GEOCHEMICAL EVOLUTION OF WATERS WITHIN THE NORTH COAST LIMESTONE AQUIFERS OF PUERTO RICO:

A CONCEPTUALIZATION BASED ON A FLOW PATH IN THE BARCELONETA AREA

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FACTORS FOR CONVERTING INCH-POUND UNITS TO INTERNATIONAL SYSTEM OF UNITS (SI)

For the convenience of readers who may want to use International System of Units (SI), the data may be converted by using the following factors:

Multiply inch-pound units	By	To obtain SI units
inches (in)	25.4	millimeters (mm)
feet (ft)	0.3048	meters (m)
square feet (ft^2)	0.09294	square meters (m^2)
miles (mi)	1.609	kilometers (km)
square miles (mi^2)	2.590	square kilometers (km^2)
gallons per minute (gal/min)	0.06308	liters per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meters per day (m^3/d)
cubic feet per second (ft^3/s)	0.02832	cubic meters per second (m^3/s)
parts per million (ppm) (for dilute solutions)	1	milligrams per liter (mg/L)
degree Fahrenheit (°F)	°C = 5/9 (°F-32)	degrees Celsius (°C)

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ABSTRACT

The report provides a preliminary description of the principal geochemical processes that determine the ground-water chemistry along the north coast limestone aquifers of Puerto Rico. Water samples along a ground-water flow path in the Barceloneta area were collected from wells screened in the Montebello Limestone Member of the Cibao Formation (artesian aquifer) and in the overlying Aguada and Aymamón Limestones (water-table aquifer).

The ground-water chemistry changes as water migrates from recharge areas to downgradient zones in the aquifers. Dissolved magnesium, dissolved sulfate, pH, and carbon-13 isotope generally increase downgradient. Total inorganic carbon and calcium decrease within the freshwater parts of the aquifer. Mass-transfer calculations show that the likely reaction model is carbon dioxide incorporation as water infiltrates through the soil zone, followed by calcite dissolution as water recharges the aquifer. As water moves downgradient within the artesian aquifer, carbon dioxide may degas as a result of calcite precipitation while gypsum and dolomite are dissolved. Within the water-table aquifer, continuous recharge of waters rich in carbonic acid maintains the dissolution of the carbonate minerals. Near the coast the mixing of fresh ground water with saltwater is the primary process affecting water chemistry within the water-table aquifer.

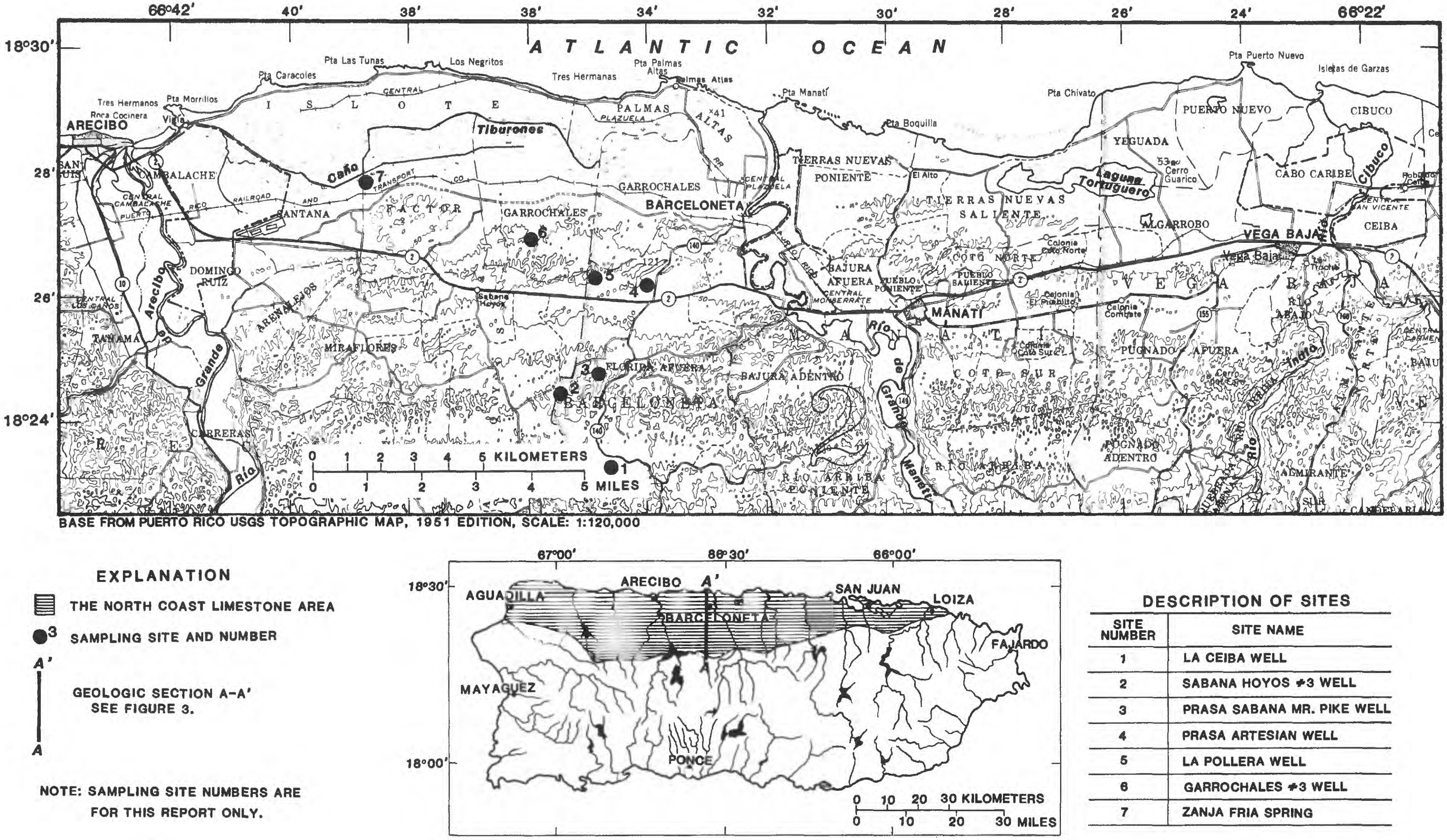
INTRODUCTION

The limestones found along the north coast of Puerto Rico contain the most productive aquifers on the island. These aquifers underlie an area of about 600 square miles (mi^2), and extend from Aguadilla on the west coast eastward to Loíza (fig. 1). During 1983, about 80 million gallons per day (Mgal/d) of fresh ground water was withdrawn from these aquifers, providing approximately 20 percent of the total water demand for the north coast area (U.S. Geological Survey, 1985, p. 370).

Two important aquifers occur within the north coast limestone area: (1) a water-table aquifer occurring within the Aguada and Aymamón Limestones and alluvial deposits, and (2) a deep, artesian aquifer system occurring within the Lares Limestone and the Montebello Limestone Member of the Cibao Formation (fig. 2). In general, water from both aquifers is suitable for public supply as well as industrial and agricultural uses.

The geochemical investigation of the north coast limestone aquifers is part of the Caribbean Islands Aquifers - Regional Aquifers Systems Analysis (CIA-RASA), a comprehensive appraisal of aquifers in Puerto Rico and the U.S. Virgin Islands. The investigation consists of three phases. Phase one includes a compilation of all historical water-quality data for the north coast limestone aquifers; with these data a series of map reports showing the areal and vertical distribution of various chemical species and hydrochemical facies were prepared. Phase one also includes a preliminary description of the principal geochemical processes that produce the observed ground-water chemistry within the north coast limestone aquifers. This aspect of phase one is the subject of this report. Phase two will include aquiring additional data and phase three will be the final geochemical modeling effort.

A sample flow path near the Barceloneta area was selected to describe the principal geochemical processes within the north coast limestone aquifers. Six wells and one spring along the flow path were sampled to determine chemical conditions representing both upgradient and downgradient zones within each aquifer identified as hydrogeologically



BASE FROM PUERTO RICO USGS TOPOGRAPHIC MAP, 1951 EDITION, SCALE: 1:120,000

NOTE: SAMPLING SITE NUMBERS ARE FOR THIS REPORT ONLY.

DESCRIPTION OF SITES

SITE NUMBER	SITE NAME
1	LA CEIBA WELL
2	SABANA HOYOS #3 WELL
3	PRASA SABANA MR. PIKE WELL
4	PRASA ARTESIAN WELL
5	LA POLLERA WELL
6	GARROCHALES #3 WELL
7	ZANJA FRIA SPRING

Figure 1.--Location of study area and sampling sites.

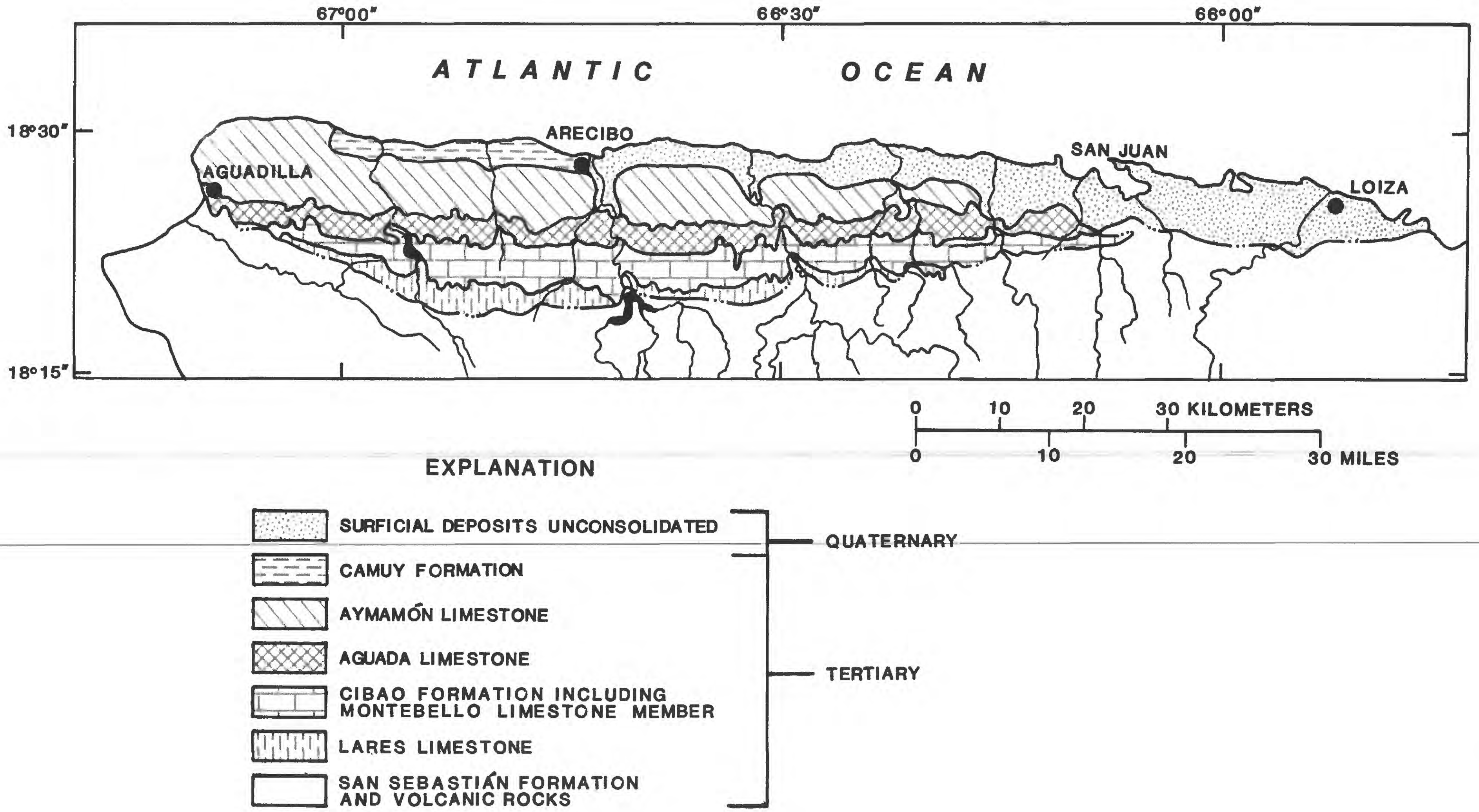


Figure 2.--Geologic formations of the north coast limestone area. (Adapted from Giusti, 1978.)

distinct. The data obtained from chemical analyses of water samples were processed using computer programs WATEQF (Plummer and others, 1976), BALANCE (Parkhurst and others, 1982) and PHREEQE (Parkhurst and others, 1980). These programs were used to construct mass-transfer and reaction-path models. The models can be used to determine: (1) The chemical reactions that have occurred, (2) the magnitude of chemical reactions, and (3) the conditions under which the reactions occurred.

GEOLOGY

The limestone formations of the north coast of Puerto Rico rest unconformably on a faulted and folded volcanic formations (Giusti, 1978, p. 2), predominantly of Cretaceous to early Tertiary age (Monroe, 1980, p. 9). Above the volcanic base, six limestone formations are recognized. General location of these formations and geologic characteristics are shown in figure 2 and table 1. The total thickness of the limestones exceeds 5,000 feet (ft) at the northern coastline. They dip seaward at about 5 degrees (Giusti, 1976, p. 1), and extend offshore an undetermined distance.

The limestone formations are overlain in different parts of the area by coastal deposits, alluvial deposits, or blanket sands of the Cenozoic age (Monroe, 1976, p. 14). The blanket sands fill in the depressions between mogotes in the North Coast limestone belt, especially in the northern part of the belt where the Aymamón Limestone outcrops. Very thick masses of alluvium fill valleys within the study area. These alluvial valleys are associated with major rivers and are the only surficial deposits that contain important aquifers.

Table 1. General geologic characteristics of the north coast limestone area

System	Series	Geologic unit	*Description of sediments	Thickness in feet
Quaternary	Holocene	Alluvial deposits	Mixture of sand, gravel, and clay	0-200
Tertiary	Pliocene	Camuy Formation	Fragmental limestone and marl containing some sandstone and hard limestone beds; some discontinuous dolomite beds	0-600
	Miocene	Aymamón Limestone	Thick-bedded and massive dense limestone and calcarenite, some dolomite beds	600-1100
		Aguada Limestone	Hard, thick-bedded to massive calcarenite and dense limestone interbedded with chalky limestone and marl.	100-600
	Lower Miocene and Oligocene	Cibao Formation (including Montebello Limestone Member)	Interbedded marl. Chalk and limestone, thin sand and clay beds. Montebello Limestone Member: fine grained nearly pure limestone	0-1000
	Oligocene	Lares Limestone	Massive, dense limestone and calcarenite	0-1650
		San Sebastián Formation	Sand, silt and clay	0-900

*Description of sediment as adapted from Giusti and Bennett, 1976.

CLIMATE

The climate of the North Coast Province of Puerto Rico is tropical humid (Wills, 1955, p.72). The island is located in the pathway of nearly constant easterly trade winds. A strong orographic effect makes the North Coast Province an area of high rainfall, averaging 70 inches per year (in/yr) (Gómez-Gómez, 1980, p. 3). A dry season extends from January to April and the wet season from September to December. Temperature for the North Coast Province averages 24°C. The high temperature and the constant winds contribute to a high evapotranspiration rate. An empirical relation of evapotranspiration or pan evaporation versus annual rainfall for Puerto Rico was developed by Giusti (1978, p. 21). Areas receiving 70 inches of annual rainfall will yield values of evapotranspiration and pan evaporation of 45 and 60 inches respectively, leaving 10 to 25 inches per year to be discharged by surface and subsurface flow.

GROUND WATER

Water-table Aquifer

A generally productive water-table aquifer occurs within the Tertiary Aguada and Aymamón Limestones as well as the alluvial deposits along the north coast of Puerto Rico. The Tertiary Lares Limestone and the Montebello Limestone Member of the Cibao Formation are similarly unconfined in their recharge areas but are not considered productive water-table aquifers. Yields to wells tapping the water-table aquifer range from 150 gallons per minute (gal/min) for the Lares Limestone and the Cibao Formation to 1,000 gal/min for the Aguada and Aymamón Limestones and some alluvial deposits (Gómez-Gómez, 1980, p. U7). The hydraulic characteristics of the principal stratigraphic units that form the water-table aquifer are summarized on table 2.

GROUND WATER (Continued)

Water-table Aquifer (Continued)

Recharge to the Aguada and Aymamón Limestones and alluvial sediments occurs principally by direct infiltration of rainfall over the outcrop area. Other sources of recharge are: (1) direct infiltration of rainfall through blanket sands and other surficial deposits, (2) leakage from rivers hydraulically connected to the aquifer.

Table 2. Hydrogeologic framework of the north coast limestone area (Adapted from Torres-González and Wolansky, 1984.)

Geologic unit	Associated aquifers	Estimated aquifer characteristics		
		Transmissivity in ft^2/d	Leakance (K'/b') in (ft/day)/ft	Storage coefficient
Alluvial deposits	Water-table aquifer	1000 to 50,000	---	0.05 to 0.2
Camuy Formation	Water-table aquifer	1000 to 3000	1×10^{-3}	2×10^{-4} to 0.1
Aymamón Limestone	Water-table aquifer	5000 to 50,000	1×10^{-3}	0.1×10^{-4} to 3×10^{-4}
Aguada Limestone	Water-table aquifer	2000 to 20,000	1×10^{-3}	0.1×10^{-4} to 2×10^{-4}
Cibao Formation (including Montebello Limestone Member)	Cibao artesian aquifer	3000	1×10^{-4}	5×10^{-4}
Lares Limestone	Lares artesian aquifer	10,000	1×10^{-4}	1×10^{-3}
San Sebastián Formation	None	---	---	---

GROUND WATER (Continued)

Water-table Aquifer (Continued)

Water entering the aquifer generally moves northward. The steeper hydraulic gradient within the Aguada Limestone reflects the lower hydraulic conductivity of this formation in comparison to the Aymamón Limestone (Giusti, 1978). The steep gradient is also associated with a relatively thin sheet-like flow through the Aguada Limestone, for which the upper part of the Cibao Formation forms a low permeability base. The gradient gradually flattens out as ground water moves from the Aguada Limestone to the Aymamón Limestone because of the higher hydraulic conductivity of the Aymamón Limestone (Giusti and Bennett, 1976, p. 13).

Artesian Aquifer

Artesian conditions within the north coast limestone area were reported by drillers in 1968. Artesian heads were first encountered in the Montebello Limestone Member of the Cibao Formation at a depth of about 1,200 feet; artesian pressure was also detected in the Lares Limestone at a depth of about 1,600 feet (Giusti and Bennett, 1976, p. 17). At present, the hydraulic connection between the two formations is not well defined.

Recharge to the artesian aquifers occurs almost entirely within the outcrop areas. This water has, through geologic time, replaced the salty connate water which originally occupied the limestones. The recharging freshwater has progressed downdip and occurs under artesian conditions near the coast. Wells that tap the artesian aquifers are capable of producing as much as 1,900 gal/min. In 1968, the piezometric head in the artesian system in the Barceloneta area was about 500 feet above mean sea level. Since then the artesian aquifer has undergone extensive development. As a consequence, piezometric heads have dropped to 300 feet above mean sea level. The principal hydraulic characteristics of each geologic unit occurring under artesian conditions are summarized on table 2.

GROUND WATER (Continued)

Ground-Water Flow Pattern

Giusti (1978, p. 28) described two flow patterns in the water-table aquifer. In the area west of Río Grande de Arecibo the occurrence and availability of ground water are speculative. It appears, from water budget data presented by Giusti (1978, p. 28), that Río Tanamá, Río Camuy and Río Guajataca act as highly efficient ground-water drains. A low percentage of the regional flow discharges into either coastal swampy areas or the sea bottom. In contrast, east of Río Grande de Arecibo, about 75 percent of the ground-water outflow occurs inland from the coast (Caño Tiburones, Laguna Tortuguero, other swampy areas, and some streams), the remaining 25 percent discharges along the sea bottom (Bennett and Giusti, 1972, p. 9).

Ground-water outflow from the artesian aquifers was described by Giusti and Bennett (1976, p. 25-26) as direct discharge to the sea at a submarine outflow face. The ground water is discharged against the static head exerted by the column of sea water above the outflow face. Assuming that values of hydraulic conductivity do not vary downdip, discharge from artesian zones will occur approximately 18 miles offshore (Giusti, 1978, p. 27). If the hydraulic conductivity decreases seaward or with statigraphic depth, head would be dissipated much closer to shore than 18 miles, and an upward discharge of ground water would occur over a large area through the confining beds.

SURFACE WATER

The north coast limestone area is traversed by 9 major rivers (fig. 1), which generally cross the area in a direction west of north and whose headwaters are found in the volcanic terrane to the south. The relationship of surface water and ground-water is an important factor in the ground-water chemistry of those areas of the water-table system where river recharge occurs.

SURFACE WATER (Continued)

There is a striking difference in the hydrologic relation between ground water and surface water in the eastern part of the area as compared to the western part, as the streams proceed from volcanic to limestone rocks. Rivers east of Arecibo (Río Grande de Arecibo, Río Grande de Manatí, and Río Cibuco), tend to lose flow to the adjoining alluvium and Aymamón Limestone. Rivers west of Arecibo (Río Guajataca, Río Camuy, and Río Tanamá) show consistent gains, as they act as drains for the water-table aquifer within that part of the study area.

GEOCHEMISTRY

Rock - Rainfall - Soil

The mineral content of the north coast limestones was studied in detail by Monroe (1980, p. 18, 32, 47, 54, 60). Calcite ($CaCO_3$) is the predominant mineral comprising the north coast limestones. The Aymamón Limestone contains up to 99 percent calcite, making it the purest limestone in Puerto Rico. Rock samples from the eastern part of the Aymamón Limestone indicate that the formation is less pure in that area. The Lares Limestone and the Montebello Limestone Member of the Cibao Formation are composed of 94 to 96 percent calcite. The Aguada Limestone, somewhat less pure, is composed of 82 to 94 percent calcite. The Cibao Formation and the Camuy Limestone are composed of 59 to 91 percent and of 50 to 95 percent calcite, respectively.

The magnesium (Mg) content of the north coast limestones is low, generally less than 2 percent MgO. However, the MgO content in some samples of the Aymamón Limestone and the Camuy Limestone are as high as 39 percent, suggesting the presence of dolomite [$CaMg(CO_3)_2$]. Silica is also present, and it comprises 81 percent of the insoluble residue from rock samples of all formations. Minor amounts of iron and aluminum are present, and traces of strontium, titanium, and other metals were detected.

GEOCHEMISTRY (Continued)

Rock - Rainfall - Soil (Continued)

Calcite in pure water hydrolyzes according to the following reactions (Krauskopf, 1967 pp. 51-54):

$$(1)\quad CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-$$

The equilibrium constant for this reaction is:

$$K = [Ca^{2+}]\,[OH^-]\,[HCO_3^-] = 10^{-12}$$

At equilibrium the solution acquires a pH near 10.

At this pH, the HCO_3^- will dissociate:

$$HCO_3^- = H^+ + CO_3^{2-} \text{ and,}$$

$$[CO_3^{2-}] / [HCO_3^-] \cong 0.5.$$

The concentrations of HCO_3^- and OH^- will be 2/3 the concentrations of Ca^{2+}:

$$[Ca^{2+}] = 3/2\ [OH^-] = 3/2\ [HCO_3^-] = \sqrt[3]{9/4 \times 10^{-12}}$$

$$[Ca^{2+}] = 1.3 \times 10^{-4}\ M.$$

Most of the water that infiltrates into the north coast ground water flow system originates as rainfall recharge. Samples of rainfall within the North Coast Province show pH values that range from 6.1 to 6.8 units. This slightly acidic condition is attributed to the formation of carbonic acid when rainwater reacts with carbon dioxide (CO_2) from the atmosphere. The reaction is as follows:

$$(2)\quad CO_2 + H_2O = H_2CO_3 \text{ (Carbonic acid)}$$

$$K = \frac{[H_2CO_3]}{PCO_2} = 10^{-1.5}$$

Atmospheric carbon dioxide partial pressure (PCO_2) is $10^{-3.5}$ atm (atmosphere), therefore:

$$[H_2CO_3] = 10^{-5} M \text{ (molar)}$$

GEOCHEMISTRY (Continued)

Rock - Rainfall - Soil (Continued)

The carbonic acid content of rainwater is capable of dissolving as much as 3.5 times more calcium carbonate than the hydrolysis reaction in pure water (Krauskopf, 1979, p. 51-54).

$$(3)\quad CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$$

$$K = \frac{[Ca^{2+}]\,[HCO_3^-]^2}{[H_2CO_3]} = 10^{-4.4}$$

In this reaction 2 moles of HCO_3^- are produced for every mole of Ca^{2+}

$$2\,[Ca^{2+}] = [HCO_3^-]$$

for equilibrium with atmosphere ($PCO_2 = 10^{-3.5}$ atm)

$[H_2CO_3] = 10^{-5}$, and,

$$K = \frac{4\,[Ca^{2+}]^3}{10^{-5}} = 10^{-4.4}$$

$$[Ca^{2+}] = 4.7 \times 10^{-4} M$$

From equations 2 and 3 it is possible to write a general equation for the dissolution of calcite.

$$(4)\quad \begin{array}{c} H_2O + CO_2 \\ \| \\ CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^- \end{array}$$

The carbonic acid present in rainwater gives it the capacity to dissolve the carbonate rocks. The equilibrium position in equation (4) is determined by the CO_2 partial pressure.

Before rainwater reaches the ground-water system it passes through the soil zone. Biological processes within the soil zone may generate relatively large amounts of acid while consuming the available dissolved oxygen in the infiltrated water.

GEOCHEMISTRY (Continued)

Rock - Rainfall - Soil (Continued)

Geochemically, the most important acid produced in the soil zone is H_2CO_3. The necessary CO_2 for the production of carbonic acid, is generated by the decay of organic matter and by respiration of plant roots.

$$(5) \quad O_{2(g)} + CH_2O \text{ (carbohydrate)} = CO_{2(g)} + H_2O$$

The partial pressure of CO_2 (PCO_2) in the soil atmosphere is much higher than that of the earth's atmosphere. Values of PCO_2 in wet soils can be as high as $10^{-0.7}$ atm (Monroe, 1976, p. 17). Miotke (1973, p. 4) found that CO_2 partial pressure of the ground air on the side of the mogotes range from $10^{-2.0}$ to $10^{-1.9}$ atm while in blanket sands soil range from $10^{-1.8}$ to $10^{-1.2}$ atm. For a CO_2 partial pressure (PCO_2) equal to 10^{-1} atm, the concentration of carbonic acid (H_2CO_3) is equal to $10^{-2.5}$M, and the pH may be near 4.4. Roberts and others (1942, p. 454) report pH values as low as 4.7 for soil waters within the north coast limestone areas. Water having a H_2CO_3 concentration of $10^{-2.5}$ M is capable of dissolving as much as 6.68 times ($[Ca^{2+}] = 3.34 \times 10^{-3}$M) more calcite than water in equilibrium with atmospheric CO_2 partial pressure.

As calcite dissolves, the pH of the water increases, reaching equilibrium values between 7 and 8. Within this range of pH values, the concentration of CO_3^{2-} is about 3×10^{-4} times the concentration of HCO_3^-. Accordingly, the dissociation of HCO_3^- into H^+ and $CO_3 2-$ was not considered in equation 3.

Water-Quality Trends

The Barceloneta area was selected for the sample flow path in which to conceptualize the geochemistry because it is representative of hydrogeologic conditions in the north coast limestone area and has not been affected by surface water recharge. Wells upgradient and down-

GEOCHEMISTRY (Continued)

Water-Quality Trends (Continued)

gradient within each aquifer and geologic unit were selected to establish trends in the evolution of ground-water chemistry along a flow path (fig. 3 and table 3). The selected flow paths are as follows:

Flow path 1: from La Ceiba well to Puerto Rico Aqueduct and Sewer Authority (PRASA) Artesian well -
Artesian aquifer (Montebello Limestone Member of the Cibao Formation)

Flow path 2: from PRASA Sabana Hoyos #3 to PRASA Sabana Pike well -
Water-table Aquifer (Aguada Limestone)

Flow path 3: from rainfall to La Pollera well -
Water-table Aquifer (Aymamón Limestone)

Flow path 4: from Garrochales #3 well to Zanja Fría Spring -
Water-table Aquifer (Aymamón Limestone)

Table 3. Well completion information

Well name	Site		Screen interval (feet)	Total depth (feet)	Geological unit
	latitude	longitude			
La Ceiba	18°21'24"N	66°35'50"W	230-335	335	Cibao Formation (Montebello Limestone Member)
PRASA Artesian	18°25'55"N	66°34'02"W	1083-1234	1234	Cibao Formation (Montebello Limestone Member)
Sabana Hoyos #3	18°24'21"N	66°36'02"W	440-680	700	Aguada Limestone
PRASA Sabana Pike	18°25'04"N	66°35'01"W	220-600	600	Aguada Limestone
La Pollera	18°26'41"N	66°34'56"W	100-350	350	Aymamón Limestone
Garrochales #3	18°27'35"N	66°36'57"W	68-81	81	Aymamón Limestone
Zanja Fría Spring	18°27'48"N	66°38'21"W	-	-	Aymamón Limestone

Water-Quality Trends (Continued)

The selected wells and spring were sampled for major anions and cations, carbon-13 ($\delta^{13}C$), and dissolved gases. Analytical results show that inland ground water within the study area was dominated by calcium and bicarbonate ions, with concentrations of total dissolved solids less than 300 mg/L (fig. 3 and table 4). Near the coast, ground water has a relatively high concentration of dissolved solids in which sodium and chloride are the dominant species (fig. 3 and table 4). The increases in sodium, chloride, and dissolved solids are due to mixing of freshwater with saltwater present in the limestone aquifers in coastal areas.

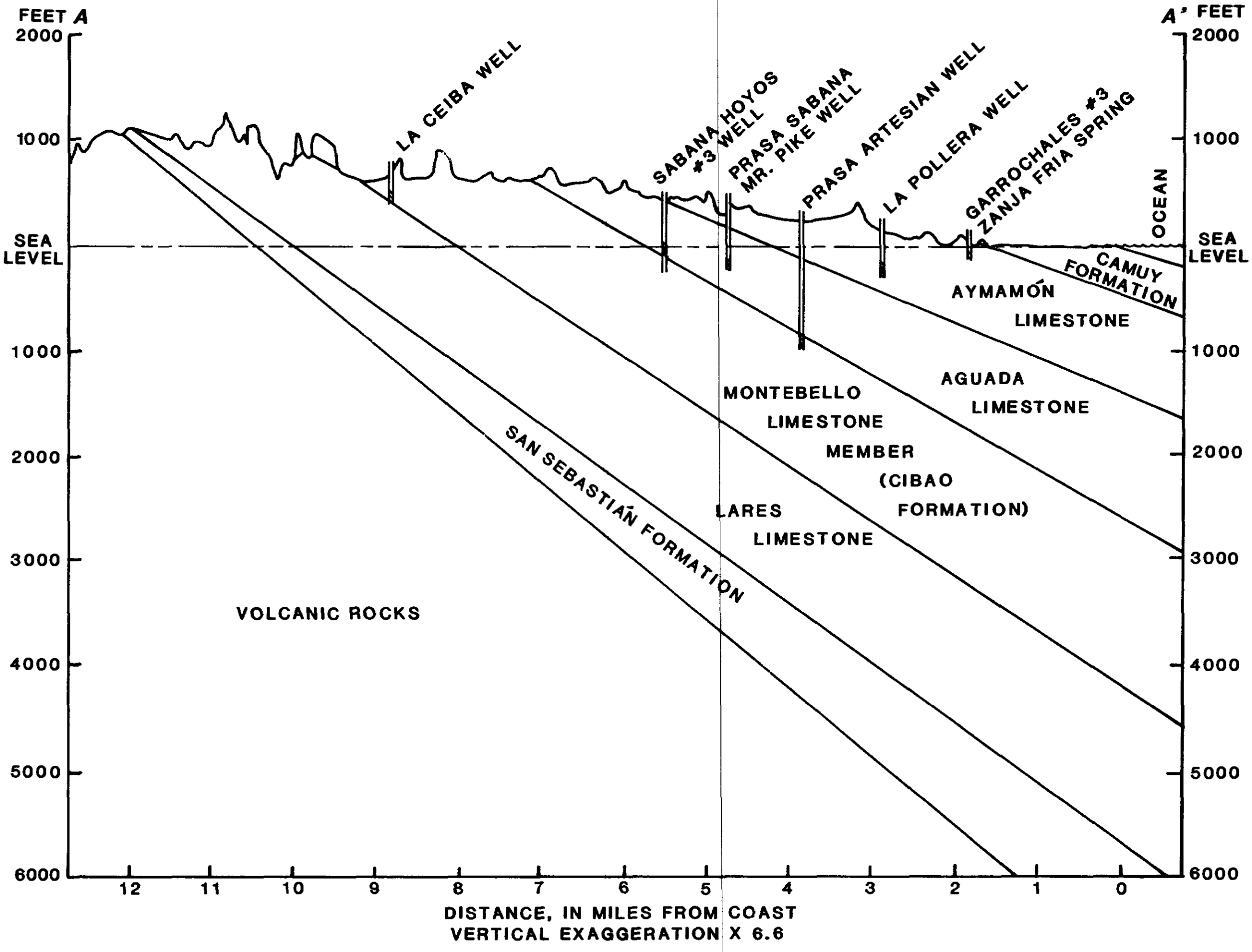


Figure 3.--Generalized geologic cross-section with sampling sites.

GEOCHEMISTRY (Continued)

Water-Quality Trends (Continued)

Consistent water-quality trends were observed in each flow path from upgradient to downgradient sampling sites. Concentration of calcium ion decreased downgradient in flow paths 1, 2, and 4, while in flow path 3 it increased. Concentration of magnesium ion increased slightly downgradient, as did sulfate ion, while concentrations of sodium and chloride ions showed pronounced increases downgradient in flow paths 3 and 4.

Total inorganic carbon, (the sum of the dissolved species of inorganic carbon, ΣCO_2) decreases downgradient as pH values increased for flow paths 2 and 4. This suggests transfer of CO_2 from solution to the solid phase as calcium carbonate (calcite), degassing of CO_2 in a partially open system, or mixing with waters containing relatively low concentrations of dissolved CO_2 (seawater).

The values for carbon-13 isotope ($\delta^{13}C$) were observed to become heavier (less negative) downgradient for flow path 1, 2, (table 4). In flow path 4, however, the water at the downgradient sampling site contains slightly lighter $\delta^{13}C$ compared to the upgradient sampling site. The observed changes in $\delta^{13}C$ within these flow paths, are so small that it is not possible to infer anything about which process dominates the inorganic carbon chemistry of the systems represented by these flow paths. Flow path 3, which is a vertical model, does show a substantial increase in $\delta^{13}C$ (table 4) (becomes heavier), suggesting that the dissolution of carbonates minerals dominates the inorganic carbon chemistry along this flow path. It was assumed that rainfall flows through the soil zone before it recharges the aquifer, reaching equilibrium with the soil atmoshpere CO_2 where the $\delta^{13}C$ is typically about -20 parts per thousand (o/oo) (Drever, J.I., 1982, p. 345).

Table 4. Water-quality data of selected wells and spring
(All values in milligrams per liter unless otherwise noted. Dash indicates no data.)

Well Name	Temp (°C)	pH (Units)	Dis-solved solids	Ca	Mg	Na	K	HCO_3	Cl	SO_4	F	SiO_2	Dissolved Gases				$\delta^{13}C$
													N_2	O_2	CO_2	Ar	
							Flow Path 1										
La Ceiba	23.5	7.09	283	89	4.8	5.9	.60	293	11	3.5	0.1	7.5	18	1.7	38	0.63	-12.20
PRASA Artesian	23.3	7.30	265	80	6.9	5.7	.38	287	11	5.0	0.1	3.7	18	3.1	26	0.64	-11.55
							Flow Path 2										
Sabana Hoyos #3	24.0	7.17	266	87	2.8	6.2	.45	274	13	5.3	0.1	5.1	22	2.8	33	0.78	-14.70
PRASA Sabana Pike	24.0	7.22	255	79	4.2	5.6	.44	263	11	13.0	0.1	5.7	22	3.1	29	0.72	-13.60
							Flow Path 3										
Rainfall	-	6.1	-	1.2	0.6	1.8	-	4.7	4.5	1.8	-	-	-	-	-	-	-20.00*
La Pollera	25.3	7.22	1,030	93	29.0	210.0	11.00	257	420	60.0	0.1	7.1	19	4.9	25	0.70	-13.10
							Flow Path 4										
Garrochales #3	25.0	7.11	509	96	11.0	68.0	3.20	314	120	25.0	0.1	6.8	21	0.9	44	0.69	-13.25
Zanja Fría	24.5	7.19	757	94	18.0	140.0	5.00	289	270	40.0	0.1	6.5	18	4.4	27	0.60	-13.40

* Assumed $\delta^{13}C$ value for rainfall before it recharges the aquifer and at equilibrium with soil atmosphere CO_2 partial pressure.

Table 5. Saturation indices of principal mineral phases

Phases	La ceiba well	PRASA artesian well	PRASA Sabana Hoyos well	PRASA Sabana Pike well	La Pollera well	Garrochales well	Zanja Fría spring
Calcite	0.026	0.180	0.028	0.025	-0.011	0.027	0.030
Dolomite	-0.883	-0.373	-1.960	-0.950	-0.240	-0.604	-0.377
Gypsum	-2.906	-2.788	-2.721	-2.366	-1.827	-2.088	-1.946

GEOCHEMISTRY (Continued)

Saturation Indices

Saturation indices (SI) for a large number of minerals were determined from the chemical analyses and field-measured values for temperature, pH, and bicarbonate. Computer program WATEQF (Plummer, and others, 1976), was used for calculating saturation indices (table 5). The saturation index is expressed as:

$$SI = \log Iap/K(T),$$

where:

Iap = ionic activity product, and

K(T) = mineral solubility product at the specified temperature.

when $SI > 0$, the solution is supersaturated with respect to the mineral;

$SI = 0$, the solution is saturated with respect to the mineral; and

$SI < 0$, the solution is undersaturated with respect to the mineral.

Within the aquifers studied, calcite, dolomite, and gypsum were considered to be the most important. The waters samples were saturated or slightly supersaturated with respect to calcite; however, water at La Pollera well was slightly undersaturated (table 5). These saturation states with respect to calcite are typical for limestone environments such as those encountered on the north coast of Puerto Rico. The data also suggest that the saturation point of calcite is reached rapidly downgradient and that calcite precipitation may occur. Calcite dissolution may not occur unless water such as rainfall, which is unsaturated with respect to calcite, reaches the flow path during ground water recharge. All water samples were undersaturated with respect to dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4.2H_2O$), revealing a propensity for ground waters to dissolve dolomite and gypsum as these minerals are encountered.

MASS-TRANSFER MODELS

The major ionic constituents occurring within a particular aquifer must have sources and sinks to account for all major chemical changes proceeding within the flow path. Dissolution and precipitation of mineral phases commonly found in carbonate rocks (e.g., calcite, dolomite, gypsum), and other processes such as ion exchange, CO_2 (gas) degassing, or dissolution, as well as saltwater and rainfall mixing should be considered in the mass transfer models. A plausible set of reactions which may affect the observed chemical behavior in the ground waters within the study area are shown in table 6.

Mass-transfer models were constructed utilizing computer programs BALANCE (Parkhurst and others, 1982) or PHREEQE (Parkhurst and others, 1980) depending upon the number of ionic species that increase or decrease in concentration, and the number of mineral phases comprising the aquifer matrix. BALANCE, because of its computation scheme, requires that the number of phases included in the calculation match the number of ionic species, while PHREEQE does not. BALANCE was utilized for flow path 1, while for flow paths 2, 3 and 4 PHREEQE was used. A positive (+) phase coefficient indicates a phase is entering the chemical system (dissolving) or a left-to-right orientation for the chemical reaction as written in table 6. A negative (-) coefficient indicates a phase is leaving the chemical system (precipitation or degassing) or a right-to-left orientation for the chemical reaction as written in table 6. Mixing models followed the methods described by Parkhurst and others (1980). Phase coefficients for mixing solutions indicate the fraction of the solution used in the mixture.

Various modeling schemes were constructed, but those included in table 7 fit best, as they are both thermodynamically feasible and consistent with the hydrology and mineralogy of these aquifers. However, those models that include seawater for the naturally occurring saltwater in these sediments are somewhat speculative. The chemical composition of the saltwater which contributes to the chemical makeup of water that occurs in the freshwater/saltwater mixing zone might be different from that of seawater.

Table 6. Chemical reactions considered in mass-transfer calculations

$$CO_2 + H_2O \longleftrightarrow H_2CO_3$$

$$CaCO_3 + H_2CO_3 \longleftrightarrow Ca^{++} + 2HCO_3^{-}$$

(Calcite)

$$CaMg(CO_3)_2 + 2H_2CO_3 \longleftrightarrow Ca^{++} + Mg^{++} + 4HCO_3^{-}$$

(Dolomite)

$$CaSO_4 . 2H_2O \longleftrightarrow Ca^{++} + SO_4^{=} + 2H_2O$$

(Gypsum)

n freshwater (upgradient) + (1 - n) (seawater) = mix (downgradient)

n freshwater (upgradient) + (1 - n) (rainfall) = mix (downgradient)

Table 7. Results of mass-transfer calculations (All values in millimoles per liter unless otherwise specified. Dashes indicate phase was not considered.)

Phase	Flow Path 1	Flow Path 2	Flow Path 3	Flow Path 4
Calcite	-0.3280	0.2251	1.9123	1.9040
Dolomite	0.0870	0.0862	0.0227	---
Gypsum	0.0160	0.0886	0.0417	---
CO2 (gas)	-0.2630	1.2564	2.3438	2.3106
Initial Solution (%)	---	76.30	---	9.50
Rainfall (%)	---	23.70	98.00	89.23
Sea Water (%)	---	---	2.00	1.26

MASS-TRANSFER MODELS (Continued)

Mass Transfer for Flow Path 1

From La Ceiba Well to PRASA Artesian Well
(Montebello Limestone Member
of the Cibao Formation, Artesian Aquifer).

Calcium and CO_2 balance for this flow path indicate net losses of both species occur downgradient. This suggests that calcite precipitation is occurring. Such a process decreases the pH of the solution because of the carbonic acid produced;

$$Ca^{+2} + 2HCO_3^- = CaCO_3 + H_2CO_3$$

However, an increase in pH is observed within this flow path, suggesting that carbon dioxide (CO_2) degasses while calcite precipitates.

$$H_2CO_3 = H_2O + CO_2$$

Mass transfer calculations indicate that calcite precipitation is the dominant process (see table 7). The 0.3280 millimoles/L of calcite that precipitates accounts for the net loss in calcium and for part of the loss in total inorganic carbon. Dissolution of minerals containing calcium or inorganic carbon, such as gypsum and dolomite, should increase the amount of calcium available for precipitation. The calculation also indicates that CO_2 gas is leaving the solution. The amount of CO_2 degassing is consistent with the gas sample analytical results (table 4) and accounts for the decrease in total inorganic carbon, as well as for the pH increase.

Gypsum and dolomite are indicated as dissolving, consistent with the mineral saturation states from WATEQF computations. The amounts of gypsum and dolomite dissolved account for the observed increases in sulfate and magnesium; but they do not contribute significantly to the calcium and inorganic carbon balance.

MASS-TRANSFER MODELS (Continued)

Mass Transfer for Flow Path 2

From Sabana Hoyos #3 Well to PRASA Sabana Pike Well
(Aguada Limestone Water-Table Aquifer)

Similar to flow path-1, calcium and total inorganic carbon concentrations decrease downgradient while magnesium and sulfate concentrations as well as pH value increase. Sodium and chloride, which are considered conservative elements for these flow paths, show net losses downgradient. This suggests that direct rainfall recharge through the many sinkholes present in the areas is occurring causing a dilution effect.

The chemical composition of rainfall as reported by Quiñones-Márquez (1975, p. 6) and the upgradient well water (PRASA Sabana Hoyos #3 Well) were used as mixing members in the calculation. Results show that final water (PRASA Sabana Pike Well) consists of 76 percent water from PRASA Sabana Hoyos Well and 24 percent rainfall (table 7). Because of the dilution effect of rainfall and the CO_2 incorporated in the soil zone, the water from the mixture is unsaturated with respect to calcite, dolomite, and gypsum. As expected, mass transfer calculations indicate the dissolution of these minerals; the CO_2 incorporated by rainfall provides the necessary carbonic acid (H_2CO_3) for the dissolution of the carbonate minerals.

MASS-TRANSFER MODELS (Continued)

Mass Transfer for Flow Path 3

From rainfall to La Pollera Well
(Aymamón Limestone)

All major ionic constituents show increases in their concentrations within this flow path. La Pollera well (end member of this flow path) produced water in which sodium and chloride are the dominant ionic species suggesting that the well screen is located within the saltwater-freshwater mixing zone.

Seawater (Stumm and Morgan, 1981, p. 567) and rainfall (Quiñones-Márquez, 1975, p. 7) were used as mixing members. Results indicate that based on chloride and sodium balance, the end water is about 98 percent rainfall and 2 percent seawater (table 7). However, the actual concentrations of calcium, magnesium, and sulfate at La Pollera well are higher than those from the mix. The calcium, magnesium, and sulfate in the final water composition are supplied by the dissolution of calcite, dolomite, and gypsum (table 7).

MASS-TRANSFER MODELS (Continued)

Mass Transfer for Flow Path 4

From Garrochales No. 3 Well to Zanja Fría Spring
(Water-table Aquifer, Aymamón Limestone)

Similar to flow paths 1 and 2, calcium and total inorganic carbon concentrations decrease downgradient while magnesium and sulfate concentrations as well as pH values increase. Sodium and chloride experience significant increases, suggesting that as in flow path 3, the saltwater-freshwater mixing zone is affecting the system.

Rainfall, seawater, and initial solution (Garrochales #3) were used as mixing members. Based on chloride and sodium balance, the final solution observed at Zanja Fría Spring is 89.23 percent rainfall, 1.26 percent seawater, and 9.50 percent initial solution. However, the actual conentrations of total inorganic carbon and calcium at Zanja Fría are higher than those from the mixture. In order to provide the required inorganic carbon and calcium, carbon dioxide (gas), and calcite were included in the calculation. Carbon dioxide (gas) increases the amount of total inorganic carbon and provides the necessary H_2CO_3 for the dissolution of calcite. Calcite dissolution provided the required calcium and inorganic carbon. Dolomite and gypsum were not included in the calculation because magnesium and sulfate concentrations resulting from the mixture were about the same as at Zanja Fría. In addition, the water resulting from the mixture was oversaturated with respect to dolomite and gypsum.

CONCLUSIONS

Mass-transfer and reaction-path model results indicate that incorporation of carbon dioxide (CO_2) at the soil zone and calcite ($CaCO_3$) dissolution are the primary processes that determine the chemistry of water as it recharges the aquifer. Water that moves downgradient into the artesian aquifer losses it's inorganic carbon by CO_2 degassing, possibly as a result of calcite precipitation, while small amounts of gypsum and dolomite dissolve. Continuous recharge to the water-table aquifer of water rich in carbonic acid, but having low-dissolved solids, promotes the dissolution of carbonate minerals as water moves downgradient. The net effect of the continuous recharge is water having a conservative mix with respect to sodium and chloride concentrations. The calcium, magnesium, sulfate, and total inorganic carbon concentrations are somewhat higher than the conservative mix because of the dissolution of calcite, dolomite, and gypsum.

In coastal areas of the water-table aquifer, fresh ground water and seawater mixing is the primary process responsible for the observed chemical changes in these areas. The seawater mixing models showed comparable amounts of calcite, CO_2 (gas), dolomite, and gypsum dissolution to the more upgradient models within the water table aquifer. It must be stated, however, that models that include seawater mixing are somewhat speculative because the chemical composition of seawater is different from that of saltwater found within the aquifer materials.

To complete and verify the mass-transfer models for these aquifers, the following data are needed: (1) Chemical data of recharge water (rainfall); (2) Chemical data of the unsaturated zone (soil) materials and biogeochemical processes within this zone and their impact on the ground-water quality; (3) mineralogic, petrologic and chemical composition of the aquifer materials including clays and total exchangeable cations; (4) Carbon-13 isotope data on gas phase CO_2; and (5) chemical data of saltwater found in these aquifer materials.

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