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 tested the P sorption properties of sediment with three endmember water sources in this region: 1) fresh groundwater from the inland Everglades; 2) bicarbonate (HCO_3^-) enriched brackish groundwater from the 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 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. This is consistent with a trend in measured zero-equilibrium SRP concentration, which was highest in ecotone groundwater (0.094 ± 0.003 µM) compared to fresh groundwater and Florida Bay surface water (0.075 ± 0.005 µM and 0.058 ± 0.004 µM respectively). The natural variability of SRP concentration in ecotone groundwater is greater than the range of zero equilibrium SRP concentration for all three waters, so all three waters have the potential to desorb SRP from sediments when ambient water P is low. Soluble reactive P would be expected to begin desorbing 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 equilibrium SRP concentration.

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 fishes, 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 the coastal estuaries (Froelich 1988). Phosphorus (P) is often 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 & 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 and particulate P (both organic and inorganic) are immobile until mineralized to dissolved inorganic P, which typically requires microbial activity (Björkman & Karl 2003). We refer to dissolved inorganic P as soluble reactive P (SRP), defined as the fraction of P in a water sample that passes through a 0.45 µm filter and responds to colorimetric tests without having been subjected to a pretreatment of hydrolysis or oxidative digestion (Murphy & Riley 1962). Soluble reactive P concentration is considered to be roughly equivalent to dissolved inorganic P concentration, but the distinction is made because there is potential for organic or colloidal P to pass through <0.45 µm and to react to colorimetric reagents (Thomson-Bulldis & Karl 1998).

The cycle through which P shifts between SRP and immobilized forms involves a great number of complex processes, and both biotic and abiotic portions of the cycle must be considered when evaluating P availability in wetlands (Reddy et al. 1999). Abiotic processes in the P cycle include leaching of P from leaf litter; sedimentation; exchange of P between sediment and the overlying water column; precipitation, dissolution, and weathering of inorganic P phases such as

apatite; and P sorption reactions (Davis & Childers 2007; Reddy et al. 1999). Phosphorus sorption is an important process in wetlands whereby P is exchanged between SRP in the ambient water and solid phase P (Froelich 1988). The process has two steps. The first step has fast kinetics (minutes to hours) and involves the accumulation (adsorption) of SRP from ambient water at sediment particle surfaces; a reversible process is desorption that releases the adsorbed SRP back to the ambient water. The second step is much slower (days to weeks), and involves solid-state diffusion of adsorbed SRP from the mineral surface into the interior of mineral grains (Froelich 1988).

In this study we discuss P sorption in terms of the rapid, reversible first step. Adsorption/desorption reactions can act as SRP buffers, analogous to pH buffers, maintaining water SRP at a constant concentration. The water SRP concentration at which zero net SRP adsorption or desorption occurs for a given system is termed the zero equilibrium SRP concentration (EPC_o). When ambient water SRP concentration is close to the EPC_o, the sediment displays the maximum capacity for buffering SRP (Froelich 1988). Slight rises or falls in ambient SRP concentration from this equilibrium may result in rapid adsorption or desorption, respectively, returning the system to a new equilibrium (Froelich 1988). A sediment is described as having high adsorption efficiency when SRP adsorption is high as water SRP concentration increases. Efficient P sorption results in high SRP buffer intensity, maintaining low water SRP concentration as long as the sediment does not become saturated (Reddy et al. 1999).

Highly variable water chemistry in coastal mixing zones causes variability in SRP availability through shifting P sorption behavior. Sorption reactions are influenced by physiochemical properties of the given sediments and their ambient water, including the composition and particle size distribution of the solid particles, temperature, pH, ionic strength, redox status, organic matter content, and ions in the ambient water (Millero et al. 2001a; Pant & Reddy 2001; Reddy et al. 1999; Zhang & Huang 2011). The sensitivity of P sorption reactions to water chemistry and sediment characteristics means that the direction and strength of sorption

reactions are hard to predict without direct experimentation with the natural sediment and water in question (Suzumura et al. 2000).

Some coastal estuaries have ambient water SRP concentration that is higher than would be predicted based on conservative mixing of the fresh river water and seawater. Typically freshwater adsorbs SRP more strongly than seawater, so seawater induces desorption of adsorbed SRP from suspended or benthic sediments (Froelich 1988; Zhang & Huang 2011). Suspended sediments in coastal rivers may release SRP as they enter the seawater mixing zone (Fox et al. 1986). Similarly, an influx of seawater due to tidal influx or seawater intrusion, can lead to rapid desorption and associated increases in measured SRP concentrations (Gardolinski et al. 2004; Sundareshwar & Morris 1999; Suzumura et al. 2000).

Many mangrove estuaries are found in carbonate lithology, including Belize, the West Indies, Bermuda, Mexico, Western Australia, Brazil and East Africa (Alongi et al. 1996; Coronado-Molina et al. 2012; Ellison 1993; Jennerjahn & Ittekkot 1997; McKee & Faulkner 2000; Woodroffe 1981). Groundwater in carbonate-based lithology can become enriched in HCO_3^- when organic matter breakdown releases acids that in turn dissolve mineral solids. Differences in HCO_3^- alkalinity play a critical role in freshwater-seawater mixing reactions. Experiments by Millero et al. (2001a) on synthetic aragonite and calcite determined that the apparent effect of salinity on P sorption behavior was actually driven by the respective HCO_3^- and SO_4^- concentrations in the solutions. The researchers found that increase in the HCO_3^- concentration decreased SRP adsorption, especially at low salinity. When HCO_3^- concentration was held constant (2 mM) adsorption was nearly independent of salinity. The slight positive charge of the calcium-on-calcium carbonate surfaces attract SRP and HCO_3^- and surface complexation reactions can result. When the relative abundance of SRP and HCO_3^- in the ambient water changes, anion exchange can occur between competing ions at the adsorption sites. Consequently, Millero et al. (2001b) predicted that for coastal rivers that have higher HCO_3^- than seawater the typical pattern of seawater-induced desorption could be reversed, such that an influx of seawater into sediment that had

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been equilibrated to the high HCO_3^- water cause the sediment to release of HCO_3^- ions and adsorb SRP.

Determining the relative behavior of P sorption in carbonate sediments and their associated waters is important to understanding the drivers of mangrove productivity in carbonate-based regions. This study examines the potential for SRP concentration of the shallow groundwater in the mangrove ecotone to be affected by in situ adsorption and desorption reactions. P sorption parameters are determined for carbonate sediments from a mangrove zone with respect to three natural endmembers: fresh groundwater, brackish high HCO_3^- groundwater, and saltwater. In so doing, this study provides insight into the fast-acting abiotic portion of the biogeochemical P cycle in this coastal mixing zone, which has implications for other estuaries with carbonate lithology and a brackish high HCO_3^- endmember water.

2. Materials and Methods

2.1. Study Area

The southern terminus of the Florida peninsula is fringed by a wide mangrove swamp, dividing the upstream freshwater marsh from Florida Bay (Fig. 1). The Everglades wetland complex of southern Florida, USA has two main drainage basins: Shark River Slough, which angles to the southwest and drains into the Gulf of Mexico, and the smaller Taylor Slough, which flows southward into the northeast corner of Florida Bay. The broad Everglades mangrove region is within 1 m of mean sea level. Tides along the western portion of Florida Bay are mixed diurnal and semidiurnal with a mean amplitude of about 0.3 m (Wang et al. 1994). As waters from the Gulf of Mexico move into Florida Bay, the tidal effects are damped by the shallow mud banks such that the Eastern bay is micro tidal, with tidal amplitudes of only about 1-5 cm (Wang et al. 1994). On a few occasions per year, high salinity bay water flows upstream into the upper mangrove fringe wetlands of Taylor Slough, particularly in the dry season during times of low freshwater head and sustained southerly winds (Castaneda 2010; Davis III et al. 2004;

Koch et al. 2012; Sutula et al. 2003). The sediment layer consists of a relatively thin layer (up to 1.5 m deep) of calcareous marl and peat (Spence 2011) with mangrove roots penetrating the shallow sediments down to the underlying limestone bedrock (Ewe et al. 2007). The limestone aquifer underlying Taylor Slough is the unconfined Biscayne Aquifer (Fish & Stewart 1991). Saltwater intrudes into the Biscayne Aquifer between 6-10 km inland in Taylor Slough (Fitterman & Deszcz-Pan 1998; Price et al. 2006).

The Taylor Slough mangrove ecotone (hereafter referred to as the "ecotone") is oligotrophic and highly P-limited (Noe et al. 2001). The groundwater in the shallow sediments of the ecotone has 3-4 times higher HCO_3^- alkalinity than either upstream freshwater or downstream Florida Bay water, and the three waters mix with a high degree of temporal and spatial variability (Millero et al. 2001b; Price et al. 2006; Zapata-Rios & Price 2012).

2.2. Water Samples

Three water types were collected representing fresh groundwater ("fresh GW"), high bicarbonate brackish groundwater ("ecotone GW"), and surface saltwater from Florida Bay ("bay SW") (Fig. 1). The fresh groundwater endmember was collected from a shallow monitoring well (TSB-15) within the bedrock underlying the freshwater sawgrass marsh region of Taylor Slough. The well is lined with a 5.5 cm diameter PVC pipe screened at 4 m depth. The well was first purged of at least five well volumes using a peristaltic pump. The high bicarbonate endmember was taken from the Taylor Slough mangrove ecotone about 4 km inland from a well that penetrates to a depth of 142 cm within the sediment layer (Castaneda 2010; Zapata-Rios 2009). This well is designated as TS/Ph 6b well C3 and is operated by the Florida Coastal Everglades Long Term Ecological Research Program. Florida Bay surface water was taken from a dock in Key Largo to represent the saltwater endmember.

Immediately after sampling, temperature, pH, and electrical conductivity were measured with a YSI 556 MPS (YSI, Yellow Springs OH). Water samples placed in HDPE Nalgene bottles and

maintained at 4°C (± 2°C) prior to analysis. Total alkalinity was determined within 24 hours by potentiometric acid titration. Major cations and anions were determined at FIU with ion chromatography. SRP was analyzed as discussed below. Selected water characteristics are presented in Table 1.

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, and the top 1 cm of cores taken at this location were darker in color then the sediment immediately below. Previous study of sediment further downstream found exceptionally high total sedimentary P in the top of the core (Koch & Reddy 1992). Calcareous marl sediment was extracted using a Russian peat corer at FCE field station TS/Ph6b (Fig. 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 μm), 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). Organic P also adsorbs to sediment but because it is considered less bioavailable and behaves differently from inorganic P (Huang & Zhang 2010), the scope of this paper is limited to measuring $MgCl_2$-exchangeable organic P for the purpose of characterizing the sediment. 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. Samples were filtered with 0.45 μm nylon syringe filters and divided into two 10 mL portions. The $MgCl_2$-exchangeable inorganic P, or P_{exch} is measured by analyzing one portion of filtrate SRP, and normalizing the value to μmoles per grams of sediment. The second portion of filtrate

was analyzed for total dissolved P by digesting the other 10 mL portion of filtrate with 1 mL of neutral potassium persulfate solution (5%, w/v, pH approximately 6.5) at 90°C for 16 hours (Huang & Zhang 2009) and analyzed for SRP after returning to room temperature. Dissolved organic P was calculated as the difference between SRP and total dissolved P, and this value was converted to $MgCl_2$-exchangeable organic P by normalizing to µmole g^{-1} (Zhang et al. 2010; Zhang et al. 2004).

A portion of the sediment was acid digested (preparation method EPA 3050) and total sedimentary P was determined inductively coupled plasma-atomic emission spectrometry (analytical method EPA 6010). Selected sediment characteristics are presented in Table 2.

2.4. Adsorption-Desorption Experiments

Phosphorus sorption parameters of the sediment in contact with the three water types were determined by batch incubation experiments based on the method of Froelich (1988). Varying amounts of SRP stock solution were added to subsamples of each water type to create batches of solutions with SRP concentrations of 0 (no added SRP), 4, 8, 16, 24, 32, and 48 µM. Biological activity was prevented in our experiments with two precautions. Prior to experimentation the natural water samples were filtered through 0.1 µm PTFE filters using a vacuum filter flask to exclude microorganisms that could uptake or release P during water storage. To inhibit biological activity that may be introduced by any microbes in the sediment, 10 µL 0.1% chloroform was added to each tube (Zhou et al. 2005). To account for any SRP reduction caused by the 0.1 µm filter step, a sub-sample of each field water-SRP solution was analyzed for SRP before the incubation, and the measured concentration was operationally defined as initial SRP concentration, $[SRP]_I$ for a given batch.

For the batch with no added SRP, so as to permit the detection of P desorption from sediment with such low P content, the solution was concentrated by reducing the water volume to 5 mL, and increasing the sediment mass to 1.5 g (and number of replicates raised to 20 for each

water type). For the other batches, 10 mL of field water-SRP solution was combined with a 200 mg subsample of ecotone sediment in a 15 mL plastic conical centrifuge tube (10 replicates per water type per batch, 30 samples total in a batch). At 48 µM SRP the fresh GW sorption curve was still relatively steep, thus not providing enough of the sorption isotherm to calculate P_{max}; five higher SRP concentrations ranging from 60-320 µM SRP were used and run exclusively for fresh GW (three replicates for each increment of added P). Each suspension was agitated at 200 rpm on a platform shaker for 24 hours at room temperature (23±0.5°C). After incubation, the water from each tube was filtered with a 0.45 µm nylon syringe filter, and immediately analyzed for their final SRP concentration, $[SRP]_f$. A total of 255 P sorption experiments were conducted.

2.5. SRP Analysis

SRP concentrations were determined the day of each experiment by filtering samples through a 0.45 µm nylon syringe filter and using the microscale malachite green method (D'Angelo et al. 2001), measuring absorbance at 630 nm in 96-well microplates on a BioTek EPOCH microplate spectrophotometer.

2.6. Sorption Isotherms

The amount of SRP adsorbed or desorbed from the sediment, ΔP_{sed}, was calculated as:

$$\Delta P_{sed} = [SRP]_i - [SRP]_f \tag{1}$$

ΔP_{sed} was normalized to the mass of sediment and volume of solution (µmole g^{-1}). A plot of ΔP_{sed} vs. $[SRP]_f$ 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 (Fig. 2a).

The linear isotherm equation is:

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

where K_d (L g^{-1}) is the P sorption coefficient or partition coefficient (slope) relating to buffering capacity, and NAP (µmole g^{-1}) is native adsorbed SRP (the y-intercept), a constant representing the amount of pre-existing loosely adsorbed inorganic P on the sediment (Fig. 2a). Negative ΔP_{sed} indicates desorption and positive ΔP_{sed} indicates adsorption. The EPC$_o$ (µmole 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$_o$:

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

The parameter K_d is a measure of the buffer intensity, 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 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 equilibrium 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 (Fig. 2a). 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:

$$\triangle \mathrm{P_{sed}} = \frac{\mathrm{K_{eq}P_{max}} \, \mathrm{[SRP]_f}}{(1 + \mathrm{K_{eq}[SRP]_f}} \qquad . \qquad\qquad [4]$$

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

$$\frac{\mathrm{[SRP]_f}}{\triangle \mathrm{P_{sed}}} = \frac{\mathrm{[SRP]_f}}{\mathrm{P_{max}}} + \frac{1}{\mathrm{K_{eq} \, P_{max}}} \qquad , \qquad\qquad [5]$$

a linear line segment is formed, in which $\mathrm{P_{max}}$ is the reciprocal of the slope, and $\mathrm{K_{eq}}$ is the inverse product of $\mathrm{P_{max}}$ and the y-intercept, as depicted in Fig. 2b.

Soil and sediment particles commonly have two adsorption sites with different affinities for SRP, and the reciprocal Langmuir plot will yield two-line segments of different slope. The Langmuir two-surface sorption isotherm generates two pairs of $\mathrm{P_{max}}$ and $\mathrm{K_{eq}}$ constants (Fetter 1977):

$$\triangle \mathrm{P_{sed}} = \frac{\mathrm{K_{eq1}P_{max1}[SRP]_f}}{(1 + \mathrm{K_{eq1}[SRP]_f}} + \frac{\mathrm{K_{eq2}P_{max2}[SRP]_f}}{(1 + \mathrm{K_{eq2}[SRP]_f}} \qquad , \qquad\qquad [6]$$

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

The endmember waters caused divergent P sorption behavior with the same sediment. Sorption efficiency followed the order: fresh GW > bay SW > ecotone GW. A sorption plot of $\Delta\mathrm{P_{sed}}$ as a function of $\mathrm{[SRP]_f}$ is given in Fig. 3a, 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 ($\mathrm{K_d}$ = 11 L g^{-1}). $\Delta\mathrm{P_{sed}}$ 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 L g^{-1}), and ecotone GW exhibited 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.

The sorption curves for the three water types exhibit an inflection in slope, which indicates the onset of saturation. The bay SW isotherm curve inflects at a low ΔP_{sed} and a low concentration of $[SRP]_f$. When $[SRP]_f$ /ΔP_{sed} is plotted as a function of $[SRP]_f$ the data for each water type form two distinct straight-line components (Fig. 3b). 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 Fig. 3b fresh GW and ecotone GW have visibly similar slopes for both line segments (high and low energy adsorption sites), resulting in similar sorption maxima for both P_{max1} (1.1 µmole g^{-1} and 1.4 µmole g^{-1}, respectively) and P_{max2} (4.7 µmole g^{-1} and 4.1 µmole g^{-1}, respectively) compared to the much lower values for bay SW (P_{max1}: 0.4 µmole g^{-1} and P_{max2}: 2.0 µmole 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 $[SRP]_f$ concentration to reach saturation. Conversely, although bay SW has strong sorption efficiency initially, it reaches saturation at a lower SRP concentration than 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 ± 0.003 µM, 0.075 ± 0.005 µM, and 0.058 ± 0.004 µM, 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. The sediment acted as a strong SRP sink in fresh GW, as reflected in the high P sorption efficiency (K_d) and high saturation concentration (P_{max}). Ecotone groundwater exhibited very low SRP buffering capacity (low K_d), which would allow ambient waters to be maintained at a higher SRP concentration. In Florida Bay seawater the sediment exhibited intermediate sorption efficiency, but very low P_{max}. 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.

The EPC_o of a given sediment-water system can be used as an indicator of the potential for desorption of SRP from sediments in response to fluctuations in ambient water SRP. 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). This would be expected for sediments with low P content, as EPC_o commonly rises with NAP (Zhou & Li 2001). Nonetheless, all three EPC_o's determined for this study are above the minimum field SRP concentration 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 μmole 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. Given that mangrove roots permeate the sediment layer in the ecotone (Ewe et al. 2007), a small release of SRP by the sediment could be immediately taken up by the mangroves. The high 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 low P content of our sediment may explain its high sorption efficiency in two of the three waters, and low EPC_o's in all three of the waters tested. In a study of soils from a range of

freshwater, estuary, and saltwater sites in the Southern Everglades, the sediment at our site had the least P_{exch} (Chambers & Pederson 2006). In a study of nearby Florida Bay sediments Zhang and Huang (2007) found low P_{exch} was associated with lower EPC_o and higher sorption efficiency. Of all of their Florida Bay sediments, the sample with the lowest P_{exch} (0.023 µmole g^{-1}; very similar to ours) was also from the most proximal Florida Bay sampling location to our study area. The mangrove swamp sediments may be a landward extension of Florida Bay pattern. Consistent with its low P_{exch}, that bay sediment exhibited one of their higher K_d values (0.579 L g^{-1}; similar to ours), and one of their lower EPC_o's (0.503 µM; still approximately an order of magnitude higher than ours). One soil in a freshwater wetland of the Everglades was determined to have 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) (Zhou & Li 2001). The other freshwater wetland soil in that study had a much higher EPC_o (0.323 µM).

The calculation of NAP for ecotone GW (0.02 µmole g^{-1}) is consistent with the measured P_{exch} of 0.022 ± 0.002 µmole 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 µmole g^{-1}, 0.20 µmole g^{-1}, and 0.02 µmole g^{-1}, respectively). Bearing in mind that 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 (Fig. 3b) 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, and that distinct adsorption sites are available when the sediment is in contact with bay SW.

Our study demonstrates how abiotic P exchange mechanisms may contribute to greater P availability in coastal estuaries, relative to upstream and downstream low-and high-salt endmembers respectively. The Everglades mangrove zone has been called a "net source" of total dissolved P (Rudnick et al. 1999) with "nutrient regeneration or retention" occurring (Childers 2006). Ecotone surface water and sediment groundwater commonly have higher total dissolved P than freshwater or coastal waters (Price et al. 2006; Rudnick et al. 1999). Our results suggest that P sorption dynamics could drive the observed elevated total dissolved P in this region due to their extremely low buffering capacity in brackish ecotone groundwater. Sorption processes within the sediment may in turn explain the surface water total dissolved P as well, as has been found elsewhere (Wang & Li 2010). Taylor Slough ecotone groundwater is a net source of total dissolved P to the overlying water column (Davis et al. 2001). Other contributing biotic and abiotic factors include transport of dissolved or particulate P from Florida Bay when Taylor River flow is reversed, mangrove leaf litter collecting and releasing SRP, coastal groundwater discharge, and hurricanes bringing P-rich particles from Florida Bay (Davis III et al. 2004; Davis & Childers 2007; Price et al. 2006; Rudnick et al. 1999; Sutula et al. 2003).

Our work merits further investigations as to prevalence and role of high HCO_3^- alkalinity brackish water in other settings. Few studies of estuary pore water include HCO_3^- alkalinity, and those undertaken do not include P sorption. Attribution of high HCO_3^- alkalinity brackish water varies. In carbonate lithology it has been attributed to dissolution of carbonate sediments at low pH:
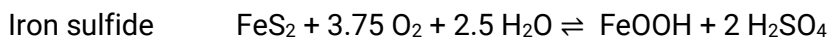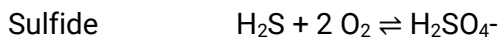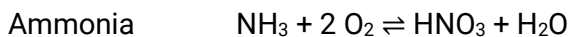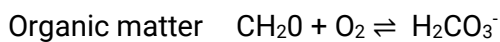
$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$
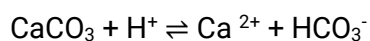
Carbonic acid reacts with calcium carbonate to produce two HCO_3^- equivalents:

$$CaCO_3 + H_2CO_3^- \rightleftharpoons Ca^{2+} + 2HCO_3^-$$
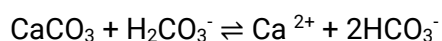
Mangroves may enhance dissolution of calcium carbonate by enhancing the production of acids in several ways. If acids are produced in sufficient quantity to consume alkalinity, the saturation state for calcium carbonate may lower sufficiently to cause dissolution of carbonate

sediment adjacent to roots. Based on work in the Taylor Slough mangrove ecotone, 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^- alkalinity, which Middelburg et al. (1996) also attribute to mangrove-facilitated carbonate dissolution, pointing to three biological activities of mangroves produce acid soils by creating oxidizing conditions 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 & Kristensen 1988; Boto & Wellington 1984). The subsequent bacterially mediated oxidation reactions produce a range of possible acids:

Organic matter $\quad CH_2O + O_2 \rightleftharpoons H_2CO_3^-$

Ammonia $\qquad\quad NH_3 + 2\ O_2 \rightleftharpoons HNO_3 + H_2O$

Sulfide $\qquad\quad H_2S + 2\ O_2 \rightleftharpoons H_2SO_4-$

Iron sulfide $\qquad FeS_2 + 3.75\ O_2 + 2.5\ H_2O \rightleftharpoons FeOOH + 2\ H_2SO_4$

Secondly, mangrove roots uptake ammonium leading the release of H^+ ions. And thirdly, mangrove roots respire carbon dioxide, which also lowers soil pH (Andersen & Kristensen 1988; Kristensen et al. 1988).

Intense sulfate reduction has been attributed to high HCO_3 pore water in salt marshes and at least one mangrove forest (Giblin & Howarth 1984; Ovalle et al. 1990). Sulfate reduction generates two moles of bicarbonate for every mole of sulfate reduced:

Sulfate reduction $\qquad 2(CH_2O) + SO_4^{2-} \rightleftharpoons H_2S + 2HCO_3^-$
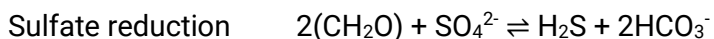
High HCO_3^- alkalinity in pore waters of a mangrove forest in Sepetiba Bay of southeast Brazil were attributed to intense sulfate reduction that produces ammonium (Ovalle et al. 1990).

Researchers examined a transect which included: upland mangroves that are rarely flooded, tidally flooded mangroves, and a mudflat. Pore water in the tidally flooded mangrove zone was enriched in both HCO_3^- and SRP compared to the upslope mangroves and the mudflat, and supplied SRP to the tidal creek at low tide. Although the researchers attribute the non-conservative SRP concentrations in the tidally flooded mangroves, it is plausible that P sorption dynamics play a role.

If exceptionally low P sorption efficiency driven by high HCO_3^--brackish water are demonstrated to be a general process for estuary sediments, the dynamics may have implications for coastal SRP availability globally. As we have outlined, there appear to be complex feedbacks between abiotic P sorption reactions and biological factors such as productivity, microbially mediated oxidation/reduction reactions, and also a suite of mangrove activities that affect the chemistry in their root zone including release of both oxygen and carbon dioxide and uptake of both ammonium and SRP. Further studies are needed to evaluate the prevalence and distribution of HCO_3^--enriched pore waters and elucidate their relationship to P sorption dynamics with the associated sediment. It would be helpful to better understand the range of conditions that are associated with this dynamic in terms of productivity, vegetation type, sediment type and texture, redox state, and tidal range and elevation. Tidal saline wetlands are found on sheltered marine coastlines, with salt marshes extending from the arctic to sub-tropical latitudes, and mangrove dominating in the sub-tropics and tropics (Mitsch & Gosselink 2000). The exceptional rates productivity by these two wetland-types rival that of productive agricultural lands (Odum & Smalley 1959). Surface water may also be affected in some regions; river HCO_3^- alkalinity in carbonate regions is higher than in any other lithology (Amiotte Suchet et al. 2003), and suspended sediment could potentially reverse P sorption behavior upon encountering coastal seawater (Millero et al. 2001b).

In our study site, and perhaps other coastal estuaries with high HCO_3^- regions as well, an influx of either fresh or marine water might cause sediments to adsorb SRP, lowering ambient water

SRP concentration. 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 both alkalinity HCO_3^- and SRP concentration. The mangrove site for this study was a freshwater marsh in 1950, before mangroves encroached 1.5 km inland from Florida Bay (Ross et al. 2000). Sea level rise is expected to exacerbate saltwater intrusion in many areas (Barlow & Reichard 2010). Long-term changes in freshwater flow could potentially cause a mangrove zone to retreat seaward, shifting P sorption dynamics as it goes. 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 seal level rise.

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 results of this study suggest that the carbonate sediment in high HCO_3^- water would have severely limited ability to remove excess SRP from the water.

The only water composition gradient (see Table 1) that can explain the exceptionally low sorption efficiency of ecotone GW is its high HCO_3^- alkalinity, which may lead to competition at adsorption sites between SRP and HCO_3^-. Sulfate ions can also compete with SRP for adsorption sites (Sigg & Stumm 1981), however if P sorption behavior were controlled more by gradients of SO_4^{2-} than HCO3-, one might predict lower sorption efficiency in bay SW compared to ecotone GW, given that bay SW has double the SO_4^{2-} concentration. The high Ca^{2+} and Mg^{2+} concentration in saltwater may provide bridges for surface complexation reactions with SRP(Spiteri et al. 2008), which would favor greater adsorption in bay SW. Differences in pH can

also be important, especially at the high and low end of the scale (Zhou et al. 2005), and goethite shows a decreasing trend of P adsorption as pH increases from 6 to 9 (Hawke et al. 1989). The trend in pH of our waters is ecotone GW (6.7) < fresh GW (7.3) < bay SW (8.2), which may cause iron (hydr)oxide sites on our sediment to adsorb more strongly in ecotone GW. Planned geochemical modeling using the empirically derived parameters from this study may help elucidate the geochemical mechanisms for the observed P sorption behavior.

Phosphorus sorption behavior can be influenced by factors held constant in our experiments, such as changing temperature or redox condition. Increased temperature has been found to increase adsorption in Florida Bay sediments (Zhang & Huang 2011). In the Indian River Lagoon, Florida, SRP was found to adsorb more efficiently in oxic vs. anoxic conditions, P binding to iron oxide in oxidizing conditions, and desorbing when the iron is reduced (Pant & Reddy 2001). The iron content of the ecotone sediments (Chambers & Pederson 2006) is similar to the Indian River Lagoon sediments (Pant & Reddy 2001), so the potential importance of redox condition in the topmost layer of Taylor Slough ecotone sediment cannot be dismissed. Under reducing conditions it can be expected that the sediment of the present study would have diminished adsorption efficiency in all three endmember water types. Future work examining temperature and redox effects would be useful in understanding P sorption behavior in the Taylor Slough ecotone.

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. The potential exists for the present study on a carbonate-based mangrove system to have implications for a broad range of settings where high HCO_3^- brackish water exists, including non-carbonate sediment, salt marshes, and 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 linear and two-surface Langmuir P sorption parameters. This study found 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 endmember waters 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 supported 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.

Table 1. Selected characteristics of the three field waters.

Field Water	pH	Salinity psu	Ca^{2+} mM	Mg^{2+} mM	Na^+ mM	K^+ mM	Cl^- mM	SO_4^{2-} mM	HCO_3^- mM	SRP µM	Si^{4+} µM
Fresh GW	7.3	0.1	1.8	0.1	0.7	0.01	0.8	*	4.0	0.050	80.4
Ecotone GW	6.7	16.0	6.7	29.6	217.9	4.16	264.1	11.2	17.5	0.177	83.6
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 µmole g^{-1}.

$MgCl_2$ inorganic SRP (P_{exch})	0.022 ± 0.002
$MgCl_2$ organic SRP	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] µmole g^{-1}	NAP [c] µmole g^{-1}	EPC_o [d] µM	P_{max1} [e] µmole g^{-1}	$K_{eq\,1}$ [f] µM	P_{max1} [g] µmole g^{-1}	$K_{eq\,2}$ [h] µM
Fresh GW	11	0.0034 ± 0.0002	0.85	0.075	1.1	3.5	4.7	0.04
	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] Adorption maximum for second surface
[h] Adsorption energy for second surface

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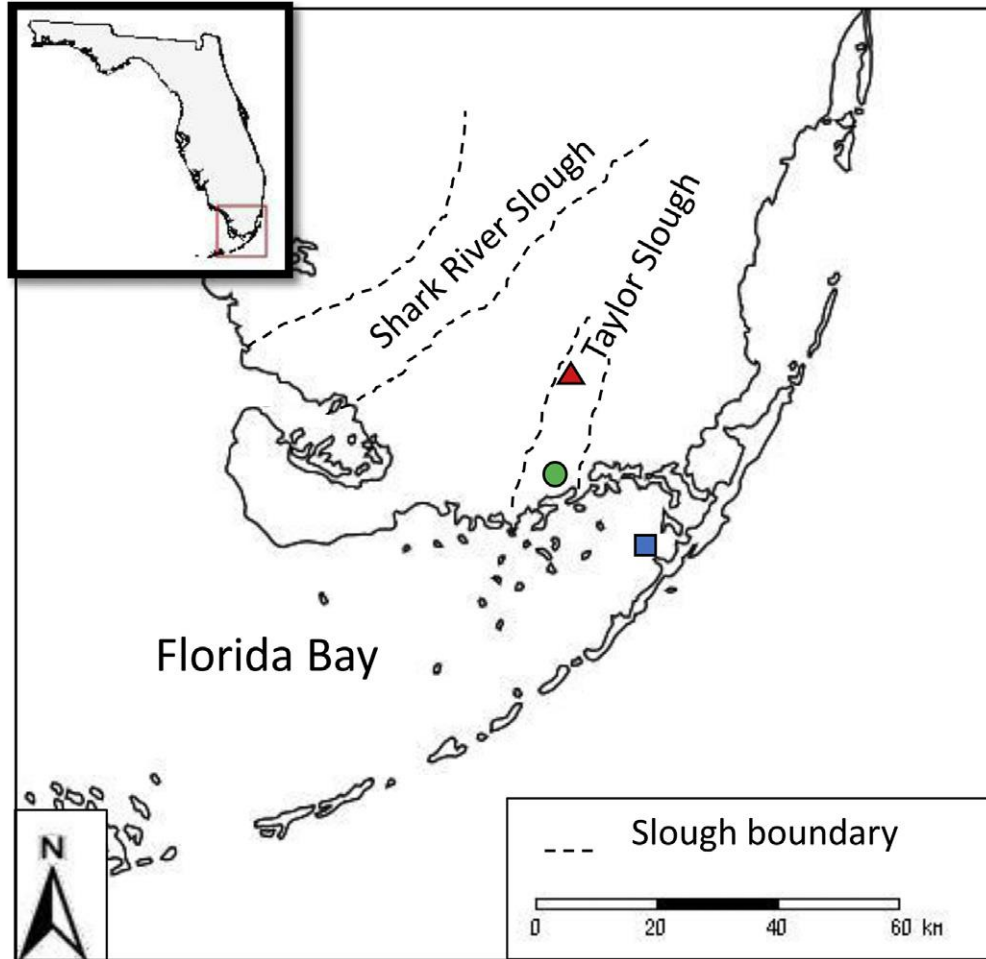
Fig. 1. Collection locations for samples: fresh GW (triangle); ecotone GW and sediment (circle); and bay SW (square).
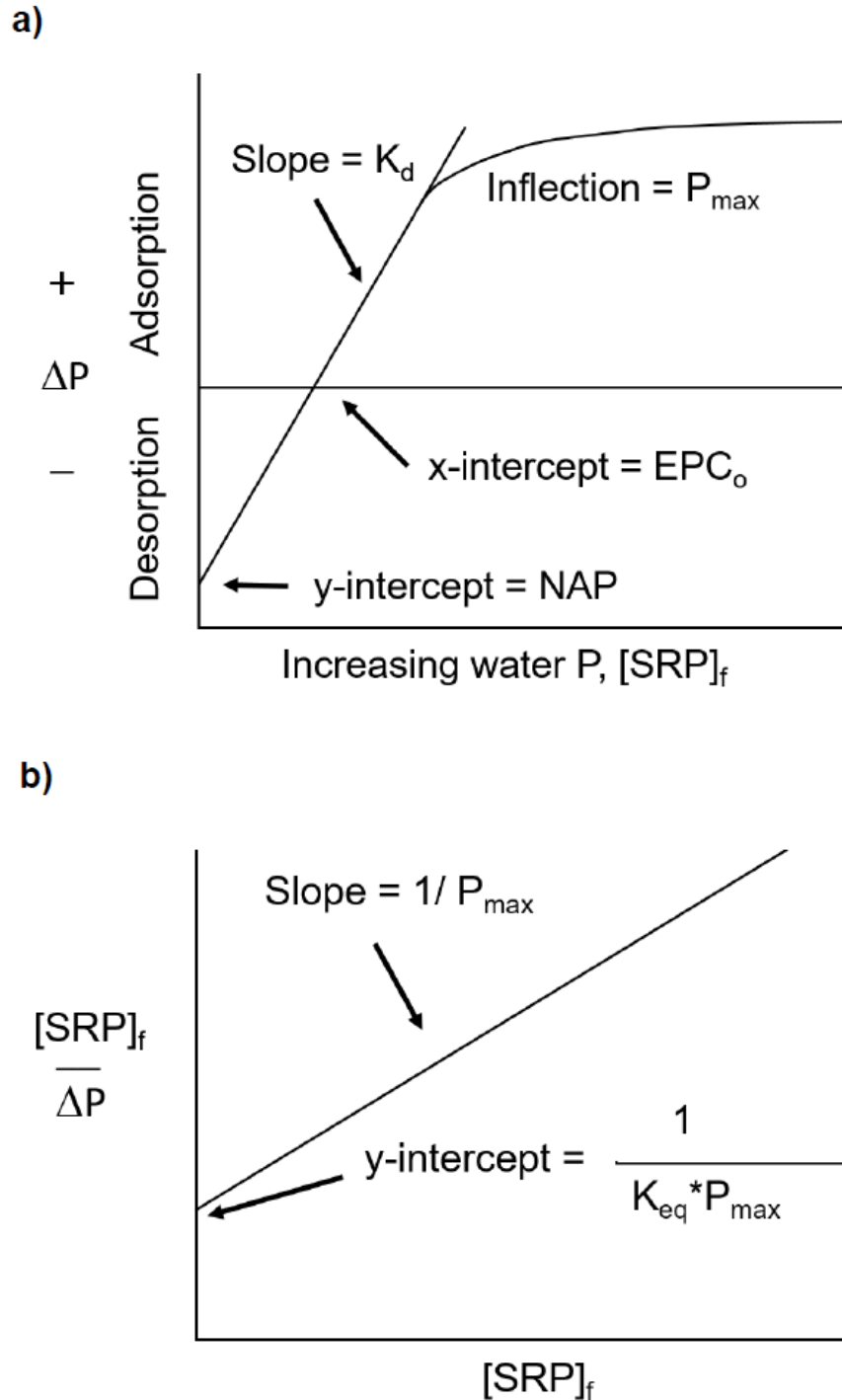
Fig. 2. (a) Schematic of P sorption isotherm. Kd= adsorption coefficient (slope); EPCo= zero equilibrium SRP concentration (x-intercept) where adsorption = desorption; NAP = native adsorbed P (y-intercept); Pmax = maximum monolayer sorption capacity, and is the point on the y-axis where the sorption curve inflects towards lower angle sorption; (b) Schematic of reciprocal Langmuir Isotherm plot; Pmax = the inverse of the slope, and Keq = the inverse product of the y-intercept and Pmax
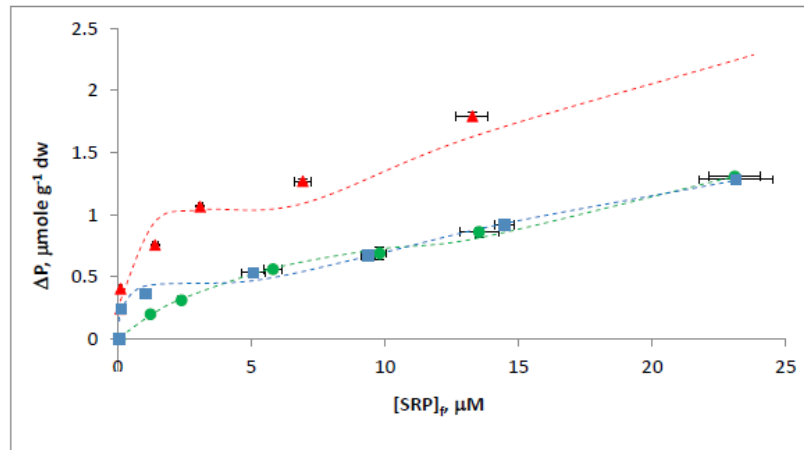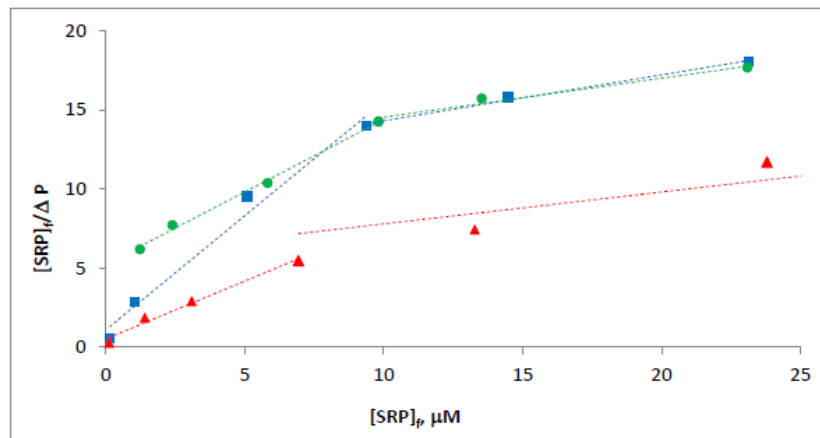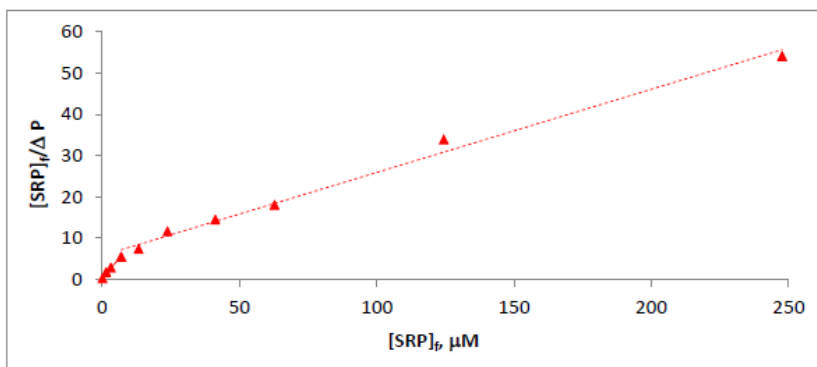
Fig. 3. Fresh GW (triangles), ecotone GW (circles), and bay SW (squares), accompanied by dashes representing the Langmuir Two-Surface Sorption isotherms: a) In standard plot; b) in reciprocal plot from which Langmuir two surface isotherm parameters were determined; and c) the extended two-surface isotherm for fresh GW.