

		Volume 25, Issue 7, July 2010 ISSN 0883-2927																										
<h1>Applied Geochemistry</h1> <p>JOURNAL OF THE INTERNATIONAL ASSOCIATION OF GEOCHEMISTRY</p>																												
Executive Editor Associate Editors	Roy Fyfe, <i>Aberystwyth</i> E. L. ANORR, <i>Nottingham</i> L. AQUILINO, <i>Rome</i> H. AMANNING, <i>Reykjavik</i> S. BOTTRELL, <i>Leeds</i> J. CAYWRIGHT, <i>Clyton</i> Z. CEYLAN, <i>Ankara</i> R. N. J. COMANS, <i>Peñen</i> A. DANNEBERG, <i>Leipzig</i> W. M. EDMUNDS, <i>Oxford</i> G. FILIPPILLI, <i>Indianapolis</i> D. FORTIN, <i>Ottawa</i> M. GAGNON, <i>Pinawa</i> D. GORDON, <i>Wallingford</i> J. E. GRAY, <i>Denver</i> R. S. HARMON, <i>Research Triangle Park</i>	M. HUDSON, <i>Reading</i> I. HUGHES, <i>Calgary</i> M. KERRIE, <i>Mant</i> A. KOKKER, <i>Reston</i> X. D. LI, <i>Kowloon</i> W. B. LYONS, <i>Columbus</i> P. B. MCMASON, <i>Denver</i> J. MAREK, <i>Jacksonville</i> L. A. MEEK, <i>Anchorage</i> B. NIKOROVA, <i>Edinburgh</i> M. NOVAK, <i>Praha</i> J. C. POTT, <i>Gij-Sur-Foyette</i> D. PATAI, <i>Manchester</i> R. M. PIRCH, <i>Miami</i> C. REIMANN, <i>Frankfurt</i> A. N. ROYCHOWDERY, <i>Stellenbosch</i>	K. S. SAVAGE, <i>Nashville</i> R. R. SEGA II, <i>Reston</i> G. SELINS, <i>Uppsala</i> B. R. T. SMITH, <i>Corvallis</i> D. B. SMITH, <i>Denver</i> L. SELLERIK, <i>Lisieux</i> Y. TARDY, <i>Nantes</i> K. G. TAYLOR, <i>Manchester</i> A. VINGOERI, <i>Durban</i> B. WANG, <i>Anchorage</i> R. B. WASTY, <i>Denver</i> R. WATKINS, <i>Perth</i> J. WEBSTER-BROWN, <i>Christchurch</i>																									
<table border="0"> <tr> <td>W.G. DARLING, D.C. GOODDY, J. RICHES and I. WALLIS: Using environmental tracers to assess the extent of river-groundwater interaction in a quarried area of the English Chalk.....</td> <td>923</td> </tr> <tr> <td>L. MARYNOWSKI and M. ZATON: Organic matter from the Callovian (Middle Jurassic) deposits of Lithuania: Compositions, sources and depositional environments.....</td> <td>933</td> </tr> <tr> <td>B. BUGGLE, G.L.B. WIESENBERG and B. GLASER: Is there a possibility to correct fossil <i>n</i>-alkane data for postdepositional alteration effects?.....</td> <td>947</td> </tr> <tr> <td>E.J. CLYDE, P. CHAMPAINE and H.E. JAMIESON: The use of passive treatment alternatives for the mitigation of acidic drainage at the Williams Brother mine, California: Bench-scale study.....</td> <td>958</td> </tr> <tr> <td>B.E. KIMBALL, J.D. RIMSTDT and S.L. BRANTLEY: Chalcopyrite dissolution rate laws.....</td> <td>972</td> </tr> <tr> <td>S. FEYTA, A. TESSIER, C. GOREL and D. COSSA: <i>In situ</i> adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments.....</td> <td>984</td> </tr> <tr> <td>J. MA, F. PAN, L. CHEN, W.M. EDMUNDS, Z. DING, J. HE, K. ZHOU and T. HUANG: Isotopic and geochemical evidence of recharge sources and water quality in the Quaternary aquifer beneath Jinchang city, NW China.....</td> <td>996</td> </tr> <tr> <td>J.M. ASTILLEROS, A. GODELITSAS, J.D. RODRIGUEZ-BLANCO, L. FERNÁNDEZ-DÍAZ, M. PRIETO, A. LAGOYANNIS and S. HARISSOPULOS: Interaction of gypsum with lead in aqueous solutions.....</td> <td>1008</td> </tr> <tr> <td>M. UJEVIĆ, Ž. DUJIC, C. CAHOT, L. SIPOS, Y. SANTO, Ž. DADIĆ and J. HALAMIC: Occurrence and geochemistry of arsenic in the groundwater of Eastern Croatia.....</td> <td>1017</td> </tr> <tr> <td>C. REIMANN, M. BERK and P. FILZMOSER: Bottled drinking water: Water contamination from bottle materials (glass, hard PET, soft PET), the influence of colour and acidification.....</td> <td>1030</td> </tr> <tr> <td>R.G. GARRETT, A.R.D. PORTER and P.A. HUNT: An occurrence of cadmiferous phosphorite soil concretions in Jamaica.....</td> <td>1047</td> </tr> <tr> <td>K. LANGE, R.K. ROWE, H. JAMIESON, R.L. FLEMING and A. LANZIBOTTI: Characterization of geosynthetic clay liner bentonite using micro-analytical methods.....</td> <td>1056</td> </tr> <tr> <td>G. BERD, P.A. BREWER, M.G. MACKLIN, M. NIKOLOVA, T. KOTSEV, M. MOLLOV and C. SWAIN: Pb isotope evidence for contaminant-metal dispersal in an international river system: The lower Danube catchment, Eastern Europe.....</td> <td>1070</td> </tr> </table>			W.G. DARLING, D.C. GOODDY, J. RICHES and I. WALLIS: Using environmental tracers to assess the extent of river-groundwater interaction in a quarried area of the English Chalk.....	923	L. MARYNOWSKI and M. ZATON: Organic matter from the Callovian (Middle Jurassic) deposits of Lithuania: Compositions, sources and depositional environments.....	933	B. BUGGLE, G.L.B. WIESENBERG and B. GLASER: Is there a possibility to correct fossil <i>n</i> -alkane data for postdepositional alteration effects?.....	947	E.J. CLYDE, P. CHAMPAINE and H.E. JAMIESON: The use of passive treatment alternatives for the mitigation of acidic drainage at the Williams Brother mine, California: Bench-scale study.....	958	B.E. KIMBALL, J.D. RIMSTDT and S.L. BRANTLEY: Chalcopyrite dissolution rate laws.....	972	S. FEYTA, A. TESSIER, C. GOREL and D. COSSA: <i>In situ</i> adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments.....	984	J. MA, F. PAN, L. CHEN, W.M. EDMUNDS, Z. DING, J. HE, K. ZHOU and T. HUANG: Isotopic and geochemical evidence of recharge sources and water quality in the Quaternary aquifer beneath Jinchang city, NW China.....	996	J.M. ASTILLEROS, A. GODELITSAS, J.D. RODRIGUEZ-BLANCO, L. FERNÁNDEZ-DÍAZ, M. PRIETO, A. LAGOYANNIS and S. HARISSOPULOS: Interaction of gypsum with lead in aqueous solutions.....	1008	M. UJEVIĆ, Ž. DUJIC, C. CAHOT, L. SIPOS, Y. SANTO, Ž. DADIĆ and J. HALAMIC: Occurrence and geochemistry of arsenic in the groundwater of Eastern Croatia.....	1017	C. REIMANN, M. BERK and P. FILZMOSER: Bottled drinking water: Water contamination from bottle materials (glass, hard PET, soft PET), the influence of colour and acidification.....	1030	R.G. GARRETT, A.R.D. PORTER and P.A. HUNT: An occurrence of cadmiferous phosphorite soil concretions in Jamaica.....	1047	K. LANGE, R.K. ROWE, H. JAMIESON, R.L. FLEMING and A. LANZIBOTTI: Characterization of geosynthetic clay liner bentonite using micro-analytical methods.....	1056	G. BERD, P.A. BREWER, M.G. MACKLIN, M. NIKOLOVA, T. KOTSEV, M. MOLLOV and C. SWAIN: Pb isotope evidence for contaminant-metal dispersal in an international river system: The lower Danube catchment, Eastern Europe.....	1070
W.G. DARLING, D.C. GOODDY, J. RICHES and I. WALLIS: Using environmental tracers to assess the extent of river-groundwater interaction in a quarried area of the English Chalk.....	923																											
L. MARYNOWSKI and M. ZATON: Organic matter from the Callovian (Middle Jurassic) deposits of Lithuania: Compositions, sources and depositional environments.....	933																											
B. BUGGLE, G.L.B. WIESENBERG and B. GLASER: Is there a possibility to correct fossil <i>n</i> -alkane data for postdepositional alteration effects?.....	947																											
E.J. CLYDE, P. CHAMPAINE and H.E. JAMIESON: The use of passive treatment alternatives for the mitigation of acidic drainage at the Williams Brother mine, California: Bench-scale study.....	958																											
B.E. KIMBALL, J.D. RIMSTDT and S.L. BRANTLEY: Chalcopyrite dissolution rate laws.....	972																											
S. FEYTA, A. TESSIER, C. GOREL and D. COSSA: <i>In situ</i> adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments.....	984																											
J. MA, F. PAN, L. CHEN, W.M. EDMUNDS, Z. DING, J. HE, K. ZHOU and T. HUANG: Isotopic and geochemical evidence of recharge sources and water quality in the Quaternary aquifer beneath Jinchang city, NW China.....	996																											
J.M. ASTILLEROS, A. GODELITSAS, J.D. RODRIGUEZ-BLANCO, L. FERNÁNDEZ-DÍAZ, M. PRIETO, A. LAGOYANNIS and S. HARISSOPULOS: Interaction of gypsum with lead in aqueous solutions.....	1008																											
M. UJEVIĆ, Ž. DUJIC, C. CAHOT, L. SIPOS, Y. SANTO, Ž. DADIĆ and J. HALAMIC: Occurrence and geochemistry of arsenic in the groundwater of Eastern Croatia.....	1017																											
C. REIMANN, M. BERK and P. FILZMOSER: Bottled drinking water: Water contamination from bottle materials (glass, hard PET, soft PET), the influence of colour and acidification.....	1030																											
R.G. GARRETT, A.R.D. PORTER and P.A. HUNT: An occurrence of cadmiferous phosphorite soil concretions in Jamaica.....	1047																											
K. LANGE, R.K. ROWE, H. JAMIESON, R.L. FLEMING and A. LANZIBOTTI: Characterization of geosynthetic clay liner bentonite using micro-analytical methods.....	1056																											
G. BERD, P.A. BREWER, M.G. MACKLIN, M. NIKOLOVA, T. KOTSEV, M. MOLLOV and C. SWAIN: Pb isotope evidence for contaminant-metal dispersal in an international river system: The lower Danube catchment, Eastern Europe.....	1070																											
<i>Continued on outside back cover</i>																												

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

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

René M. Price^{a,*}, M. Reza Savabi^b, Jean L. Jolicoeur^{a,1}, Srikumar Roy^{b,2}^a Dept. of Earth and Environment and the Southeast Environmental Research Center Florida International University, Miami, FL, United States^b US Department of Agriculture, Agricultural Research Service, Miami, FL, United States

ARTICLE INFO

Article history:

Received 18 September 2009

Accepted 20 April 2010

Available online 24 April 2010

Editorial handling by R. Fuge

ABSTRACT

This study investigates the potential release of 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 showed strong adsorption of PO_4^{3-} in DIW, while adsorption was significantly less in the presence of seawater. Dissolution of CaCO_3 was found to prevent PO_4^{3-} adsorption at salinities less than 30 psu. Adsorption of PO_4^{3-} was limited at higher salinities (30–33 psu), due to competition with HCO_3^- ions for adsorption sites. At a salinity <33, some PO_4^{3-} adsorption occurred as CaCO_3 precipitated. Concentrations of PO_4^{3-} between 2 and 5 $\mu\text{mol/L}$ 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. Consequently, adsorbed PO_4^{3-} is expected to be released from coastal carbonate aquifers world-wide as sea level continues to rise exposing more of the freshwater aquifer to seawater.

© 2010 Elsevier Ltd. All rights reserved.

1. 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., 1986; Plummer et al., 1976; Sayles and Mangelsdorf, 1977). Many studies have focused on the concentrations of major cations and anions as related to carbonate mineral dissolution (Price and Herman, 1991; Stoessel et al., 1993; Wicks et al., 1995). Investigations of nutrients, such as N and P, 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 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 exists in the freshwater wetlands and coastal bays of south Florida where the values of PO_4^{3-} are typically less than 0.05 $\mu\text{mol/L}$ (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 P (TP) concentrations were found to increase linearly with salinity in mixing zone groundwater (Price et al., 2006). Once in the groundwater, the TP may be transported to surface coastal waters via either submarine groundwater discharge (Moore, 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 as 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 P. In an effort to investigate the potential release of PO_4^{3-} in mixing zone groundwaters from the aquifer matrix, adsorption/desorption experiments of PO_4^{3-} on limestone were conducted using both deionized water (DIW) and seawater. The DIW experiments

* Corresponding author. Tel.: +1 305 348 3119; fax: +1 305 348 3877.

E-mail address: pricer@fiu.edu (R.M. Price).¹ Present address: Broward Community College, Broward County, FL, United States.² Present address: Institute of Geophysics, Swiss Federal Institute of Technology (ETH) Zurich, Switzerland.

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 $\mu\text{mol/L}$, 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 have often been 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.

2. Methods and materials

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 and 138 ka ago during the Sangamon interglacial (Hoffmeister, 1974). The formation is composed of about 30% coral skeleton and 70% interstitial calcarenite (Stanley, 1966). Most but not all of the original aragonite has been dissolved and replaced by calcite (Stanley, 1966). The Key Largo limestone is a member of the Biscayne Aquifer in south Florida (Parker et al., 1955). Limestone core collected from the upper 6 m of the Biscayne Aquifer contained on average 2 $\mu\text{g/g}$ of loosely adsorbed P as determined by extraction in a 1 M solution of MgCl (Price unpublished data). Approximately 35 $\mu\text{g/g}$ of P was obtained from the same limestone samples when completely dissolved in 1 N HCl.

The limestone block used in this study was dominantly composed of the interstitial calcarenite and has been described in detail by DiFrenna et al. (2008). The hydrologic properties of the limestone cube were previously identified, 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 L.

Stock solutions of P (1 mM) 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 $\mu\text{mol/L}$ using NaCl (Fisher Scientific). The seawater was collected from the Gulf Stream just offshore of Key Largo, Florida and filtered through a 0.45 μm filter. The 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 $\mu\text{mol kg}^{-1}$ (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 $\mu\text{mol/L}$ 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 20–60 L of PO_4^{3-} -containing DIW were used. The PO_4^{3-} concentrations in these experiments 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 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/h. The second phase (phase II) of the experiments consisted of alternating between Gulf Stream seawater and DIW containing 8 $\mu\text{mol/L}$ and 0 $\mu\text{mol/L}$ of PO_4^{3-} (Table 1). These tests along with those in phase III were conducted at a slightly higher head difference of 60–75 mm (hydraulic gradient of 0.3) with a discharge rate of 2.1 L/h. 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 liter for PO_4^{3-} analysis. Concentration of PO_4^{3-} was determined on a spectrophotometer with a method detection limit of 0.02 $\mu\text{mol/L}$. 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

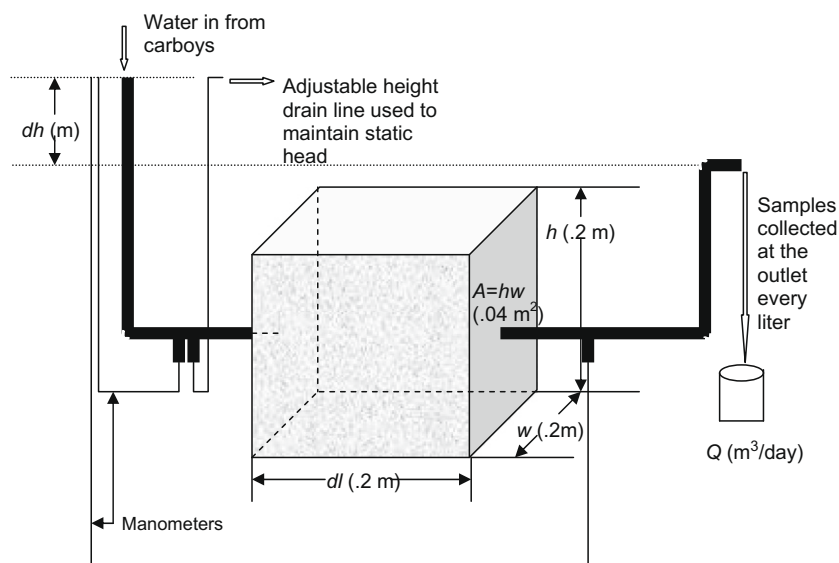


Fig. 1. Experimental apparatus used for adsorption/desorption experiments. Figure originally published in DiFrenna et al. (2008) and used here with kind permission of Springer Science & Business Media.

Table 1Mass of PO_4^{3-} adsorbed relative to inputs in deionized water (DIW) and seawater (SW) matrix as determined in the phases I–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)	Cumulative mass of PO_4^{3-} adsorbed (μmoles)
<i>Phase I</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
<i>Phase II</i>					
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
<i>Phase III</i>					
DIW	36	0	0.00	23.3	1438.1
SW	60	0	0.00	219	1219.1

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 the HCO_3^- and CO_3^{2-} 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.

3. Results

3.1. Adsorption of phosphate in DIW

When concentrations of 1–5 $\mu\text{mol/L}$ with 57 L of DIW were discharged through the limestone all of the introduced PO_4^{3-} was adsorbed (Table 1). As the PO_4^{3-} concentration increased in the DIW to 8 $\mu\text{mol/L}$, detectable concentrations of PO_4^{3-} were observed in the first 1 L discharged from the limestone (Fig. 2). The ratio of the input concentration to the output concentration of PO_4^{3-} ($C_{\text{in}}/C_{\text{out}}$) increased quickly to 0.1 within 3 L of discharge, and then increased slowly throughout the remaining 45 L to just over 0.2 (Fig. 2). The final concentration of P discharged from the limestone was 1.9 $\mu\text{mol/L}$. 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 $\mu\text{mol/L}$, PO_4^{3-} was detected in the first liter discharged, and the PO_4^{3-} ratio increased slowly to near 0.45 for the remaining 45 L (Fig. 2). The final P concentration was 9 $\mu\text{mol/L}$. 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.

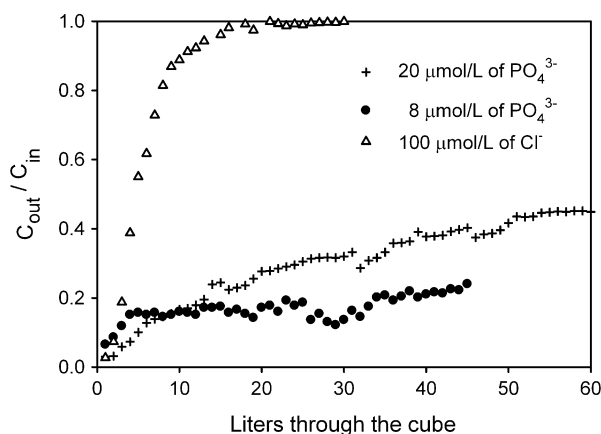


Fig. 2. The effect of increase of PO_4^{3-} concentrations from 8 to 20 $\mu\text{mol/L}$ in DIW on the adsorption of PO_4^{3-} on limestone as compared to 100 $\mu\text{mol/L}$ of Cl^- . The ratio $C_{\text{in}}/C_{\text{out}}$ represents the input concentration to the output concentration of PO_4^{3-} or Cl^- .

3.2. 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 $\mu\text{mol/L}$ 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 L (Fig. 3), corresponding to a salinity increase from 0 to 30 psu (Fig. 3). For the next 6 L the salinity increased from 30 to 33.6 and the $C_{\text{in}}/C_{\text{out}}$ of PO_4^{3-} exceeded that for salinity (Fig. 3). For the remainder of the experiment, salinity increased to 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-} discharged was 6.7 $\mu\text{mol/L}$. 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 $\mu\text{mol/L}$ (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 PO_4^{3-} (Table 1). During these flushes, an additional 150 μmoles of PO_4^{3-}

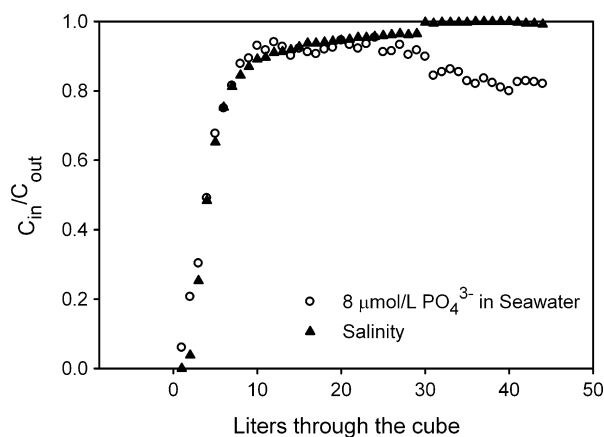


Fig. 3. Comparison of the ratio C_{in}/C_{out} for $8 \mu\text{mol/L}$ of PO_4^{3-} in Gulf Stream seawater compared to salinity.

were desorbed. As a final test to determine if the adsorption sites on the limestone were close to being filled, DIW containing $8 \mu\text{mol/L}$ was input to the stone as the final experiment of phase II. During this last test, $299 \mu\text{moles}$ 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.

3.3. 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 $1.5 \mu\text{mol/L}$ but then decreased to $0.3 \mu\text{mol/L}$ in 30 L (Fig. 4). In the subsequent flushing with blank seawater, significantly more PO_4^{3-} , with concentrations ranging from 2 to $5 \mu\text{mol/L}$, was released from the limestone. A total of $219 \mu\text{moles}$ of PO_4^{3-} was desorbed from the limestone by the Gulf Stream seawater as compared to $23 \mu\text{moles}$ with the DIW (Table 1).

3.4. 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. Through-

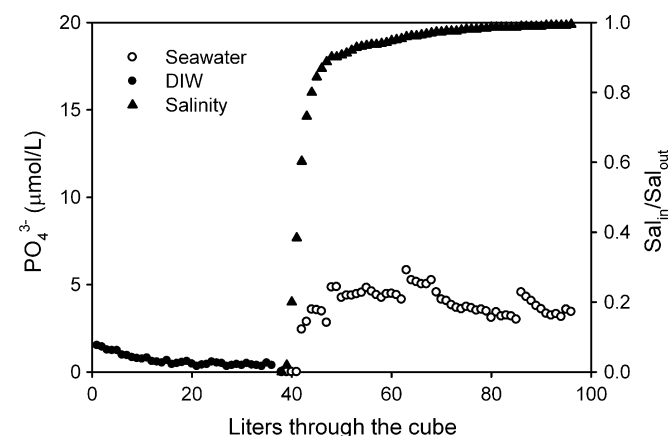


Fig. 4. Desorbed PO_4^{3-} ($\mu\text{mol/L}$) measured in blank DIW and Gulf Stream seawater. The C_{in}/C_{out} ratio for salinity ($\text{Sal}_{in}/\text{Sal}_{out}$) is compared on the second y-axis.

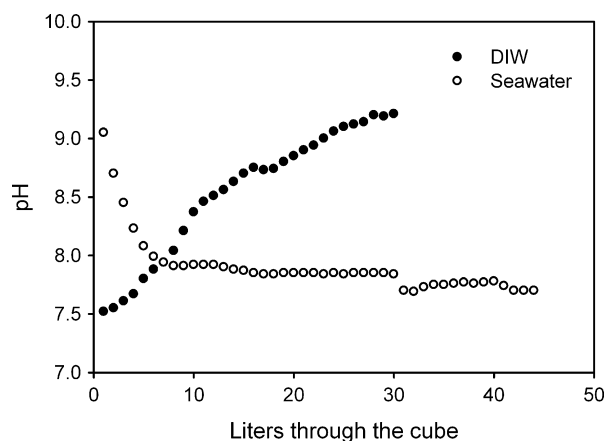


Fig. 5. Variation in pH between the DIW and Gulf Stream seawater experiments.

out the experiments using DIW, the pH increased in the discharge water to values greater than 9 (Fig. 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 (Fig. 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 (Figs. 6–8). The dashed line on the plots represents the theoretical mixing between the DIW and seawater. Concentrations of Mg^{2+} were found to be enriched in most of the seawater samples containing P (Fig. 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 4–8 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 (Fig. 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

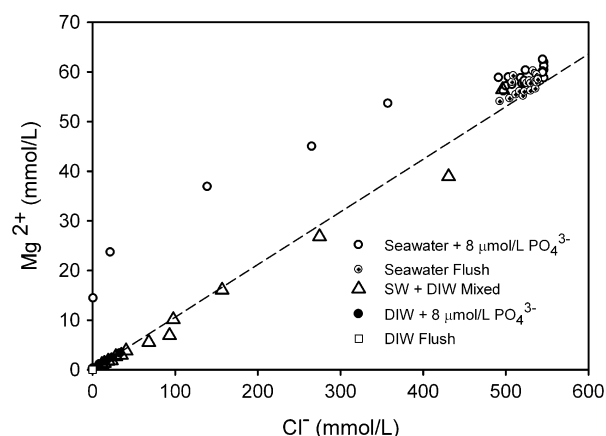


Fig. 6. Magnesium concentrations versus chloride in DIW, seawater, and mixtures of seawater and DIW.

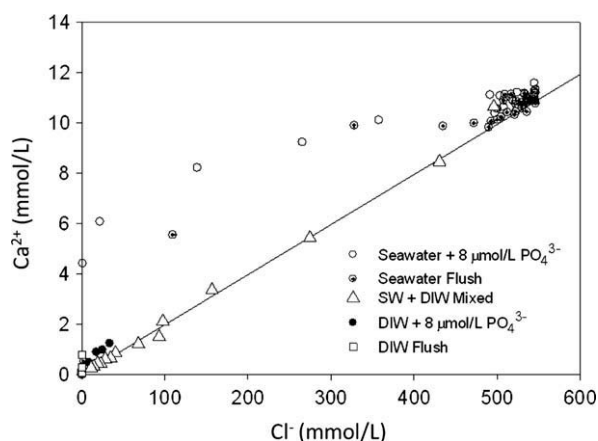


Fig. 7. Calcium concentrations versus chloride in DIW, seawater, and mixtures of seawater and DIW.

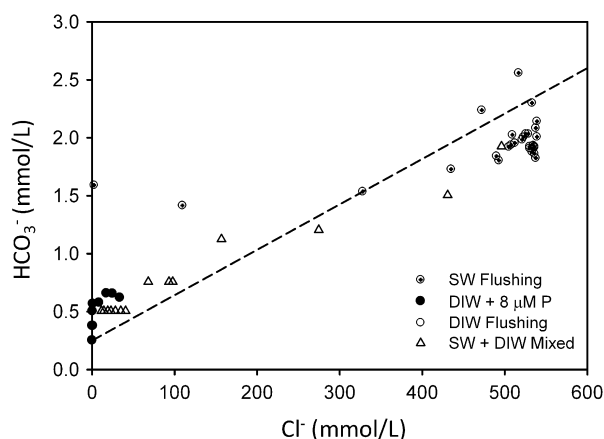


Fig. 8. Bicarbonate concentrations versus chloride in DIW, seawater, and mixtures of seawater and DIW.

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 (Fig. 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 (Fig. 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 CO_2 (Fig. 8).

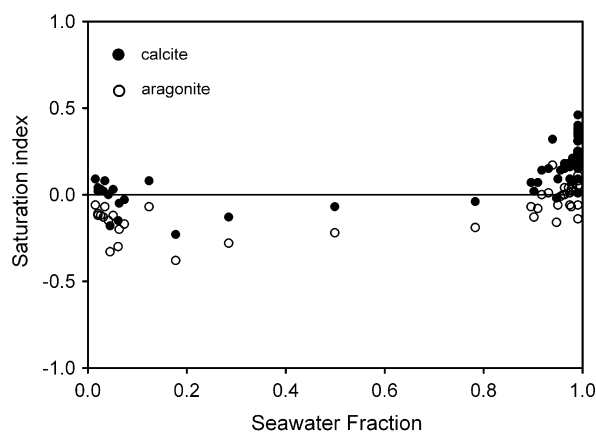


Fig. 9. Saturation indices of calcite and aragonite with respect to mixing seawater and DIW water.

4. Discussion

4.1. 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 P (TP) concentrations in south Florida rainfall averaged 0.3 $\mu\text{mol/L}$. 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 $\mu\text{mol/L}$ (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 μM added to low salinity (<5) wastewater and then injected into the Key Largo limestone aquifer was removed from solution within 5 m of the injection site in 20–50 h.

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 CaCO_3 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 and 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 percentage 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 CaCO_3 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.

4.2. 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 and 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 CaCO_3 was greater in seawater as compared to the DIW (Figs. 7 and 8). The dissolution of CaCO_3 would be expected to release adsorbed PO_4^{3-} 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 increases 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 0–28, was greater than expected for dissolution of a low-Mg 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 C in mixing zone groundwaters has been previously explained by an outgassing of CO_2 across the water table (Price and Herman, 1991). 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 $C_{\text{in}}/C_{\text{out}}$ 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 33.6–36.5 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 the 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 limited PO_4^{3-} adsorption. The overall results of the 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 CaCO_3 dissolution, and at higher salinity (30–33 psu) due to competition with HCO_3^- for adsorption sites. At salinity values greater than 33 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 cannot 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 $\mu\text{mol/L}$ dissolved in low salinity (<5 psu) wastewater (that was originally groundwater) injected into the Key Largo limestone aquifer was removed from solution, most likely by adsorption, within 5 m of the injection site in 20–50 h. The results of their experiments are similar to those

described here 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 P (TP) ranging from 1 to 2.5 $\mu\text{mol/L}$ 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 $\mu\text{mol/L}$. The TP values observed by Price et al. (2006) are similar to the PO_4^{3-} values of 2–3.5 $\mu\text{mol/L}$ 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 $\mu\text{mol/L}$ (Corbett et al., 2000; Fourqurean et al., 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 the experiments.

Furthermore, the 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. The 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 479.

References

- Ahn, H., James, R.T., 2001. Variability, uncertainty, and sensitivity of phosphorus deposition load estimates in south Florida. *Water Air Soil Pollut.* 126, 37–51.
- Back, W., Hanshaw, B.B., Herman, J.S., 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., Fourqurean, J.W., Jones, R.D., 1999. Seasonal and long-term trends in water quality of Florida Bay (1989–1997). *Estuaries* 22, 417–430.
- Corbett, R., Kump, L., Dillon, K., Burnett, W.C., Chanton, J., 2000. Fate of wastewater-borne nutrients under low discharge conditions in the subsurface of the Florida Keys. *USA. Mar. Chem.* 69, 99–115.
- Cunningham, K.J., Renken, R.A., Wacker, M.A., Zygnerski, M.R., Robinson, E., Shapiro, A.M., 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: Harmon, R.S., Wicks, C. (Eds.), *Perspectives on Karst Geomorphology, Hydrology, and Geochemistry – A Tribute Volume to Derek C. Ford and William B. White*. *Geol. Soc. Am. Special Paper* 404, pp. 191–208.
- DiFrenna, V.J., Price, R.M., Savabi, M.R., 2008. Identification of a hydrodynamic threshold in karst rocks from the Biscayne Aquifer, south Florida, USA. *Hydrogeol. J.* 16, 31–42.
- Fourqurean, J.W., Zieman, J.C., 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*. *Limnol. Oceanogr.* 37, 162–171.
- Gaiser, E.E., Zafiris, A., Ruiz, P.L., Tobias, F.A.C., Ross, M.S., 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.
- Lopez, P., Lluch, X., Vidal, M., Morgu, J.A., 1996. Adsorption of phosphorus on sediment of the Balearic Islands (Spain) related to their composition. *Estuar Coast. Shelf Sci.* 42, 185–196.
- Millero, F., Huang, F., Zhu, X., Liu, X., Zhang, J.-Z., 2001. Adsorption and desorption of phosphate on calcite and aragonite in seawater. *Aquat. Geochem.* 7, 33–56.
- Moore, W.S., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature* 380, 612–614.
- Parker G.G., Gerguson, G.E., Love, S.K., et al., 1955. Water resources of southeastern Florida with special reference to geology and groundwater of the Miami areas. US Geol. Surv. Water Supply Paper 1255.
- Parkhurst, D.L., 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. US Geol. Surv. Water-Resour. Invest. Rep. 99-4259.
- Plummer, L.N., Vacher, H.L., Mackenzie, F.T., Bricker, O.P., Land, L.S., 1976. Hydrogeochemistry of Bermuda: a case history of ground-water diagenesis of biocalcarenes. *Geol. Soc. Am. Bull.* 87, 1301–1316.
- Price, R.M., 2001. Geochemical investigation of groundwater and surface water flow in Everglades National Park. Ph.D. Dissertation, Univ. Miami.
- Price, R.M., Herman, J.S., 1991. Geochemical investigation of salt water intrusion into a coastal carbonate aquifer: Mallorca, Spain. *Geol. Soc. Am. Bull.* 103, 1270–1279.
- Price, R.M., Swart, P.K., 2006. Geochemical indicators of groundwater recharge in the surficial aquifer system: Everglades National Park, Florida, USA. In: Harmon, R.S., Wicks, D. (Eds.), *Perspectives on Karst Geomorphology, Hydrology, and Geochemistry – A Tribute Volume to Derek C. Ford and William B. White*. *Geol. Soc. Am. Special Paper* 404, pp. 251–266.
- Price, R.M., Swart, P.K., 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. In: 2008 Florida Bay and Adjacent Marine Systems. Science Conf., Program and Abstract Book, Naples, Florida, USA, pp. 145–146.
- Reddy, K.R., Diaz, O.A., Scinto, L.J., Agami, M., 1995. Phosphorus dynamics in selected wetlands and streams of the Lake Okeechobee Basin. *Ecol. Eng.* 5, 183–207.
- Ross, M.S., O'Brien, J.J., Sternberg, L., 1994. Sea-level rise and the reduction in pine forests in the Florida Keys. *Ecol. Appl.* 4, 144–156.
- Sayles, F.L., Mangelsdorf, P.C., 1977. The equilibrium of clay minerals with sea water: exchange reactions. *Geochim. Cosmochim. Acta* 41, 951–960.
- Simmons, G.M., 1992. Importance of submarine groundwater discharge (SGWD) and seawater cycling to material flux across sediment/water interfaces in marine environments. *Mar. Ecol. Prog. Ser.* 84, 173–184.
- Sivan, O., Yechieli, Y., Herut, B., Lazar, B., 2005. Geochemical evolution and timescale of seawater intrusion into the coastal aquifer of Israel. *Geochim. Cosmochim. Acta* 69, 579–592.
- Stanley, S.M., 1966. Paleogeology and diagenesis of Key Largo limestone, Florida. *Am. Assoc. Petrol. Geol. Bull.* 50, 1927–1947.
- Stoessel, R.K., Moore, Y.H., 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., Morgan, J.J., 1981. *Aquatic Chemistry*, second ed. John Wiley & Sons, New York.
- Wanless, H.R., Parkinson, R.W., Tedesco, L.P., 1994. Sea level control on stability of Everglades wetlands. In: Davis, S.M., Ogden, J.C. (Eds.), *Everglades: the Ecosystem and its Restoration*. Lucie Press, pp. 199–222.
- 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., Jee, J.L., 1995. Water–rock interactions in a modern coastal mixing zone. *Geol. Soc. Am. Bull.* 107, 1023–1032.
- Zhou, M., Li, Y., 2001. Phosphorus-sorption characteristics of calcareous soils and limestone from the southern Everglades and Adjacent Farmlands. *Soil Sci. Soc. Am. J.* 65, 1404–1412.