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

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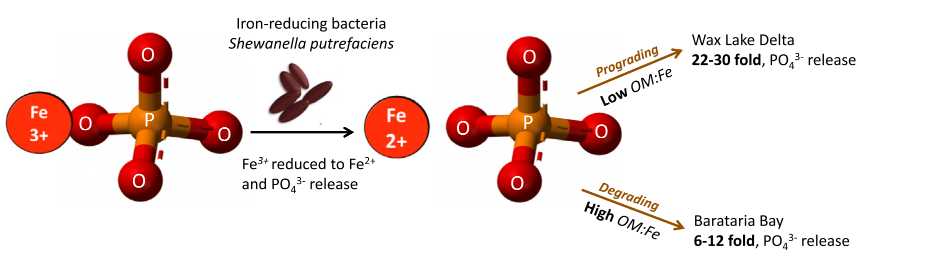
## HIGHLIGHTS

- First study to report microbial mediated potential P mobilization in coastal Louisiana
- P release increased by up to 30 fold in presence of iron reducing bacteria.
- P release was correlated with Fe bound P in sediments than organic matter content.
- Iron bound P was found to be higher in prograding delta than degrading delta.

## GRAPHICAL ABSTRACT

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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 $g^{-1}$ in the ridge and from 0.079 ± 0.007 to 2.407 ± 0.001 μmol $g^{-1}$ in the marsh substrates. In Barataria bay, $PO_4^{3-}$ release increased from 0.103 ± 0.006 μmol $g^{-1}$ to 0.601 ± 0.008 μmol $g^{-1}$ in the channel and 0.050 ± 0.000 to 0.618 ± 0.026 μmol $g^{-1}$ 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.



## 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: 16 N: 1P; Redfield, 1958). Thus, excessive

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P loading can promote growth of harmful algal blooms, exacerbate eutrophication, and lead to hypoxia (Heisler et al., 2008; 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 ($2.04 \times 10^7$ 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 and 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 and 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 and 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 μM; White et al., 2009) while the suspended sediment can contain a large amount of total particulate P (9,645 μM; Zhang et al., 2012). A major portion of the particulate P associated within the sediment is eventually deposited in estuarine benthic substrates (McDowell and Sharpley, 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., 1995a, 1995b; 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., 1995b), 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 and 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 and Twilley, 2013; 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 Jr. 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)