Control of Phosphorus concentration through adsorption and desorption in shallow groundwater
of subtropical carbonate estuary

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Abstract

The balance of fresh and marine water sources in coastal mixing zones can affect phosphorus (P) availability, one of the important drivers of primary productivity. This study focuses on an abiotic portion of the P cycle in the mangrove ecotone of Taylor Slough, coastal Everglades, Florida. We investigated the P sorption properties of sediment with three distinct water sources in this region: 1) fresh groundwater from the inland Everglades, 2) bicarbonate enriched groundwater from the mangrove ecotone, and 3) surface saltwater from Florida Bay. Ecotone groundwater caused soluble reactive P (SRP) to exhibit markedly low sorption efficiency ($K_d=0.2 \text{ L g}^{-1}$) compared to fresh groundwater and Florida Bay water (11.3 L g^{-1} and 3.4 L g^{-1} , respectively). The low SRP buffering capacity of the sediment in ecotone groundwater would maintain higher ambient water SRP concentration in ecotone groundwater than in the other two waters, and would trigger desorption if the sediment changed from one of them to ecotone groundwater. The relative sorption efficiency is consistent with the measured zero equilibrium SRP concentration being highest in ecotone groundwater ($0.094 \pm 0.003 \text{ } \mu\text{M}$) and lower in fresh groundwater and Florida Bay surface water ($0.075 \pm 0.005 \text{ } \mu\text{M}$ and $0.058 \pm 0.004 \text{ } \mu\text{M}$ respectively). The temporal variability of SRP concentration in groundwater at the ecotone field station is greater than the range of zero equilibrium SRP concentration for all three waters, so very low SRP concentration in the ambient water would induce desorption from the sediment. Soluble reactive P would be expected to begin desorbing from the sediments at a higher ambient SRP concentration in ecotone groundwater than the other two water types. Our results suggest that ecotone groundwater would release more SRP from mangrove sediments compared to the upstream and downstream waters, due to both its lower P sorption efficiency and its higher zero equilibrium SRP concentration.

Key words

bicarbonates, mangroves, sediment dynamics, abiotic factors, phosphates

Regional index terms

USA, Florida, Everglades, Taylor Slough

1. Introduction

Mangrove swamps are ubiquitous along sheltered coasts between latitudes 25°N and 30°S, covering an estimated 20 million hectares worldwide (Tomlinson, 1994). Mangrove forests provide important ecosystem services, including the maintenance of water quality, stabilization of shorelines and coastal community protection, and carbon sequestration (Donato et al., 2011; Gedan et al., 2011). Mangroves provide nursery and spawning grounds for many coastal crustaceans and fish, thereby supporting local fisheries and ocean biodiversity (Lugendo et al., 2007).

A detailed assessment of the controls on bioavailability of the essential nutrients is critical to understanding coastal estuaries (Froelich, 1988). Phosphorus (P) is commonly a limiting nutrient in mangrove swamps (Castañeda-Moya et al., 2011; Coronado-Molina et al., 2012). The bioavailable form of P is dissolved inorganic P (Karl and Tien, 1992), which is dominated by the orthophosphate species H_2PO_4^- at pH less than 7.2, and HPO_4^{2-} above that. Dissolved organic P

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4 and particulate P (both organic and inorganic) are immobile until mineralized to dissolved
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6 inorganic P, which typically requires microbial activity (Björkman and Karl, 2003). We refer to
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8 dissolved inorganic P as soluble reactive P (SRP), defined as the fraction of P in a water sample
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10 that passes through a 0.45 μm filter and responds to colorimetric tests without having been
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12 subjected to a pretreatment of hydrolysis or oxidative digestion (Murphy and Riley, 1962). The
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14 soluble reactive P concentration is considered to be roughly equivalent to dissolved inorganic P
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16 concentration, but the distinction is made because there is potential for organic or colloidal P to
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18 pass through $<0.45 \mu\text{m}$ and to react to colorimetric reagents (Thomson-Bulldis and Karl, 1998).
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26 The cycle through which P shifts between SRP and immobilized forms involves a great number
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28 of complex processes, and both biotic and abiotic portions of the cycle must be considered when
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30 evaluating P availability in wetlands (Reddy et al., 1999). Abiotic processes in the P cycle
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32 include leaching of P from leaf litter; sedimentation; exchange of P between sediment and the
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34 overlying water column; processes with inorganic P phases such as apatite, eg., precipitation,
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36 dissolution, and weathering; and P sorption reactions (Davis and Childers, 2007; Reddy et al.,
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38 1999). Phosphorus sorption is an important process in wetlands whereby P is exchanged between
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40 SRP in the ambient water and solid phase P (Froelich, 1988). The process has two steps. The first
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42 step has fast kinetics (minutes to hours) and involves the accumulation (adsorption) of SRP from
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44 ambient water at sediment particle surfaces. This step is rapidly reversible; as conditions change,
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46 desorption can release the adsorbed SRP back to the ambient water. The second adsorption step
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48 is much slower (days to weeks), and involves solid-state diffusion of adsorbed SRP from the
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50 mineral surface into the interior of mineral grains (Froelich, 1988).
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4 In this study we discuss P sorption in terms of the rapid, reversible first step.
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6 Adsorption/desorption reactions can act as SRP buffers, analogous to pH buffers, maintaining
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8 water SRP at a constant concentration. The water SRP concentration at which zero net SRP
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10 adsorption or desorption occurs for a given system is termed the zero equilibrium SRP
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12 concentration (EPC_o). When ambient water SRP concentration is close to the EPC_o , the sediment
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14 displays the maximum capacity for buffering SRP (Froelich, 1988). Slight rises or falls in
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16 ambient SRP concentration from this equilibrium may result in rapid adsorption or desorption,
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18 respectively, returning the system to a new equilibrium (Froelich, 1988). A sediment is described
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20 as having high adsorption efficiency when SRP adsorption increases intensely as water SRP
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22 concentration increases. Efficient P sorption results in high SRP buffer intensity, maintaining
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24 low water SRP concentration as long as the sediment does not become saturated (Reddy et al.,
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26 1999).
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36 Highly variable water chemistry in coastal mixing zones causes variability in SRP availability
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38 through shifting P sorption behavior. Sorption reactions are influenced by physiochemical
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40 properties of the given sediments and their ambient water, including the composition and particle
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42 size distribution of the solid particles, temperature, pH, ionic strength, redox status, organic
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44 matter content, and ions in the ambient water (Millero et al., 2001a; Pant and Reddy, 2001;
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46 Reddy et al., 1999; Zhang and Huang, 2011). The sensitivity of P sorption reactions to water
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48 chemistry and sediment characteristics means that the direction and strength of sorption reactions
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50 are hard to predict without direct experimentation with the natural sediment and water in
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52 question (Suzumura et al., 2000).
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4 Some coastal estuaries have ambient water SRP concentration that is higher than would be
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6 predicted based on conservative mixing of the fresh river water and seawater. Typically
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8 freshwater causes SRP to adsorb more effectively to the substrate, so an influx of seawater
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10 induces desorption of loosely adsorbed SRP from suspended or benthic sediments (Froelich,
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12 1988; Zhang and Huang, 2011). Suspended sediments in coastal rivers may release SRP as they
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14 enter the seawater mixing zone (Fox et al., 1986). Similarly, an incursion of seawater due to tidal
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16 influx or seawater intrusion can lead to rapid desorption from suspended and benthic sediment
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18 particles, accompanied by increases in measured SRP concentrations (Gardolinski et al., 2004;
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20 Sundareshwar and Morris, 1999; Suzumura et al., 2000).
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29 Microbial activity enriches groundwater HCO_3^- concentration above saltwater levels in some
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31 coastal wetlands. Millero et al. (2001b) predicted that along coastlines where saltwater mixes
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33 with a water that has high HCO_3^- concentration, the typical pattern of seawater-induced
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35 desorption could be reversed, such that an influx of seawater into sediment that had been
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37 equilibrated to the water with HCO_3^- concentration could cause the sediment to release HCO_3^-
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39 ions and adsorb SRP. Experiments by Millero et al. (2001a) on synthetic calcite determined that
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41 especially at low salinity the apparent effect of salinity on P sorption behavior of calcium
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43 carbonate is driven by the higher concentrations of HCO_3^- and SO_4^{2-} in saltwater. When HCO_3^-
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45 concentration was held constant (2 mM) adsorption was nearly independent of salinity. The
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47 slight positive charge of the calcium atom on calcium carbonate surfaces attract SRP anions,
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49 forming surface complexation reactions. An influx of HCO_3^- ions can induce anion exchange at
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51 the positive sorption sites.
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4 Many mangrove estuaries are found in carbonate lithologies, including Belize, the West Indies,
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6 Bermuda, Mexico, Western Australia, Brazil and East Africa (Alongi et al., 1996; Coronado-
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8 Molina et al., 2012; Ellison, 1993; Jennerjahn and Ittekkot, 1997; McKee and Faulkner, 2000;
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10 Woodroffe, 1981). To understand the drivers of coastal wetland productivity in carbonate-based
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12 regions it is essential to determine the behavior of P sorption in carbonate sediments with respect
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14 to high bicarbonate water, fresh water and saltwater. This study examines the potential for SRP
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16 concentration of the shallow groundwater in a mangrove swamp to be affected by *in situ*
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18 adsorption and desorption reactions in response to mixing of these three water types. In so doing,
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20 this study provides insight into the fast-acting abiotic portion of the biogeochemical P cycle in a
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22 coastal mixing zone, which has implications for other estuaries with carbonate lithology and a
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24 water enriched in HCO_3^- .
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34 **2. Materials and Methods**

35 **2.1. Study Area**

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38 The southern terminus of the Florida peninsula is fringed by a wide mangrove swamp, dividing
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40 the upstream freshwater marsh from Florida Bay (Figure 1). The Everglades wetland complex of
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42 southern Florida, USA has two main drainage basins: Shark River Slough, which angles to the
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44 southwest and drains into the Gulf of Mexico, and the smaller Taylor Slough, which flows
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46 southward into the northeast corner of Florida Bay. The Everglades mangrove region is within 1
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48 m of mean sea level. Tides along the western portion of Florida Bay are mixed diurnal and
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50 semidiurnal with a mean amplitude of about 0.3 m (Wang et al., 1994). As waters from the Gulf
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52 of Mexico move into Florida Bay, the tidal effects are dampened by the shallow mud banks such
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4 that the Eastern bay is micro tidal, with tidal amplitudes of only about 1-5 cm (Wang et al.,
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6 1994). On a few occasions per year, bay saltwater flows upstream into the upper mangrove
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8 fringe wetlands of Taylor Slough, particularly in the dry season during times of low freshwater
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10 hydraulic head and sustained southerly winds (Castaneda, 2010; Davis III et al., 2004; Koch et
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12 al., 2012; Sutula et al., 2003). The sediment layer consists of a relatively thin layer (up to 1.5 m
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14 deep) of calcareous marl and peat (Spence, 2011) with mangrove roots penetrating the shallow
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16 sediments down to the underlying limestone bedrock (Ewe et al., 2007). The limestone aquifer
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18 underlying Taylor Slough is the unconfined highly transmissive Biscayne Aquifer (Fish and
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20 Stewart, 1991). Saltwater intrudes into the Biscayne Aquifer between 6-10 km inland in Taylor
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22 Slough (Fitterman and Deszcz-Pan, 1998; Price et al., 2006).
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33 The Taylor Slough mangrove ecotone (hereafter referred to as the “ecotone”) is oligotrophic and
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35 highly P-limited (Noe et al., 2001). The groundwater in the shallow sediments of the ecotone has
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37 much higher HCO_3^- concentration than either the upstream freshwater or the downstream Florida
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39 Bay saltwater, and the three waters mix with a high degree of temporal and spatial variability
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41 (Millero et al., 2001b; Price et al., 2006; Zapata-Rios and Price, 2012).
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49 **2.2. Water Samples**

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52 Three water types were collected representing fresh groundwater (“fresh GW”), high bicarbonate
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54 groundwater (“ecotone GW”), and surface saltwater from Florida Bay (“bay SW”) (Figure 1).
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56 Our fresh GW was collected from a shallow monitoring well (TSB-15) within the bedrock
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58 underlying the freshwater sawgrass marsh region of Taylor Slough. The well is lined with a 5.5
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4 cm diameter PVC pipe screened at 4 m depth. The well was first purged of at least five well
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6 volumes using a peristaltic pump. The high bicarbonate water was taken from well C3 in the
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8 Taylor Slough mangrove ecotone about 4 km inland at monitoring station TS/Ph 6b operated by
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10 the Florida Coastal Everglades Long Term Ecological Research Program(Castaneda, 2010). The
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12 well penetrates to a depth of 142 cm within the sediment layer (Castaneda, 2010; Zapata-Rios,
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14 2009). Florida Bay surface water was taken from a dock at Key Largo to represent saltwater.
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23 Immediately after sampling, temperature, pH, and electrical conductivity were measured with a
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25 YSI 556 MPS (YSI, Yellow Springs OH). Water samples placed in HDPE Nalgene bottles and
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27 maintained at 4°C ($\pm$ 2°C) prior to analysis. Total alkalinity was determined within 24 hours by
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29 potentiometric acid titration. Given the high total alkalinity of our ecotone GW and the pH
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31 measurements, we refer to these measurements as HCO_3^- concentration, while recognizing that
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33 small amounts of the other bases may be included in the measured quantity. Major cations and
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35 anions were determined at FIU with ion chromatography. The SRP concentration of the field
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37 samples were analyzed as discussed in section 2.5. Selected water characteristics are presented in
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39 Table 1 and Figure 2.
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49 The water that was to be refrigerated in 9 L HDPE Nalgene carboys for later experimentation
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51 was first filtered through 0.1 μm PTFE filters using a vacuum filter flask to exclude
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53 microorganisms that could uptake or release P during water storage.
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2.3. Sediment Samples

Sediment composition was held constant by running all experiments using a representative sample from a homogenized 1-5 cm depth increment extracted from a single sampling date and location (same location as ecotone GW). This depth increment was chosen so as to have a sufficiently large sample with little variation by depth. The top 1 cm of cores taken at this location were not used because they were darker in color than the sediment immediately below, and because exceptionally high total sedimentary P was found in the top 1 cm sediment in a pond further downstream (Koch and Reddy, 1992). Calcareous marl sediment was extracted using a Russian peat corer at FCE field station TS/Ph6b (Figure 1). The sediment was placed in ziplock bags, and was kept on ice for transport to the lab, where it was air dried, passed through stainless steel sieves ($<125\ \mu\text{m}$), and kept refrigerated prior to use.

Loosely adsorbed or readily exchangeable P (P_{exch}) was defined as the SRP released from sediment by MgCl_2 solution at pH 8.0 (Ruttenberg, 1992). A 0.5 g of dry sieved sediment was combined with 1 M MgCl_2 solution, and pH was adjusted with dilute NaOH solution. Sediment and solution were placed in 60 mL high density polypropylene digestion tubes and agitated for 2 hours on a platform shaker at 200 rotations per minute at room temperature, with a total of 5 replicates. Slurries were filtered with $0.45\ \mu\text{m}$ nylon syringe filters and divided into two 10 mL subsamples. The first subsample was analyzed for SRP (section 2.5) so as to determine MgCl_2 -exchangeable inorganic P, or P_{exch} , with the resulting concentration normalized to $\mu\text{moles per grams}$ of sediment. We also measured MgCl_2 -exchangeable organic P for the purpose of characterizing the sediment, but its dynamics are beyond the scope of this paper because it is

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4 considered less bioavailable and behaves differently from inorganic P (Huang and Zhang, 2010).
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6 The organic MgCl_2 -exchangeable P fraction is determined by measuring total dissolved P
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8 concentration in the subsample that had been set aside, and subtracting from that the SRP
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10 concentration measured previously in the undigested subsample; the difference is assumed to be
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12 the dissolved organic fraction liberated by MgCl_2 (Zhang et al., 2010; Zhang et al., 2004). To
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14 measure total dissolved P, 10 mL of filtrate is first digested with 1 mL of neutral potassium
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16 persulfate solution (5%, w/v, pH approximately 6.5) at 90°C for 16 hours (Huang and Zhang,
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18 2009) and analyzed for SRP (section 2.5) after returning to room temperature.
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28 A portion of the sediment was acid digested (preparation method EPA 3050) and total
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30 sedimentary P was determined inductively coupled plasma-atomic emission spectrometry
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32 (analytical method EPA 6010). Selected sediment characteristics are presented in Table 2.
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39 **2.4. Adsorption-Desorption Experiments**

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42 Phosphorus sorption parameters of the sediment in contact with the three water types were
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44 determined by batch incubation experiments based on the method of Froelich (1988).
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47 Subsamples of each water type received variable portions of stock SRP solution to establish
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49 batches with SRP concentrations of 0 (no added SRP), 4, 8, 16, 24, 32, and 48 μM . To inhibit
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51 biological activity from microbes in the sediment, 10 μL 0.1% chloroform was added to each
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53 tube (Zhou et al., 2005). The initial SRP concentration, $[\text{SRP}]_i$, for each batch of field water-SRP
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55 solution was analyzed directly for SRP before the incubation began.
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8 For the batch with no added SRP, so as to permit the detection of P desorption from sediment
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10 with such low P content, the solution was concentrated by using 5 mL of a given field water and
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12 1.5 g sediment, and with 20 replicates for each water type. For the other batches, 10 mL of field
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14 water-SRP solution was combined with a 200 mg subsample of ecotone sediment in a 15 mL
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16 plastic conical centrifuge tube (10 replicates per water type per batch, 30 samples total in a
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18 batch). At 48 μM SRP the fresh GW sorption curve was still relatively steep, thus not providing
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20 sufficient of the sorption isotherm curve for calculating P_{max} (described in section 2.6). So as to
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22 better characterize P_{max} , five additional SRP concentrations ranging from 60-320 μM SRP were
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24 used for fresh GW (with three replicates for each increment of added P). In all batch incubation
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26 experiments, each suspension was agitated at 200 rpm on a platform shaker for 24 hours at room
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28 temperature ($23 \pm 0.5^\circ\text{C}$). Next, each suspension was filtered with a 0.45 μm nylon syringe filter,
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30 and immediately analyzed for final SRP concentration, $[\text{SRP}]_f$ (section 2.5). A total of 255 P
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32 sorption experiments were conducted.
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44 **2.5. Soluble reactive P Analysis**

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47 Soluble reactive P concentrations were determined the day of each experiment by first filtering
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49 samples through a 0.45 μm nylon syringe filter and then using the microscale malachite green
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51 method (D'Angelo et al., 2001), measuring absorbance at 630 nm in 96-well microplates on a
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53 BioTek EPOCH microplate spectrophotometer.
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2.6. Sorption Isotherms The amount of SRP adsorbed or desorbed from the sediment, ΔP_{sed} , was calculated as:

$$\Delta P_{\text{sed}} = [\text{SRP}]_i - [\text{SRP}]_f \quad . \quad [1]$$

ΔP_{sed} was normalized to the mass of sediment and volume of solution ($\mu\text{mol g}^{-1}$). A plot of ΔP_{sed} vs. $[\text{SRP}]_f$ was used to describe a sediment's adsorption behavior when in contact with each of the three water types.

Various sorption models exist for providing empirically-fit parameters that summarize the resulting isotherm. At the very low range of SRP, where the number of available adsorption sites is much higher than the concentration of SRP available in solution, sorption increases in direct proportion to added SRP and a linear model provides the best fit (Figure 3a).

The linear isotherm equation is:

$$\Delta P_{\text{sed}} = K_d [\text{SRP}]_f - \text{NAP} \quad , \quad [2]$$

where K_d (L g^{-1}) is the slope, and NAP ($\mu\text{mol g}^{-1}$) is native adsorbed SRP (the y-intercept), a constant representing the amount of pre-existing loosely adsorbed inorganic P on the sediment (Figure 3a). Negative ΔP_{sed} indicates desorption from the sediment and positive ΔP_{sed} indicates adsorption onto the sediment. The EPC_0 ($\mu\text{mol g}^{-1}$) is obtained from x-intercept, the measured equilibrium SRP concentration at which neither desorption nor adsorption occurs. The linear equation can be rearranged to solve for EPC_0 .

$$EPC_o = EPC_o = \frac{NAP}{K_{eq}}, \quad \text{when } \Delta P_{sed} = 0 \quad . \quad [3]$$

The sorption coefficient K_d is a measure of the buffer intensity (also described as sorption efficiency), and is formally defined as the number of moles of SRP required to be added to or subtracted from the system to change $[SRP]_f$ by 1 μM near the EPC_o (Froelich, 1988). A steep slope (high K_d) near the EPC_o indicates a system with high sorption efficiency.

The purpose of experimentally increasing SRP concentration beyond what is realistic for field conditions is to characterize certain characteristics of the sorption behavior of a given sediment-water combination that can only be calculated as the sediment responds to artificially high SRP concentrations, such as saturation concentration and the possibility of two adsorption sites with different affinities for SRP. As the final SRP concentration increases in solution, the adsorption of SRP to sediment decreases, resulting in the sorption curve bending from linear to an increasingly low angle curve (Figure 3a). The Langmuir sorption model assumes the sediment surface has a finite number of available adsorption sites, with sorption reaching saturation at a maximum monolayer sorption capacity, P_{max} . Such behavior can be modeled as:

$$\Delta P_{sed} = \frac{K_{eq}P_{max} [SRP]_f}{(1+K_{eq}[SRP]_f)} \quad . \quad [4]$$

The constant K_{eq} (μM) is different from K_d and is related to the binding energy of the adsorption sites (also described as the affinity of SRP for the sediment in the given water. When sorption data are evaluated by using the reciprocal plot of the Langmuir adsorption equation:

$$\frac{[SRP]_f}{\Delta P_{sed}} = \frac{[SRP]_f}{P_{max}} + \frac{1}{K_{eq} P_{max}} \quad , \quad [5]$$

a linear line segment is formed, in which P_{max} is the reciprocal of the slope, and K_{eq} is the inverse product of P_{max} and the y-intercept, as depicted in Figure 3b.

If the solid particle has two adsorption sites with different affinities for SRP, its reciprocal Langmuir plot will exhibit two line segments with different slope. The Langmuir two-surface sorption isotherm generates two pairs of P_{max} and K_{eq} constants (Fetter, 1977):

$$\Delta P_{sed} = \frac{K_{eq1} P_{max1} [SRP]_f}{(1 + K_{eq1} [SRP]_f)} + \frac{K_{eq2} P_{max2} [SRP]_f}{(1 + K_{eq2} [SRP]_f)} \quad , \quad [6]$$

where the subscripts “1” and “2” indicate the adsorption sites with higher and lower bonding energies, respectively. Model parameters for equation 6 were estimated by minimizing log weighted error.

3. Results

In spite of only one sediment being used in our sorption experiments, we observed very different P sorption behavior based on water type. Sorption efficiency followed the order: fresh GW > bay SW > ecotone GW. A sorption plot of ΔP_{sed} as a function of $[SRP]_f$ is given in Figure 4a, and the parameters derived from the isotherm models are listed in Table 3. Soluble reactive P adsorbed to sediments most efficiently in fresh GW, as it has the steepest slope ($K_d = 11 \text{ L g}^{-1}$). ΔP_{sed} in fresh GW was 20-40% higher than ecotone GW and bay SW across all SRP concentrations. Bay

SW adsorbed efficiently at low SRP concentrations ($K_d=3.4 \text{ L g}^{-1}$), and ecotone GW exhibits low sorption efficiency across all SRP concentrations; its K_d (0.21 L g^{-1}) is 63 and 17 times lower than fresh GW and bay SW, respectively.

Sorption curves typically begin linear and then the slope begins to decrease at the onset of saturation. The bay SW isotherm curve inflects at a low ΔP_{sed} and a low concentration of $[\text{SRP}]_f$. When $[\text{SRP}]_f / \Delta P_{\text{sed}}$ is plotted as a function of $[\text{SRP}]_f$ the data for each water type form two distinct straight-line components (Figure 4b and c). Soils commonly exhibit distinct line segments in reciprocal plots, indicating two types of adsorption sites may have different kinetics (Holford et al., 1974; Syers et al., 1973). Accordingly, the two-surface Langmuir isotherm equation is applied so as to derive separate sorption parameters for the high and low energy adsorption sites (Fetter, 1977). The P saturation, P_{max} , is calculated as the reciprocal of the slope, and in Figure 4b fresh GW and ecotone GW have visibly similar slopes for both line segments (high and low energy adsorption sites), resulting in similar values as each other for both P_{max1} ($1.1 \mu\text{mol g}^{-1}$ and $1.4 \mu\text{mol g}^{-1}$, respectively) and P_{max2} ($4.7 \mu\text{mol g}^{-1}$ and $4.1 \mu\text{mol g}^{-1}$, respectively) compared to the much lower values for bay SW (P_{max1} : $0.4 \mu\text{mol g}^{-1}$ and P_{max2} : $2.0 \mu\text{mol g}^{-1}$).

Although fresh GW and ecotone GW reach saturation at similar thresholds, the low sorption efficiency of ecotone GW means that it takes a much higher $[\text{SRP}]_f$ concentration to reach the same saturation point. Conversely, although bay SW has high sorption efficiency initially, it reaches saturation at a very lower SRP concentration compared to the other two waters.

The EPC_o 's for the three water types follow a different order: ecotone GW > fresh GW > bay SW ($0.094 \pm 0.003 \mu\text{M}$, $0.075 \pm 0.005 \mu\text{M}$, and $0.058 \pm 0.004 \mu\text{M}$, respectively).

4. Discussion

Our results support the hypothesis of Millero et al. (2001a) that high bicarbonate water causes sediment to have lower sorption efficiency than it does in either fresh water or saltwater. Our sediment acted as a high SRP sink in fresh GW, as reflected in the high P sorption efficiency (K_d) and high saturation concentration (P_{max}). In Florida Bay seawater the sediment exhibits intermediate sorption efficiency. The sediment in ecotone GW exhibits very low SRP buffering capacity (low K_d), which would maintain higher ambient water SRP concentration.

Risk of eutrophication from outside sources is also higher in a sediment with low buffering capacity. Portions of the freshwater Everglades that have received water with elevated SRP from canals have exhibited high buffering capacity, sequestering some of the excess P, as measured in high sedimentary total P (Osborne et al., 2014; Wang et al., 2011). The P retention capacity of the sediments in both freshwater marshes and bays protect the overlying water column from rapid P release (Wang and Li, 2010), although where P-loading is intense, such as the Everglades Agricultural Area even freshwater can induce significant desorption from the sediment (Das et al., 2012). The results of this study suggest that carbonate sediment in water with high HCO_3^- concentration would have severely limited ability to remove excess SRP from the water and would readily desorb P from sediments.

Given that the mangrove ecotone is an active mixing zone, it is important to recognize that if the sediment were equilibrated to ecotone GW, an influx of either bay SW or fresh GW would be expected to lead to adsorption of P to the sediment. Conversely, the same sediment immersed in either bay SW or fresh GW would undergo desorption upon a change to ecotone GW. Many coastal wetlands are subject to influxes of fresh and tidal seawater, such as during storm and tide events, and also on diurnal, seasonal, and long term time scales, which could result in frequent rapid reversals in P sorption. Conversely encroachment of mangroves into a former freshwater wetland may be accompanied by increase in concentration of both HCO_3^- and SRP. The mangrove site for this study was a freshwater marsh in 1950, before mangroves encroached from Florida Bay (Ross et al., 2000). Sea level rise is expected to exacerbate saltwater intrusion in many areas (Barlow and Reichard, 2010). Long-term increases in freshwater flow could recharge the aquifer and potentially cause a mangrove zone to retreat seaward, shifting P sorption dynamics as it goes. The Comprehensive Everglades Restoration Plan is a multibillion dollar project launched in 2000, one of the largest restoration projects ever undertaken. A key goal of this restoration plan is to increase freshwater flows so as to mitigate or delay the effects of sea level rise.

The EPC_o 's of this study are at the low end of the 0.03-6.20 μM range found in P sorption studies in the freshwater Everglades under aerobic conditions (Reddy et al., 2011), Zhou and Li (2001) investigated two soils from a freshwater marsh in the Everglades, of which one had an EPC_o (0.065 μM) similar to the values for our sediment in bay SW (0.058 μM) and fresh GW (0.075 μM), and the other had a much higher EPC_o (0.323 μM). By contrast, P-polluted canal sediments in the Everglades Agricultural Area were found to have EPC_o 's ranging from 1.9 to

3.9 μM (Das et al., 2012). This is consistent with a finding in the Northern Everglades and agricultural areas in southeastern Florida, where soil EPC_o has been found to increase with increasing P enrichment (Richardson and Vaithiyathan, 1995; Zhou and Li, 2001).

Nonetheless, all three EPC_o 's determined for this study are intermediate to the range of ambient water SRP concentration seen in monthly monitoring efforts at the ecotone field location (range 0.02-0.27 μM SRP; Price, René, unpublished data). On the occasions when the ambient water SRP concentration is at a low point, the ecotone sediment may desorb SRP on the order of 0.003 $\mu\text{mol g}^{-1}$ (Table 3). When magnified by the high *in situ* sediment:water ratio, desorption of this magnitude could provide a critical SRP subsidy when most needed. Any release of SRP by the sediment would be immediately ecologically relevant given that mangrove roots permeate the sediment layer here (Ewe et al., 2007),. The higher EPC_o for ecotone GW compared to fresh GW and bay SW indicates that SRP desorbs from the sediment at a higher ambient water SRP concentration and over a wider range of water SRP concentrations. The times when the ambient water exceeds the EPC_o for ecotone GW is unlikely to produce much adsorption due to the low sorption efficiency of the sediment in this water.

The low P content of our sediment may explain its high sorption efficiency in fresh and saltwater, and low EPC_o 's in all three of our water types. In a study of soils from a range of freshwater, estuary, and saltwater sites in the Southern Everglades, mangrove ecotone sediment at the same monitoring station as ours had the least P_{exch} of the 17 Everglades sediments investigated (Chambers and Pederson, 2006). Zhang and Huang (2007) determined that low P_{exch}

was associated with lower EPC_o and higher sorption efficiency in Florida Bay. They measured P_{exch} for sediments at 40 stations and their lowest P_{exch} was $0.023 \mu\text{mol g}^{-1}$; very similar to our $0.022 \pm 0.002 \mu\text{mol g}^{-1}$, was from their sampling station nearest to our study area. The mangrove swamp sediments may be a landward extension of the Florida Bay pattern of P_{exch} variability. Consistent with its low P_{exch} , that bay sediment exhibits a higher K_d values (0.579 L g^{-1}) which was intermediate to our sediment in ecotone GW and bay SW), and lower EPC_o 's ($0.503 \mu\text{M}$) which was approximately an order of magnitude higher than ours.

The NAP for ecotone GW ($0.02 \mu\text{mol g}^{-1}$) is consistent with the measured P_{exch} of $0.022 \pm 0.002 \mu\text{mol g}^{-1}$ for the sediment (Tables 2 and 3), an agreement that could be causally related to the fact that it had been equilibrated to ecotone GW at the time of collection. Our NAP estimates followed fresh GW > bay SW > ecotone GW ($0.85 \mu\text{mol g}^{-1}$, $0.20 \mu\text{mol g}^{-1}$, and $0.02 \mu\text{mol g}^{-1}$, respectively). Since NAP is the negative of the y-intercept on the sorption plot, a steep sorption slope (high K_d), as seen in the fresh GW and bay SW, forces a more negative y-intercept and higher NAP. In this way, the experimental determination of higher NAP in fresh GW and bay SW suggests that if the sediment had been immersed in one of these waters at the time of collection, it may have exhibited a higher P_{exch} . The two-surface Langmuir isotherm (Figure 4b) also suggests that SRP encountered distinct site density and energetics for the same sediment depending on which water it was in. It is plausible that SRP attaches to similar adsorption sites in fresh GW and ecotone GW, as reflected in the similar kinetics of the two waters, and that these adsorption sites are not available (or are less favorable) when the sediment is in contact with bay SW.

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4 The behavior of our sediment in high bicarbonate groundwater is consistent with local field
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6 measurements that show ecotone surface water and sediment groundwater often have higher total
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8 dissolved P than freshwater or coastal waters (Price et al., 2006; Rudnick et al., 1999). The
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10 Everglades mangrove zone has been called a “net source” of total dissolved P (Rudnick et al.,
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12 1999) and that some form of “nutrient regeneration or retention” must be occurring (Childers,
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14 2006). Our results suggest that P sorption dynamics could drive the observed elevated total
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16 dissolved P in this region due to their extremely low buffering capacity in ecotone groundwater
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18 as well as direct desorption from the sediment when the ambient water concentration drops
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20 below the EPCo, or the sediment is subjected to high bicarbonate groundwater after a period of
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22 immersion in fresh water or saltwater. Our study demonstrates how abiotic P exchange
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24 mechanisms may contribute to greater P availability in coastal estuaries, relative to waters with
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26 low salinity upstream and high salinity downstream. It has also been determined that Taylor
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28 Slough ecotone groundwater is a net source of total dissolved P to the overlying water column
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30 (Davis et al., 2001), so P sorption dynamics in the groundwater may be an important source of P
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32 for the surface water as well. Other contributing biotic and abiotic factors include transport of
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34 dissolved or particulate P from Florida Bay when Taylor River flow is reversed, mangrove leaf
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36 litter collecting and releasing SRP, coastal groundwater discharge, and hurricanes bringing P-
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38 rich particles from Florida Bay (Davis III et al., 2004; Davis and Childers, 2007; Price et al.,
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40 2006; Rudnick et al., 1999; Sutula et al., 2003).

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55 Our work merits further investigations as to prevalence and effects of water with high HCO_3^-
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57 concentration in other settings. Few studies of estuary pore water include total alkalinity, and
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59 those undertaken do not include P sorption. Attribution as to the cause of high HCO_3^-
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concentration in ambient water varies. In carbonate lithology it has been attributed to dissolution of carbonate sediments at low pH:

Carbonic acid reacts with calcium carbonate to produce two HCO_3^- equivalents:

Mangroves may enhance dissolution of calcium carbonate by enhancing the production of acids in several ways. If acids are produced in sufficient quantity, the saturation state for calcium carbonate may lower sufficiently to cause dissolution of carbonate sediment adjacent to roots. Millero et al. (2001b) postulated that mangroves acidify their soils as a result of the high volume of leaf litter associated with them, causing an unusual degree of photochemical and bacterial oxidation of organic material. Pore waters in a mangrove forest in East Africa also exhibited high HCO_3^- concentration, which Middelburg et al. (1996) also attribute to mangrove-facilitated carbonate dissolution, due to three biological activities through which mangroves produce acid soils at their roots. First, mangrove roots translocate oxygen from their leaves to their roots and leak it to the soil, as inferred from Eh levels and microelectrode measurements (Andersen and Kristensen, 1988; Boto and Wellington, 1984). The subsequent bacterially mediated oxidation reactions produce a range of possible acids:

7 Secondly, mangrove roots uptake ammonium leading the release of H^+ ions. And thirdly,
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9 mangrove roots respire carbon dioxide, which also lowers soil pH (Andersen and Kristensen,
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11 1988; Kristensen et al., 1988).
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16 Pore water with high HCO_3^- concentration in a salt marsh at Great Sippewissett Marsh,
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18 Massachusetts was attributed to intense sulfate reduction of organic material (Giblin and
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20 Howarth, 1984). Sulfate reduction generates two moles of bicarbonate for every mole of sulfate
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22 reduced:
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32 High HCO_3^- pore water in a mangrove creek in Sepetiba Bay of southeast Brazil was attributed to
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34 intense sulfate reduction that produces ammonium (Ovalle et al., 1990). For that study,
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36 researchers examined a coastal transect which included: upland mangroves that are rarely
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38 flooded, tidally flooded mangroves, and a mudflat. Pore water in the tidally flooded mangrove
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40 zone was enriched in both HCO_3^- and SRP compared to the upslope mangroves and the mudflat,
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42 and these pore waters supplied SRP to the tidal creek at low tide. Although the researchers
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44 attribute the non-conservative SRP concentrations in the tidally flooded mangroves to
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46 groundwater discharge from below, it is plausible that *in situ* HCO_3^- related P sorption dynamics
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48 play a role.
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4 If exceptionally low P sorption efficiency driven by HCO_3^- concentration are demonstrated to be
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6 a general process for estuary sediments, the dynamics may have implications for coastal SRP
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8 availability globally. Tidal wetlands are found on sheltered marine coastlines, with salt marshes
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10 extending from the arctic to sub-tropical latitudes, and mangrove dominating in the sub-tropics
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12 and tropics (Mitsch and Gosselink, 2000). Further studies are needed to evaluate the prevalence
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14 of this water type is, what conditions are required to produce it, and how this water type affects
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16 sediment P sorption dynamics in other regions. As we have outlined, there appear to be complex
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18 feedbacks between abiotic P sorption reactions and biological factors such as productivity,
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20 microbially mediated oxidation/reduction reactions, and also a suite of mangrove activities that
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22 affect the chemistry in their root zone. It would be helpful to better understand the range of
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24 conditions that are associated with high HCO_3^- concentration in terms of productivity, vegetation
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26 type, sediment type and texture, redox state, salinity, tidal range and elevation. The exceptional
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28 rates of productivity by salt marshes and mangrove swamps rival that of productive agricultural
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30 lands (Odum and Smalley, 1959). River HCO_3^- concentration in carbonate regions is higher than
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32 in any other lithology (Amiotte Suchet et al., 2003), and suspended sediment could potentially
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34 reverse P sorption behavior upon encountering coastal seawater (Millero et al., 2001b).
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46 The only water composition gradient among the three water types (see Table 1) that can explain
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48 the exceptionally low sorption efficiency of ecotone GW is its high HCO_3^- concentration, which
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50 may lead to competition at adsorption sites between SRP and HCO_3^- . Sulfate ions can also
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52 compete with SRP for adsorption sites (Sigg and Stumm, 1981), however SO_4^{2-} concentration in
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54 the ecotone GW is intermediate to the fresh GW and bay SW (Figure 2). If SO_4^{2-} were the
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56 primary driver of the relative sorption efficiency of the three water types, bay SW (with double
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4 the SO_4^{2-} concentration of ecotone GW) would exhibit lower sorption efficiency than ecotone
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6 GW. The high Ca^{2+} and Mg^{2+} concentration in saltwater may provide bridges for surface
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8 complexation reactions with SRP (Spiteri et al., 2008), which would favor greater adsorption in
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10 bay SW. A decreasing trend of P adsorption as pH increases from 6 to 9 has been observed in
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12 natural lake sediments (Zhou et al., 2005) and goethite (Hawke et al., 1989). The trend in pH of
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14 our waters is ecotone GW (6.7) < fresh GW (7.3) < bay SW (8.2), which would favor more
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16 efficient adsorption in ecotone GW compared to bay SW. Future geochemical modeling is
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18 planned that uses the empirically derived parameters from this study as input to help elucidate
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20 the geochemical mechanisms for the observed P sorption behavior.
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29 Phosphorus sorption behavior can be influenced by factors held constant in our experiments,
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31 such as changing temperature or redox condition. Increased temperature has been found to
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33 increase adsorption in Florida Bay sediments (Zhang and Huang, 2011). In the Indian River
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35 Lagoon, Florida, SRP was found to adsorb more efficiently in oxic vs. anoxic conditions, P
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37 binding to iron oxide in oxidizing conditions, and desorbing from the sediment when the iron is
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39 reduced (Pant and Reddy, 2001). The iron content of sediments at our ecotone field station
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41 (Chambers and Pederson, 2006) is similar to the Indian River Lagoon sediments (Pant and
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43 Reddy, 2001), so the potential importance of redox condition in the topmost layer of Taylor
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45 Slough ecotone sediment cannot be dismissed. Under reducing conditions it can be expected that
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47 the sediment of the present study would have diminished adsorption efficiency in all three water
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49 types. Future work examining temperature and redox effects would be useful in understanding P
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51 sorption behavior in the Taylor Slough ecotone.
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Coastal wetlands are highly vulnerable to anthropological impacts such as rising sea levels, saltwater intrusion, reductions in freshwater availability and eutrophication (Rivera-Monroy et al., 2011). Better understanding of sediment-groundwater interactions in the mangrove zone provides useful guidance to restoration efforts and improves our understanding of mangrove productivity in the face of climate change. Our results may have implications for a broad range of settings where high HCO_3^- water exists, including non-carbonate sediment, salt marshes, and suspended and benthic sediment of coastal rivers.

5. Conclusion

This is the first information on P sorption dynamics in a sub-tropical carbonate mangrove wetland and provides a basis for understanding the geochemical contribution to SRP availability in these important biomes. We have evaluated the adsorption/desorption reactions between calcareous sediments and three ambient coastal waters and determined P sorption parameters for both linear and two-surface Langmuir models. This study finds that ecotone groundwater, by interacting with mangrove sediment, can provide more available SRP than fresh groundwater and Florida Bay seawater. Distinct P sorption behavior for these three water types with the mangrove ecotone sediment has important implications for both sea level rise and increased freshwater flows, namely that both hydrologic changes would be expected to decrease SRP availability in the mangrove ecotone. Our experiments support the hypothesis that adsorption/desorption reactions between the sediment and ambient waters could be a significant abiotic control of SRP availability in the shallow groundwater of the Taylor Slough ecotone.

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Table 1 Selected characteristics of the three field waters

Water Type	pH	Salinity	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	Total	SRP	Si(OH) ₄
		psu	mM	mM	mM	mM	mM	mM ⁻	alkalinity as HCO ₃ ⁻ mM	μM	μM
Fresh GW	7.3	0.1	1.8	0.1	0.7	0.01	0.8	*	4.0	0.050	80.4
Ecotone	6.7	16.0	6.7	29.6	217.9	4.16	264.1	11.2	17.5	0.177	83.6
GW											
Bay SW	8.2	31.4	9.1	50.0	425.9	9.29	512.4	28.4	2.9	0.076	9.2

* Below detection

Table 2 Selected P analysis of the sediment, in μmol g⁻¹

MgCl ₂ inorganic P (P _{exch})	0.022 ± 0.002
MgCl ₂ organic P	0.025 ± 0.002
Total Sedimentary P	1.3

Table 3 Phosphorus sorption characteristics of the ecotone sediment with respect to the field waters

Field Water	K_d , ^a L g ⁻¹	Desorbed SRP ^b μmol g ⁻¹	NAP ^c μmol g ⁻¹	EPC _o ^d μM	P_{max1} ^e μmol g ⁻¹	K_{eq1} ^f μM ⁻¹	P_{max1} ^g μmol g ⁻¹	K_{eq2} ^h μM ⁻¹
Fresh GW	11	0.0034 ± 0.0002	0.85	0.075	1.1	3.5	4.7	0.04
Ecotone GW	0.21	0.0028 ± 0.0002	0.02	0.094	1.2	0.2	4.1	0.02
Bay SW	3.40	0.0024 ± 0.0002	0.20	0.058	0.4	12.6	2.0	0.06

^a Linear adsorption coefficient

^b Desorbed SRP from natural water (no added P)

^c Native adsorbed P

^d Equilibrium SRP concentration

^e Adsorption maximum for first surface

^f Adsorption energy for first surface

^g Adsorption maximum for second surface

^h Adsorption energy for second surface

Figure captions:

Figure 1 Collection locations for samples: fresh GW (triangle), ecotone GW and sediment (circle), and bay SW (square)

(2 column width)

Figure 2 Selected water composition for fresh GW (triangle), ecotone GW (circle), and bay SW (square) with SRP concentration in filled shapes, and Total alkalinity as HCO_3^- in open shapes.

(1 column width)

Figure 3 a) Schematic of P sorption isotherm. K_d = adsorption coefficient (slope); EPC_0 = zero equilibrium SRP concentration (x-intercept) where adsorption = desorption; NAP = native adsorbed P (y-intercept); P_{max} = maximum monolayer sorption capacity, and is the point on the y-axis where the sorption curve inflects towards lower angle sorption; (b) Schematic of reciprocal Langmuir Isotherm plot; P_{max} = the inverse of the slope, and K_{eq} = the inverse product of the y-intercept and P_{max}

(1 column width)

Figure 4 Fresh GW (triangles), ecotone GW (circles), and bay SW (squares), accompanied by dashes representing the Langmuir Two-Surface Sorption isotherms, a) In standard plot; b) in reciprocal plot from which Langmuir two surface isotherm parameters were determined; and c) the extended two-surface isotherm for fresh GW

(1 column width)

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Figure(s)