

Saltwater intrusion as potential driver of phosphorus release from limestone bedrock in a coastal aquifer

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Abstract

An important but often overlooked consequence of saltwater intrusion is the potential increase of groundwater soluble reactive phosphorus concentrations. The phosphorus sorption dynamics of two limestone rocks of different composition were investigated by simulating seawater intrusion over a wide range of mixing ratios between freshwater and saltwater. Both rocks exhibited a logarithmic loss of sorption efficiency in mixtures containing more than approximately 3 mM Cl^- concentration (100 mg Cl^-/L ; about 0.5% saltwater). We infer that aquifer solids immersed in freshwater would undergo phosphorus desorption in response to the introduction of this minor amount of seawater. This Cl^- concentration is within the range designated as fresh water. Thus we conclude that increased soluble reactive phosphorus availability from saltwater-induced desorption may occur at the ion exchange front, which is actually landward of the saltwater intrusion front as it is commonly defined. Sorption efficiency in our experiments continued to decline as salinity increased, until Cl^- concentration reached a second threshold of 50 or 200 mM (1,700 or 7,700 mg Cl^-/L), depending on the rock composition, particularly iron content. Further increase in salinity would produce little increase in groundwater soluble reactive phosphorus concentration. Our results have implications for soluble reactive phosphorus availability in estuaries that receive mixing zone groundwater discharge.

Key words: Phosphate, mixing zone, groundwater, desorption, carbonate, Everglades

Introduction

Geochemical studies of coastal aquifers worldwide have established that intensive water-rock interactions are a globally important consequence of saltwater intrusion (Sivan et al., 2005). Where fresh water and saltwater meet in the aquifer, saltwater typically forms a wedge beneath the more buoyant fresh water, with a flat base at an impermeable layer. Due to the hydraulic gradient between the freshwater and marine waters, fresh and brackish water from the aquifer mix and flow seaward and upward along the saltwater wedge to discharge near the coastline in a process known as submarine groundwater discharge (Moore, 1999). In this way, the products of mixing zone reactions affect water quality in coastal estuaries.

Phosphorus (P) commonly adsorbs to the surfaces of suspended riverine particles, soils, sediments and aquifer solids. An influx of saltwater can induce mineral solids to desorb P, raising the ambient water P concentration. These reactions are important because the species of P that participates in adsorption/desorption reactions is the bioavailable form, dissolved inorganic P (H_2PO_4^- and HPO_4^{2-} , measured as soluble reactive P, SRP). As a result of these reactions, saltwater intrusion causes coastal groundwater to be many orders of magnitude higher in SRP than the overlying surface waters in many regions (Valiela et al., 1990; Slomp and Van Cappellen, 2004). Phosphorus desorption reactions that occur at depth in the aquifer are considered to be one of the major abiotic controls of coastal water SRP concentration where P-enriched brackish groundwater discharges to overlying ecosystems (Froelich, 1988). In some estuary P-budgets, groundwater discharge exceeds the input from rivers and atmospheric deposition (Slomp and Van Cappellen, 2004). Phosphorus-enriched brackish groundwater increases the productivity of many P-limited coastal ecosystems such as seagrass beds near Perth, Australia (Johannes and Hearn, 1985), many coral reefs worldwide (Paytan et al., 2006),

salt marshes in North Carolina, USA (Krest et al., 2000), and the mangrove swamps of the Everglades, in Florida, USA (Price et al., 2006).

In many coastal aquifers, the transition from freshwater to saltwater is gradational, with mixing zones from meters to kilometers wide (Slomp and Van Cappellen, 2004). Increments of increasing salinity within the transition zone are commonly represented by sets of contours delineating equal Cl^- concentration (isochlors) (Figure 1). The locations and possible movements of these isochlors are determined by salinity measurements of groundwater in monitoring wells and remote methods such as geophysical mapping (Dimova et al., 2012; Prinos et al., 2014; Spiteri et al., 2008a; Swarzenski et al., 2006). In regions with a broad mixing zone, incremental increases in salinity may be accompanied by incremental or abrupt changes in a variety of chemical constituents resulting from non-conservative mixing and chemical reactions triggered by various proportions of freshwater and seawater at the solid-solution interface. The best known example of this is the ion exchange front, located where freshwater first contacts saltwater; here the major changes in concentration of Ca^{2+} , Na^+ , HCO_3^- , Li^+ , K^+ , B^{3+} , SO_4^{2-} and Mg^{2+} occur due to ion exchange (Prinos et al., 2014). The reason that low salinity groundwater mixtures can have such a large effect is the high ionic strength of seawater compared to the density of limited exchange sites on solid surfaces. Once exchange sites on the mineral surfaces are filled by competing ions, further increase in saltwater content may have little effect.

Inorganic P ions are highly surface-reactive, and SRP is known to change concentration in freshwater-saltwater mixing zones. We hypothesize that, like other highly reactive ions, SRP is actively cycled in the ion exchange front within the aquifer, and thus P desorption is triggered at a very low threshold of saltwater content. We chose to test our hypothesis on limestone because carbonate aquifers are extensive in coastal settings, and many have undergone saltwater

intrusion. Examples include Florida, USA (Fitterman, 2014), Mallorca, Spain (Price and Herman, 1991), and Apulia, Italy (Cotecchia et al., 1974). With many carbonate coastlines under threat of increased saltwater intrusion due to sea level rise (Barlow and Reichard, 2010; Carter et al., 2014; Loáiciga et al., 2012; Webb and Howard, 2011; Wong et al., 2014), and many coastal estuaries subject to mixing zone groundwater discharge, it is important to predict how SRP concentrations change as a function of incremental increases in saltwater content. The southern coastal Everglades was chosen as a field location because it has a carbonate aquifer, significant saltwater intrusion, the potential for rapid movement of the freshwater-saltwater interface, a highly gradational transition zone, and SRP-enriched brackish groundwater discharging to a P-limited estuary (Price et al., 2006).

To date, most studies of seawater-induced P desorption focus on soil, sediment (e.g., suspended river sediment and bottom sediment of lakes, rivers and lagoons), or pure phase minerals (e.g., calcite or goethite) (Clavero et al., 1990; Gao and Mucci, 2001; Gardolinski et al., 2004). In many studies, NaCl or KCl solutions substitute for seawater (Wang et al., 2006), which excludes reactive seawater ions such as Mg^{2+} , Ca^{2+} , SO_4^{2-} , and HCO_3^- (Millero et al., 2001).

Freshwater-seawater mixing is commonly simulated with no more than 4 mixtures (Gao and Mucci, 2003). The few that have considered a wider range of salinity report that sorption behavior changed at the low salinity end of the continuum. Fox et al. (1986) immersed sediments from the Amazon estuary in seawater diluted with deionized water, and observed that the sediments began to desorb P at salinities above 4. A laboratory study of calcite and aragonite in seawater diluted with 2mM $NaHCO_3$ solution found that the crystal grains gained the most adsorption efficiency (29%) when the salinity was lowered from 5 to 0 (Millero et al., 2001). A sorption study using Florida Bay sediment and seawater diluted with 2 mM $NaHCO_3$ solution

reported that adsorption decreased with increasing salinity, and the effect was much greater for sediment samples with a higher amount of loosely adsorbed P (Zhang and Huang, 2011).

Suzumura et al. (2000) investigated sand from a coastal aquifer, at Tokyo Bay, Japan; among eight evenly proportioned mixtures of deionized water and artificial seawater, the largest change in P sorption behavior of the sand was observed between the lowest two salinity solutions. An important limitation of these previous studies is that mixtures were created by diluting seawater with deionized water or 2mM NaHCO₃ solution, resulting in mixtures that are not equivalent to mixing seawater with a naturally occurring freshwater, wherein non-conservative mixing reactions may occur due to the reactive ions in the freshwater.

There is no systematic study of the influence of salinity of seawater on P sorption by bedrock, but our recent work in the Everglades has highlighted the importance of seawater-induced desorption of P in groundwater. Price et al. (2010) conducted a flow chamber experiment with a large block of Key Largo limestone from the Florida Keys. After first loading the rock with P-enriched water, the researchers measured significant increases in leachate SRP concentration when the chamber inflow solution was changed to seawater. Although studies of rock pre-loaded with P can provide indications of how a system may behave where the aquifer itself has a high degree of adsorbed P (for instance where sewage has been injected into wells (Cable et al., 2002; Corbett et al., 2000; Parkhurst et al., 2003)), such studies cannot be related directly to carbonate aquifers with low P content, because the amount of loosely adsorbed P on the solids strongly influences P sorption behavior (Wang and Li, 2010; Zhang and Huang, 2007; Zhou and Li, 2001).

In order to understand how carbonate systems with low P content behave with respect to P sorption it is necessary to use unadulterated solids. Accordingly, we recently conducted a

column study using crushed limestone with low P content immersed in natural fresh groundwater (Flower, in review). The initial influx of seawater caused a rapid and intense release of SRP. Indeed, the first 1 mL sample of leachate that exhibited a detectable increase in salinity also exhibited an increase in SRP concentration, lending further credence to the possibility that SRP increase may accompany the leading edge of saltwater intrusion into carbonate aquifers with low P content.

The question remains as to the threshold of salinity that triggers desorption, and the pattern with which sorption efficiency changes with incremental increases in saltwater content. Such information would permit connections to be drawn between changes in desorption-enhanced SRP concentration and specific isochlors along the freshwater-saltwater mixing zone. Being able to identify the isochlor associated with the initiation of P desorption would allow saltwater intrusion monitoring efforts to take nutrient changes into account when considering the ramifications of a movement landward or seaward of a given isochlor. Further, whether desorption changes in a linear or non-linear fashion with incremental increases in saltwater content will, in turn, affect how SRP availability varies with salinity in the overlying estuary receiving the subsequent groundwater discharge (Figure 2).

The objective of this study is to quantify, at high salinity resolution, how P sorption behavior of pristine (no added P) carbonate solids may be affected by ambient waters that gradationally change in the relative proportion of fresh groundwater and saltwater. Two limestones of different chemical composition were used in order to provide indications as to how different geographic regions may respond differently to the same increment of saltwater intrusion. Fresh groundwater samples from the Everglades and seawater from Florida Bay were used to better simulate the complex reactions that occur when natural waters mix. In order to

examine the effects of saltwater intrusion on P sorption efficiency of carbonate solids, it is necessary to quantify the change in P sorption efficiency at equilibrium with different ambient waters. An equilibrium SRP concentration, obtained in ambient water containing carbonate solids, reflects the net P-sorption effect of all surface reactive species in the ambient water.

The purpose of this work is to enable water managers and those engaged in restoration efforts in carbonate coastal regions to tie isochlors from saltwater intrusion monitoring efforts to the likelihood of desorption-enhanced water SRP concentrations (Price et al., 2006; Prinos et al., 2014). The Everglades is the focus of an \$8 billion restoration effort intensely concerned with both sea level rise (including saltwater intrusion) and water SRP concentrations (Team, 2014). Salinity is thought to come from the south with sea level rise, and excess SRP to flow from the canals north of the Everglades National Park, and this water quality paradigm drives projections of sea level rise effects on future coastal foundational communities, wildlife and vegetation communities, and soil accretion (Aumen et al., 2015; Catano et al., 2015; Koch et al., 2015; Nungesser et al., 2015; van der Valk et al., 2015). The potential for saltwater intrusion from sea level rise to bring with it a P subsidy from water-rock interactions may indicate an unanticipated linkage between these dual concerns. Increased SRP accompanying brackish groundwater discharge could substantially bolster the chances that mangrove soil accretion could keep up with sea level rise, delaying or preventing the drowning of mangroves and encroachment of saltwater into freshwater marshes.

Methods

Study Area

The southern Everglades has a flat coastline with surface water flowing southward through two main pathways (Figure 3). The larger drainage basin, Shark River Slough, flows to

the southwest and drains to the Gulf of Mexico. The smaller drainage to the east is Taylor Slough, where surface water flows south into Florida Bay. This flow-way is largely disconnected from tidal influence due to an embankment running along the coastline.

The southern Everglades is underlain by an unconfined karstic limestone aquifer known as the Biscayne Aquifer (Fish and Stewart, 1991). This limestone and sand aquifer is thickest (> 35 m) along the eastern coastline in Miami- Dade County, thinning westward in a wedge shape (Klein and Hull, 1978). Fish and Stewart (1991) define the Biscayne Aquifer as having hydraulic conductivities commonly exceeding 3 km per day. Water levels respond rapidly when the groundwater system is stressed by such factors as drainage and recharge from canals, recharge from rainfall, evapotranspiration, and abstraction from supply wells. The Biscayne Aquifer saltwater interface is highly mobile, and has been found to move seaward in response to an intense storm or prolonged rainfall in a wet season (Kohout, 1964).

Saltwater has intruded into approximately 1,200 km² of the Biscayne Aquifer (Prinos et al., 2014). In the Everglades the saltwater intrusion zone extends 6-28 km inland (Price et al., 2006). In Taylor Slough the freshwater-saltwater interface is sharp and parallel to a historical road which is no longer used (the Old Ingraham Highway), because a borrow canal created for the construction of this road was open to the sea and brought saltwater inland (Fitterman and Deszcz-Pan, 1998). In Shark River Slough the transition is highly gradational due to tidally connected river channels (Price et al., 2006).

The inland extent of the Everglades mangrove forest coincides with the saltwater intrusion front (Saha et al., 2011). Mangroves encroached 1.5 km inland from Florida Bay after 1950 (Ross et al., 2000). Measurements of total dissolved P (i.e., SRP plus dissolved organic P) in the brackish groundwater of the mangrove zone ranged from 0.1 to 2.3 μM, and were typically

higher than the freshwater and seawater both at the surface and within the aquifer (Price et al., 2006). Price et al. (2006) emphasized that an additional P source is needed, since elevated total dissolved P in brackish groundwater cannot be explained from conservative mixing between the freshwater and saltwater with lower P concentration. Based on the further observation that groundwater total dissolved P exhibited a direct relationship with salinity (albeit with considerable variability; $R^2 = 0.67$) they suggested that water-rock interactions, such as dissolution of the aquifer matrix or ion exchange, could provide the additional source of dissolved P. Zapata-Rios and Price (2012) followed up on this work by quantifying several hydrodynamic and geochemical indicators of spatially and temporally variable brackish groundwater discharge in the mangrove swamp of Taylor Slough. The generation of a groundwater source of P is particularly important to understand given that the Everglades is so P-limited that it has been described as “P-starved” (Noe et al., 2001; Rivera-Monroy et al., 2011). As such, slight additions of SRP are immediately uptaken by plants and periphyton. In the freshwater marsh, sustained low-level SRP subsidy (as little as 0.2 μM over five years) doubled plant biomass and eliminated native calcareous periphyton mats (Gaiser et al., 2005).

Water Samples

Fresh groundwater (hereafter referred to as “freshwater”) was collected from a shallow monitoring well (TSB-15) within the bedrock underlying the freshwater marsh (sampling locations provided in Figure 3) (Price, 2001). Our representative saltwater sample (“saltwater”) is from Florida Bay surface water taken from a dock in Key Largo. We chose Florida Bay saltwater rather than the Gulf of Mexico because a significant portion of saltwater intrusion in the area is from the south. Sulfate concentration was 28.4 ± 0.01 mM in our saltwater, and below detection limit in our freshwater. Total alkalinity was 4.0 ± 0.02 and 2.9 ± 0.02 mM for our

saltwater and freshwater respectively. The SRP concentration was 0.05 ± 0.02 and 0.08 ± 0.01 μM for our saltwater and freshwater respectively. Procedures for determining water properties and more complete results are described elsewhere (Flower et al., 2016). All SRP concentrations were determined by the microscale malachite green method (D'Angelo et al., 2001), measuring absorbance at 630 nanometers (nm) in 96-well microplates on a BioTek EPOCH microplate spectrophotometer. For experiments, all SRP concentrations were measured the day of the experiment.

Rock Samples

The limestone samples used for this study were well cores derived from the drilling of monitoring wells known as Canepatch and RB (Price et al., 2006), which are in Shark River Slough close to the western edge of the Biscayne Aquifer as delineated by Klein and Hull (Figure 3) (Klein and Hull, 1978). The two wells lie on opposite sides of the freshwater-saltwater interface as it was determined by resistivity measurements by Fitterman and Deszcz-Pan (1998), with RB on the landward side and Canepatch on the seaward side. The interface was considered to be unmoved in a 2014 study (Prinos et al., 2014). Water quality measurements at Canepatch and RB wells conducted between 1997-1999 indicated that surface water ranged from fresh to brackish, with Cl^- concentration varying from 0.4-173 mM (Price, 2001). In contrast the groundwater at both field sites was brackish during this period: groundwater in the RB well (screened at of 6.7 m depth) was found to range from 52-101 mM Cl^- concentration, 1.6-4.9 mM SO_4^{2-} concentration, and 6.01-8.06 in pH (Price, 2001); in 2003 total dissolved P was measured at 0.37 μM (Price et al., 2006). Groundwater in the Canepatch well (screened at 15.5 m depth) was found in the years 1997-1999 to have a range of 222-251 mM Cl^- , 9.9-11.6 mM SO_4^{2-} , and

6.75-8.06 in pH (Price, 2001); and in 2003 total dissolved P was reported as 1.9 μM (Price et al., 2006).

For our experiments, the top 30 cm of the two limestone bedrock well cores were crushed and passed through a brass sieve ($<125 \mu\text{m}$). We measured four aspects of the rocks' chemical composition that may affect P sorption behavior: total sedimentary P, carbonate-bound Fe, and both inorganic and organic $\text{MgCl}_2\text{-P}$. Inorganic $\text{MgCl}_2\text{-P}$, also known as loosely adsorbed or readily exchangeable P (P_{exch}) (Zhang et al., 2004), is defined as the inorganic P released from rock powder by 1 M MgCl_2 solution at pH 8.0, following the protocol established by Ruttenberg (1992). Organic $\text{MgCl}_2\text{-P}$ was determined using the protocol of Zhang et al. (2010), with the exception that total dissolved P was measured using the sub-boiling temperature method of Huang and Zhang (2009).

Total sedimentary P was determined by high temperature combustion (Zhang et al., 2004). The sediment samples were placed in 100-mL Pyrex beakers and wetted with a few drops of 1 M $\text{Mg}(\text{NO}_3)_2$ solution and then ashed in a combustion furnace at 550°C for 2 hours. After the samples were cooled to room temperature, 50 mL of a 1 M HCl solution was added to each sample. The samples were then agitated at 25°C for 24 hours to extract P. Samples were filtered to remove any particulate residuals and the filtrates analyzed for dissolved phosphate. The carbonate-bound Fe in rock powders was determined by dissolution of solid phase Fe in 1 N HCl solution. The total dissolved iron ($\text{Fe}^{3+} + \text{Fe}^{2+}$) in the solution was reduced with ascorbic acid to Fe^{2+} . The Fe^{2+} was then spectrophotometrically determined with a ferrozine reagent in a pH 5.5 buffer solution at a maximum absorption wavelength of 562 nm (Zhang et al., 2001).

In addition to rock composition, the density of surface reactive sites has a great effect on P sorption behavior. Both rock powders underwent single-point Brunauer, Emmett, and Teller

Model (BET) specific surface area analysis (nitrogen gas physisorption) using a Micromeritics Tristar II instrument.

Mixing Continuum Sorption Experiments

The relative magnitude of P adsorbed by the rock powders was investigated in solutions ranging from freshwater (0.8 mM Cl^- concentration) to saltwater (512 mM Cl^- concentration). We designate our freshwater-saltwater mixtures by the Cl^- concentration added by the saltwater, so that our results could readily be applied to isochlors in saltwater monitoring studies; Cl^- concentration is used as a conservative tracer of saltwater content. In order to choose mixing proportions to focus on for our study, we first conducted a preliminary study with fourteen mixing ratios between pure freshwater and pure saltwater (results not shown). We observed the most significant decrease in P adsorption between freshwater and the mixture with the least saltwater (26 mM added Cl^- concentration, or 5% saltwater), and we observed no change after 256 mM added Cl^- concentration from saltwater (50% saltwater). Based on these observations, the decision was made to examine the very low (0-26 mM Cl^- concentration) interval at high resolution, and not to include a mixture between pure saltwater and the mixture with 256 mM added Cl^- concentration. Accordingly, the two water types were mixed in 14 proportions with saltwater content increasing from pure fresh water along a log-scale of added Cl^- concentration from saltwater (i.e., pure freshwater; pure saltwater; and mixtures with 0.03, 0.04, 0.08, 0.15, 0.36, 0.85, 2, 5, 11, 26, 51, 256 mM added Cl^- concentration from saltwater).

A stock P solution (made from reagent grade KH_2PO_4) was added to give both the freshwater and saltwater solutions an 8.0 μM initial SRP concentration ($[\text{SRP}]_i$). In each test tube a sample of 100 mg of Canepatch or RB rock powder was mixed with 30 mL of either pure freshwater, full strength saltwater, or one of the mixed solutions. To inhibit microbial activity

which could affect SRP concentration, 20 μ L of chloroform solution was added to each test tube (Zhou et al., 2005). The test tubes were incubated for 24 hours on a platform shaker at 200 rotations per minute (rpm) at room temperature ($23 \pm 0.5^\circ\text{C}$). The slurry from each test tube was filtered with 0.45 μm nylon syringe filters and analyzed for final SRP concentration ($[\text{SRP}]_f$), using the colorimetric method described previously. The percent P adsorbed by the rock powder in a given mixture was calculated as:

$$\% \text{Adsorbed P} = \frac{[\text{SRP}]_i - [\text{SRP}]_f}{[\text{SRP}]_i} \times 100 \quad (1)$$

To explain our calculations for the threshold of saltwater content at which P sorption efficiency of limestone rocks begins to decline, and the second threshold at which it ceases to decline, it is helpful to invoke a horizontal line being intersected by a curve of known equation. If the data initially exhibit a plateau of similar sorption at the freshwater end of the mixing continuum, this sub-group of data can be assigned a mean value and a standard deviation. In turn this can be expressed using the equation for a horizontal line ($y =$ the mean of the % Adsorption values of the sub-group of data). The uncertainty around that value can be expressed as the mean value plus or minus one standard deviation (i.e., within 95% certainty the upper y value = (mean y) + (1 standard deviation), and the lower y value = (mean y) – (1 standard deviation). Where the data ceases to scatter about the horizontal line and begins instead to decrease according to an equation that can be calculated (and evaluated using R^2), the x -value for this intersection can be calculated using the equations of the curves. Specifically, the three y -values (mean, upper, lower) can be plugged into the equation of the intersecting curve, allowing one to solve for the x -value (with a lower and upper range within 95% certainty).

Sorption Isotherm Experiments

To glean further details as to the differences in sorption behavior by rock sample and by water type, we undertook sorption isotherm batch experiments. Based on the batch incubation method of Froelich (1988), P-sorption parameters were determined for the two rock powders (RB and Canepatch) in three water types: freshwater, saltwater, and a mixture of freshwater with 10% saltwater (51 mM Cl^- concentration added by saltwater). Into each test tube was placed 100 mg of one of the two rock types, 30 mL of one of the three water types, 20 μL chloroform, and a measure of SRP stock solution to yield one of 11 different $[\text{SRP}]_i$ between 0.6 and 8.1 μM . After incubation at 200 rpm for 24 hours, filtrate was analyzed for $[\text{SRP}]_f$, as described previously.

Sorption Isotherm Parameters

Data from sorption isotherm experiments can be fit to isotherm models that help quantify disparate aspects of P sorption behavior for a given rock-water combination, including buffer intensity, binding energy, adsorption capacity, and P exchange site density. The relationship between experimental data and isotherm models can be visualized using a plot of the amount of P adsorbed to the solids (ΔP) compared to the final P concentration in the solutions $[\text{SRP}]_f$. The final SRP concentration in the test tubes differs between water-rock combinations, and is thus more informative than the initial SRP concentration, since that is the same for all. The amount of SRP adsorbed to the mineral solids, ΔP ($\mu\text{mol g}^{-1}$), was calculated as:

$$\Delta\text{P} = ([\text{SRP}]_i - [\text{SRP}]_f) \times \frac{0.03 \text{ L solution}}{0.1 \text{ g rock powder}} \quad (2)$$

A modified Freundlich equation was used to parameterize the adsorption isotherm data:

$$\Delta P + \text{NAP} = K_f [\text{SRP}]_f^n, \quad (3)$$

where NAP ($\mu\text{mol g}^{-1}$) is the native adsorbed inorganic P, n is the exponent factor, and K_f is the Freundlich coefficient with units $(\text{L g}^{-1})^{1/n}$, which indicates the relative adsorption capacity of the mineral surface. The value of $[\text{SRP}]_f$ at $\Delta P = 0$ is known as the zero equilibrium concentration, EPC_0 , the SRP concentration at which there is no net change in adsorbed P. The distribution coefficient, K_d (L g^{-1}) is a measure of the buffer intensity and can be calculated from the Freundlich equation (Zhang and Huang, 2011) by taking the derivative of equation (3) with respect to the EPC_0 :

$$K_d = n K_f [\text{EPC}_0]^{n-1}. \quad (4)$$

At higher concentrations of SRP_i, isotherm curves may begin to flatten, indicating the onset of saturation of monolayer sorption sites on the mineral surface. The Langmuir sorption model provides an indication of the point at which the system reaches saturation, the maximum monolayer sorption capacity, P_{max} . Such behavior can be modeled as:

$$\Delta P = \frac{K_{\text{eq}} P_{\text{max}} [\text{SRP}]_f}{1 + K_{\text{eq}} [\text{SRP}]_f} - \text{NAP}. \quad (5)$$

The Langmuir constant K_{eq} (μM^{-1}) is related to the heat of adsorption and the affinity of the adsorption sites. When sorption data are evaluated by using the reciprocal plot of the Langmuir adsorption equation:

$$\frac{[\text{SRP}]_f}{\Delta P} = \frac{[\text{SRP}]_f}{P_{\text{max}}} + \frac{1}{K_{\text{eq}} P_{\text{max}}}, \quad (6)$$

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 of the reciprocal Langmuir plot. We fit these curves to data from our sorption isotherm experiments and estimated parameters K_f , K_d , K_{eq} , and P_{\max} so as to learn in more detail about how the rocks' P sorption behavior differs from each other (Canepatch vs. RB) and based on water type (freshwater, full strength saltwater, or a mixture with 10% saltwater).

Results and Discussion

Small additions of saltwater made a large difference in how our limestone bedrock samples adsorbed SRP. The pattern of P sorption change occurred at the extremely low salinity end of the mixing continuum and the response was non-linear with respect to added saltwater (Figure 4a). Our results support the hypothesis that loosely adsorbed SRP is released at the ion exchange front within carbonate aquifer mixing zones, and responds in a non-linear fashion to added saltwater (i.e., Figure 4a resembles curve C in Figure 2).

When the low salinity end of the mixing continuum is displayed on a log scale, a plateau of high freshwater P sorption efficiency becomes apparent for both rocks. The pure freshwater solution and the first seven mixtures for both rocks vary about a mean value of $77\% \pm 2\%$ for RB and $48\% \pm 4.0\%$ for Canepatch (uncertainties are reported as one standard deviation). Similarly, a second plateau exists at the high salinity end of the spectrum, representing a reduction in sorption efficiency of nearly half for both rocks, to $41\% \pm 1\%$ for RB, and $25\% \pm 1\%$ for Canepatch. The sub-group of data that connect the first plateau (the high P sorption sub-group) to the second plateau (low P sorption sub-group) fit a logarithmic equation well (R^2 of 0.9697 for RB rock and 0.9972 for Canepatch rock; Figure 4b).

Departure from the initial plateau of high P sorption efficiency was abrupt and occurred at extremely low amounts of added saltwater. The total Cl^- concentration at the low salinity threshold was 2.9 mM (103 mg Cl^-/L) for RB rock (with a 95% confidence interval ranging from 2.4-3.6 mM) and 3.4 mM (121 mg Cl^-/L) for Canepatch rock (95% confidence interval spanning 2.4-5.0 mM) (these values are the added Cl^- concentration from saltwater added to the initial freshwater Cl^- concentration of 0.8 mM). These threshold mixtures contain less than 1% added saltwater (0.57% and 0.67% saltwater for RB rock and Canepatch rock, respectively).

Accordingly, we infer that in a freshwater portion of the aquifer with similar rocks, desorption of P from mineral surfaces might be expected in response to an influx of <1% saltwater. This low salinity threshold implies that increased P desorption would be expected to occur landward of the apparent saltwater intrusion front. Water with a Cl^- concentration ≤ 7.1 mM (250 Cl^-/L) is considered fresh and meets secondary drinking water standards for chloride set by the U.S. Environmental Protection Agency (Agency, 2015). Although some monitoring efforts designate the saltwater intrusion front as salinity in excess of background concentration, generally considered to be 3 mM Cl^- concentration (100 mg Cl^-/L) (Sonenshein, 1996), more commonly fronts are designated by 28 mM Cl^- concentration (1000 mg Cl^-/L) (Barlow and Reichard, 2010) or higher (Fitterman, 2014; Langevin, 2001).

Knowing that the 3 mM Cl^- concentration isochlor may indicate increased P availability in the aquifer is particularly useful because the low-salinity edge of saltwater intrusion may move landward or seaward in the coming decades. One study predicted the 7.1 mM (250 mg Cl^-/L) isochlor would move inland in the Everglades by 40-1800 m by 2100 depending on the sea level rise rate (Langevin et al., 2005). Conversely, one of the goals of Everglades restoration is increased fresh water flow, in part to resist the landward encroachment of saltwater intrusion, and

ideally cause it to retreat seaward. Our results indicate that locating and monitoring very low salinity isochlors would provide useful indications of P availability in saltwater intrusion zones that discharge to an overlying ecosystem. A subsidy of P accompanying encroaching saltwater intrusion may help mitigate the effects of sea level rise by enhancing soil accretion in mangrove zones.

For RB the second threshold occurs at 316 mM Cl^- concentration (95% confidence interval 217-462 mM), which is a 62% saltwater mixture. For Canepatch rock, the second threshold mixture corresponded to 49 mM Cl^- concentration (95% confidence interval 45-54 mM), approximately 10% saltwater. From this we infer that within a carbonate aquifer mixing zone, little or no additional SRP release would be expected as salinity increases from these “second threshold” salinities.

The sorption isotherm curves (Figure 5) provide additional detail as to the non-linear loss in sorption efficiency with increasing saltwater content: the 10% saltwater isotherm is visibly closer to full strength saltwater despite its compositional proximity to pure freshwater. With the addition of 10% saltwater sorption efficiency (K_d) was halved for both rocks, and binding energy (K_{eq}) decreased by two thirds for RB, and a quarter for Canepatch (Table 1). The other parameters offer a more complex picture. It could be that saltwater requires a greater portion of chloroform to fully prevent microbial activity. For RB, the relative sorption capacity of the mineral surface (K_f) and native adsorbed P (NAP) are similar in freshwater and 10% saltwater, and much lower in saltwater, suggesting adsorption capacity may not respond to the same threshold as sorption efficiency. For Canepatch, both K_f and NAP are higher in 10% saltwater than freshwater. The saltwater sorption data yield a poor fit to the Langmuir isotherm model

($R^2 = 0.63$) for both RB and Canepatch rocks, and a poor fit to the Freundlich isotherm model for Canepatch ($R^2 = 0.69$).

The similarity of the two rock samples' response to saltwater is particularly striking given the large difference between the two rocks in magnitude and intensity of adsorption. In this way, our results hint that seawater-induced P desorption may function somewhat independently from compositional differences among limestone that affect the rocks' P sorption behavior in other ways. In our mixing continuum study, RB adsorbed approximately 50% more than Canepatch in all mixtures; its lowest percentage of adsorption was similar to highest adsorption for Canepatch (Figure 4b). The isotherm curves exhibit a similar contrast between the rock samples (Figure 5). The mineral surface of RB rock exhibited a freshwater adsorption capacity (K_f) seven times higher than Canepatch, and high salinity K_f was more than double in RB compared to Canepatch. The buffer intensity (K_d) was approximately four times higher in RB rock compared to Canepatch rock for all water types. Also in all water types, RB was higher than Canepatch in exchange site density (P_{max}) and affinity of binding sites for SRP (K_{eq}). The higher density of exchange sites in RB suggests that it would require more saltwater to cause the same reduction in P adsorption, which helps explain the higher second threshold of saltwater content for RB compared to Canepatch.

The greater exchange site density (P_{max}) in RB compared to Canepatch is consistent with specific surface area measurements of $2.43 \text{ m}^2 \text{ g}^{-1}$ for RB and $1.42 \text{ m}^2 \text{ g}^{-1}$ for Canepatch. Specific surface area is a measurement of adsorption site density. Both of our measured values are lower than the $5.84\text{-}6.99 \text{ m}^2 \text{ g}^{-1}$ specific surface areas measured for Florida Bay sediments that were high in Fe and low in P_{exch} . In addition to specific surface area, other limestone characteristics that may contribute to differential P sorption behavior include differences in iron and aluminum

oxides, P content (especially P_{exch}), permeability, and proportion of clay and detrital content. Iron oxide is known to have a high affinity for P; RB rock has more than twice the carbonate-bound iron content (36.33 vs. $14.09 \mu\text{mol g}^{-1}$ for RB and Canepatch respectively). These values coincide almost exactly with the range of carbonate-bound iron content measured in Taylor Slough and Shark River Slough sediments in a study by Chambers and Pederson (2006); in which the lowest value was $14 \mu\text{mol g}^{-1}$, from downstream estuary sediment from Taylor Slough, and the highest value was $36 \mu\text{mol g}^{-1}$, from freshwater marsh sediment from Taylor Slough.

We consider it unlikely that P content is responsible for the difference in P sorption behavior between our two rock samples, since their P_{exch} and total sedimentary P are similarly low. Rock RB has slightly lower total sedimentary P (1.2 ± 0.1 vs. $1.7 \pm 0.2 \mu\text{mol g}^{-1}$ for RB and Canepatch respectively). The average P content of continental rock is much higher (given as $21 \mu\text{mol P g}^{-1}$ by Rudnick and Gao (2003)) but our values are close to the lower end of Florida Bay carbonate sediments found in the eastern region of the bay (Zhang et al., 2004). The P_{exch} was 0.019 ± 0.003 and $0.011 \pm 0.001 \mu\text{mol g}^{-1}$ (for RB and Canepatch respectively) which is about 10% of total sedimentary P, a similar ratio to that exhibited by Florida Bay carbonate sediment. For organic MgCl_2 -P, RB has $0.031 \pm 0.004 \mu\text{mol g}^{-1}$ and Canepatch had $0.024 \pm 0.004 \mu\text{mol g}^{-1}$.

We infer that the relatively large differences in both specific surface area and carbonate-bound iron content between our two limestone samples are jointly responsible for their contrasting sorption efficiency. The importance of iron in low P content sediments was highlighted in the previously mentioned study on carbonate sediments in Florida Bay (Zhang and Huang, 2007), in which surface reactive iron dominated as a driver of P sorption behavior in

sediments with low P_{exch} ($< 0.12 \mu\text{mol g}^{-1}$). The reason for this is that Fe oxides only lose their sorption efficiency by saturation of surface sites with P in sediment with high P content (Pant and Reddy, 2001; Zhang and Huang, 2007). Although we have not directly measured the surface reactive Fe oxide content of rock samples, it is reasonable to assume the surface reactive iron is proportional to carbonate-bound Fe dissolved by 1 M HCl, since we crushed the rock samples to powder in the lab and new powder surfaces essentially have the same composition as bulk rock.

The finding that a miniscule amount of added saltwater can trigger significant geochemical exchanges at the solid-solution interface makes intuitive sense given the high concentration of reactive ions comprising seawater compared to the limited density of surface reactive sites on solids. This effect is well understood in the $\text{Na}^+ - \text{Ca}^{2+}$ cation exchange at the ion exchange front. Which ions or characteristics of seawater are responsible for driving seawater-induced P desorption is as yet uncertain, although progress is being made on this question. Although higher ionic strength and higher pH are factors known to favor desorption, seawater also contains components that favor adsorption. The Ca^{2+} and Mg^{2+} ions introduced by seawater appear strongly favor P adsorption (Gao and Mucci, 2003; Millero et al., 2001; Spiteri et al., 2008b). These cations are thought to favor adsorption by forming bridges between negative sorption sites and negatively charged H_2PO_4^- , or by forming polar complexes such as CaHPO_4 which may adsorb to surface sites (Gao and Mucci, 2003; Millero et al., 2001).

Since seawater nonetheless consistently induces desorption, Millero et al. (2001) has postulated that the anions SO_4^{2-} and HCO_3^- in the presence of Ca^{2+} and Mg^{2+} cause P to lose sorption efficiency on calcite and aragonite, perhaps by forming ion pairs such as CaSO_4^0 and MgSO_4^0 , which reduce the formation of cation-bridged sites (Millero et al., 2001). Lending credence to this hypothesis, P exhibited significantly lower sorption efficiency when carbonate

sediment was immersed in high HCO_3^- brackish water (6 times higher than seawater), highlighting the importance of bicarbonate as a likely driver of desorption (Flower et al., 2016). In an *in situ* geochemical study of 23 aquatic systems, Caraco et al. (1989) found that SO_4^{2-} concentration was strongly correlated with P release (while pH and conductivity did not correlate with P release), with the transition from low to high P release occurring between 40-100 μM SO_4^{2-} concentration. In the experiments of the present study, the small percentage of seawater that triggered lower sorption efficiency corresponds to SO_4^{2-} concentrations of 160 and 190 μM , for RB and Canepatch respectively.

Thus, the possibility that HCO_3^- and SO_4^{2-} are key drivers of seawater-induced P desorption appears to be a promising hypothesis. Further research will be necessary to resolve the question as to the precise geochemical mechanism responsible for seawater-induced desorption. Results from this study will be used as input to a geochemical modeling effort to better understand this process.

Nonetheless, the fact that RB adsorbs more P than Canepatch, and yet exhibits a similar response to seawater (50% loss of sorption efficiency, beginning at a threshold of <1% saltwater) suggests that the fundamental mechanism of seawater-induced desorption may be independent of the loss of sorption sites if iron reduction occurs. Our data indicate that the salinity threshold of releasing P from the carbonate rocks by saltwater intrusion is independent of either specific surface area or carbonate-bound Fe content, although the concentrations of P released would be expected to be proportional to the adsorbed P (P_{exch}) on the carbonate rocks.

To relate our experimental results more generally to conditions within the aquifer requires consideration of how redox potential may affect P sorption. Both rock samples were taken from the top of the core in a location with a thin layer of overlying sediment (1-4 m), a

portion of the aquifer in which groundwater may have more oxygen than would be available at greater depths. Organic matter oxidation within the limestone aquifer is likely to consume oxidants in the groundwater system, rendering much of the groundwater sub-oxic. Electron acceptors follow the sequence of O₂, NO₃, Mn(IV), Fe(III), and SO₄²⁻ (Stumm and Morgan, 2012). Iron reduction would be expected to release much P bound to ferric iron (hydr)oxides (Pant and Reddy, 2001). A limestone rock with enhanced P adsorption efficiency resulting from iron oxides may adsorb less efficiently under sub-oxic conditions.

If SO₄²⁻ ions are the active agent behind saltwater-induced desorption, the potential for SO₄²⁻ reduction to affect P sorption must also be considered. Substantial SO₄²⁻ reduction to H₂S is only possible under extremely anoxic condition (such as in deep sediments or bedrock). In the Biscayne aquifer, from which our rock samples were extracted, there is abundant SO₄²⁻ in brackish and saline groundwater (Price, 2001). The investigators indicated that a degree of SO₄²⁻ reduction was present in the brackish wells because H₂S odors were commonly detected while sampling (H₂S was not directly measured), and a minority of groundwater samples exhibited a slight depletion in SO₄²⁻ relative to the seawater mixing line. In the study previously mentioned by Caraco et al. (1989) investigators found that aquatic systems with low SO₄²⁻ concentrations have low P release under both oxic or anoxic conditions, and that systems with only slightly elevated SO₄²⁻ concentrations exhibited significantly elevated P release, particularly under anoxic conditions.

Our results may provide an explanation for anomalous field observations in the Everglades. Specifically, desorption of P and the indirect effects of low P buffering efficiency within the aquifer mixing zone of the Everglades may contribute to the higher dissolved P

concentrations in the brackish groundwater in the Florida Coastal Everglades reported by Price et al. (2006).

The magnitude of increased SRP availability in an aquifer resulting from seawater-induced desorption would vary depending on several variables, including desorption kinetics (magnitude, rate, and duration), characteristics of the aquifer solids (e.g., total Fe content, P_{exch} and specific surface area), and hydrogeologic factors (e.g., permeability and thickness of the affected portion of the aquifer). In order to obtain high resolution observations of seawater mixtures, we chose to use rock powder so as to increase sorption site density per mass of aquifer material. The low surface area of intact limestone would be expected to severely dampen the magnitude of P desorption to accompany saltwater intrusion, compared to our experimental observations. Further, the location, timing, rate and extent of subsequent groundwater discharge to the overlying estuary will be important as well. In addition to P desorption, possible dissolution of aquifer solids in the mixing zone may also contribute to the apparent linear relationship between total dissolved P and higher salinity groundwater in the coastal Everglades (Price et al., 2006). In addition, the amount SRP in brackish groundwater may also be increased or decreased by other portions of the P cycle *en route* to the surface, such as dissolution or precipitation of P-bearing minerals, and microbial processes.

Despite these difficulties in estimating the amount of SRP concentration increase to be expected from seawater-induced desorption, almost any increase in SRP can be considered ecologically relevant due to the extreme P-limitation in the Everglades, it is likely that saltwater intrusion into an aquifer matrix like RB and Canepatch could contribute an ecologically relevant amount of SRP to the estuary P budget. The fate of SRP entering the mangrove root zone may include biological uptake (e.g., by mangrove roots, periphyton, grasses, or microbes) or

adsorption to the sediment. In the case of the Everglades, high HCO_3^- content in the mangrove sediment groundwater appears to inhibit P adsorption, allowing ambient groundwater SRP concentration to be maintained at an elevated concentration (Flower et al., 2016).

In conclusion, our results indicate that P is active in the ion exchange front of saltwater intrusion. A very small amount of saltwater mixing with fresh groundwater, i.e., a Cl^- concentration of as little as 3 mM (100 mg Cl^-/L), has the potential to cause mineral surfaces to dramatically lose sorption efficiency for P. Because of its association with elevated water SRP concentration due to desorption, this very low salinity isochlor would be valuable to monitor, particularly in coastal regions where groundwater discharges to P-limited ecosystems. Further study is required to understand the P sorption dynamics of limestone bedrocks over a range of P contents, iron contents, and redox conditions, so as to understand these processes along coastlines globally.

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Table 1. Phosphorus sorption characteristics for RB rock and Canepatch rock.

Rock Name	Water type	Freundlich Model						Langmuir Model		
		K_f^{ft} (L g ⁻¹) ^{1/n}	n ^b	NAP ^c μmol g ⁻¹	K _d ^d L g ⁻¹	EPC ₀ ^e μM	R ² ^f	P _{max} ^g μmol g ⁻¹	K _{eq} ^h μM ⁻¹	NAP R ² ⁱ μmol g ⁻¹
RB	Freshwater									
	10% Saltwater	5.2	0.09	4.0	6.3	0.059	0.97	1.8	2.4	1.71 0.95
	Saltwater	4.9	0.06	4.3	2.1	0.116	0.97	1.3	0.7	0.08 0.96
		0.4	0.44	0.1	1.8	0.015	0.91	0.6	1.2	0.00 0.63
Canepatch	Freshwater									
	10% Saltwater	0.7	0.33	0.2	2.7	0.023	0.97	1.1	0.9	0.08 0.96
	Saltwater	1.7	0.07	1.5	0.8	0.143	0.87	0.6	0.6	0.00 0.88
		0.2	0.43	---	---	---	0.69	0.4	0.8	0.00 0.63

^aFreundlich adsorption coefficient.

^bFreundlich exponent, dimensionless.

^cNative adsorbed P.

^dLinear adsorption coefficient.

^eEquilibrium zero P concentration.

^fR² for Freundlich adsorption parameters.

^gAdsorption maximum.

^hAdsorption energy.

ⁱR² for Langmuir adsorption parameters (P_{max} and K_{eq}).

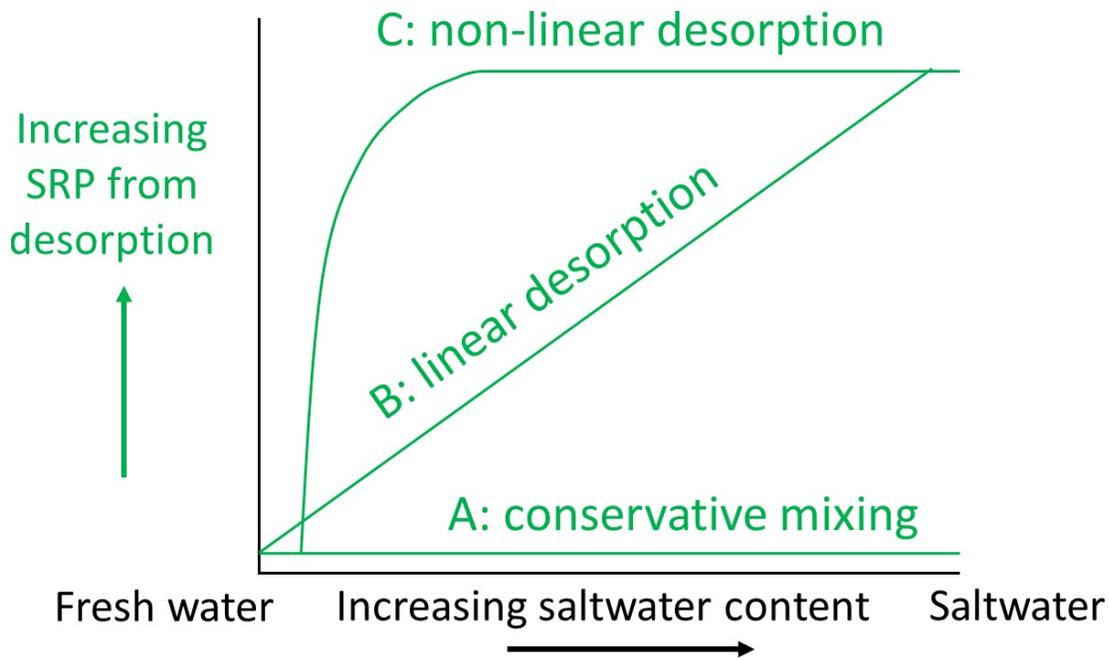


Figure 2. Schematic comparison of three hypothetical patterns of P sorption response to gradational increases in saltwater content, where the two mixing water types have identical low SRP concentration: (A) conservative mixing; (B) SRP availability from desorption increasing in direct proportion to saltwater content; (C) non-linear response, here depicted as a logarithmic increase in SRP from desorption at the freshwater end of the mixing continuum.

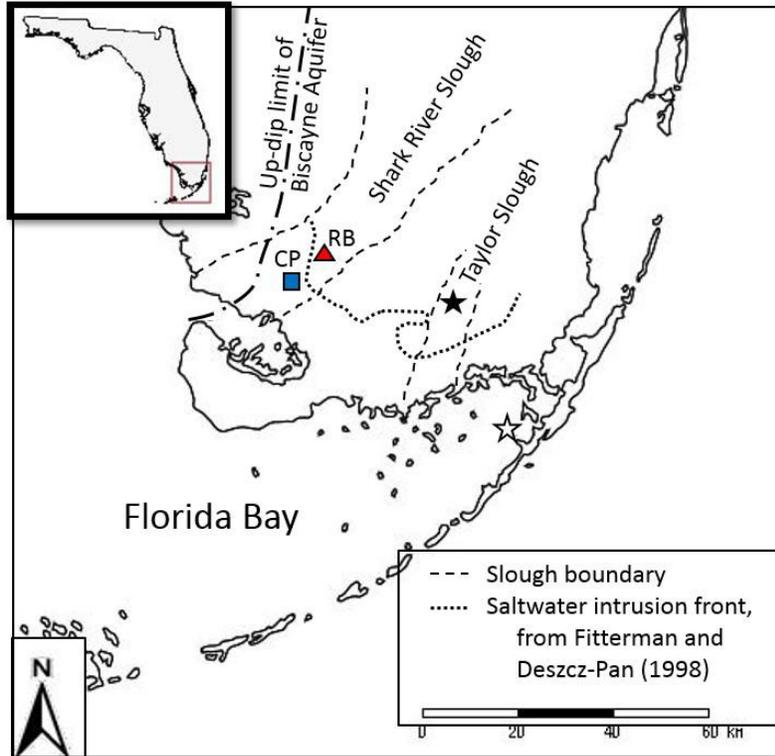


Figure 3. Map of southern Everglades, showing the two major flow-ways, Shark River Slough and Taylor Slough; sampling sites for rock samples Canepatch (CP; square) and RB (triangle); and sampling location for fresh groundwater (solid star), and saltwater from Florida Bay (open star). The saltwater intrusion front corresponds to the 5 m depth horizon within the aquifer and is based on interpreted resistivity measurements by Fitterman and Deszcz-Pan (1998).

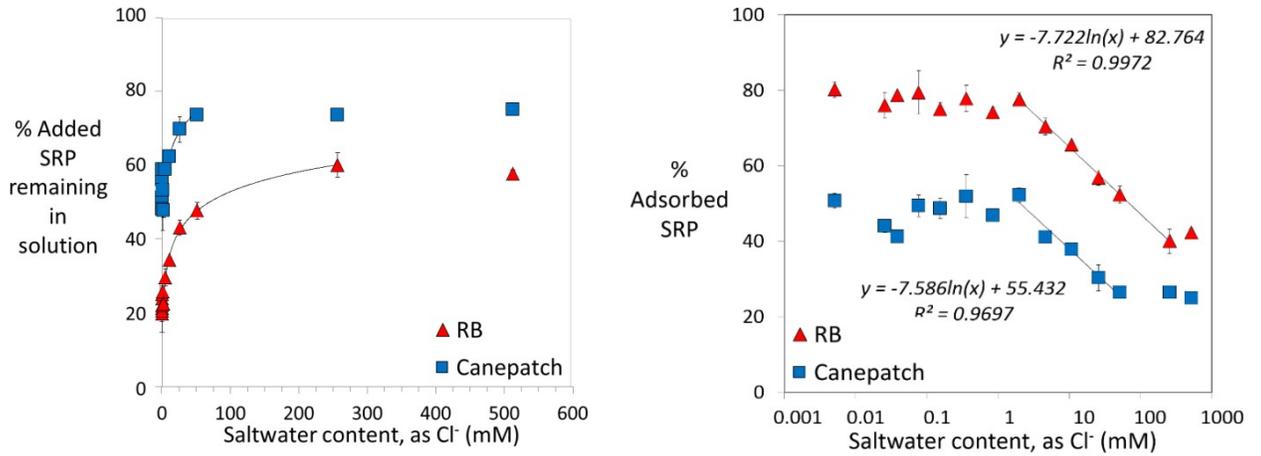


Figure 4. (a) Percent of added SRP remaining in solution (not adsorbed) after equilibration to mixtures of varying amounts of saltwater content for RB rock (red triangles) and Canepatch rock (blue squares); (b) same data set represented on a log scale so as to better display trends at the low salinity end of the mixing continuum, and with the y-axis expressing % of added SRP adsorbed, (removed from solution); the logarithmic function equations with respect to Cl^- concentration are provided.

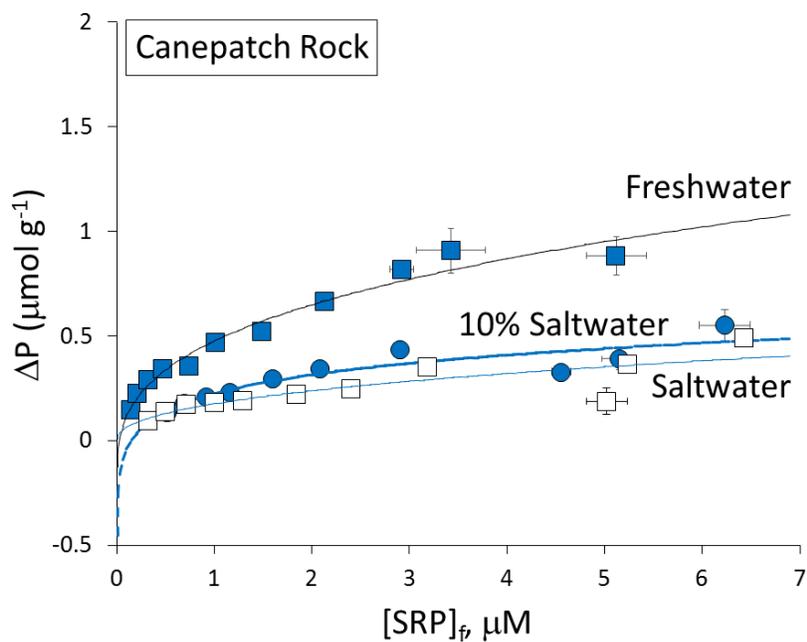
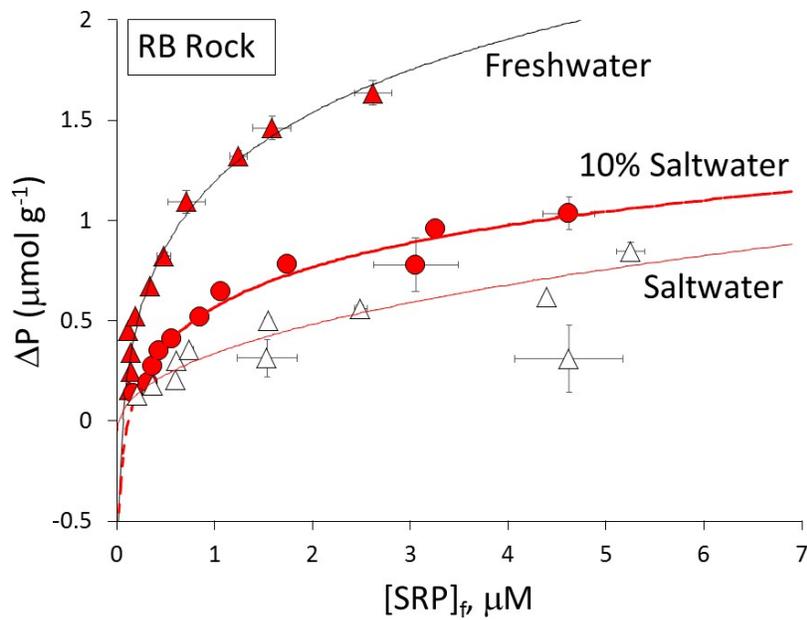


Figure 5. Freundlich sorption isotherms: (a) RB rock with freshwater (solid triangle with solid line), 10% saltwater mixture (solid circle with dashed line) and saltwater (open triangle with solid line); and (b) Canepatch rock with freshwater (solid square with solid line), 10% saltwater mixture (solid circle with dashed line) and saltwater (open square with solid line). Error bars indicate the standard deviation for replicate samples with the same treatment.