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Adsorption and desorption of phosphate on limestone in experiments simulating seawater intrusion

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Key Words: Phosphate, Adsorption, Desorption, Karst, Limestone, seawater intrusion, aquifer
Abstract

This study investigates the potential release of phosphate (PO$_4^{3-}$) from carbonate aquifers exposed to seawater intrusion. Adsorption and desorption of PO$_4^{3-}$ in the presence of deionized water (DIW) and seawater were conducted on a large block of Pleistocene age limestone to simulate the effects of seawater intrusion into a coastal carbonate aquifer at the laboratory scale. The limestone had a high affinity to adsorb PO$_4^{3-}$ in DIW, while PO$_4^{3-}$ adsorption was significantly less in the presence of seawater. Dissolution of calcium carbonate was found to prevent PO$_4^{3-}$ adsorption at salinities less than 30 psu. Adsorption of PO$_4^{3-}$ was limited at higher salinities (30 – 36 psu), due to competition with bicarbonate ions for adsorption sites. At a salinity of 36, some PO$_4^{3-}$ absorption occurred as calcium carbonate precipitated. Concentrations of PO$_4^{3-}$ between 2 and 5 µmol/L were released by desorption when the limestone was exposed to seawater. The results of this study suggest that as seawater intrudes into an originally freshwater coastal aquifer, adsorbed PO$_4^{3-}$ may be released into the groundwater. Additionally, adsorbed PO$_4^{3-}$ is expected to be released from coastal carbonate aquifers world-wide as sea level continues to rise and expose more of the freshwater aquifer to seawater.
Introduction

As seawater intrudes into a coastal carbonate aquifer and mixes with the fresh groundwater, the geochemistry of the resulting mixing zone groundwater is often not a simple mixing of the two end-member waters (Sivan et al. 2005). Processes such as cation exchange, carbonate mineral dissolution or precipitation, and CO$_2$ exchange have all been attributed to either an excess or depletion of ion concentrations as predicted by conservative mixing of freshwater and seawater (Back et al. 1979; Plummer et al. 1976; Sayles 1997). Many studies have focused on the concentrations of major cations and anions as related to carbonate mineral dissolution (Price and Herman 1991; Stroessell et al. 1993; Wicks et al. 1995). Investigations of nutrients, such as nitrogen and phosphorus, in mixing zone waters have reported these constituents in terms of their concentrations transported to coastal zones with submarine groundwater discharge (Simmons 1992). Few studies have investigated the geochemical reactions of phosphate (PO$_4^{3-}$) in seawater intruding into a carbonate aquifer.

Phosphate is often a limiting nutrient in many freshwater and coastal ecosystems located in carbonate terrains (Fourqurean et al. 1992; Reddy et al. 1995). Phosphate limitation exits in the freshwater wetlands and coastal bays of south Florida where the values of PO$_4^{3-}$ are typically less than 0.05 µmol/L (Boyer et al. 1999). These regions are low lying and are most susceptible to sea level rise (Gaiser et al. 2006; Ross et al. 1994; Wanless et al. 1994). Seawater has intruded into the coastal carbonate aquifer in south Florida as far as 30 km inland (Price et al. 2006). Furthermore, total phosphorus (TP) concentrations were found to increase linearly with salinity in mixing zone groundwater (Price et al. 2006). Once in the groundwater, the TP maybe transported to surface coastal waters via either submarine groundwater discharge (Moore 1999;
Moore and Church 1996) or coastal groundwater discharge (Price et al. 2006) where it can serve as an additional source of this important ecosystem nutrient.

The source and mechanisms for the elevated TP observed in the mixing zone groundwaters by Price et al. (2006) are yet unknown. Likely mechanisms involve water-rock interactions such as ion exchange and carbonate mineral dissolution. Although TP was measured by Price et al. (2006), dissolved concentrations of PO$_4^{3-}$ are considered to be the most reactive form of phosphorus. In an effort to investigate the potential release of PO$_4^{3-}$ in mixing zone groundwaters from the aquifer matrix we conducted adsorption/desorption experiments of PO$_4^{3-}$ on limestone using both deionized water (DIW) and seawater. The DIW experiments represented low ionic strength water such as infiltrating rainwater with PO$_4^{3-}$, while the seawater experiments simulated seawater intrusion into a coastal aquifer. The concentrations of PO$_4^{3-}$ used were low, ranging from 1 to 20 µmol/L, in order to mimic the low levels of PO$_4^{3-}$ typically found in groundwaters and surface waters in south Florida unaffected by agricultural practices (Price et al. 2006). The objectives of the study were: 1) to determine the adsorption/desorption characteristics of PO$_4^{3-}$ on limestone in DIW versus seawater; and 2) to identify the geochemical reactions responsible for the release of PO$_4^{3-}$ from the limestone as a result of seawater intrusion.

The uniqueness of this study was the size of the limestone used. Other PO$_4^{3-}$ adsorption/desorption experiments were often conducted on small pieces of limestone weighing 5 g or less (Zhou and Li 2001; Lopez et al. 1996). The limestone used in this experiment was a cube measuring 0.2 m on each side. This experimental set-up allowed for examining PO$_4^{3-}$ adsorption/desorption as seawater intrudes into the natural pore spaces and conduits of a limestone aquifer, but in a laboratory setting.
Methods and Material

The limestone used in this investigation was a cube 0.2 m on each side cut from a large block of the Key Largo limestone extracted from Key Largo, Florida. The Pleistocene age Key Largo limestone was formed between 125,000 to 138,000 years ago during the Sangamon interglacial (Hoffmeister, 1974). The formation is composed of about 30 percent coral skeleton and 70 percent interstitial calcarenite (Stanley, 1996). Most but not all of the original aragonite has been dissolved and replaced by calcite (Stanely, 1996). The Key Largo limestone is a member of the Biscayne Aquifer in south Florida (Parker and others, 1955). Limestone core collected from the upper 6 m of the Biscayne Aquifer contained on average 2 µg/g of loosely adsorbed P as determined by extraction in a 1 M solution of MgCl (Price unpublished data). Approximately 35 µg/g of P was obtained from the same limestone samples when completed dissolved in 1 N HCl.

The limestone block used in this study was dominantly composed of the interstitial calcarenite and was described in detail by (DiFrenna et al. 2008). The hydrologic properties of the limestone cube were previously identified as having a bulk density of 1.47 g/cm$^3$, an effective porosity of 0.30 and an average horizontal hydraulic conductivity of 4.05 m/day (DiFrenna et al, 2008). One pore volume of the cube was approximately 2.4 liters.

Stock solutions of P (1mM) were prepared using reagent grade Sodium Phosphate dibasic anhydrous powder (Fisher Scientific). The P was added to either 18 megohm deionized water (DIW) or seawater. Chloride was added to the DIW at a concentration of 100 µmol/L using sodium chloride (Fisher Scientific). The seawater was collected from the Gulf Stream just offshore of Key Largo, Florida and filtered through a 0.45µm filter. Salinity of the Gulf Stream
seawater was 36.6 practical salinity units (psu). The PO$_4^{3-}$ in the Gulf Stream was determined to be below 0.05 $\mu$mol kg$^{-1}$ (Millero et al. 2001).

The adsorption/desorption experiments were conducted with the limestone block sealed in a Plexiglas permeameter (DiFrenna et al., 2008). A constant head was maintained throughout each experiment using a 20 L carboy at the inlet of the apparatus (Fig. 1). The carboy was filled with a solution of PO$_4^{3-}$ varying from 1 to 20 $\mu$mol/L in either DIW or Gulf Stream seawater. The adsorption/desorption experiments were conducted in three phases. The first phase (phase I) of the experiments investigated the adsorption of PO$_4^{3-}$ in DIW only. For these experiments 20 to 60 L of PO$_4^{3-}$-containing DIW were used. The PO$_4^{3-}$ concentrations in these experiments varied from 1 to 20 $\mu$mol/L (Table 1). Following 2, 8, and 20 $\mu$mol/L tests, 9 L of DIW containing no PO$_4^{3-}$ was flushed through the stone as a blank rinse. A constant head difference of 40 and 45 mm (hydraulic gradient of 0.2) was maintained during these tests with a discharge rate of 1.5 L/hr. The second phase (phase II) of the experiments consisted of alternating between Gulf Stream seawater and DIW containing 8 $\mu$mol/L and 0 $\mu$mol/L of PO$_4^{3-}$ (Table 1). These tests along with those in phase III were conducted at a slightly higher head difference of 60 to 75 mm (hydraulic gradient of 0.3) with a discharge rate of 2.1 L/hr. The final phase (phase III) of the experiments consisted of flushing the stone with blank DIW and then blank Gulf Stream seawater to observe PO$_4^{3-}$ desorption.

During phase I, discharge water was sampled every L for PO$_4^{3-}$ analysis. Concentration of PO$_4^{3-}$ was determined on a spectrophotometer with a method detection limit of 0.02 $\mu$mol/L. Temperature of the discharge water was also monitored and ranged from 21.8 to 22.4°C. During phases II and III, pH, salinity, and temperature of the inlet and discharge water was monitored every liter using Orion pH and S/C/T meters, respectively. A 40 mL subsample for every liter
discharged was collected for PO$_4^{3-}$ and other chemical analyses. Dissolved concentrations of major cations (K$^+$, Ca$^{2+}$, Na$^+$, and Mg$^{2+}$) were determined on a subset of the samples collected across the salinity range using an Inductively Coupled-Plasma (ICP-OES) Vista Pro CCD Simultaneous. The concentrations of major anions (Cl$^-$ and SO$_4^{2-}$) were obtained by ion chromatography on a Dionex DX-120. Total alkalinity was determined by acid titration according to the Gran method (Stumm and Morgan 1981). Concentrations of bicarbonate and carbonate ions were determined from the total alkalinity measurements. The concentrations of the major ions, pH, and temperature, were input to the geochemical reaction path model PHREEQC version 2.14.2. Saturation indices (SI) of aragonite and calcite were determined by PHREEQC using the Davies and Truesdell-Jones equations to calculate activity coefficients for aqueous species (Parkhurst and Appelo 1999). The Davies equation was used for the higher ionic strength seawater.

Results

Adsorption of phosphate in DIW

All of the introduced PO$_4^{3-}$ was adsorbed onto the limestone at concentrations of 1µmol/L to 5 µmol/L with 57 L of DIW discharged through the limestone (Table 1). As the PO$_4^{3-}$ concentration increased in the DIW to 8 µmol/L, detectable concentrations of PO$_4^{3-}$ were observed during the first 1 L discharged from the limestone (Figure 2). The ratio of the input concentration to the output concentration of PO$_4^{3-}$ ($C_{in}/C_{out}$) increased quickly to 0.1 within 3 L discharged, and then increased slowly throughout the remaining 45 L to just over 0.2 (Figure 2). The final concentration of P discharged from the limestone was 1.9 µmol/L. The mass of PO$_4^{3-}$...
adsorbed to this point was 421 µmoles (Table 1). Upon flushing with blank DIW, only about 6
µmoles was desorbed from the limestone.

With a PO$_4^{3-}$ input concentration of 20 µmol/L, PO$_4^{3-}$ was detected in the first L
discharged, and the PO$_4^{3-}$ ratio increased slowly to near 0.45 for the remaining 45 L (Figure 2).
The final P concentration was 9 µmol/L. The total mass of PO$_4^{3-}$ input to the limestone in the
first phase of the experiments was 1676 µmoles (Table 1). The amount of PO$_4^{3-}$ desorbed from
the limestone ranged from 3 to 25 µmoles upon flushing with blank DIW. The limestone
retained 1235 µmoles of PO$_4^{3-}$ or about 75% of the input PO$_4^{3-}$ during phase I.

Adsorption of Phosphate in Seawater

In the phase II experiments, the results of PO$_4^{3-}$ adsorption in seawater using a PO$_4^{3-}$
concentration of 8 µmol/L were compared to those obtained at a similar PO$_4^{3-}$ concentration in
DIW during the phase I experiments (Table 1). In seawater, PO$_4^{3-}$ appeared to act similarly to
salinity for the first 7 liters (Figure 3), corresponding to a salinity increase from 0 to 30 psu
(Figure 3). For the next 6 liters the salinity increased from 30 to 33.6 and the C$_{in}$/C$_{out}$ of PO$_4^{3-}$
exceeded that for salinity (Figure 3). For the remainder of the experiment, salinity increased to
36.8 and the C$_{in}$/C$_{out}$ of PO$_4^{3-}$ was lower than that of salinity. The final concentration of PO$_4^{3-}$
 discharged was 6.7 µmol/L. Only 20%, or 76 µmoles of the 360 µmoles of PO$_4^{3-}$ input was
retained by the limestone in the seawater matrix at an input concentration of 8 µmol/L (Table 1).

The amount of PO$_4^{3-}$ adsorbed in the seawater experiment was significantly lower than
the 75% retention observed for a similar PO$_4^{3-}$ concentration in DIW from the Phase I
experiments (Table 1). To determine if the low amount of PO$_4^{3-}$ retained on the limestone in the
seawater was not a factor of adsorption sites filled during the phase I experiments, the stone was
first flushed with 23 L of seawater and then with 31 L of DIW, both with no added phosphate (Table 1). During these flushes, an additional 150 µmoles of PO$_4^{3-}$ were desorbed. As a final test to determine if the adsorption sites on the limestone were close to being filled, DIW containing 8 µmol/L was input to the stone as the final experiment of phase II. During this last test, 299 µmoles or 80% of the initial PO$_4^{3-}$ in the DIW was retained on the limestone. This amount exceeded the amount desorbed during the two previous flushing steps (Table 1), and therefore, all of the available adsorption surface sites were not filled in phase I.

Desorption of Phosphate in DIW and Seawater

The phase III desorption experiments consisted of flushing the limestone first with blank DIW and then with blank seawater (Table 1). In the blank DIW experiment, the output PO$_4^{3-}$ concentrations were initially high at 1.5 µmol/L but then decreased to 0.3 µmol/L in 30 liters (Figure 4). In the subsequent flushing with blank seawater, significantly more PO$_4^{3-}$, with concentrations ranging from 2 to 5 µmol/L, was released from the limestone. A total of 219 µmoles of PO$_4^{3-}$ was desorbed from the limestone by the Gulf Stream seawater as compared to 23 µmoles with the DIW (Table 1).

Geochemical Analysis

The initial pH of the DIW ranged from 5.06 to 5.90. For the Gulf Stream seawater, the initial pH varied from 8.06 to 8.14. Throughout the experiments using DIW, the pH increased in the discharge water to values greater than 9 (Figure 5). In one DIW experiment, the pH increased to a value as high as 9.89. Conversely, in the seawater experiments the pH decreased
in the discharge water from a high value above 9.05, as a consequence of the DIW flushing, to a
low value of 7.55 (Figure 5).

The ions Mg$^{2+}$, Ca$^{2+}$ and HCO$_3^-$ were found to be non-conservative compared to Cl$^-$
during the phase II and III experiments (Figures 6 – 8). The dashed line on the plots represents
the theoretic mixing between the DIW and seawater. Concentrations of Mg$^{2+}$ were found to be
enriched in most of the seawater samples containing P (Figure 6). The enrichment of Mg$^{2+}$
ranged from 14 to 22 mmol/L with an average of 19 mmol/L for Cl$^-$ concentrations less than 400
mmol/L. At higher Cl$^-$ values, the Mg$^{2+}$ enrichment was less and ranged from 4 mmol/L to 8
mmol/L. When the limestone was flushed with blank seawater, the Mg$^{2+}$ concentrations tended
to be either similar to the theoretical mixing line or slightly elevated by 4 to 8 mmol/L. When
the limestone was flushed with blank DIW following the seawater experiments, the discharge
water was initially enriched with Mg$^{2+}$, but then the concentrations of Mg$^{2+}$ in the discharge water
was either depleted or similar to the theoretical mixing line.

Concentrations of Ca$^{2+}$ were slightly elevated as compared to the theoretical mixing line
in the DIW matrix with P (Figure 7). Conversely, Ca$^{2+}$ was enriched relative to the theoretical
mixing line in the seawater matrix. At Cl$^-$ concentrations of less than 400 mmol/L, Ca$^{2+}$ was
enriched in the seawater matrix between 3 and 5.4 mmol/L with an average of 4.4 mmol/L. At
higher Cl$^-$ concentrations, Ca$^{2+}$ concentrations were either similar to the theoretical mixing line or
were enriched at concentrations of 1 mmol/L or less. Upon flushing the limestone with blank
DIW, the Ca$^{2+}$ concentrations decreased according to the theoretical mixing line. Concentrations
of HCO$_3^-$ were enriched in both the seawater and DIW matrix at Cl$^-$ concentrations of 200
mmol/L or less (Figure 8). Except for a few samples, HCO$_3^-$ concentrations tended to be depleted
in the discharge water at Cl$^-$ concentrations greater than 200 mmol/L.
The PHREEQC results showed differences in the saturation indices of calcite and
aragonite with respect to seawater and DIW water (Figure 9). Saturation indices (SI) with respect
to calcite varied from -0.23 to 0.65 while saturation indices with respect to aragonite varied from
-0.38 to 0.50. The SI values tended to be negative, indicating dissolution of the carbonate
minerals between 0 and 80% seawater. Calcite SI values were negative between 10 and 80%
seawater. Above 80% seawater, the SI values for both calcite and aragonite were positive
indicating supersaturation and possible precipitation of these minerals from solution. The SI
values observed in the discharge water were similar to those expected for conservative mixing of
the seawater with DIW in a system closed with respect to carbon dioxide (Figure 8).

Discussion

Adsorption/desorption of phosphate in DIW

The results of this study indicated that the Key Largo limestone had a high capacity to
adsorb PO$_4^{3-}$ in low salinity waters such as infiltrating rain water. Ahn and James (2001) reported
that total phosphorus (TP) concentrations in south Florida rainfall averaged 0.3 $\mu$mol/L. Dust
and larger particles collected as dry deposition in south Florida and then dissolved in 1 L of DIW
had TP concentrations up to 2.2 $\mu$mol/L (Ahn and James 2001). Phosphate concentrations are
expected to be lower than TP, therefore, the low concentrations of PO$_4^{3-}$ expected in rainfall
would be easily adsorbed onto the Key Largo limestone used in this study. In another study,
Corbett et al. (2000) found that 95% of dissolved PO$_4^{3-}$ at concentrations ranging from 30 to 100
$\mu$M added to low salinity (<5) wastewater and then injected into the Key Largo limestone aquifer
was removed from solution within 5 meters of the injection site in 20 to 50 hrs.
The unusually high pH values (>9) observed at the end of the DIW adsorption tests were indicative that the experimental apparatus was kept closed with respect to CO$_2$ while calcium carbonate dissolved. The slight excess of Ca$^{2+}$ and HCO$_3^-$ compared to Cl$^-$ observed in the DIW experiments indicated that the limestone was dissolving (Figs. 7-8). In this study, 80% and 60% of the input PO$_4^{3-}$ was adsorbed in the DIW experiments using PO$_4^{3-}$ concentrations of 10 and 20 mmol/L, respectively. This percent removal remained constant despite the change in pH, suggesting that there was ample solid surface area available for PO$_4^{3-}$ adsorption despite the concurrent calcium carbonate dissolution. In an unconfined limestone aquifer, the groundwater is often not closed with respect to CO$_2$ but instead is expected to be enriched with CO$_2$ due to organic matter decomposition as well as respiration of plant roots within the soil zone, and therefore, high pH values (>9) are not expected. For instance, fresh groundwaters of the Biscayne Aquifer typically have pH values that range from 6.1 to 7.8 (Price 2001) and average 7.1 (Price and Swart 2006). Additional experiments using natural groundwater enriched with CO$_2$ would be useful to better understand the adsorption of P in a fresh limestone aquifer.

**Phosphate adsorption/desorption during seawater intrusion**

The results of the adsorption/desorption tests conducted on the Key Largo limestone block indicated that carbonate mineral dissolution was occurring at low to moderate salinity (0-30) as observed by the relatively large enrichment of Mg$^{2+}$, Ca$^{2+}$ and HCO$_3^-$ ions versus Cl$^-$ (Figs. 6-8). The enrichment of Ca$^{2+}$ and HCO$_3^-$ ions versus Cl$^-$ in the seawater experiments were significantly higher than that observed in the DIW experiments suggesting that the dissolution of calcium carbonate was greater in seawater as compared to the DIW (Figs. 7-8). The dissolution of CaCO$_3$ would be expected to release adsorbed phosphate and could explain the lack of PO$_4^{3-}$
adsorption observed between salinity values of 0 and 30 (Fig. 3). Ion exchange reactions such as
the exchange of Na\(^+\) and K\(^+\) ions in seawater for Ca\(^{2+}\) and Mg\(^{2+}\) ions on the limestone could also
account for some of the observed increased of Ca\(^{2+}\) and Mg\(^{2+}\) (Sivan et al., 2005), but not the
HCO\(_3^−\) ions which were best described by CaCO\(_3\) dissolution. For instance, the amount of Mg\(^{2+}\)
released in the salinity range of 0 to 28, was greater than expected for dissolution of a low-
magnesium calcite (<10% MgCO\(_3\)).

For salinity values greater than 30 psu, HCO\(_3^−\) concentrations were depleted relative to
conservative mixing (Fig. 8). A depletion of inorganic carbon in mixing zone groundwaters was
previously explained by an outgassing of CO\(_2\) across the water table (Price and Herman, 1999).
Since the experimental apparatus used in these experiments did not lend to an exchange of CO\(_2\),
then adsorption of HCO\(_3^−\) onto the limestone most likely explained the HCO\(_3^−\) depletion. Millero
et al (2001) reported that HCO\(_3^−\) competition for adsorption sites reduced PO\(_4^{3−}\) adsorption onto
CaCO\(_3\) in seawater. A similar competition for adsorption sites between HCO\(_3^−\) and PO\(_4^{3−}\) could
explain the higher ratio of C\(_{in}/C_{out}\) for PO\(_4^{3−}\) compared to salinity between salinity values of 30
and 33.6 psu (Fig. 3). A moderate amount of PO\(_4^{3−}\) adsorption was observed in the seawater
experiments over a salinity range of 33.6 to 36.5 psu (Fig. 3). At these high salinity values,
precipitation of CaCO\(_3\) was expected (Fig. 9), which in turn would increase the surface area
available for PO\(_4^{3−}\) adsorption (Millero et al 2001). The results of our experiments suggest that at
high salinities (>33 psu), PO\(_4^{3−}\) adsorption could co-occur with CaCO\(_3\) precipitation, but HCO\(_3^−\)
competition for adsorption sites results in limiting the PO\(_4^{3−}\) adsorption. The overall results of
our experiments indicate that as seawater intrudes into a coastal carbonate aquifer, PO\(_4^{3−}\)
desorption is expected at salinities less than 30 psu due to calcium carbonate dissolution, and at
higher salinity (30 – 33 psu) due to competition with HCO\(_3^−\) for adsorption sites. At salinity
values greater than 36 psu, some \( \text{PO}_4^{3-} \) adsorption is expected to occur concomitantly with calcite precipitation.

Water flow in karst aquifers including the Biscayne Aquifer is often characterized as having triple porosity consisting of 1) matrix or primary porosity 2) fractures or small vugs less than 1 cm in size; and 3) touching vugs or conduits which tend to transport most of the groundwater flow (White 2002; Cunningham et al. 2006). Laboratory experiments that use small pieces of limestone weighing 5 g or less (Zhou and Li 2001; Lopez et al. 1996) for adsorption/desorption studies can not adequately capture surfaces sites along conduits.

Furthermore, those studies require the limestone to be broken or crushed exposing fresh surfaces that may have not have been available for adsorption if the limestone was intact. The limestone block used in the present study is more representative of an intact limestone. All three types of porosity were observed in the 0.2 m limestone block used in this study (DiFrenna et al., 2008), and therefore the results are more representative of field conditions than for small pieces of limestone.

The experiments conducted herein used DIW and natural seawater to simulate seawater intrusion. Although the use of a natural groundwater instead of DIW would have been more appropriate, the results obtained from the present study seem to compare well with field studies conducted under a range of salinities. For instance, Corbett et al. (2000) found that 95% of \( \text{PO}_4^{3-} \) at concentrations ranging from 30 to 100 \( \mu \text{mol/L} \) dissolved in low salinity (<5 psu) wastewater (that was originally groundwater) and then injected into the Key Largo limestone aquifer was removed from solution, most likely by adsorption, within 5 meters of the injection site in 20 to 50 hrs. The results of their experiments are similar to ours in the finding that the Key Largo limestone has a high affinity to adsorb low concentrations of \( \text{PO}_4^{3-} \) in fresh water. In the natural
brackish mixing zone located along the southern coastline of the Florida peninsula, Price et al. (2006) found concentrations of total phosphorus (TP) ranging from 1 to 2.5 µmol/L over a range of salinities from 3 to 30 psu. The concentrations of TP observed by Price et al. (2006) could not be explained by conservative mixing of fresh groundwater and Gulf of Mexico seawater, both with TP concentrations less than 0.5 µmol/L. The TP values observed by Price et al. (2006) are similar to the PO$_4^{3-}$ values of 2 to 3.5 µmol/L P observed in the Phase III desorption experiments conducted in this investigation.

In Florida Bay, an estuary bounded by peninsular Florida to the north, and the Florida Keys to the south, the concentrations of TP in the groundwater were reported to vary between 0.03 and 1.3 µmol/L (Corbett et al. 2000; Fourqurean 1992). Groundwater in Florida Bay was found to be saline to hypersaline (Price et al. 2008). The low concentrations of TP reported in the groundwater in Florida Bay were expected given the low concentrations of PO$_4^{3-}$ released in the highest salinity conditions observed in our experiments.

Furthermore, our results indicate that subsequent exposure of the Key Largo limestone to seawater intrusion would result in a release of the sorbed PO$_4^{3-}$ into the brackish groundwater. Continued advancement of seawater intrusion in response to sea level rise would continue to release PO$_4^{3-}$ from the limestone into the groundwater as more of the fresh water portion of the aquifer becomes brackish. Our findings have applicability beyond the coastal aquifers of south Florida, including coastal carbonate aquifers world-wide such as those found in Caribbean islands, the Yucatan Peninsula, the Balearic Islands of Spain, the Philippines, and Australia.
Acknowledgments

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References


Table 1. Mass of phosphate (PO$_4^{3-}$) adsorbed relative to inputs in deionized water (DIW) and Seawater (SW) matrix as determined in the Phase I through Phase III experiments.

<table>
<thead>
<tr>
<th>Experiment/Matrix</th>
<th>Volume of Water (L)</th>
<th>Input Concentration of PO$_4^{3-}$ (µmol/L)</th>
<th>Input Mass of PO$_4^{3-}$ (µmoles)</th>
<th>Output Mass of PO$_4^{3-}$ (µmoles)</th>
<th>Cumulative Mass of PO$_4^{3-}$ Adsorbed (µmoles)</th>
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<td></td>
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<td></td>
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List of Figures.

Figure 1. Experimental apparatus used for adsorption/desorption experiments. Figure from DiFrenna et al. 2008 (note if published in Applied Geochemistry, then permission to print this figure will be requested from Hydrogeology Journal).

Figure 2. The effect of increase of PO$_4^{3-}$ concentrations from 8 to 20 µmol/L in DIW on the adsorption of PO$_4^{3-}$ on limestone as compared to 100 µmol/L of Cl$^-$. The ratio C$_{in}$/C$_{out}$ represents the input concentration to the output concentration of PO$_4^{3-}$ or Cl$^-$. 

Figure 3. Comparison of the ratio C$_{in}$/C$_{out}$ for 8 µmol/L of PO$_4^{3-}$ in Gulf Stream seawater compared to salinity.

Figure 4. Desorbed PO$_4^{3-}$ (µmol/L) measured in blank DIW and Gulf Stream seawater. The C$_{in}$/C$_{out}$ ratio for salinity (Sal$_{in}$/Sal$_{out}$) is compared on the second y-axis.

Figure 5. Variation in pH between the DIW and Gulf Stream seawater experiments.

Figure 6. Magnesium concentrations vs. chloride in DIW, seawater, and mixtures of seawater and DIW.

Figure 7. Calcium concentrations vs. chloride in DIW, seawater, and mixtures of seawater and DIW.
Figure 8. Bicarbonate concentrations vs. chloride in DIW, seawater, and mixtures of seawater and DIW.

Figure 9. Saturation indices of calcite and aragonite with respect to mixing seawater and DIW water.
Water in from carboys

Adjustable height drain line used to maintain static head

Manometers

$A = hw$ (.04 m$^2$)

$Q (\text{m}^3/\text{day})$

Samples collected at the outlet every liter

$Q = \frac{A}{t}$

$A = d^2/2$ (.04 m$^2$)

$Q = \frac{dh}{t}$ (.04 m$^2$)

$Q = \frac{d^2}{2t}$ (.04 m$^2$)

$Q = \frac{h}{2\tau}$ (.04 m$^2$)

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$Q = \frac{d^2}{2\tau}$ (.04 m$^2$)
[Diagram showing pH values for DIW and seawater as liters through the cube increase.]