^{3-} compared to control, highlighting the role of bacteria in modulating PO_4^{3-} release rate from sediments (Figure 4c). Concurrent with these changes we also observed a 3 to 4-fold increase in Fe (II) between spike and control. The changes in PO_4^{3-} and Fe (II) concentration had significant positive regression ($r^2=0.96$, $p<0.005$) throughout the duration of the experiment. This finding suggests that reductive dissolution of Fe (III) oxides is leading to release of Fe (III) bound

524 PO_4^{3-} in presence of the bacteria *S. putrefaciens* CN32. There is a general lack of data about what prevailing conditions are favorable to such microbial community. Our current
526 understanding suggests that iron reducing bacteria such as *Shewanella putrefaciens* are positively impacted by amount of available organic matter in the soil (Cooper et al., 2017;
528 Richardson and Simpson 2011) and can be negatively impacted by high concentration of Fe^{2+} leading to saturation of the metal binding sites in the bacterial cell wall (Hyacinthe et al.,
530 2008).

532 Bacterial enhanced PO_4^{3-} mobilization has not been studied in coastal Louisiana. Similar studies have been conducted in other coastal area such as Chesapeake Bay. Fe (III) reducing
534 bacterium, GS-15 isolated from Potomac River sediments showed increase in Fe (II) by 1.5-7.0 times during 14 days of slurry incubation (Lovley & Phillips, 1988). Similar increase in
536 both PO_4^{3-} and Fe (II) by 4-15 and 4-10 times, respectively were reported from East Creek, Chesapeake Bay when the sediment slurries were spiked with *Shewanella putrefaciens*
538 (Upreti et al., 2015). Similarly, Borch et al., (2007) evaluated alterations in surface composition induced by PO_4^{3-} adsorption on reduction of ferrihydrite and found an increase
540 in PO_4^{3-} surface coverage when spiked with *Shewanella putrefaciences.* These patterns highlight the importance of Fe reducers and the role of *Shewanella putrefaciens* CN32 in
542 PO_4^{3-} mobilization suggesting that our study regions follow similar trends as observed in temperate coastal zones. Other Fe reducing bacteria such as *Geobacter species*, capable of
544 dissimilatory Fe III reduction has also been detected in fresh water sediments during microbially mediated redox cycling of Fe in Talladega wetland in Alabama (Weber et al.,
546 (2006).

4.2.2 Variability in PO_4^{3-} mobilization between habitats

548 PO_4^{3-} concentration in both WLD and BLC increased significantly irrespective of habitat when spiked with bacteria Sp-CN32. However, the response was different among regions and
550 habitats (Figure 4a, c). The PO_4^{3-} release from sediment slurries spiked with Sp-CN32 was the highest in the WLD marsh (30 fold) followed by the WLD ridge (22 fold), BLC marsh
552 (12 fold), and BLC channel (6 fold) (Figure 4a, c). Such variability in PO_4^{3-} release with different habitats might be driven to some extent by organic carbon content in the sediments.
554 Higher organic matter content results in faster DO consumption leading to more reducing conditions while sustaining a larger microbial population, which would facilitate reductive
556 dissolution of Fe (II) and associated release of PO_4^{3-}.

558 PO_4^{3-} release rates from different habitats when compared with their OM content showed no such correlation ($p< 0.2107$; MSE 18.9321; $F_{(3, 32)} = 1.5913$). In fact, our results show that
560 the trend is opposite. WLD is associated with higher PO_4^{3-} release compared to BLC, although BLC has higher average OM content. Hence, organic matter content alone cannot
562 explain the higher PO_4^{3-} release from WLD habitats compared to BLC. Thus, the finding that organic carbon is the major driver of this release (Joshi et al., 2015) does not hold true for our
564 study sites; this indicate that the availability of iron oxides in the sediment must also be an important driver of PO_4^{3-} release process, i.e., the reductive process. Therefore, the amount of
566 PO_4^{3-} bound to such iron oxide/hydroxides minerals should be considered a critical factor towards determining the rates of PO_4^{3-} release, especially in case of WLD where iron oxide
568 concentration is high.

570 Sequential extraction of sedimentary PO_4^{3-} indicates that WLD wetland marsh has highest Fe bound PO_4^{3-} content and the highest PO_4^{3-} release (Figure 4a, c, 5). Overall, PO_4^{3-} release was 572 higher for both WLD habitats compared to BLC, which could be due to higher Fe-bound PO_4^{3-} in WLD soils, particularly in the wetland marsh (Figure 4a, c, 5). Fe bound PO_4^{3-} in 574 WLD was almost a factor of two higher compared to BLC. In BLC, Fe bound PO_4^{3-} was similar in both habitats since there was no difference in PO_4^{3-} and Fe (II) release from both 576 habitats. Our findings are supported by the strong correlation between the pre and post incubation decrease in iron bound PO_4^{3-} in sediments and net release in PO_4^{3-} ($r^2 = 0.98$) and 578 Fe (r^2=0.99) from the sediment (Figure 6). In general, the higher the release, the larger the loss of the sediment fraction across all habitats especially in wetland habitats.

580

4.2.3 Relationship between PO_4^{3-} and Fe (II) release

582 To explore what is the source of PO_4^{3-} and Fe (II) released throughout the course of the experiment, we calculated the ratio of PO_4^{3-} and Fe (II) released at each time step. This ratio 584 is determined as the change in concentration of PO_4^{3-} and Fe (II) between two consecutive time steps and denoted as $\Delta PO_4^{3-}/\Delta$Fe (II). This release ratio was not constant throughout the 586 duration of the experiment (Figure 7). In the first 24 hours, $\Delta PO_4^{3-}/\Delta$Fe (II) ratio steadily increased from 1.26 to 1.96 in the WLD wetland ridge and from 0.26 to 1.02 in the WLD 588 wetland marsh. After this period, $\Delta PO_4^{3-}/\Delta$Fe (II) started decreasing reaching a value of 0.84 in WLD ridge and 0.27 in WLD marsh by the end of the experiment (Figure 7a). A similar 590 trend was also observed in the BLC benthic channel and wetland marsh habitats (Figure 7b). This variability in $\Delta PO_4^{3-}/\Delta$Fe (II) ratio over time indicate that Fe bound PO_4^{3-} is not the only 592 source of PO_4^{3-} and/or there are other sinks of PO_4^{3-}. One possibility is that some of the

loosely bound PO_4^{3-} is contributing to the PO_4^{3-} release as evidenced by the pre and post incubation loss of loosely bound PO_4^{3-}. Another alternative explanation is the initial bacterial uptake of the loosely bound PO_4^{3-} pool when bacteria respired on oxygen. This pattern is consistent with the other studies showing that bacteria prefer loosely sorbed PO_4^{3-} over less bioavailable PO_4^{3-} pools in sediments (Jaisi et al., 2011). It is also possible that new PO_4^{3-} released from reductive dissolution of iron can be transformed to loosely bound over the course of the experiment. It is beyond the scope of our experiments to determine how both sources and sinks of P are changing throughout the duration of experiment, but it is quite evident that this net release of PO_4^{3-} is driven by more dynamic processes than just reductive release of iron-bound PO_4^{3-}.

Conclusion

Phosphorus biogeochemistry across freshwater/brackish system is influenced by the inundation of river waters during flood-pulse events. Thus, it is important to understand the biogeochemical function of nutrients such as P in deltaic systems before it enters the coastal waters. PO_4^{3-} mobilization from wetlands in coastal Louisiana is negligible under aerobic condition. This is an important finding from the point of eutrophication and water quality management. Our study sites are heavily influenced by the water outflow from various flood control and diversion structures and as such the flow of water is heavily controlled. Thus, we can expect soil P remobilization to be significant under pulsed water release which can lead to more O_2 depleted stagnant water compared to continuous release of water that can supply relatively oxygen rich moving water. Under low oxygen, a prevalent condition in these coastal areas, there is a potential for the significant release of PO_4^{3-} from sediment and

wetland soils. Under the low or no oxygen condition, biologically mediated redox processes can contribute significantly to the release of PO_4^{3-} from these substrates. Substrates amended with a commonly found sediment bacteria such as Sp-CN32 resulted in significant PO_4^{3-} and Fe (II) release rates. Therefore, bacterially mediated release of iron bound PO_4^{3-} in wetland soils and benthic sediments could be an important source; and with other environmental parameters remaining constant, this flux can vary significantly as a function of Fe bound PO_4^{3-} present in the sediments.

This study advances our understanding of microbial mechanisms and processes controlling the coupling between sediment/soil and overlying water exchange of dissolved constituents across the sediment/soil−water interface. Such bacterial mediated processes need to be better quantified in coastal Louisiana since the sediment/soil bacterial community is sensitive to major alterations in pH, salinity and temperature. Louisiana coastline is facing one of the highest sea level rise in the world (Jankowski et al., 2017) and future changes in salinity regimes in these fresh water wetlands can greatly impact the microbial mediate P cycling as increases in pore water salinity can result in a decrease of iron oxide-bound P (Jordan et al., 2008). However, the direct impact of such salinity increase to iron reducing microbial community is still unknown. Further studies are needed to better understand the impact of such microbial mediated processes, not only in freshwater dominated systems but also in brackish and saline wetlands along coastal Louisiana. Such studies should include isolation and characterization of these microbial communities at higher spatial resolution across salinity gradients, including temporal variability, to fully understand the role of microbial P cycling in coastal wetlands and how it might change in the future along with climate.

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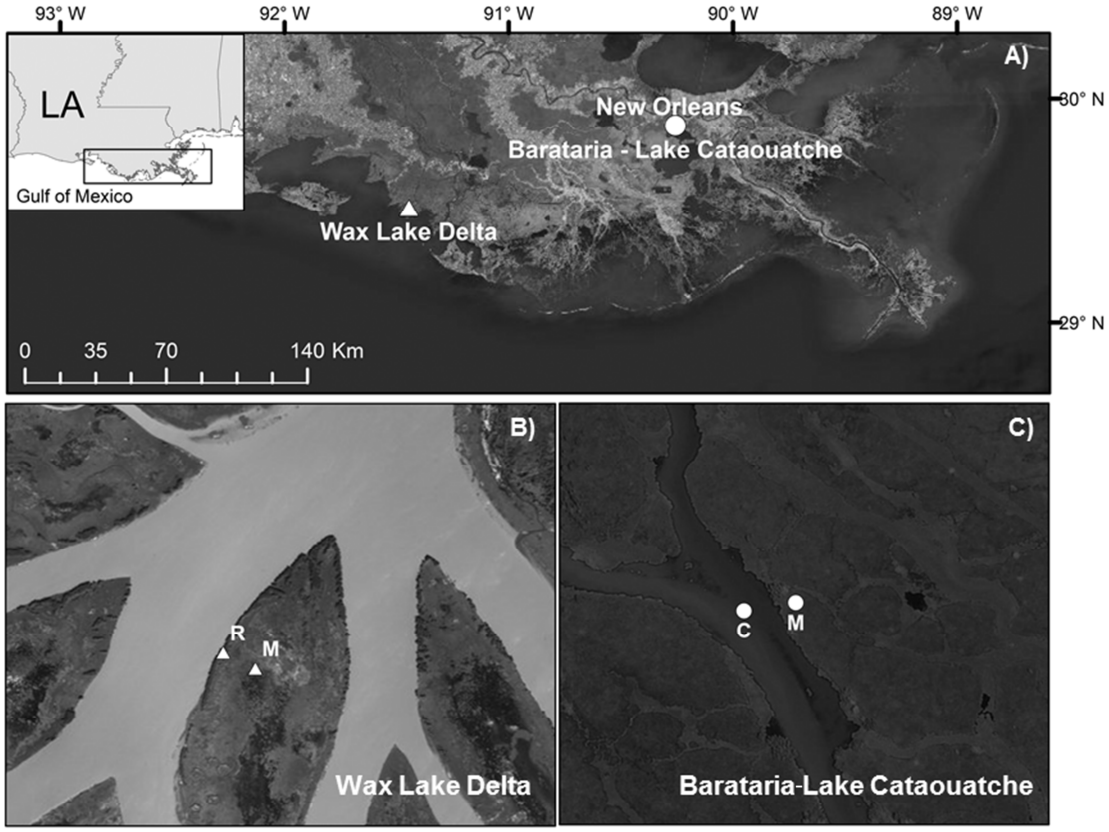

Figure 1 A) Atchafalaya and Mississippi Delta Regions, Louisiana (LA); (B) Wax Lake Delta habitats ridge (R) and marsh (M); (C) Upper Barataria Lake Cataouatche habitats channel (C), and marsh (M). White dots show sampling locations (marsh and canals).

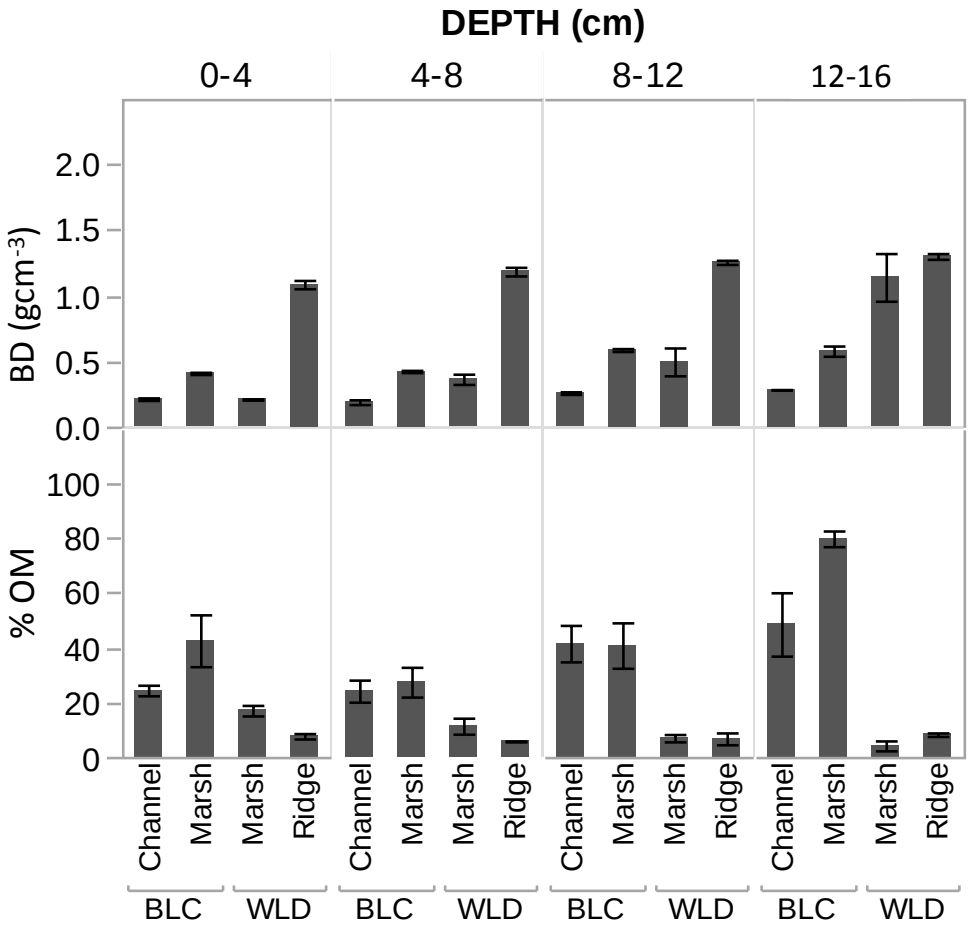

Figure 2: Sediment properties (Mean ±SE): Bulk density (BD) and organic matter content (%OM) in different habitats of Wax Lake Delta (WLD) and Barataria (BLC) at different substrate depths in spring incubation (April; 20^{o}C).

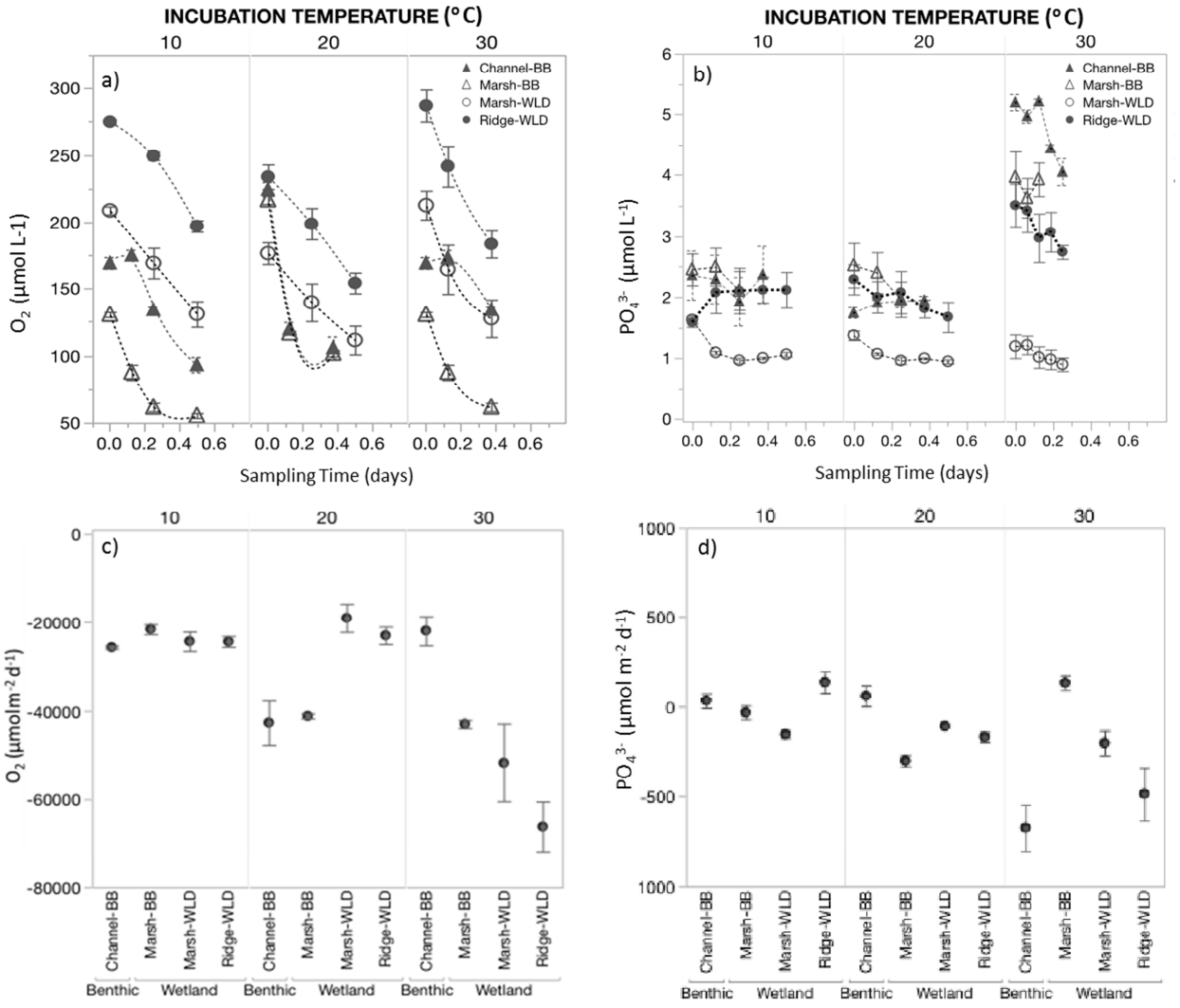

Figure 3: a) Change in dissolved oxygen and b) PO_4^{3-} concentrations with time and c) associated sediment O_2 consumption, and d) PO_4^{3-} fluxes during intact core incubation experiments (Mean ±SE).

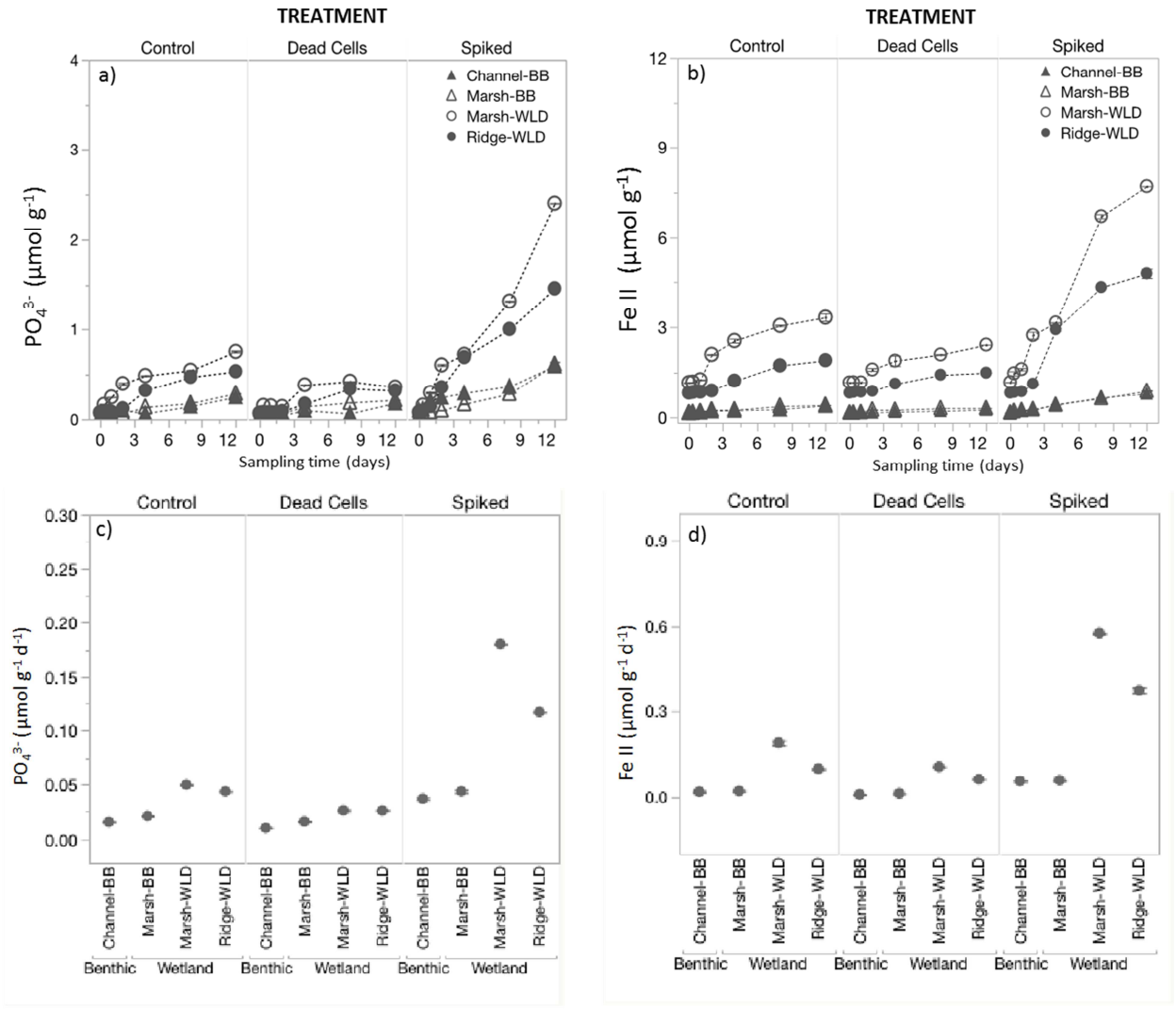

Figure 4: a) Changes in PO_4^{3-} concentration, b) Fe (II) concentration, c) PO_4^{3-} fluxes, and d) Fe (II) fluxes during the sediment slurry laboratory incubation experiment (Mean ±SE).

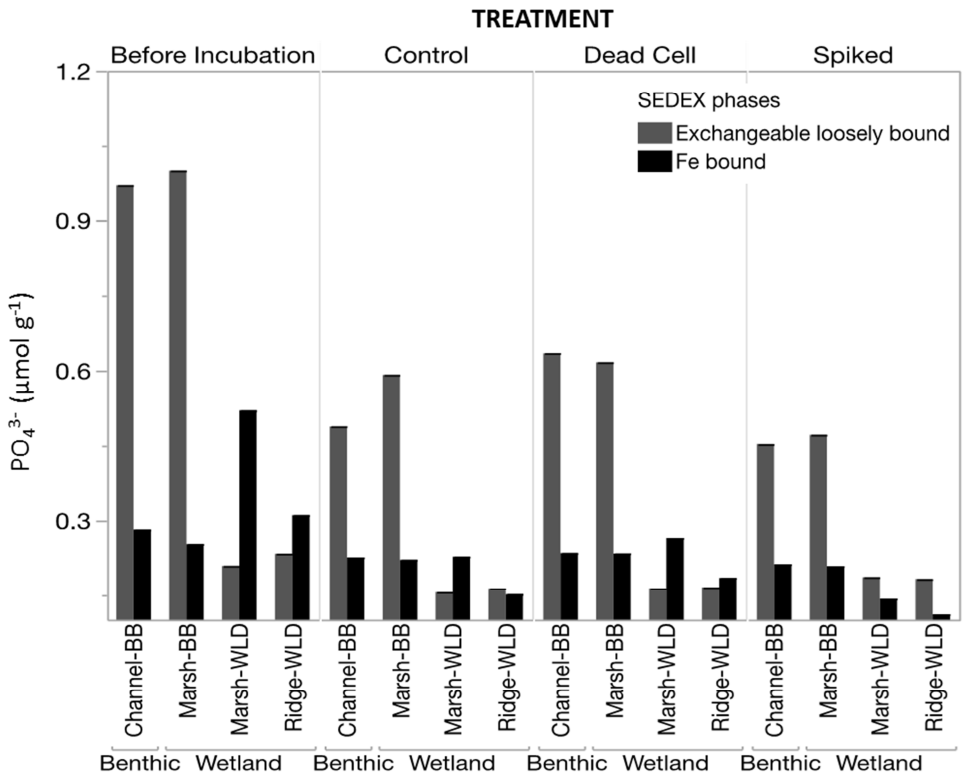

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Figure 5: Sediment bound PO_4^{3-} concentrations before and after sediment slurry experiments

40 in Wax Lake Delta (WLD) and Barataria (BLC) habitats.

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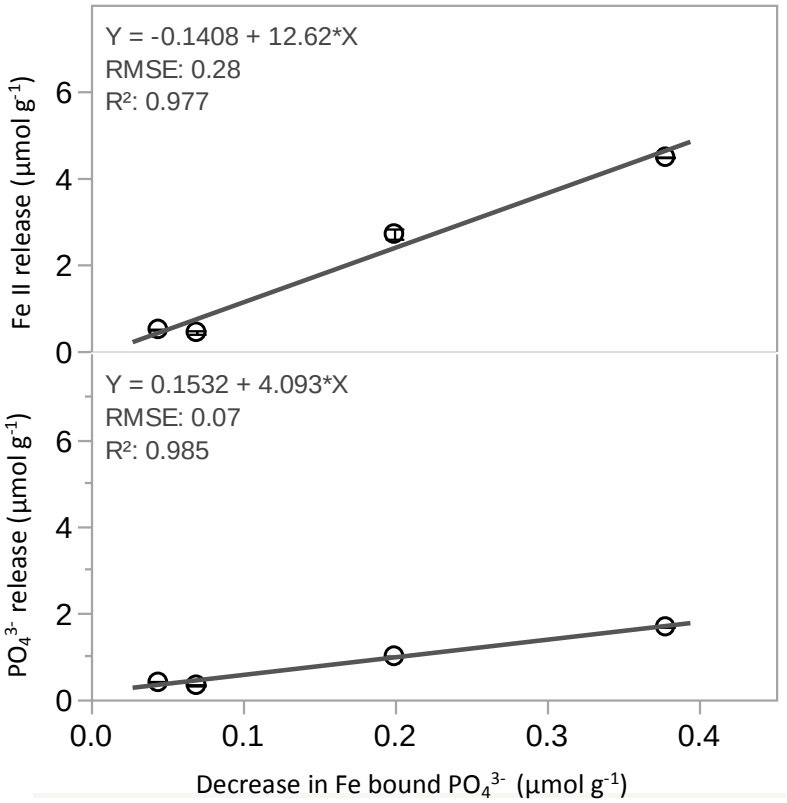


Figure 6: a) Relation between loss of Fe bound PO_4^{3-} in sediments and net PO_4^{3-} release, and b) Fe (II) release during sediment slurries spiked with *Shewanella putrefaciens* CN32 bacteria.

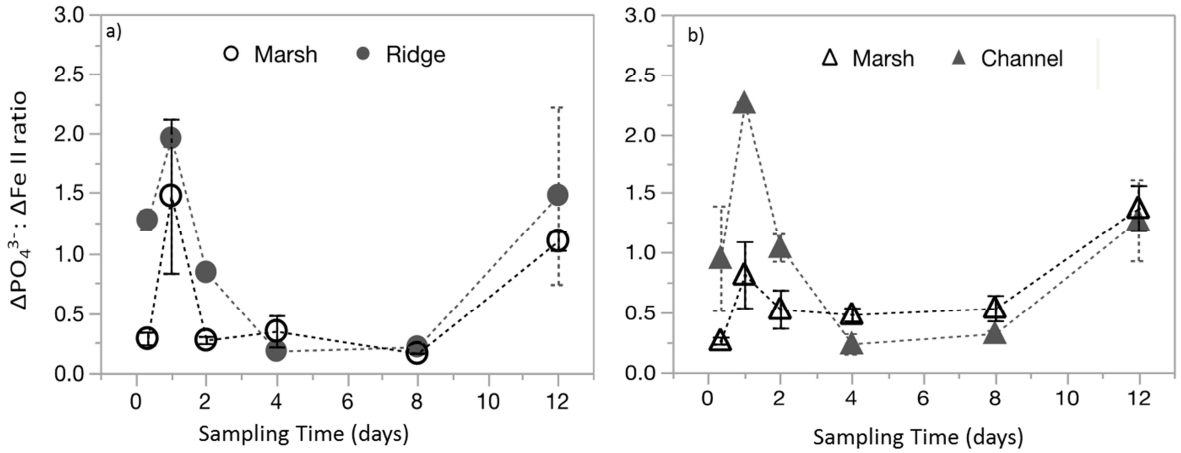


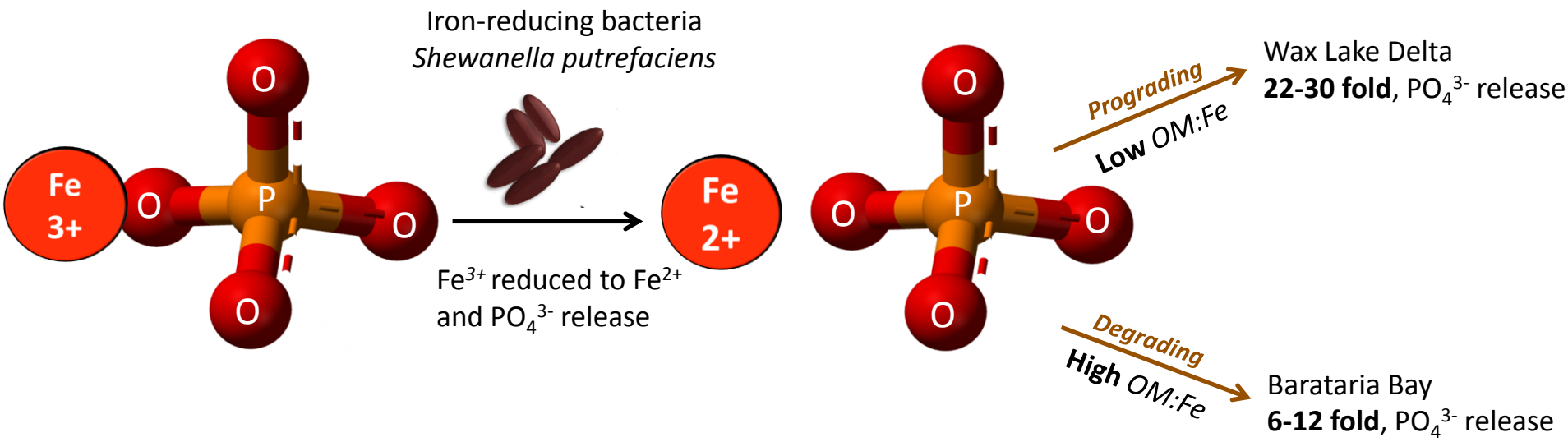
Figure 7: Observed changes in ΔPO_4^{3-}: ΔFe (II) release ratio in a) Wax Lake Delta (WLD) and b) Barataria Lake Cataouatche (BLC) habitats during sediment slurry experiment spiked with *Shewanella putrefaciens* CN32 bacteria (Mean ±SE).

Table 1: Water column and pore water physicochemical properties in Wax Lake Delta (WLD) and Barataria Lake Cataouatche (BLC). Data not available is represented by (-).

Year	Sampling Season	Region	Habitat	Substrate	Temperature (^{o} C)	Salinity (ppt)	Surface water PO_4^{3-} (uM)	Pore water PO_4^{3-} (uM)
2015	Winter	WLD	Channel	Benthic	12.7	0.4	1.51	-
			Ridge	Wetland	-	-	-	1.908
			Marsh	Wetland	-	-	-	1.258
2015	Spring	WLD	Channel	Benthic	25.9	0.1	2.1	-
			Ridge	Wetland	-	-	-	1.33
			Marsh	Wetland	-	-	-	2.05
2015	Summer	WLD	Channel	Benthic	25.8	0.2	2.55	-
			Ridge	Wetland	-	-	-	-
			Marsh	Wetland	26.3	0.2	-	0.598
2016	Winter	BLC	Channel	Benthic	12.5	0.1	1.899	-
			Marsh	Wetland	16.4	0.2	-	0.472
2016	Spring	BLC	Channel	Benthic	22.2	0.2	3.983	-
			Marsh	Wetland	25.05	0.2		0.96
2016	Summer	BLC	Channel	Benthic	26.5	0.2	4.977	-
			Marsh	Wetland	27.2	0.2	-	0.284

Table 2: Summary of analysis of variance (ANOVA)

Incubation Type	Source	DF	Sum of Squares	Mean Square	F Ratio	P value
Intact Core Incubation						
O_2	Model	3	156906.61	52302.2	9.5355	0.0001
	Error	32	175519.35	5485		
	C.Total	35	332425.96			
PO_4^{3-}	Model	3	90.37997	30.1267	1.5913	0.2107
	Error	32	605.82601	18.9321		
	C.Total	35	696.20599			
Sediment Slurry Incubation						
PO_4^{3-}	Model	5	0.07653849	0.015308	73.6367	<0.0001
	Error	30	0.00623644	0.000208		
	C.Total	35	0.08277493			
Fe II	Model	5	0.92251898	0.184504	72.6632	<0.0001
	Error	30	0.07617489	0.002539		
	C.Total	35	0.99869386			


Iron-reducing bacteria
Shewanella putrefaciens
Fe 3+
O
P
O
O
O
Fe 2+
Fe^{3+} reduced to Fe^{2+}
and PO_4^{3-} release
O
P
O
O
O
Prograding
Low *OM:Fe*
Wax Lake Delta
22-30 fold, PO_4^{3-} release
Degrading
High *OM:Fe*
Barataria Bay
6-12 fold, PO_4^{3-} release