2010

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

René M. Price
Southeast Environmental Research Center and Department of Earth and Environment, Florida International University, pricer@fiu.edu

M. Reza Savabi
US Department of Agriculture, Agricultural Research Service

Jean L. Jolicoeur
Southeast Environmental Research Center and Department of Earth and Environment, Florida International University

Srikumar Roy
Southeast Environmental Research Center and Department of Earth and Environment, Florida International University

Recommended Citation

Price, R.M., M.R. Savabi, J.L. Jolicoeur, S. Roy. 2010. Adsorption and desorption of phosphate on limestone in experiments simulating seawater intrusion. Applied Geochemistry 25(7): 1085-1091.

This material is based upon work supported by the National Science Foundation through the Florida Coastal Everglades Long-Term Ecological Research program under Cooperative Agreements #DBI-0620409 and #DEB-9910514. Any opinions, findings, conclusions, or recommendations expressed in the material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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

René M. Price [1*], M. Reza Savabi [2] Jean L. Jolicoeur[1a], Srikumar Roy[1b]

1) Dept. of Earth and Environment and the Southeast Environmental Research Center Florida International University, Miami, FL

2) US Department of Agriculture, Agricultural Research Service, Miami, FL

a) Currently at Broward Community College, Broward County, FL

b) Currently at Institute of Geophysics, Swiss Federal Institute of Technology (ETH) Zurich, Switzerland

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-} maybe 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 μmol 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 μmol/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 μmol/L (Table 1). Following 2, 8, and 20 μmol/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 μmol/L and 0 μmol/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 μmol/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 μmol/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 μmol/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 μM 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 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 PO_4^{3-} at concentrations ranging from 30 to 100 µmol/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 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.

Futhermore, 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

This research was supported by grants from the Southeast Environmental Research Center (SERC) of Florida International University (FIU), the National Park Service-Everglades National Park, NSF Grant number DBI-0620409, and the USDA, Agricultural Research Service. We thank Jim Fourqurean FIU for assistance with the phosphate analysis, and Peter Swart from RSMAS for assistance with the ICP analysis. This is SERC contribution number XXX.

References

Ahn. H and James, R.T. (2001) Variability, Uncertainty, and Sensitivity of Phosphorus Deposition Load Estimates in South Florida. Water, Air & Soil Pollution 126: 37-51.

Back W., Hanshaw B. B., Herman J. S., and Van Driel J. N. (1986) Differential dissolution of a Pleistocene reef in the ground-water mixing zone of coastal Yucatan, Mexico. Geology 14: 137-140.

Boyer, J. N., J. W. Fourqurean, and Jones, R. D. 1999. Seasonal and long-term trends in water quality of Florida Bay (1989-97). Estuaries 22: 417-430.

Corbett R., Kump L., Dillon K., Burnett W. C., and Chanton J. (2000) Fate of wastewater-borne nutrients under low discharge conditions in the subsurface of the Florida Keys, USA. Marine Chemistry 69: 99-115.

Cunningham K. J., Renken R. A., Wacker M. A., Zygnerski M. R., Robinson E., Shapiro A. M., and Wingard G. L. (2006) Application of carbonate cyclostratigraphy and borehole geophysics to delineate porosity and preferential flow in the karst limestone of the Biscayne aquifer, SE Florida. In *Perspectives on karst geomorphology, hydrology, and geochemistry-A tribute volume to Derek C. Ford and William B. White* (ed. R. S. Harmon and C. Wicks), pp. 191-208. Geological Society of America Special Paper 404.

DiFrenna V. J., Price R. M., and Savabi M. R. (2008) Identification of a hydrodynamic threshold in karst rocks from the Biscayne Aquifer, south Florida, USA. Hydrogeology Journal 16: 31-42.

Fourqurean J. W., Zieman J. C., and Powel G. V. N. (1992.) Phosphorus limitation of primary production in Florida Bay: Evidence from the C:N:P ratios of the dominant seagrass Thalassia testudinum. Limnology and Oceanography 37: 162-171.

Gaiser, E. E., A. Zafiris, P. L. Ruiz, F. A. C. Tobias and M. S. Ross. (2006) Tracking rates of ecotone migration due to salt-water encroachment using fossil mollusks in coastal south Florida. Hydrobiologia 569: 237-257.

Hoffmeister, J. E, 1974, Land from the Sea, University of Miami Press, Coral Gables, FL. 143 p.

Lopez, P., Lluch, X., Vidal, M., and Morgu, J.A. (1996) Adsorption of phosphorus on sediment of the Balearic Islands (Spain) related to their composition. Estuarine, coastal and shelf science, 42: 185-196.

Millero F., Huang F., Zhu X., Liu X., and Zhang J.-Z. (2001) Adsorption and Desorption of Phosphate on Calcite and Aragonite in Seawater. Aquatic Geochemistry 7: 33-56.

Moore W. S. and Church T. M. (1996) Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380: 612-614 & 121-122.

Parker G. G., Gerguson G. E., Love S. K., and others. (1955) Water resources of Southeastern Florida with special reference to geology and groundwater of the Miami areas, pp. 965. USGS.

Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC (Version 2)--a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.

Plummer L. N., Vacher H. L., Mackenzie F. T., Bricker O. P., and Land L. S. (1976) Hydrogeochemistry of Bermuda: A case history of ground-water diagenesis of biocalcarenites. Geological Society of America Bulletin 87: 1301-1316.

Price, R.M., (2001) Geochemical Investigation of groundwater and surface water flow in Everglades National Park, Ph.D. Dissertation, University of Miami, 307 pp.

Price, R. M. and Herman, J.S. (1991) Geochemical Investigation of Salt Water Intrusion into a Coastal Carbonate Aquifer: Mallorca, Spain. Geological Society of America Bulletin, Vol. 103: No. 10, pp. 1270-1279.

Price, R. M. and Swart, P.K. (2006) Geochemical Indicators of Groundwater Recharge in the surficial aquifer system: Everglades National Park, Florida, USA, in Harmon, R.S. and Wicks, D., eds. Perspectives on karst geomorphology, hydrology, and geochemistry -A Tribute volume to Derek C. Ford and William B. White: GSA Special Paper 404, p 251-266, doi: 10.1130/2006.2404(21).

Price R. M., Swart P. K., and Fourqurean J. W. (2006) Coastal Groundwater Discharge - an additional source of phosphorus for the oligotrophic wetlands of the Everglades. Hydrobiologia 569: 23-36.

Price, R.M. Stalker, J.C., Zapata-Rios, X. Jolicoeur, J.L., Rudnick, D.T. (2008) Geochemical and Nutrient Concentrations in the Florida Bay Groundwater. 2008 Florida Bay and Adjacent Marine Systems Science Conference, Program and Abstract Book, December 8-11, 2008, Naples, Florida, USA: 145-146.

Reddy K. R., Diaz O. A., Scinto L. J., and Agami M. (1995) Phosphorus dynamics in selected wetlands and streams of the lake Okeechobee Basin. Ecological Engineering 5: 183-207.

Ross M. S., O'Brien J. J., and Sternberg L. (1994) Sea-Level Rise and the Reduction in Pine Forests in the Florida Keys. Ecological Applications 4: 144-156

Simmons, G.M. (1992) Importance of submarine groundwater discharge (SGWD) and seawater cycling to material flux across sediment/water interfaces in marine environments. Marine Ecology Progress Series 84: 173-184.

Sivan O., Yechieli Y., Herut B., and Lazar B. (2005) Geochemical evolution and timescale of seawater intrusion into the coastal aquifer of Israel Geochimica et Cosmochimica Acta 69: 579-592.

Stanley, S.M. (1966) Paleoecology and diagenesis of Key Largo Limestone, Florida. AAPG Bulletin 50:1927-1947.

Stoesell, R.K., Moore, Y.H., and Coke J.G. (1993) The occurrence and effect of sulfate reduction and sulfide oxidation on coastal limestone dissolution in Yucatan cenotes. Ground Water 31: 566-575.

Stumm, W. and Morgan, J. J. (1981): Aquatic chemistry, 2nd Ed.; John Wiley & Sons, New York.

Wanless H. R., Parkinson R. W., and Tedesco L. P. (1994) Sea Level Control on Stability of Everglades Wetlands. In *Everglades; the ecosystem and its restoration.* (ed. Davis, S.M. and Ogden, J.C.), pp. 199-222. St. Lucie Press.

White, W.B. (2002) Karst hydrology: recent developments and open questions. Eng. Geol. 65: 85-105.

Wicks, C.M., Herman, J.S., Randazzo A.F., and Jee, J.L. (1995) Water-rock interactions in a modern coastal mixing zone Geological Society of America Bulletin. 107:1023-1032.

Zhou M. and Li Y. (2001) Phosphorus-Sorption characteristics of calcareous soils and limestone from the southern Everglades and Adjacent Farmlands. Soil Scientists Society of American Journal 65: 1404-1412.

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.

Experiment/ Matrix	**Volume of Water (L)**	**Input Concentration of PO_4^{3-} (µmol/L)**	**Input Mass of PO_4^{3-} (µmoles)**	**Output Mass of PO_4^{3-} (µmoles)**	**Cummulative Mass of PO_4^{3-} Adsorbed (µmoles)**
Phase I					
DIW	10	1	10.0	0.0	10.0
DIW	10	2	20.0	0.0	30.0
DIW	9	0	0.0	3.4	26.6
DIW	20	3	60.0	0.0	86.6
DIW	17	5	85.0	0.0	171.6
DIW	43	8	301	51.7	420.9
DIW	9	0	0.00	5.9	415.0
DIW	60	20	1200	354	1261.0
DIW	22	0	0.00	25.4	1235.6
Phase II					
SW	45	8	360	284	1311.6
SW	23	0	0.00	110	1201.6
DIW	31	0	0.00	39.7	1161.9
DIW	45	8	360	60.5	1461.4
Phase III					
DIW	36	0	0.00	23.3	1438.1
SW	60	0	0.00	219	1219.1

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.

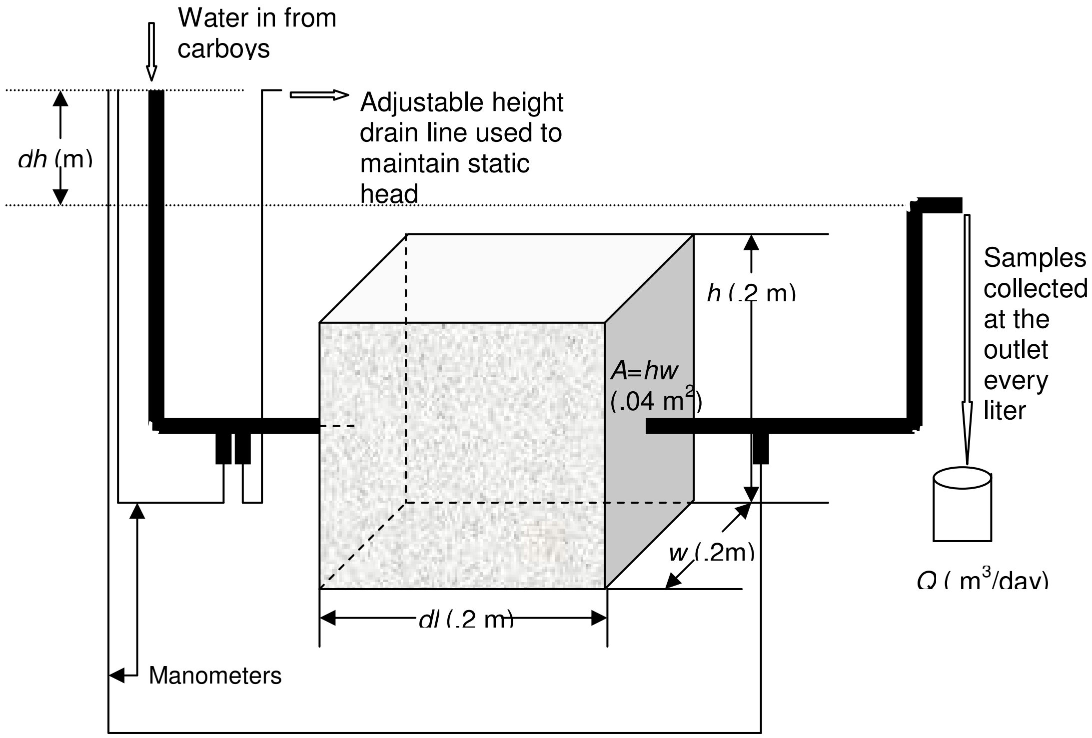
Figure 5. Variation in pH between the DIW and Gulf Stream seawater experiments.

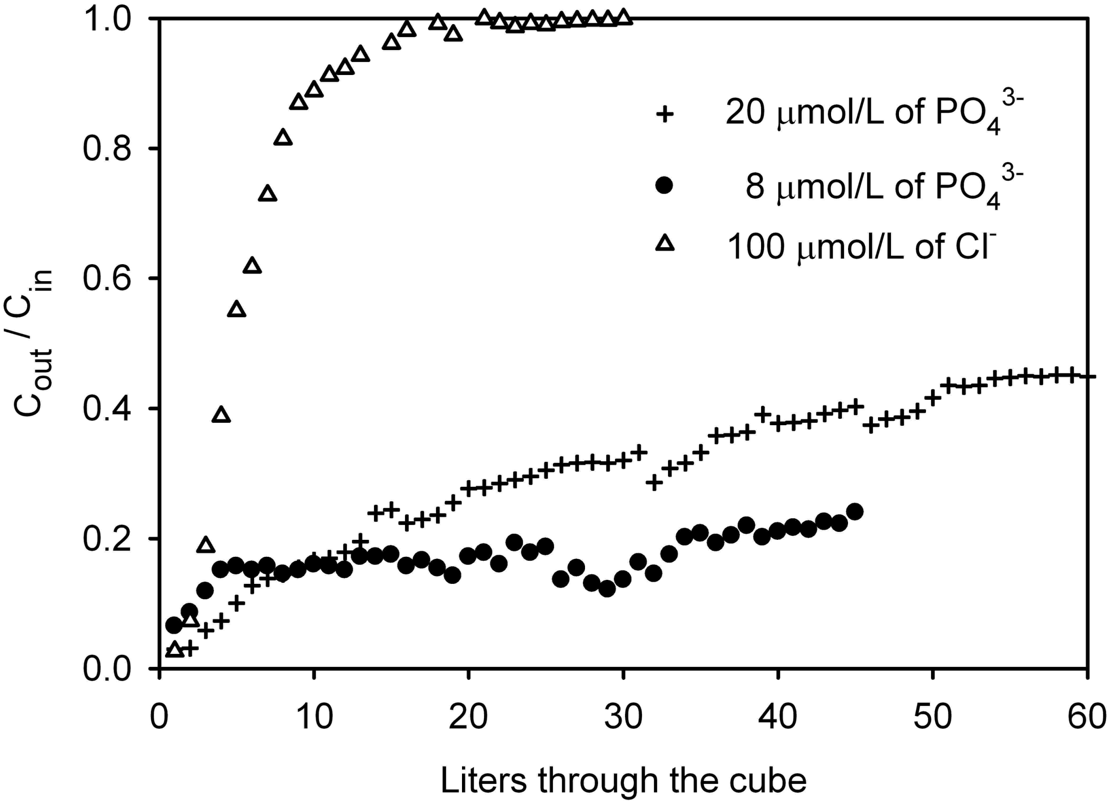
Figure 6. Magnesium concentrations vs. chloride in DIW, seawater, and mixtures of seawater and DIW.

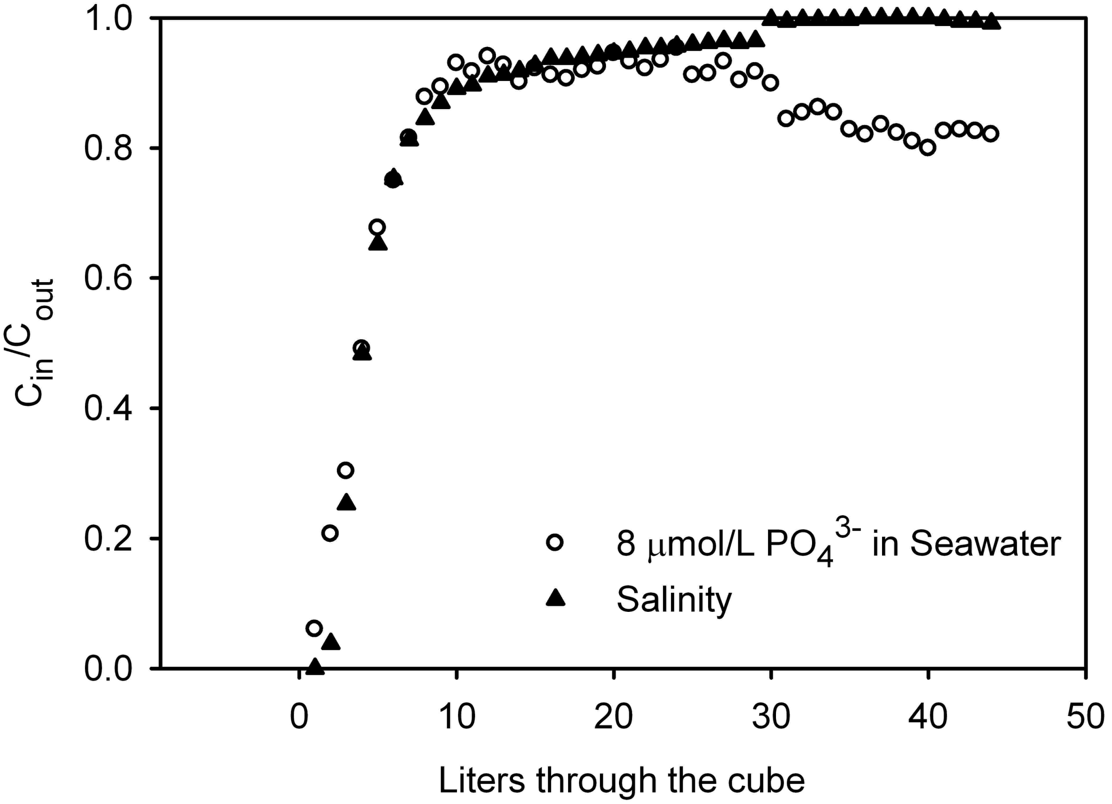
Figure 7. Calcium concentrations vs. chloride in DIW, seawater, and mixtures of seawater and DIW.

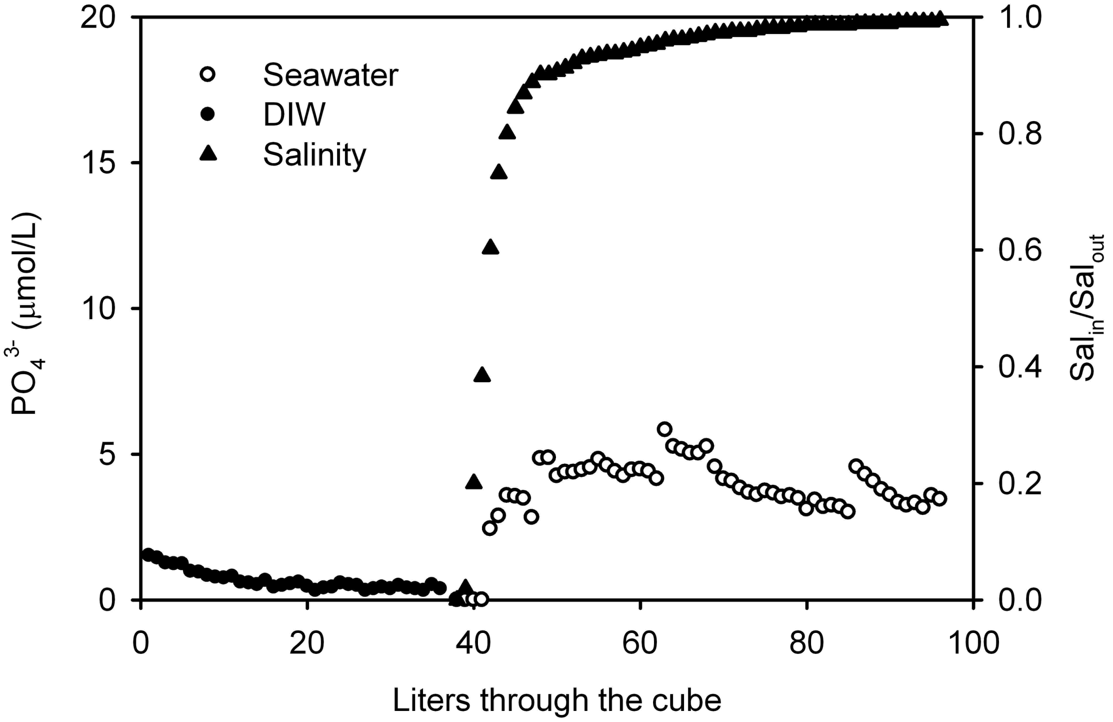
Figure 8. Bicarbonate concentrations vs. chloride in DIW, seawater, and mixtures of seawater and DIW.

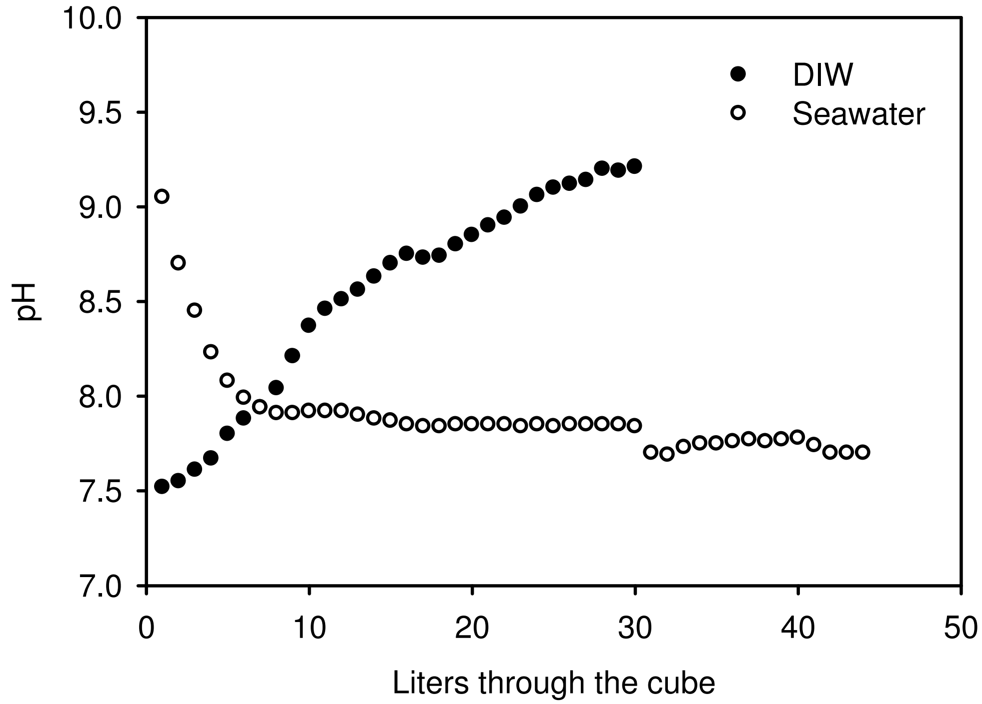
Figure 9. Saturation indices of calcite and aragonite with respect to mixing seawater and DIW water.

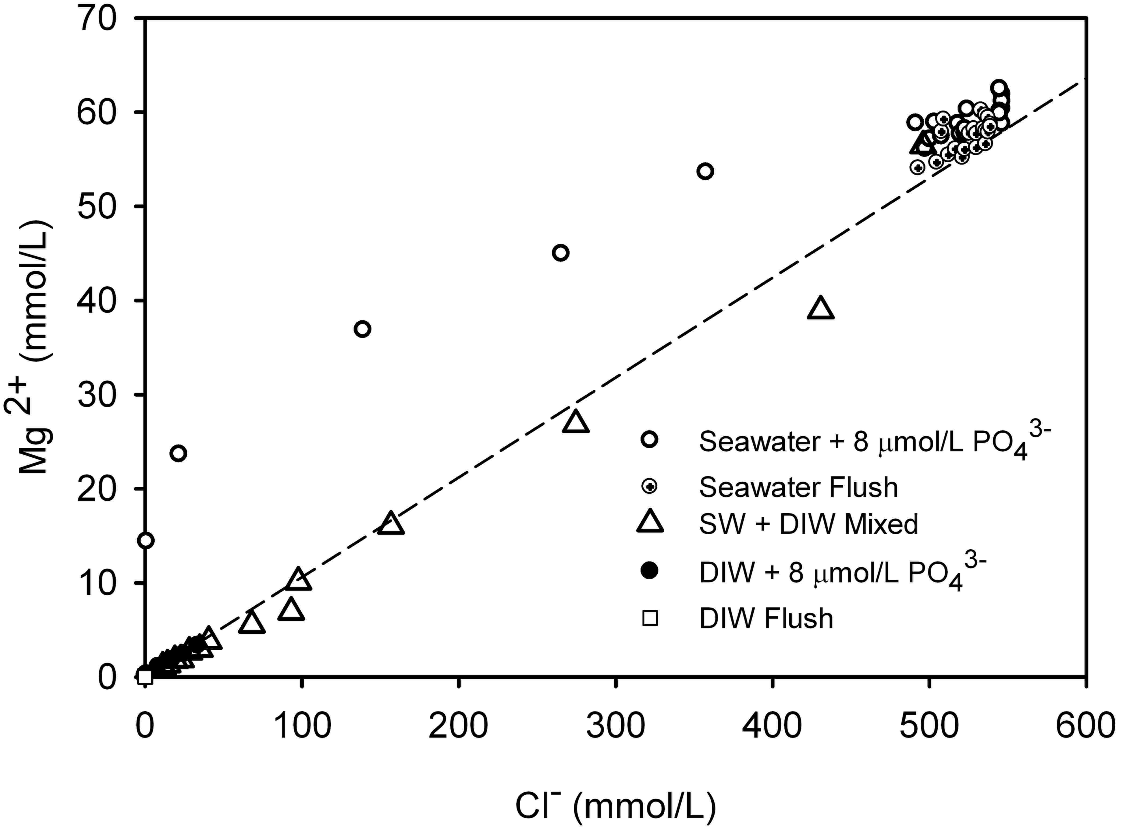

Water in from carboys
Adjustable height drain line used to maintain static head
dh (m)
h (.2 m)
A=hw (.04 m2)
w (.2m)
dl (.2 m)
Samples collected at the outlet every liter
Q (m3/day)
Manometers

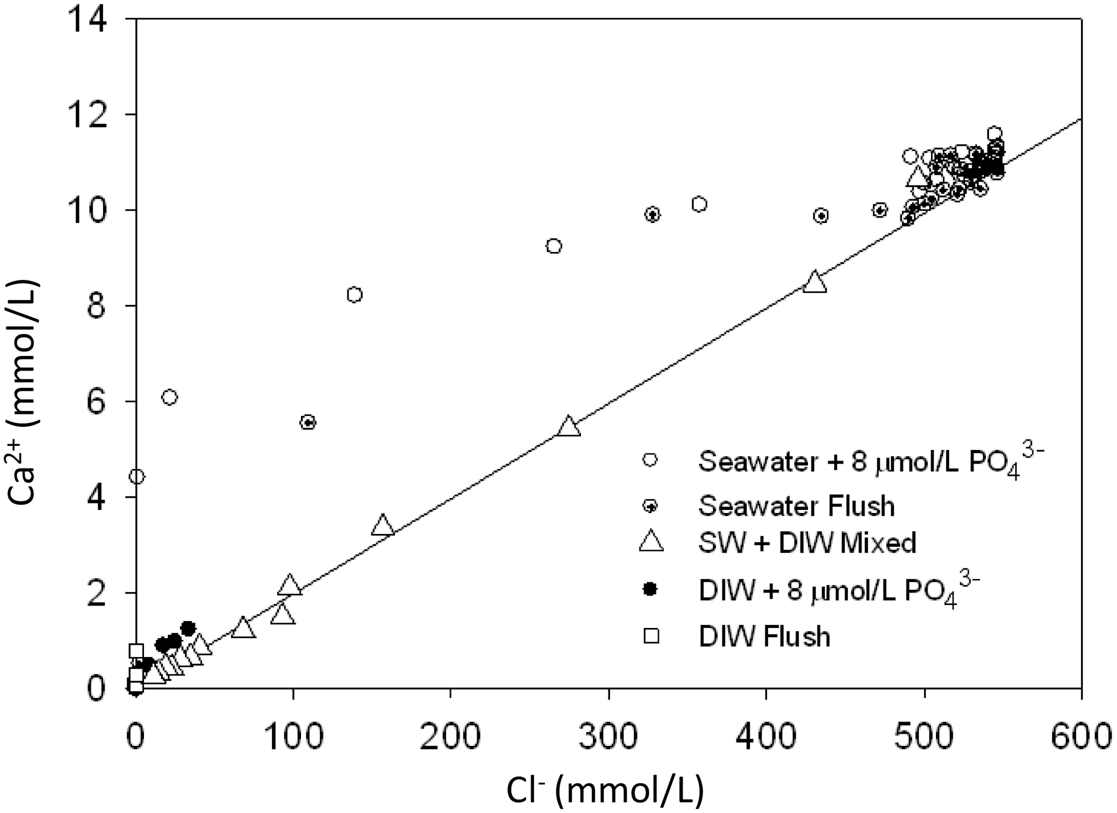

1.0
0.8
0.6
0.4
0.2
0.0
C_{out} / C_{in}
0
10
20
30
40
50
60
Liters through the cube
+ 20 μmol/L of PO_4^{3-}
● 8 μmol/L of PO_4^{3-}
△ 100 μmol/L of Cl^-

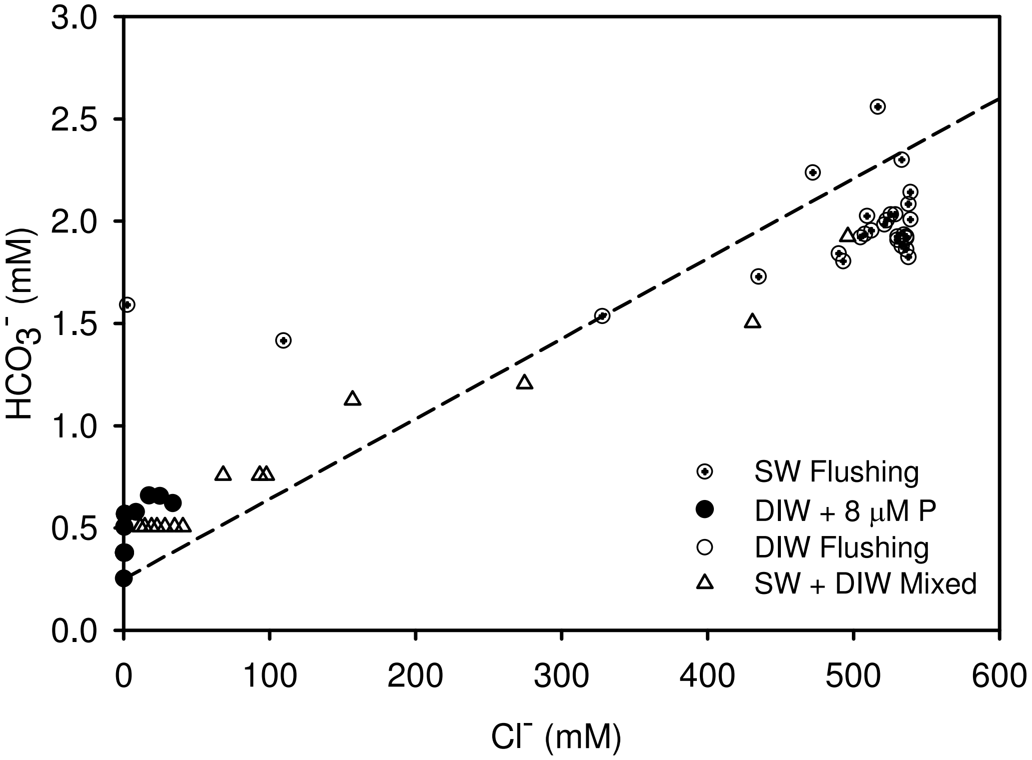

1.0
0.8
0.6
0.4
0.2
0.0
C_{in}/C_{out}
0
10
20
30
40
50
Liters through the cube
○ 8 µmol/L PO_4^{3-} in Seawater
▲ Salinity

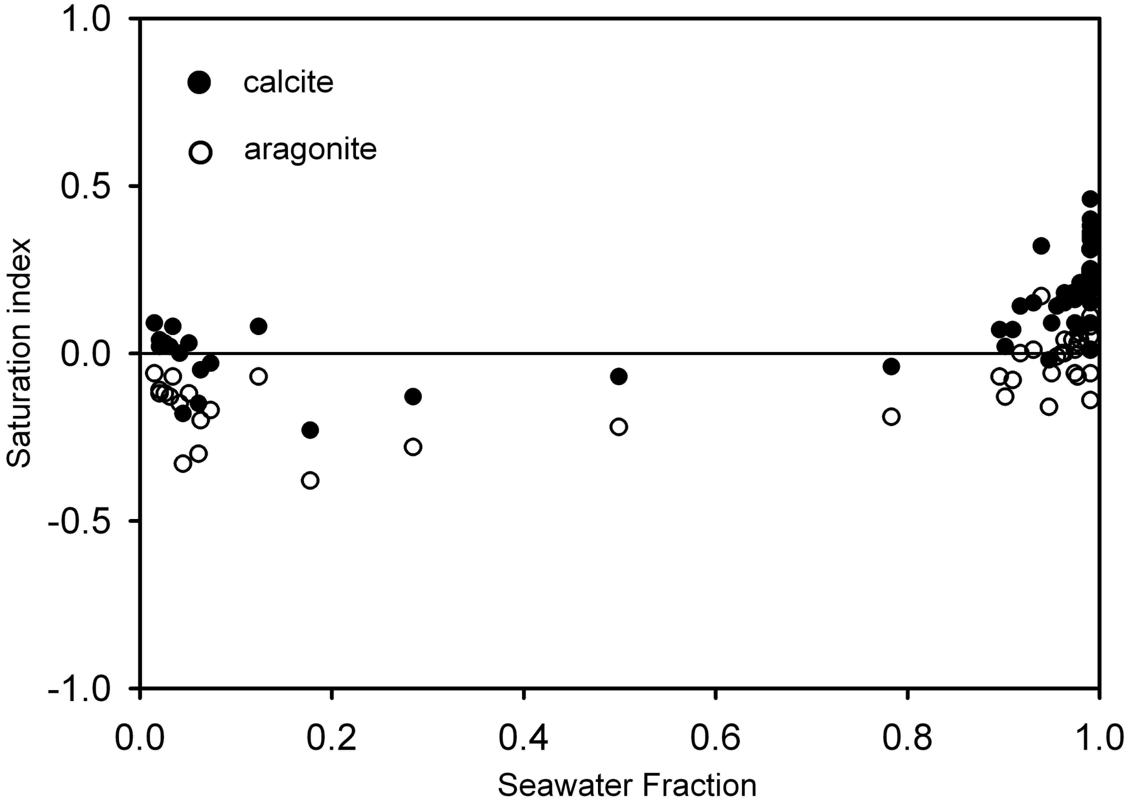

20
15
10
5
0
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
100
○ Seawater
● DIW
▲ Salinity
PO_4^{3-} (μmol/L)
Sal_{in}/Sal_{out}
Liters through the cube


10.0
9.5
9.0
8.5
8.0
7.5
7.0
pH
0
10
20
30
40
50
Liters through the cube
● DIW
○ Seawater


Mg 2+ (mmol/L)
Cl⁻ (mmol/L)
0
10
20
30
40
50
60
70
0
100
200
300
400
500
600
○ Seawater + 8 μmol/L PO4 3-
⊛ Seawater Flush
△ SW + DIW Mixed
● DIW + 8 μmol/L PO4 3-
□ DIW Flush


14
12
10
8
6
4
2
0
Ca2+ (mmol/L)
0
100
200
300
400
500
600
Cl- (mmol/L)
Seawater + 8 µmol/L PO43-
Seawater Flush
SW + DIW Mixed
DIW + 8 µmol/L PO43-
DIW Flush


3.0
2.5
2.0
1.5
1.0
0.5
0.0
HCO_3^- (mM)
0
100
200
300
400
500
600
Cl^- (mM)
SW Flushing
DIW + 8 μM P
DIW Flushing
SW + DIW Mixed


1.0
0.5
0.0
-0.5
-1.0
Saturation index
● calcite
○ aragonite
0.0
0.2
0.4
0.6
0.8
1.0
Seawater Fraction