

16 **Abstract**

17 This study investigates the potential release of phosphate (PO_4^{3-}) from carbonate aquifers
18 exposed to seawater intrusion. Adsorption and desorption of PO_4^{3-} in the presence of deionized
19 water (DIW) and seawater were conducted on a large block of Pleistocene age limestone to
20 simulate the effects of seawater intrusion into a coastal carbonate aquifer at the laboratory scale.
21 The limestone had a high affinity to adsorb PO_4^{3-} in DIW, while PO_4^{3-} adsorption was
22 significantly less in the presence of seawater. Dissolution of calcium carbonate was found to
23 prevent PO_4^{3-} adsorption at salinities less than 30 psu. Adsorption of PO_4^{3-} was limited at higher
24 salinities (30 – 36 psu), due to competition with bicarbonate ions for adsorption sites. At a
25 salinity of 36, some PO_4^{3-} adsorption occurred as calcium carbonate precipitated. Concentrations
26 of PO_4^{3-} between 2 and 5 $\mu\text{mol/L}$ were released by desorption when the limestone was exposed
27 to seawater. The results of this study suggest that as seawater intrudes into an originally
28 freshwater coastal aquifer, adsorbed PO_4^{3-} maybe released into the groundwater. Additionally,
29 adsorbed PO_4^{3-} is expected to be released from coastal carbonate aquifers world-wide as sea level
30 continues to rise and expose more of the freshwater aquifer to seawater.

31

32

33 **Introduction**

34 As seawater intrudes into a coastal carbonate aquifer and mixes with the fresh
35 groundwater, the geochemistry of the resulting mixing zone groundwater is often not a simple
36 mixing of the two end-member waters (Sivan et al. 2005). Processes such as cation exchange,
37 carbonate mineral dissolution or precipitation, and CO₂ exchange have all been attributed to
38 either an excess or depletion of ion concentrations as predicted by conservative mixing of
39 freshwater and seawater (Back et al. 1979; Plummer et al. 1976; Sayles 1997). Many studies
40 have focused on the concentrations of major cations and anions as related to carbonate mineral
41 dissolution (Price and Herman 1991; Stroessell et al. 1993; Wicks et al. 1995). Investigations of
42 nutrients, such as nitrogen and phosphorus, in mixing zone waters have reported these
43 constituents in terms of their concentrations transported to coastal zones with submarine
44 groundwater discharge (Simmons 1992). Few studies have investigated the geochemical
45 reactions of phosphate (PO₄³⁻) in seawater intruding into a carbonate aquifer.

46 Phosphate is often a limiting nutrient in many freshwater and coastal ecosystems located
47 in carbonate terrains (Fourqurean et al. 1992; Reddy et al. 1995). Phosphate limitation exists in
48 the freshwater wetlands and coastal bays of south Florida where the values of PO₄³⁻ are typically
49 less than 0.05 μmol/L (Boyer et al. 1999). These regions are low lying and are most susceptible
50 to sea level rise (Gaiser et al. 2006; Ross et al. 1994; Wanless et al. 1994). Seawater has
51 intruded into the coastal carbonate aquifer in south Florida as far as 30 km inland (Price et al.
52 2006). Furthermore, total phosphorus (TP) concentrations were found to increase linearly with
53 salinity in mixing zone groundwater (Price et al. 2006). Once in the groundwater, the TP maybe
54 transported to surface coastal waters via either submarine groundwater discharge (Moore 1999;

55 Moore and Church 1996) or coastal groundwater discharge (Price et al. 2006) where it can serve
56 as an additional source of this important ecosystem nutrient.

57 The source and mechanisms for the elevated TP observed in the mixing zone
58 groundwaters by Price et al. (2006) are yet unknown. Likely mechanisms involve water-rock
59 interactions such as ion exchange and carbonate mineral dissolution. Although TP was measured
60 by Price et al. (2006), dissolved concentrations of PO_4^{3-} are considered to be the most reactive
61 form of phosphorus. In an effort to investigate the potential release of PO_4^{3-} in mixing zone
62 groundwaters from the aquifer matrix we conducted adsorption/desorption experiments of PO_4^{3-}
63 on limestone using both deionized water (DIW) and seawater. The DIW experiments represented
64 low ionic strength water such as infiltrating rainwater with PO_4^{3-} , while the seawater experiments
65 simulated seawater intrusion into a coastal aquifer. The concentrations of PO_4^{3-} used were low,
66 ranging from 1 to 20 $\mu\text{mol/L}$, in order to mimic the low levels of PO_4^{3-} typically found in
67 groundwaters and surface waters in south Florida unaffected by agricultural practices (Price et al.
68 2006). The objectives of the study were: 1) to determine the adsorption/desorption
69 characteristics of PO_4^{3-} on limestone in DIW versus seawater; and 2) to identify the geochemical
70 reactions responsible for the release of PO_4^{3-} from the limestone as a result of seawater intrusion.

71 The uniqueness of this study was the size of the limestone used. Other PO_4^{3-}
72 adsorption/desorption experiments were often conducted on small pieces of limestone weighing
73 5 g or less (Zhou and Li 2001; Lopez et al. 1996). The limestone used in this experiment was a
74 cube measuring 0.2 m on each side. This experimental set-up allowed for examining PO_4^{3-}
75 adsorption/desorption as seawater intrudes into the natural pore spaces and conduits of a
76 limestone aquifer, but in a laboratory setting.

77

78

79 **Methods and Material**

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

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

96 Stock solutions of P (1mM) were prepared using reagent grade Sodium Phosphate dibasic
97 anhydrous powder (Fisher Scientific). The P was added to either 18 megohm deionized water
98 (DIW) or seawater. Chloride was added to the DIW at a concentration of 100 $\mu\text{mol/L}$ using
99 sodium chloride (Fisher Scientific). The seawater was collected from the Gulf Stream just
100 offshore of Key Largo, Florida and filtered through a 0.45 μm filter. Salinity of the Gulf Stream

101 seawater was 36.6 practical salinity units (psu). The PO_4^{3-} in the Gulf Stream was determined to
102 be below $0.05 \mu\text{mol kg}^{-1}$ (Millero et al. 2001).

103 The adsorption/desorption experiments were conducted with the limestone block sealed
104 in a Plexiglas permeameter (DiFrenna et al., 2008). A constant head was maintained throughout
105 each experiment using a 20 L carboy at the inlet of the apparatus (Fig. 1). The carboy was filled
106 with a solution of PO_4^{3-} varying from 1 to $20 \mu\text{mol/L}$ in either DIW or Gulf Stream seawater.
107 The adsorption/desorption experiments were conducted in three phases. The first phase (phase I)
108 of the experiments investigated the adsorption of PO_4^{3-} in DIW only. For these experiments 20
109 to 60 L of PO_4^{3-} -containing DIW were used. The PO_4^{3-} concentrations in these experiments
110 varied from 1 to $20 \mu\text{mol/L}$ (Table 1). Following 2, 8, and $20 \mu\text{mol/L}$ tests, 9 L of DIW
111 containing no PO_4^{3-} was flushed through the stone as a blank rinse. A constant head difference of
112 40 and 45 mm (hydraulic gradient of 0.2) was maintained during these tests with a discharge rate
113 of 1.5 L/hr. The second phase (phase II) of the experiments consisted of alternating between
114 Gulf Stream seawater and DIW containing $8 \mu\text{mol/L}$ and $0 \mu\text{mol/L}$ of PO_4^{3-} (Table 1). These
115 tests along with those in phase III were conducted at a slightly higher head difference of 60 to 75
116 mm (hydraulic gradient of 0.3) with a discharge rate of 2.1 L/hr. The final phase (phase III) of
117 the experiments consisted of flushing the stone with blank DIW and then blank Gulf Stream
118 seawater to observe PO_4^{3-} desorption.

119 During phase I, discharge water was sampled every L for PO_4^{3-} analysis. Concentration
120 of PO_4^{3-} was determined on a spectrophotometer with a method detection limit of $0.02 \mu\text{mol/L}$.
121 Temperature of the discharge water was also monitored and ranged from 21.8 to 22.4°C . During
122 phases II and III, pH, salinity, and temperature of the inlet and discharge water was monitored
123 every liter using Orion pH and S/C/T meters, respectively. A 40 mL subsample for every liter

124 discharged was collected for PO_4^{3-} and other chemical analyses. Dissolved concentrations of
125 major cations (K^+ , Ca^{2+} , Na^+ , and Mg^{2+}) were determined on a subset of the samples collected
126 across the salinity range using an Inductively Coupled-Plasma (ICP-OES) Vista Pro CCD
127 Simultaneous. The concentrations of major anions (Cl^- and SO_4^{2-}) were obtained by ion
128 chromatography on a Dionex DX-120. Total alkalinity was determined by acid titration
129 according to the Gran method (Stumm and Morgan 1981). Concentrations of bicarbonate and
130 carbonate ions were determined from the total alkalinity measurements. The concentrations of
131 the major ions, pH, and temperature, were input to the geochemical reaction path model
132 PHREEQC version 2.14.2. Saturation indices (SI) of aragonite and calcite were determined by
133 PHREEQC using the Davies and Truesdell-Jones equations to calculate activity coefficients for
134 aqueous species (Parkhurst and Appelo 1999). The Davies equation was used for the higher ionic
135 strength seawater.

136

137 **Results**

138 Adsorption of phosphate in DIW

139 All of the introduced PO_4^{3-} was adsorbed onto the limestone at concentrations of $1\ \mu\text{mol/L}$
140 to $5\ \mu\text{mol/L}$ with 57 L of DIW discharged through the limestone (Table 1). As the PO_4^{3-}
141 concentration increased in the DIW to $8\ \mu\text{mol/L}$, detectable concentrations of PO_4^{3-} were
142 observed during the first 1 L discharged from the limestone (Figure 2). The ratio of the input
143 concentration to the output concentration of PO_4^{3-} ($C_{\text{in}}/C_{\text{out}}$) increased quickly to 0.1 within 3 L
144 discharged, and then increased slowly throughout the remaining 45 L to just over 0.2 (Figure 2).
145 The final concentration of P discharged from the limestone was $1.9\ \mu\text{mol/L}$. The mass of PO_4^{3-}

146 adsorbed to this point was 421 $\mu\text{mol/L}$ (Table 1). Upon flushing with blank DIW, only about 6
147 $\mu\text{mol/L}$ was desorbed from the limestone.

148 With a PO_4^{3-} input concentration of 20 $\mu\text{mol/L}$, PO_4^{3-} was detected in the first L
149 discharged, and the PO_4^{3-} ratio increased slowly to near 0.45 for the remaining 45 L (Figure 2).
150 The final P concentration was 9 $\mu\text{mol/L}$. The total mass of PO_4^{3-} input to the limestone in the
151 first phase of the experiments was 1676 $\mu\text{mol/L}$ (Table 1). The amount of PO_4^{3-} desorbed from
152 the limestone ranged from 3 to 25 $\mu\text{mol/L}$ upon flushing with blank DIW. The limestone
153 retained 1235 $\mu\text{mol/L}$ of PO_4^{3-} or about 75% of the input PO_4^{3-} during phase I.

154

155 Adsorption of Phosphate in Seawater

156 In the phase II experiments, the results of PO_4^{3-} adsorption in seawater using a PO_4^{3-}
157 concentration of 8 $\mu\text{mol/L}$ were compared to those obtained at a similar PO_4^{3-} concentration in
158 DIW during the phase I experiments (Table 1). In seawater, PO_4^{3-} appeared to act similarly to
159 salinity for the first 7 liters (Figure 3), corresponding to a salinity increase from 0 to 30 psu
160 (Figure 3). For the next 6 liters the salinity increased from 30 to 33.6 and the $C_{\text{in}}/C_{\text{out}}$ of PO_4^{3-}
161 exceeded that for salinity (Figure 3). For the remainder of the experiment, salinity increased to
162 36.8 and the $C_{\text{in}}/C_{\text{out}}$ of PO_4^{3-} was lower than that of salinity. The final concentration of PO_4^{3-}
163 discharged was 6.7 $\mu\text{mol/L}$. Only 20%, or 76 $\mu\text{mol/L}$ of the 360 $\mu\text{mol/L}$ of PO_4^{3-} input was
164 retained by the limestone in the seawater matrix at an input concentration of 8 $\mu\text{mol/L}$ (Table 1).

165 The amount of PO_4^{3-} adsorbed in the seawater experiment was significantly lower than
166 the 75 % retention observed for a similar PO_4^{3-} concentration in DIW from the Phase I
167 experiments (Table 1). To determine if the low amount of PO_4^{3-} retained on the limestone in the
168 seawater was not a factor of adsorption sites filled during the phase I experiments, the stone was

169 first flushed with 23 L of seawater and then with 31 L of DIW, both with no added phosphate
170 (Table 1). During these flushes, an additional 150 μmoles of PO_4^{3-} were desorbed. As a final
171 test to determine if the adsorption sites on the limestone were close to being filled, DIW
172 containing 8 $\mu\text{mol/L}$ was input to the stone as the final experiment of phase II. During this last
173 test, 299 μmoles or 80% of the initial PO_4^{3-} in the DIW was retained on the limestone. This
174 amount exceeded the amount desorbed during the two previous flushing steps (Table 1), and
175 therefore, all of the available adsorption surface sites were not filled in phase I.

176

177 Desorption of Phosphate in DIW and Seawater

178 The phase III desorption experiments consisted of flushing the limestone first with blank
179 DIW and then with blank seawater (Table 1). In the blank DIW experiment, the output PO_4^{3-}
180 concentrations were initially high at 1.5 $\mu\text{mol/L}$ but then decreased to 0.3 $\mu\text{mol/L}$ in 30 liters
181 (Figure 4). In the subsequent flushing with blank seawater, significantly more PO_4^{3-} , with
182 concentrations ranging from 2 to 5 $\mu\text{mol/L}$, was released from the limestone. A total of 219
183 μmoles of PO_4^{3-} was desorbed from the limestone by the Gulf Stream seawater as compared to
184 23 μmoles with the DIW (Table 1).

185

186 Geochemical Analysis

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

191 in the discharge water from a high value above 9.05, as a consequence of the DIW flushing, to a
192 low value of 7.55 (Figure 5).

193 The ions Mg^{2+} , Ca^{2+} and HCO_3^- were found to be non-conservative compared to Cl^-
194 during the phase II and III experiments (Figures 6 – 8). The dashed line on the plots represents
195 the theoretic mixing between the DIW and seawater. Concentrations of Mg^{2+} were found to be
196 enriched in most of the seawater samples containing P (Figure 6). The enrichment of Mg^{2+}
197 ranged from 14 to 22 mmol/L with an average of 19 mmol/L for Cl^- concentrations less than 400
198 mmol/L. At higher Cl^- values, the Mg^{2+} enrichment was less and ranged from 4 mmol/L to 8
199 mmol/L. When the limestone was flushed with blank seawater, the Mg^{2+} concentrations tended
200 to be either similar to the theoretical mixing line or slightly elevated by 4 to 8 mmol/L. When
201 the limestone was flushed with blank DIW following the seawater experiments, the discharge
202 water was initially enriched with Mg^{2+} , but then the concentrations of Mg^{2+} in the discharge water
203 was either depleted or similar to the theoretical mixing line.

204 Concentrations of Ca^{2+} were slightly elevated as compared to the theoretical mixing line
205 in the DIW matrix with P (Figure 7). Conversely, Ca^{2+} was enriched relative to the theoretical
206 mixing line in the seawater matrix. At Cl^- concentrations of less than 400 mmol/L, Ca^{2+} was
207 enriched in the seawater matrix between 3 and 5.4 mmol/L with an average of 4.4 mmol/L. At
208 higher Cl^- concentrations, Ca^{2+} concentrations were either similar to the theoretical mixing line or
209 were enriched at concentrations of 1 mmol/L or less. Upon flushing the limestone with blank
210 DIW, the Ca^{2+} concentrations decreased according to the theoretical mixing line. Concentrations
211 of HCO_3^- were enriched in both the seawater and DIW matrix at Cl^- concentrations of 200
212 mmol/L or less (Figure 8). Except for a few samples, HCO_3^- concentrations tended to be depleted
213 in the discharge water at Cl^- concentrations greater than 200 mmol/L.

214 The PHREEQC results showed differences in the saturation indices of calcite and
215 aragonite with respect to seawater and DIW water (Figure 9). Saturation indices (SI) with respect
216 to calcite varied from -0.23 to 0.65 while saturation indices with respect to aragonite varied from
217 -0.38 to 0.50. The SI values tended to be negative, indicating dissolution of the carbonate
218 minerals between 0 and 80% seawater. Calcite SI values were negative between 10 and 80%
219 seawater. Above 80% seawater, the SI values for both calcite and aragonite were positive
220 indicating supersaturation and possible precipitation of these minerals from solution. The SI
221 values observed in the discharge water were similar to those expected for conservative mixing of
222 the seawater with DIW in a system closed with respect to carbon dioxide (Figure 8).

223

224 **Discussion**

225 Adsorption/desorption of phosphate in DIW

226 The results of this study indicated that the Key Largo limestone had a high capacity to
227 adsorb PO_4^{3-} in low salinity waters such as infiltrating rain water. Ahn and James (2001) reported
228 that total phosphorus (TP) concentrations in south Florida rainfall averaged $0.3 \mu\text{mol/L}$. Dust
229 and larger particles collected as dry deposition in south Florida and then dissolved in 1 L of DIW
230 had TP concentrations up to $2.2 \mu\text{mol/L}$ (Ahn and James 2001). Phosphate concentrations are
231 expected to be lower than TP, therefore, the low concentrations of PO_4^{3-} expected in rainfall
232 would be easily adsorbed onto the Key Largo limestone used in this study. In another study,
233 Corbett et al. (2000) found that 95% of dissolved PO_4^{3-} at concentrations ranging from 30 to 100
234 μM added to low salinity (<5) wastewater and then injected into the Key Largo limestone aquifer
235 was removed from solution within 5 meters of the injection site in 20 to 50 hrs.

236 The unusually high pH values (>9) observed at the end of the DIW adsorption tests were
237 indicative that the experimental apparatus was kept closed with respect to CO₂ while calcium
238 carbonate dissolved. The slight excess of Ca²⁺ and HCO₃⁻ compared to Cl⁻ observed in the DIW
239 experiments indicated that the limestone was dissolving (Figs. 7-8). In this study, 80% and 60%
240 of the input PO₄³⁻ was adsorbed in the DIW experiments using PO₄³⁻ concentrations of 10 and 20
241 mmol/L, respectively. This percent removal remained constant despite the change in pH,
242 suggesting that there was ample solid surface area available for PO₄³⁻ adsorption despite the
243 concurrent calcium carbonate dissolution. In an unconfined limestone aquifer, the groundwater
244 is often not closed with respect to CO₂ but instead is expected to be enriched with CO₂ due to
245 organic matter decomposition as well as respiration of plant roots within the soil zone, and
246 therefore, high pH values (>9) are not expected. For instance, fresh groundwaters of the
247 Biscayne Aquifer typically have pH values that range from 6.1 to 7.8 (Price 2001) and average
248 7.1 (Price and Swart 2006). Additional experiments using natural groundwater enriched with
249 CO₂ would be useful to better understand the adsorption of P in a fresh limestone aquifer.

250

251 Phosphate adsorption/desorption during seawater intrusion

252 The results of the adsorption/desorption tests conducted on the Key Largo limestone
253 block indicated that carbonate mineral dissolution was occurring at low to moderate salinity (0-
254 30) as observed by the relatively large enrichment of Mg²⁺, Ca²⁺ and HCO₃⁻ ions versus Cl⁻ (Figs.
255 6-8). The enrichment of Ca²⁺ and HCO₃⁻ ions versus Cl⁻ in the seawater experiments were
256 significantly higher than that observed in the DIW experiments suggesting that the dissolution of
257 calcium carbonate was greater in seawater as compared to the DIW (Figs. 7-8). The dissolution
258 of CaCO₃ would be expected to release adsorbed phosphate and could explain the lack of PO₄³⁻

259 adsorption observed between salinity values of 0 and 30 (Fig. 3). Ion exchange reactions such as
260 the exchange of Na^+ and K^+ ions in seawater for Ca^{2+} and Mg^{2+} ions on the limestone could also
261 account for some of the observed increased of Ca^{2+} and Mg^{2+} (Sivan et al., 2005), but not the
262 HCO_3^- ions which were best described by CaCO_3 dissolution. For instance, the amount of Mg^{2+}
263 released in the salinity range of 0 to 28, was greater than expected for dissolution of a low-
264 magnesium calcite (<10% MgCO_3).

265 For salinity values greater than 30 psu, HCO_3^- concentrations were depleted relative to
266 conservative mixing (Fig. 8). A depletion of inorganic carbon in mixing zone groundwaters was
267 previously explained by an outgassing of CO_2 across the water table (Price and Herman, 1999).
268 Since the experimental apparatus used in these experiments did not lend to an exchange of CO_2 ,
269 then adsorption of HCO_3^- onto the limestone most likely explained the HCO_3^- depletion. Millero
270 et al (2001) reported that HCO_3^- competition for adsorption sites reduced PO_4^{3-} adsorption onto
271 CaCO_3 in seawater. A similar competition for adsorption sites between HCO_3^- and PO_4^{3-} could
272 explain the higher ratio of $C_{\text{in}}/C_{\text{out}}$ for PO_4^{3-} compared to salinity between salinity values of 30
273 and 33.6 psu (Fig. 3). A moderate amount of PO_4^{3-} adsorption was observed in the seawater
274 experiments over a salinity range of 33.6 to 36.5 psu (Fig. 3). At these high salinity values,
275 precipitation of CaCO_3 was expected (Fig. 9), which in turn would increase the surface area
276 available for PO_4^{3-} adsorption (Millero et al 2001). The results of our experiments suggest that at
277 high salinities (>33 psu), PO_4^{3-} adsorption could co-occur with CaCO_3 precipitation, but HCO_3^-
278 competition for adsorption sites results in limiting the PO_4^{3-} adsorption. The overall results of
279 our experiments indicate that as seawater intrudes into a coastal carbonate aquifer, PO_4^{3-}
280 desorption is expected at salinities less than 30 psu due to calcium carbonate dissolution, and at
281 higher salinity (30 – 33 psu) due to competition with HCO_3^- for adsorption sites. At salinity

282 values greater than 36 psu, some PO_4^{3-} adsorption is expected to occur concomitantly with
283 calcite precipitation.

284 Water flow in karst aquifers including the Biscayne Aquifer is often characterized as
285 having triple porosity consisting of 1) matrix or primary porosity 2) fractures or small vugs less
286 than 1 cm in size; and 3) touching vugs or conduits which tend to transport most of the
287 groundwater flow (White 2002; Cunningham et al. 2006). Laboratory experiments that use small
288 pieces of limestone weighing 5 g or less (Zhou and Li 2001; Lopez et al. 1996) for
289 adsorption/desorption studies can not adequately capture surfaces sites along conduits.
290 Furthermore, those studies require the limestone to be broken or crushed exposing fresh surfaces
291 that may have not have been available for adsorption if the limestone was intact. The limestone
292 block used in the present study is more representative of an intact limestone. All three types of
293 porosity were observed in the 0.2 m limestone block used in this study (DiFrenna et al., 2008),
294 and therefore the results are more representative of field conditions than for small pieces of
295 limestone.

296 The experiments conducted herein used DIW and natural seawater to simulate seawater
297 intrusion. Although the use of a natural groundwater instead of DIW would have been more
298 appropriate, the results obtained from the present study seem to compare well with field studies
299 conducted under a range of salinities. For instance, Corbett et al. (2000) found that 95% of PO_4^{3-}
300 at concentrations ranging from 30 to 100 $\mu\text{mol/L}$ dissolved in low salinity (<5 psu) wastewater
301 (that was originally groundwater) and then injected into the Key Largo limestone aquifer was
302 removed from solution, most likely by adsorption, within 5 meters of the injection site in 20 to
303 50 hrs. The results of their experiments are similar to ours in the finding that the Key Largo
304 limestone has a high affinity to adsorb low concentrations of PO_4^{3-} in fresh water. In the natural

305 brackish mixing zone located along the southern coastline of the Florida peninsula, Price et al.
306 (2006) found concentrations of total phosphorus (TP) ranging from 1 to 2.5 $\mu\text{mol/L}$ over a range
307 of salinities from 3 to 30 psu. The concentrations of TP observed by Price et al. (2006) could not
308 be explained by conservative mixing of fresh groundwater and Gulf of Mexico seawater, both
309 with TP concentrations less than 0.5 $\mu\text{mol/L}$. The TP values observed by Price et al. (2006) are
310 similar to the PO_4^{3-} values of 2 to 3.5 $\mu\text{mol/L}$ P observed in the Phase III desorption experiments
311 conducted in this investigation.

312 In Florida Bay, an estuary bounded by peninsular Florida to the north, and the Florida
313 Keys to the south, the concentrations of TP in the groundwater were reported to vary between
314 0.03 and 1.3 $\mu\text{mol/L}$ (Corbett et al 2000; Fourqurean 1992). Groundwater in Florida Bay was
315 found to be saline to hypersaline (Price et al. 2008). The low concentrations of TP reported in
316 the groundwater in Florida Bay were expected given the low concentrations of PO_4^{3-} released in
317 the highest salinity conditions observed in our experiments.

318 Furthermore, our results indicate that subsequent exposure of the Key Largo limestone to
319 seawater intrusion would result in a release of the sorbed PO_4^{3-} into the brackish groundwater.
320 Continued advancement of seawater intrusion in response to sea level rise would continue to
321 release PO_4^{3-} from the limestone into the groundwater as more of the fresh water portion of the
322 aquifer becomes brackish. Our findings have applicability beyond the coastal aquifers of south
323 Florida, including coastal carbonate aquifers world-wide such as those found in Caribbean
324 islands, the Yucatan Peninsula, the Balearic Islands of Spain, the Philippines, and Australia.

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326

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333

334 **References**

- 335 Ahn. H and James, R.T. (2001) Variability, Uncertainty, and Sensitivity of Phosphorus
336 Deposition Load Estimates in South Florida. *Water, Air & Soil Pollution* 126: 37-51.
- 337 Back W., Hanshaw B. B., Herman J. S., and Van Driel J. N. (1986) Differential dissolution of a
338 Pleistocene reef in the ground-water mixing zone of coastal Yucatan, Mexico. *Geology*
339 14: 137-140.
- 340 Boyer, J. N., J. W. Fourqurean, and Jones, R. D. 1999. Seasonal and long-term trends in water
341 quality of Florida Bay (1989-97). *Estuaries* 22: 417-430.
- 342 Corbett R., Kump L., Dillon K., Burnett W. C., and Chanton J. (2000) Fate of wastewater-borne
343 nutrients under low discharge conditions in the subsurface of the Florida Keys, USA.
344 *Marine Chemistry* 69: 99-115.
- 345 Cunningham K. J., Renken R. A., Wacker M. A., Zygnerski M. R., Robinson E., Shapiro A. M.,
346 and Wingard G. L. (2006) Application of carbonate cyclostratigraphy and borehole
347 geophysics to delineate porosity and preferential flow in the karst limestone of the
348 Biscayne aquifer, SE Florida. In *Perspectives on karst geomorphology, hydrology, and*
349 *geochemistry-A tribute volume to Derek C. Ford and William B. White* (ed. R. S. Harmon
350 and C. Wicks), pp. 191-208. Geological Society of America Special Paper 404.
- 351 DiFrenna V. J., Price R. M., and Savabi M. R. (2008) Identification of a hydrodynamic threshold
352 in karst rocks from the Biscayne Aquifer, south Florida, USA. *Hydrogeology Journal* 16:
353 31-42.
- 354 Fourqurean J. W., Zieman J. C., and Powel G. V. N. (1992.) Phosphorus limitation of primary
355 production in Florida Bay: Evidence from the C:N:P ratios of the dominant seagrass
356 *Thalassia testudinum*. *Limnology and Oceanography* 37: 162-171.

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

360 Hoffmeister, J. E, 1974, *Land from the Sea*, University of Miami Press, Coral Gables, FL.
361 143 p.
362

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

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

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

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

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

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

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

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

385 Price, R. M. and Swart, P.K. (2006) Geochemical Indicators of Groundwater Recharge in the
386 surficial aquifer system: Everglades National Park, Florida, USA, in Harmon, R.S. and
387 Wicks, D., eds. Perspectives on karst geomorphology, hydrology, and geochemistry -A
388 Tribute volume to Derek C. Ford and William B. White: GSA Special Paper 404, p 251-
389 266, doi: 10.1130/2006.2404(21).

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

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

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

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

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

404 Sivan O., Yechieli Y., Herut B., and Lazar B. (2005) Geochemical evolution and timescale of
405 seawater intrusion into the coastal aquifer of Israel *Geochimica et Cosmochimica Acta*
406 69: 579-592.

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

409 Stoesell, R.K., Moore, Y.H., and Coke J.G. (1993) The occurrence and effect of sulfate reduction
410 and sulfide oxidation on coastal limestone dissolution in Yucatan cenotes. *Ground Water*
411 31: 566-575.

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

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

417 White, W.B. (2002) Karst hydrology: recent developments and open questions. *Eng. Geol.* 65:
418 85-105.

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

421 Zhou M. and Li Y. (2001) Phosphorus-Sorption characteristics of calcareous soils and limestone
422 from the southern Everglades and Adjacent Farmlands. *Soil Scientists Society of*
423 *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-} ($\mu\text{mol/L}$)	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 $\mu\text{mol/L}$ in DIW on the adsorption of PO_4^{3-} on limestone as compared to 100 $\mu\text{mol/L}$ of Cl^- . The ratio $C_{\text{in}}/C_{\text{out}}$ represents the input concentration to the output concentration of PO_4^{3-} or Cl^- .

Figure 3. Comparison of the ratio $C_{\text{in}}/C_{\text{out}}$ for 8 $\mu\text{mol/L}$ of PO_4^{3-} in Gulf Stream seawater compared to salinity.

Figure 4. Desorbed PO_4^{3-} ($\mu\text{mol/L}$) measured in blank DIW and Gulf Stream seawater. The $C_{\text{in}}/C_{\text{out}}$ ratio for salinity ($\text{Sal}_{\text{in}}/\text{Sal}_{\text{out}}$) 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.

















