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GROUNDWATER GEOCHEMISTRY OF ISLA DE MONA, PUERTO RICO

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In this study, we explore the differences between the hydrogeochemical processes observed in a setting that is open to input from the land surface and in a setting that is closed with respect to input from the land surface. The closed setting was a water-filled passage in a cave. Samples of groundwater and of a solid that appeared to be suspended in the relatively fresh region of saline-freshwater mixing zone were collected. The solid was determined to be aragonite. Based on the analyses of the composition and saturation state of the groundwater, the mixing of fresh and saline water and precipitation of aragonite are the controlling geochemical processes in this mixing zone. We found no evidence of sulfate reduction. Thus, this mixing zone is similar to that observed in Caleta Xel Ha, Quintana Roo, also a system that is closed with respect to input from the land surface.

The open setting was an unconfined aquifer underlying the coastal plain along which four hand-dug wells are located. Two wells are at the downgradient ends of inferred flowpaths and one is along a flowpath. The composition of the groundwater in the downgradient wells is sulfide-rich and brackish. In contrast, at the well located along a flow line, the groundwater is oxygenated and brackish. All groundwater is oversaturated with respect to calcite, aragonite, and dolomite. The composition is attributed to mixing of fresh and saline groundwater, CO_2 outgassing, and sulfate reduction. This mixing zone is geochemically similar to that observed in blue holes and cenotes.

In coastal carbonate aquifers, the saline-freshwater mixing zone is an area of enhanced calcite dissolution, aragonite neomorphism, and dolomitization (Back *et al.* 1979; Randazzo & Bloom 1985; Randazzo & Cook 1987; Smart *et al.* 1988; Budd 1988; Stoessell *et al.* 1989; Whitaker *et al.* 1994). The water-rock interactions that occur in the mixing zone can lead to changes in the chemical composition of the groundwater, the mineralogical composition of the bedrock, and the porosity and permeability of the aquifer. Summarizing the geochemical reactions in saline-freshwater mixing zones and their role in the evolution of carbonate-aquifer systems, Hanshaw and Back (1980) conclude that mineral dissolution and precipitation in the mixing zone could enhance, or at least redistribute, porosity and permeability.

Physical heterogeneities, such as cenotes, blue holes, and caves, are common on the low-lying carbonate islands of the Caribbean. These features can be flooded by fresh, brackish, or saline water. Cenotes and blue holes are collapse depressions that are directly open to the earth's surface, thus rainfall and detritus can enter cenotes and blue holes directly (Mylroie *et al.* 1995, Ford & Williams 1989). A subaqueous cave passage has a roof and is not as open to the earth's surface as are cenotes or blue holes. Therefore, subaqueous cave passages probably do not directly receive rainfall or detritus material inputs.

In a series of studies of the blue holes of Andros Island, Bahamas, Smart *et al.* (1988) and Bottrell *et al.* (1991) demonstrated that pervasive dissolution of carbonate wall rock was driven by mixing of fresh and saline groundwater and by bacterial processes. Organic matter was observed suspended on the saline-freshwater interface. In detailed studies of the cenotes and blue holes in the Yucatan, Stoessell *et al.* (1993) found that dissolution was enhanced by bacterial-driven processes. It seems that in cenotes and blue holes that are open to the earth's surface, bacterial reactions influence processes within the mixing zone.

From detailed sampling along a subaqueous cave passage, Back *et al.* (1986) determined that mixing of fresh and saline groundwater in the Yucatan Peninsula resulted in dissolution of the carbonate bedrock and the development of caves and crescent-shaped beaches. Three of the five groundwater samples collected from a cave system were in equilibrium with respect to aragonite (Back *et al.* 1986). Subsequently, Stoessell *et al.* (1989) showed that aragonite was dissolved in the Xcaret Cave. In the studies based on the Xcaret Cave, no mention of bacterial-driven processes is given. In subaqueous cave passages, bacterial processes appear to be of minor importance.

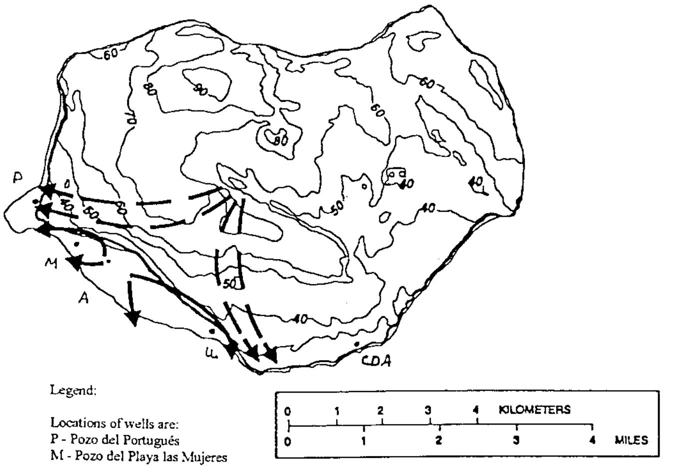
In our study, we explore the contrasts between the hydrogeochemical processes observed in open and closed settings and seek a better understanding of the controls on the geochemical processes that occur in these two distinct settings. In this study, we document the mixing and geochemical processes that control the composition of groundwater in the saline-freshwater mixing zone on Isla de Mona, Puerto Rico.

FIELD SITE DESCRIPTION

Descriptions of the geologic setting and history of Isla de Mona are found in Frank *et al.* (1998), Ruiz (1993), and Kaye (1959). Frank *et al.* (1998) includes a map showing the location of the island in the Caribbean.

COASTAL PLAIN AREA

Access to the water table is limited to hand-dug wells (Pozo del Aeropuerto, Pozo del Playa las Mujeres, Pozo del Portugués, and Pozo de Playa del Uvero) located along the coastal plain (Fig. 1). The wells intersect carbonate sand and reef deposits (Jordan 1973). The description of the configuration of the water table is based the results of a geophysical survey (TEM and TC) on the island (Richards *et al.* 1998; Richards *et al.* 1995; Martinez *et al.* 1995). A groundwater mound exists near the center of the coastal plain and flowpaths were constructed from the groundwater mound outward in all directions (Martinez *et al.* 1995) (Fig. 1). Where the coastal plain abuts the meseta, Martinez *et al.* (1995) have constructed flowpaths that originate under the meseta and divert around the coastal plain. This behavior was attributed to the lower permeability of coastal plain sediments compared to the permeability of the karstified rocks of the meseta. Thus, the coastal plain sediments are thought to act as a barrier preventing groundwater flow from the plateau to the coastal plain (Martinez *et al.* 1995). Vacher (1978) and Wallis *et al.* (1991) report that regions with different hydraulic conductivity influence the shape and position of the freshwater lens. The vegetation of the coastal plain consists of a coastal lowland forest and mahogany plantation, which form closed canopies, and a Casuarai plantation, which has an open canopy (Cintron & Rogers 1991).



Legend:

Locations of wells are:
P - Pozo del Portugués
M - Pozo del Playa las Mujeres
A - Pozo del Aeropuerto
U - Pozo de Playa del Uvero

Location of Cueva del Agua (Punta Los Ingleses) is CDA.

Contours are in meters above sea level.
Inferred flowpaths are shown as bold dashed arrows.

Figure 1. Map of Isla de Mona, Puerto Rico, located in the Mona Passage midway between Puerto Rico and Hispaniola showing the coastal plain that is along the southern and southwestern edge of the plateau. The sampling locations are noted. Flowpaths are based on the work by Martinez *et al.* (1995) and Richards *et al.* (1995).

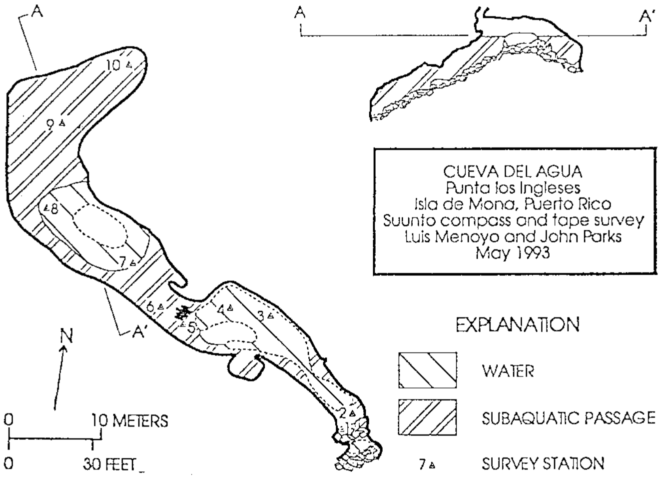


Figure 2. Map of Cueva de Agua (Punta Los Ingleses).

MESETA AREA

Access to the water table is limited to Cueva de Agua (Punta los Ingleses) that penetrates through Mio-Pliocene carbonates (Frank 1993) (Fig. 1). This cave is thought to have formed during the substage 5-e sea level highstand about 125 Ka (Frank *et al.* 1998). The cave has been referred to as Cueva de Agua Playa Brava in Nieves-Rivera *et al.* (1995). The main cave passage extends into the island and under the meseta. The cave passage is generally flat-lying with a series of air bells (Fig. 2). There is one steeply sloping passage located toward the seaward edge of the cave where the saline-freshwater mixing zone is intersected. Groundwater flow is outward from the central portion of the meseta (Richards *et al. 1*998; Richards *et al.* 1995; Martinez *et al.* 1995) (Fig. 1). About 94% of the meseta is covered with a dry forest and shrublands, which is an open association of shrubby trees (Cintron & Rogers 1991). Soil coverage is greater along the western portion of the meseta than along the eastern portion of the meseta (Briggs & Seiders 1972). Along the eastern portion and overlying Cueva de Agua (Punta los Ingleses), the meseta surface is either exposed bare rock or covered with cacti (Briggs & Seiders 1972; Frank *et al.* 1998).

METHODS

Samples of groundwater were collected from the wells along the coastal plain in May 1992, May 1993, and June 1994, from the Caribbean in May 1993, and from Cueva de Agua (Punta los Ingleses) in May 1993 and June 1994. The amount of precipitation delivered to Isla de Mona during the months of the sampling trips were 30, 11, and 3 cm in May 1992, May 1993, and June 1994, respectively (NOAA 1996).

Table 1. The chemical composition (in mmol/L, mixing ratio (MR), specific conductance (Cond, µS/cm), dissolved oxygen concentration (DO, in mg/L), sulfide concentration (H_2S, mg/L), log of the partial pressure of CO_2, and saturation indices with respect to calcite (SI_c), aragonite (SI_a) and dolomite (SI_d) of the groundwater collected from Isla de Mona, Puerto Rico.

	depth	cond	pH	MR[1]	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	DO[3]	H_2S	$logCO_2$[2]	SI_c	SI_a	SI_d
1993																	
Cueva del Agau																	
5	2.0	5000	7.37	0.00	82.	2.8	5.07	3.4	8.6	67.	1.5	7.	0	-1.97	0.20	0.06	1.00
7	4.0	6100	7.32	0.03	96.	4.2	5.16	3.7	10.	78.	1.8	6.	0	-1.92	0.17	0.03	1.00
6	6.0	8200	7.24	0.14	150.	6.3	4.95	5.2	16.	120.	3.1	7.	0	-1.88	0.14	0.02	1.00
3	8.0	11000	7.29	0.23	200.	8.5	4.77	5.4	19.	170.	3.3	6.	0	-1.96	0.14	0.00	1.02
2	10.0	18000	7.27	0.44	310.	16.	3.70	8.5	35.	260.	6.4	4.	0	-2.09	0.12	-0.02	1.10
4	12.0	24500	7.30	0.62	400.	20.	3.20	10.	43.	330.	8.4	4.	0	-2.21	0.13	0.00	1.10
1	14.0	47000	7.21	0.86	520.	24.	2.64	13.	56.	430.	10.	4.	0	-2.22	.02	-0.12	0.90
SW[1]	33.7‰[2]		8.24	1.00	592.	31.3	3.54	14.0	66.	480.	13.	8.	0	-3.25	1.06	0.92	2.99
1994																	
Cueva del Agau																	
1	1.21	8200	7.33	0.00	68.	3.1	5.11	3.4	7.2	45.	1.5	4.	0	-1.92	0.20	0.05	0.88
2	2.74	10200	7.30	0.03	81.	3.9	5.15	3.8	9.8	150.	1.7	6.	0				
6	5.79	15000	7.22	0.16	150.	6.7	5.07	4.6	14.	92.	1.9	4.	0				
5	4.27	16500	7.23	0.17	150.	8.0	5.02	5.0	15.	101.	2.2	6.	0	-1.86	0.11	-0.03	0.88
4	7.62	27400	7.21	0.42	260.	13.	4.20	8.5	27.	181.	5.1	2.	0	-1.96	0.14	0.00	0.96
7	9.14	44500	7.28	0.95	500.	26.	1.25	12.	44.	460.	9.5	1.	0	-2.63	-0.28	-0.42	0.18
3	10.4	45200	7.24	0.99	520.	26.	2.55	12.	46:	440.	9.8	1.	0	-2.27	0.00	-0.14	0.77
1992																	
Pozo																	
Aeropuerto	nd	1400	7.54	0.00	8.7	0.49	4.09	1.4	1.5	7.0	0.25	4.8	0	-2.20	0.15	0.10	0.49
Portugues-u[3]	nd	2300	7.32	0.04	31.	1.9	3.77	2.1	3.2	29.	1.9	3.1	0	-2.00	-0.05	-0.19	0.06
Portugues-u[3]	nd	4300	7.24	0.02	16.	1.0	4.10	1.8	1.9	14.	0.31	2.7	0	-1.90	-0.12	-0.26	0.10
Portugues-u[3]	nd	3200	7.26	0.02	24.	1.5	4.92	2.5	2.6	2.0	0.31	1.6	0	-1.80	0.11	-0.03	0.40
Uvero	nd	3250	7.53	0.02	21.	2.0	5.25	2.4	2.8	19.	1.4	3.8	1	-2.10	0.37	0.23	0.99
1993																	
Aeropuerto	2.80	3170	7.43	0.02	20.	1.0	7.54	2.8	3.6	17.	0.38	0.4	0	-1.80	0.53	0.39	1.40
Portugues-1[4]	1.34	2430	7.63	0.02	19.	1.1	4.10	1.9	2.1	17.	0.41	1.0	0	-2.30	0.34	0.20	0.91
Portugues-2	1.70	3250	7.59	0.02	20.	1.0	3.77	2.0	2.3	17.	0.41	0.8	0	-2.30	0.24	0.10	0.71
Uvero	nd	5‰[2]	7.63	0.11	73.	3.0	8.03	5.0	7.8	56.	2.2	<0.2	1	-2.00	0.83	0.69	2.00
1994																	
Aeropuerto	2.61	4150	7.65	0.03	25.	1.0	9.18	3.3	3.7	15.4	0.31	1.0	0	-1.95	0.87	0.73	2.00
Portugues-1	1.10	2900	7.36	0.01	48.2	2.17	4.10	2.89	4.59	21.3	0.28	1.0	0	-2.10	-0.18	-0.33	-0.25
Portugues-2	1.71	6000	7.34	0.07	16.6	18.7	3.68	2.36	2.28	49.6	0.29	0.8	0	-2.00	0.12	-0.02	0.62
Mujeres	1.20	15200	7.85	0.19	118.	1.0	11.1	5.67	13.6	75.5	1.8	<0.2	1	-2.10	1.20	1.0	2.92
Uvero[5]	2.25	12500	7.72	0.20	119.	4.45	88.	1.61	7.4	12.4	0.15			-2.09	1.06	0.92	2.53

1. SW is Caribbean seawater
2. Salinity is reported instead of conductivity.
3. Sampled several times during rain event on 5-22-93 at 10am (1), on 5-22-93 at 12 pm (2), and on 5-25-93 at 11 am (3).
4. Pozo del Portugues is often stratified. Samples collected from the upper water body are number 1 and those from the lower water body are number 2.
5. Represents an average composition of samples collected hourly over a 26-hour period.

All samples of water were filtered and split for subsequent analyzes of cations (acidified to pH < 2) and anions. Due to the remoteness of Isla de Mona, water samples could not be refrigerated. In the field, potentiometric titrations were performed for determination of bicarbonate alkalinity. The concentration of dissolved oxygen in each water sample was determined using a Hach® kit*. The temperature and conductivity of each groundwater were also measured. Upon return to the laboratory, the concentrations of calcium, magnesium, sodium, and potassium were determined by atomic absorption spectrophotometry, and the concentrations of chloride and sulfate were determined by ion chromatography. The total inorganic carbon content and the partial pressure of carbon dioxide were calculated using the numerical model, PHREEQE (Parkhurst *et al.* 1990). The quality of the chemical analyses was affirmed by fifty-one of the fifty-three samples having a charge balance error of less than 10% (Tables 1 & 2) and only those fifty-one samples were used in the interpretation of water-rock interactions.

Theoretical mixing calculations were performed based on a presumed linear relationship between the solute concentrations in the fresh endmember and the saline endmember. This relationship results from conservative mixing with all solutes remaining in solution, that is, with no mineral dissolution or precipitation reactions and no gas exchange. For the groundwater collected from the wells in the coastal plain, the freshest groundwater collected (Pozo del Aeropuerto sample collected in 1992) and Caribbean seawater were used as the fresh and saline endmembers, respectively (Table 1). For the water collected from Cueva de Agua (Punta los Ingleses), the freshest groundwater (CDA1-94 sample collected in 1994) and Caribbean seawater were used as the fresh and saline end-

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*The use of trade names in this article is for descriptive purposes only and does not imply endorsement by the University of Missouri or the U.S. Government.

Table 2. The mixing ratio(MR), the pH and calcium concentration in theoretical mixtures of fresh and saline endmembers (CDA1-94 and Seawater), the mass of aragonite that could be removed from each mixture at equilibrium with respect to aragonite (Δ), and the concentration of calcium of each mixture at equilibrium with respect to aragonite.

MR	Ca$^{2+}_{init}$ (mM)	Ca$^{2+}_{final}$ (mM)	Δ (mmol/kg)	pH$_{final}$
0	3.43	3.39	0.038	7.29
0.05	3.97	3.93	0.041	7.29
0.1	4.5	4.45	0.050	7.29
0.15	5.03	4.97	0.064	7.29
0.2	5.56	5.48	0.080	7.29
0.25	6.10	6.00	0.098	7.29
0.35	7.16	7.02	0.138	7.29
0.4	7.69	7.53	0.158	7.29
0.45	8.23	8.05	0.180	7.29
0.5	8.76	8.55	0.202	7.30
0.55	9.29	9.07	0.224	7.30
0.6	9.82	9.57	0.247	7.30
0.65	10.4	10.0	0.271	7.30
0.7	10.9	10.6	0.293	7.31
0.75	11.4	11.1	0.318	7.32
0.8	11.9	11.6	0.342	7.33
0.85	12.5	12.1	0.367	7.33
0.9	13.0	12.6	0.392	7.34
0.95	13.6	13.1	0.418	7.36
1	14.1	13.6	0.448	7.37

members, respectively. Concentrations of solutes observed in the groundwater were compared to concentrations predicted by theoretical mixing calculations based on the mixing ratio of each groundwater. The mixing ratio was calculated based on the chloride concentrations of the groundwater and of the fresh and saline endmembers (Plummer & Back 1980). Differences between the observed concentrations of solutes in the groundwater and the concentrations predicted based on theoretical mixing were attributed to sources or sinks for the various solutes (Plummer & Back 1980). For each groundwater and for each theoretical mixture, the saturation state of the sample with respect to calcite, aragonite, and dolomite were calculated using PHREEQE (Parkhurst *et al.* 1990). The saturation state of a groundwater was compared to the saturation state of a theoretical mixture with the same mixing ratio. The difference between the saturation state observed in the groundwater and the saturation state of the theoretical mixture was attributed to water-rock interactions (Plummer & Back 1980).

In theoretical calculations, the amount of mineral that could be dissolved (if the conservative mixture is undersaturated) or precipitated (if the conservative mixture is oversaturated) from a conservative mixture was calculated using PHREEQE (Parkhurst *et al.* 1990). By forcing a conservative mixture to equilibrium with respect to the specified mineral, the mass of mineral added to or removed from solution was calculated. The change in the concentration of Ca^{2+} and total inorganic carbon and of the pH in the conservative mixture as a result of the dissolution or precipitation was also calculated using PHREEQE (Parkhurst *et al.* 1990).

In December 1996, a Campbell CR10® data logger, which was equipped with Druck® pressure transducers and Campbell® conductivity and temperature probes, was installed at Pozo de Playa del Uvero to monitor the water level in the well and the temperature and conductivity of the groundwater. Also recorded was the tidal signal of the Caribbean. (Precipitation data from December 1996 were not available.) All sensors were sampled every second and averaged for 5 minutes. The 5 minute averages were recorded in the data logger. The tidal data were smoothed using a one-hour running average. Both the tidal data and the water-level response of Pozo de Playa del Uvero were normalized to the overall average of the entire set of data. We do not know the elevation of Pozo de Playa del Uvero relative to sea level. The data were reduced using a Fourier transform to determine the peak amplitude.

RESULTS

COASTAL PLAIN AREA

The composition of the groundwater from the coastal plain wells ranged from 1.5 to 19% seawater and represented a relatively fresh-water environment (Table 1). The concentration of dissolved oxygen in the groundwater ranged from 0.2 mg/L to 1.0 mg/L. On a Piper diagram, the composition of the groundwater falls within the Na-K-Cl-SO$_4$ field (Fig. 3) and the compositions cluster near the theoretical mixing line.

Most of the groundwater was oversaturated with respect to calcite, aragonite, and dolomite (Fig. 4). Over the limited range of mixing ratios that include samples from the wells, the theoretical mixing curves are basically flat. The saturation index (SI = log IAP/Kt) of most groundwater with respect to calcite, aragonite, and dolomite was greater than that predicted by theoretical mixing calculations.

The results from the December 1996 tidal monitoring showed that the depth to the water table exhibited a tidal cycle. The peak amplitudes of the water-level response and of the tidal data indicate both are 26.7 hours (Fig. 5). The tidal cycle response (peak amplitude of 26.7 hours) is also apparent in the temperature and conductivity data (Fig. 5). Based on the method and assumptions outlined in Erskine (1991), the ratio of storativity (specific yield) to the transmissivity of the aquifer is $5.2 \times 10^{-3} \pm 6.1 \times 10^{-3}$ day/m^2 (n = 28). Assuming a storativity of 0.01, the transmissivity would be 1.9×10^2 m^2/day.

MESETA AREA

The cave divers noted that a material appeared to be suspended in the water column along the flat-lying passage inland from the first air bell in Cueva de Agua (Punta los Ingleses) (Fig. 2). They collected samples of the material during the dive in May 1993. The samples were analyzed by XRD and

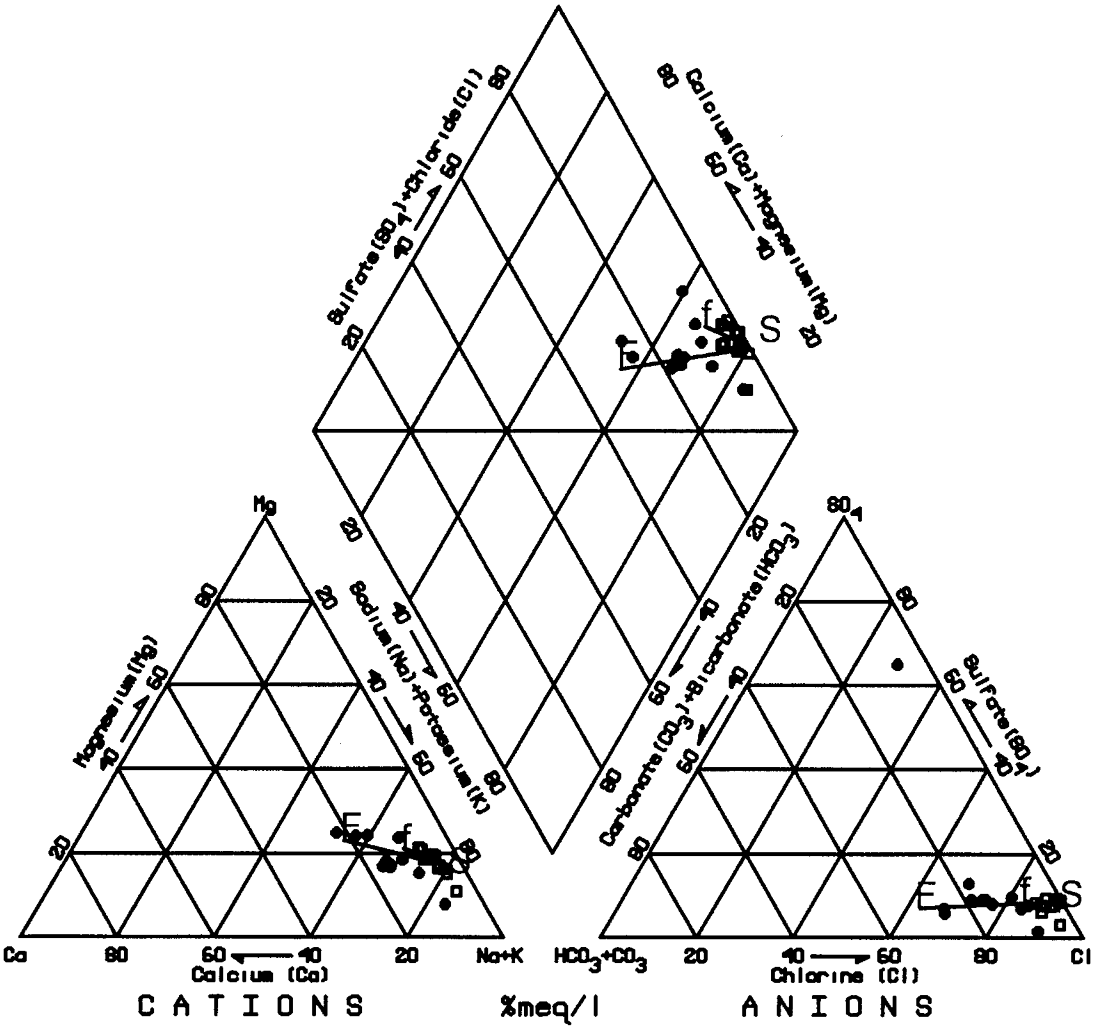

Figure 3. A piper diagram showing the composition of the groundwater. Observations from Cueva de Agua (Punta Los Ingleses) are plotted as hollow squares and from wells along the coastal plain as solid circles. The lines are theoretical mixing lines between the fresh and saline endmembers. The F, f, and S denote the composition of the fresh endmember for the coastal plain, the fresh endmember for Cueva de Agua (Punta Los Ingleses), and the saline endmember for both settings, respectively.

found to be aragonite (R. Deike, pers. comm. 1994).

Samples of groundwater were collected at different depths as the divers traversed from near the surface to the bottom of the cave along the steeply sloping passage (Fig. 2). The conductivity of the groundwater along the steeply sloping passage increased from 5000 µS/cm (measured 10 cm below the surface of the water) to 47000 µS/cm (measured 10 cm above the bottom of the cave) (Table 1). The concentration of dissolved oxygen in the groundwater ranged from 2 to 14 mg/L with the concentration decreasing as the salinity increased. The composition of the groundwater ranged from relatively fresh to nearly saline and closely matched the composition of the theoretical mixtures and, on a Piper diagram, cluster near the theoretical mixing line (Table 1 & Fig. 3). Some differences in observed compositions relative to the mixing line were noted, and they fell on either side of the line.

Most groundwater was in equilibrium with respect to aragonite and slightly oversaturated with respect to calcite up to a mixing ratio of 0.6 (Fig. 4). For mixing ratios greater than 0.8, the groundwater was undersaturated with respect to aragonite and approximately in equilibrium with respect to calcite. All groundwater was oversaturated with respect to dolomite. The saturation index of theoretical mixtures of fresh and saline endmembers with respect to aragonite, calcite, and dolomite increases as the mixing ratio increases. The observed saturation state of the water with respect to calcite, aragonite, and dolomite was less than that predicted by theoretical mixing calculations.

DISCUSSION

The groundwater geochemistry as observed on the island, and particularly underlying the coastal plain, may not reflect long-term conditions. The island was formerly known as a watering port and now, the water resources of the island are supplemented to provide drinking water for the few rangers that reside on the island. Further, the geochemistry is probably not representative of the chemistry of the water during the development of the unconfined aquifers or of the chemistry of the water during the development of the caves that ring the

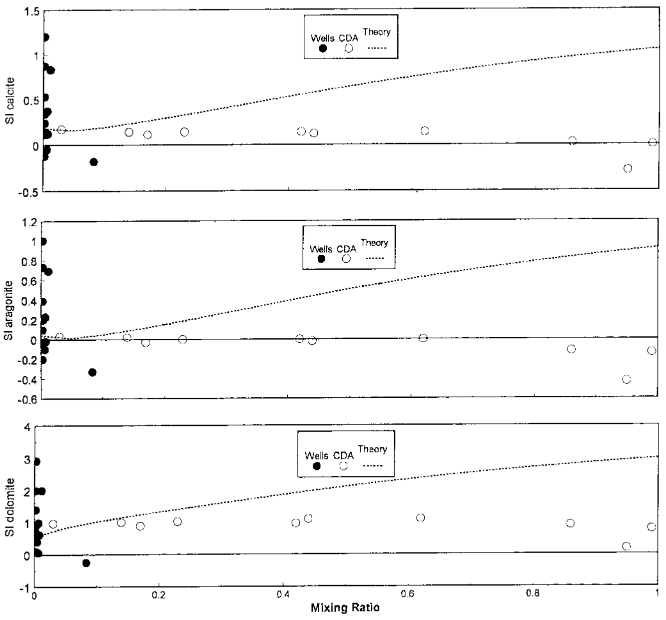

Figure 4. Graph of the saturation indices of the groundwater with respect to (a) calcite, (b) aragonite, and (c) dolomite plotted against the mixing ratio. Observations from Cueva de Agua (Punta Los Ingleses) are plotted as hollow circles and from the coastal plain as solid circles. The curves (dashed) are the theoretical mixing curves between the fresh and saline endmembers.

island. However, it does represent the conditions during the sampling events and probably current conditions.

COASTAL PLAIN AREA

The observed compositions and saturation states are consistent with an interpretation of mixing fresh and saline endmembers, outgassing of carbon dioxide, and reduction of sulfate to sulfide. We suggest that outgassing occurs from the surface of the water in the large-diameter open-bore hand-dug wells, and that results in sampled waters that are more oversaturated with respect to the carbonate minerals than predicted by conservative mixing alone (Fig. 4). These samples might not represent the composition of the groundwater due to the large open-bore nature of the wells. However, installation of sampling wells along the coastal plain was not feasible.

Changes in the chemistry of the groundwater were observed over tidal periods and over the three-year study period. The change in the composition of the groundwater at a particular well relative to the three sampling periods showed the influence of the yearly weather pattern on the composition (Table 1). In the wet year of 1992, the groundwater was the freshest observed and the chloride concentration of the groundwater collected at Pozo del Aeropuerto was 8.7 mM. Whereas, the concentration was 20 mM in 1993 (a normal precipitation year) and 24.5 mM in 1994 when there was a drought on Isla de Mona. These observed changes in the composition of the groundwater with annual fluctuations in precipitation suggest that a strong evaporative flux could change the composition of the water in the large-diameter open-bore wells. The correlation between the tidal fluctuation, the water level in the well, and the changes in the temperature and conductivity of the water allow us to conclude that tidal pumping is the cause of those changes. The coastal plain aquifer appears to be transmissive and to respond to changing hydrological boundary conditions (tidal and evaporative) readily.

MESETA AREA

The chemical composition of the groundwater was closely matched by theoretical mixing alone (Fig. 3), whereas the saturation states of the groundwater were not accurately reproduced by theoretical mixing alone (Fig. 4). Theoretically, all mixtures are oversaturated with respect to aragonite (Fig. 4). However, the saturation state of the groundwater is in equilibrium with respect to aragonite (Fig. 4). These two interpretations suggest that aragonite has precipitated from the ground-

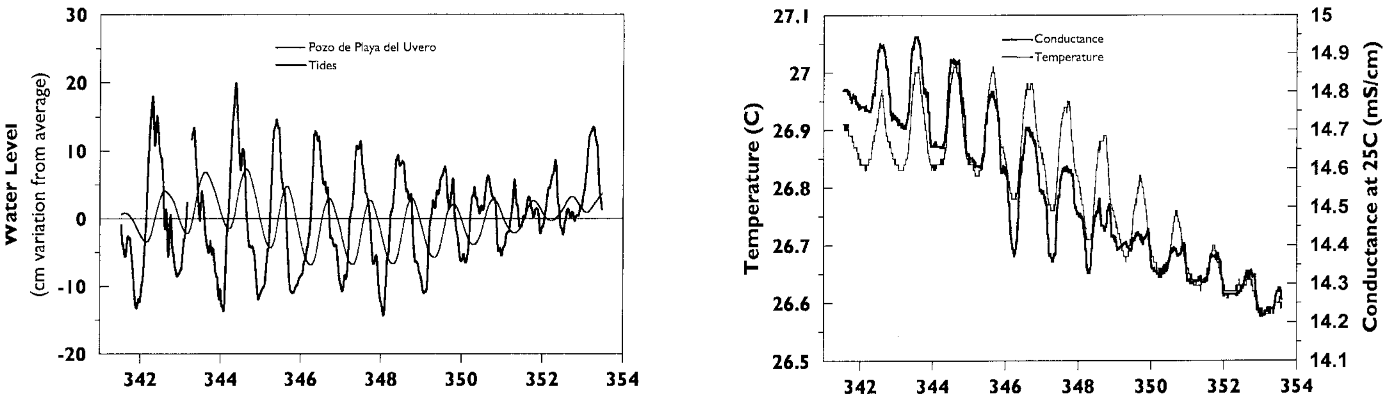

Figure 5. Graph of the results of the tidal monitoring effort of December 1996 showing (a) the response of the tides and the elevation of the water table and (b) the conductivity and temperature of the groundwater.

water in Cueva de Agua (Punta los Ingleses). However, if aragonite had precipitated from the groundwater in the cave, the composition of the water should have been depleted in calcium and total inorganic carbon relative to theoretical mixing. This was not observed (Fig. 3).

This discrepancy can be understood using geochemical modeling. Based on mixing of the fresh and saline endmembers, the mass of aragonite that would be precipitated from a theoretical mixture and the resultant composition of that mixture were calculated using PHREEQE (Parkhurst *et al.* 1990). The mass of aragonite could be theoretically precipitated ranged from 0.038 to 0.448 mmol/kg (Table 2). Precipitation of that amount of aragonite from a mixture results in a proportional change in the concentration of calcium in that mixture (Table 2). A loss of 0.038 mmol/L of calcium from the fresher groundwaters and of 0.448 mmol/L of calcium from the more saline groundwaters in the Cueva de Agua (Punta los Ingleses) represents a loss of two to three percent of the calcium in the groundwaters (Table 1). A 3-4% deviation in the composition of the groundwater is within the charge-balance error and is therefore not detectable.

The pH of the mixtures that were forced to equilibrium with respect to aragonite ranged from 7.29 to 7.37 (Table 2). The pH of the groundwater in Cueva de Agua (Punta los Ingleses) ranged from 7.21 to 7.37 (Table 1). The agreement between the expected pH of the mixtures in equilibrium with respect to aragonite and the measured pH of the groundwater supports the idea that aragonite has precipitated within the mixing zone in Cueva de Agua (Punta los Ingleses).

In Cueva de Agua (Punta los Ingleses), it appears that the saturation state of the groundwater is a more sensitive indicator of water-rock interactions than is the composition of the groundwater. Stoessell *et al.* (1989) also concluded that the saturation state of the groundwater was a more sensitive indicator of water-rock interactions based on their results from the Yucatan Peninsula. The composition of the saline-freshwater mixing zone underlying the meseta of Isla de Mona appears to be controlled by mixing of the fresh and saline endmembers and precipitation of aragonite. There were no indications that microbial processes were occurring in this mixing zone.

OPEN AND CLOSED SYSTEMS

In blue holes and cenotes, the water becomes sulfidic because of sulfate reduction (Bottrell *et al.* 1991; Smart *et al.* 1988; Stoessell *et al.* 1993). This bacterial process is driven by an abundance of sulfate (seawater source) and organic matter (for example, Berner 1980). The seawater, and therefore sulfate, enters into the cenotes and blue holes through either subaqueous cave passages or diffuse groundwater flow. The organic matter seems to added to the blue holes and cenotes from the land surface as detritus material. The blue holes and cenotes represent an open system with respect to input from the land surface. Subaqueous cave passages are open to the entry of seawater through the subaqueous passages but are closed with respect to input from the land surface. In these systems, there is source of sulfate to the mixing zone. However, the roof of the cave prevents or reduces the delivery of detrital organic matter to the mixing zone. Therefore microbially driven sulfate reduction cannot occur as there is no organic matter available.

On Isla de Mona, it appears that the geochemistry of the coastal plain aquifer more closely resembles that of cenotes or blue holes. The source of sulfate is the seawater and the source of organic matter is the abundant plant communities (mahogany, lowland forest, and Casuarai) on the coastal plain. We believe that dissolved organic carbon is delivered to the groundwater environment through infiltration through the soil zone. As oxygen is consumed by organic matter degradation along a flowpath, the dissolved oxygen concentration decreases. At the terminus of flowpaths (Fig. 1), the groundwater becomes sulfidic and similar to that of cenotes and blue holes. This represents a different hydrologic setting than the blue holes and cenotes, but similar microbial and geochemical reactions occur (Bottrell *et al.* 1991; Smart *et al.* 1988).

On Isla de Mona, it appears that the geochemistry of the groundwater in Cueva de Agua (Punta los Ingleses) closely resembles that of other subaqueous cave passage (Back *et al.* 1986; Stoessell *et al.* 1989 & 1993). These systems are closed with respect to input from the land surface. Sulfate is delivered into Cueva de Agua (Punta los Ingleses) by seawater, yet very little organic matter can enter the cave because of the roof. Further, given the lack of plant communities and the presence of bare rock on the overlying meseta, there is very little organic matter that could be decayed, dissolved in soil water, and delivered to the groundwater. There is no indication that any sulfate reduction is occurring in the mixing zone of Cueva de Agua (Punta los Ingleses). The observations of the groundwater geochemistry and the geochemical modeling have lead us to conclude that mixing and precipitation of aragonite control the carbonate geochemistry. This is similar to the mixing zone studied in a Xcaret Cave in the Yucatan (Back *et al.* 1986; Stoessell *et al.* 1989 & 1993).

CONCLUSIONS

In our study, we explored the differences between the hydrogeochemical processes observed in open and closed settings and sought a better understanding of the controls on those geochemical processes. We documented that the geochemistry of the groundwater in the coastal plain aquifer represents a system open to input from the land surface and influenced by microbial processes, similar to blue holes and cenotes. We documented that the geochemistry of the groundwater in the meseta aquifer represents a system that is closed to input from the land surface and that is not influenced by microbial processes, similar to other subaqueous caves.

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REFERENCES

Back, W., Hanshaw, B.B., Pyle, T.E., Plummer, L.N. & Weidie, A.E. (1979). Geochemical significance of groundwater discharge and carbonate solution to the formation of Caleta Xel Ha, Quintana Roo, Mexico. *Water Resources Research 15*: 1521-1535.

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 4*: 137-140.

Berner, R.A. (1980). *Early Diagenesis: A theoretical approach*. Princeton University Press, Princeton, NJ: 241 pp.

Bottrell, S.H., Smart, P.L., Whitaker, F.F. & Raiswell, R. (1991). Geochemistry and isotope systematics of sulphur in the mixing zone of Bahamian blue holes. *Applied Geochemistry 6*: 97-103.

Briggs, R.P. & Seiders, V.M. (1972). Geologic map of the Isla de Mona quadrangle, Puerto Rico. *U.S. Geological Survey Miscellaneous Geologic Investigations Map I-718, scale 1:20,000*.

Budd, D.A. (1988). Aragonite to calcite transformation during freshwater diagenesis of carbonates: Insights from pore-water chemistry. *Geological Society of America Bulletin 100*: 1260-1270.

Cintron, B. & Rogers, L. (1991). Plant communities of Mona Island In *Acta Cientifica. Asociación de Maestros de Ciencia de Puerto Rico 5*(1-3): 10-64.

Erskine, A.D. (1991). The effect of tidal fluctuation on a coastal aquifer in the UK. *Ground Water 29*: 556-562.

Ford, D. & Williams, P. (1989). *Karst Geomorphology and Hydrology*. Unwin Hyman Publishing: 601 pp.

Frank, E.F. (1993). *Aspects of karst development and speleogenesis Isla de Mona, Puerto Rico: An analogue for Pleistocene speleogenesis in the Bahamas*. MS thesis, Mississippi State University: pp. 132.

Frank, E.F., Wicks, C.M., Mylroie, J.M., Troester, J.W., Alexander, E.C. Jr. & Carew, J.L. (1998). Geology of Isla de Mona, Puerto Rico. *Journal of Cave and Karst Studies 60*(2): 69-72.

Hanshaw, B.B. & Back, W. (1980). Chemical mass-wasting of the northern Yucatan Peninsula by groundwater dissolution. *Geology 8*: 222-224.

Jordan, D.G. (1973). A summary of the actual and potential water resources Isla de Mona, Puerto Rico. In *Isla de Mona - Volume II: Junta de Calidad Ambiental*: D1-8.

Kaye, C.A. (1959). Geology of Isla Mona Puerto Rico, and notes on age of Mona Passage. *U.S. Geological Survey Professional Paper 317-C*: 178.

Martínez, M.I., Troester, J. W. & Richards, R.T. (1995). Surface electromagnetic geophysical exploration of the ground-water resources of Isla de Mona, Puerto Rico, A Caribbean carbonate island. *Carbonates and Evaporites 10* (2): 184-192.

Mylroie, J.E., Carew, J.L., Frank, E.F., Panuska, B.C., Taggart, B.E., Troester, J.W. & Carrasquillo, R. (1995). Development of flank margin caves on San Salvador Island, Bahamas and Isla de Mona, Puerto Rico. In Boardman, M.R., (ed.), *Proceedings of the Seventh Symposium on the Geology of the Bahamas: San Salvador Island, Bahamas, Bahamian Field Station*: 49-81.

Nieves-Rivera, A.M., Mylroie, J.E. & McFarlane, D.A. (1995). Bones of *Puffinus lherminieri* Lesson (Aves: Procellaridae) and two other vertebrates from Cueva de Agua, Mona Island, Puerto Rico (West Indies). *National Speleological Society Bulletin 57*: 99-102.

National Oceanic and Atmospheric Association. (1996). National Climatic Data Center World Wide Web, www.ncdc.noaa.gov/pub/data/coop-precip/others.txt.

Parkhurst, D.L., Thorstenson, D.C. & Plummer, L.N. (1990). PHREEQE - a computer program for geochemical calculations. *U.S. Geological Survey Water Resources Investigations 80-96*: 210 p.

Plummer, L.N. & Back, W. (1980). The mass balance approach: Application to interpreting the chemical evolution of hydrologic systems. *American Journal of Science 280*: 130-142.

Randazzo, A.F. & Bloom, J.I. (1985). Mineralogical changes along the freshwater/saltwater interface of a modern aquifer. *Sedimentary Geology 43*: 219-239.

Randazzo, A.F. & Cook D.J. (1987). Characterization of dolomitic rocks from the coastal mixing zone of the Floridan aquifer, USA. *Sedimentary Geology 54*: 169-192.

Richards, R. T., Troester, J.W. & Martínez, M.I. (1998). An electromagnetic geophysical survey of the freshwater lens of Isla de Mona, Puerto Rico. *Journal of Cave and Karst Studies 60*(2): 115-120.

Richards, R. T., Troester, J.W. & Martínez, M.I. (1995). A comparison of electromagnetic techniques used in a reconnaissance of ground-water resources under the coastal plain of Isla de Mona, Puerto Rico. *The symposium on the Applications of Geophysics to Environmental and Engineering Problems (SAGEEP'95) Proceeding, Orlando, Florida*: 251-260.

Ruiz, H.M. (1993). *Sedimentology and diagenesis of Isla de Mona, Puerto Rico*. MS thesis, University of Iowa: 86p.

Smart, P.L., Dawans, J.M. & Whitaker, F. (1988). Carbonate dissolution in a modern mixing zone. *Nature 335*: 881-813.

Stoessell, R.K., Ward, W.C., Ford, B.H. & Schuffert, J.D. (1989). Water chemistry and $CaCO_3$ dissolution in the saline part of an open-flow mixing zone, coastal Yucatan Peninsula, Mexico. *Geologic Society of America Bulletin 101*: 159-169.

Stoessell, 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.

Vacher, H.L. (1978). Hydrogeology of Bermuda - Significance of an across-the-island variation in permeability. *Journal of Hydrology 39*: 207-226.

Wallis, T.N., Vacher, H.L. & Stewart, M.T. (1991). Hydrogeology of freshwater lens beneath a holocene strandplain, Great Exuma, Bahamas. *Journal of Hydrology 125*: 93-109.

Whitaker, F.F., Smart, P.L., Vahrenkamp, V.C., Nicholson, H. & Wogelius, R.A. (1994). Dolomitization by near-normal seawater? Field evidence from the Bahamas. *Special Publications of the International Association of Sedimentology 21*: 111-132.