

ORIGINS AND DISTRIBUTION OF SALINE GROUND WATERS
IN THE FLORIDAN AQUIFER IN COASTAL SOUTHWEST FLORIDA

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ABSTRACT

Present and future urban development in the coastal parts of southwest Florida depend to a large extent on the availability of a satisfactory water supply. The Floridan aquifer is a regionally extensive geohydrologic system of Tertiary carbonate rocks that contains water of variable quality in the 2,085 square-mile study area. Downgradient in the flow system, to the south and west, ground-water grades from a fresh calcium magnesium bicarbonate sulfate type water to a very saline sodium magnesium chloride type water. The saline water is the probable result of past marine inundations and subsequent mixing and reaction.

Bromide chloride and specific conductance ratios indicate that dilution of marine-like ground water is a significant mechanism in the evolution of the different water types found. Calcium, magnesium, and bicarbonate concentrations occur within a relatively narrow range and are primarily a function of mineral equilibria. Magnesium and strontium concentration distributions suggest several mineral-water interactions, including aragonite inversion, incongruent solution of magnesian calcite to a lower magnesian form, and dedolomitization. Sulfate concentrations increase downgradient and evince gypsum-anhydrite solution, particularly in the fresher waters. The extent to which each factor affects dissolved specie concentrations is a function of the location of the water in the flow system.

INTRODUCTION

The coastal sections of southwest Florida (fig. 1) have experienced extensive urban development in the past 10 years (table 1). Development will likely continue and conceivably intensify in the future. Coincident increases in water demand have led to water-supply questions and problems concerning availability, source, and quality. Answers and solutions can come only from a comprehensive, rational, resource-management plan.

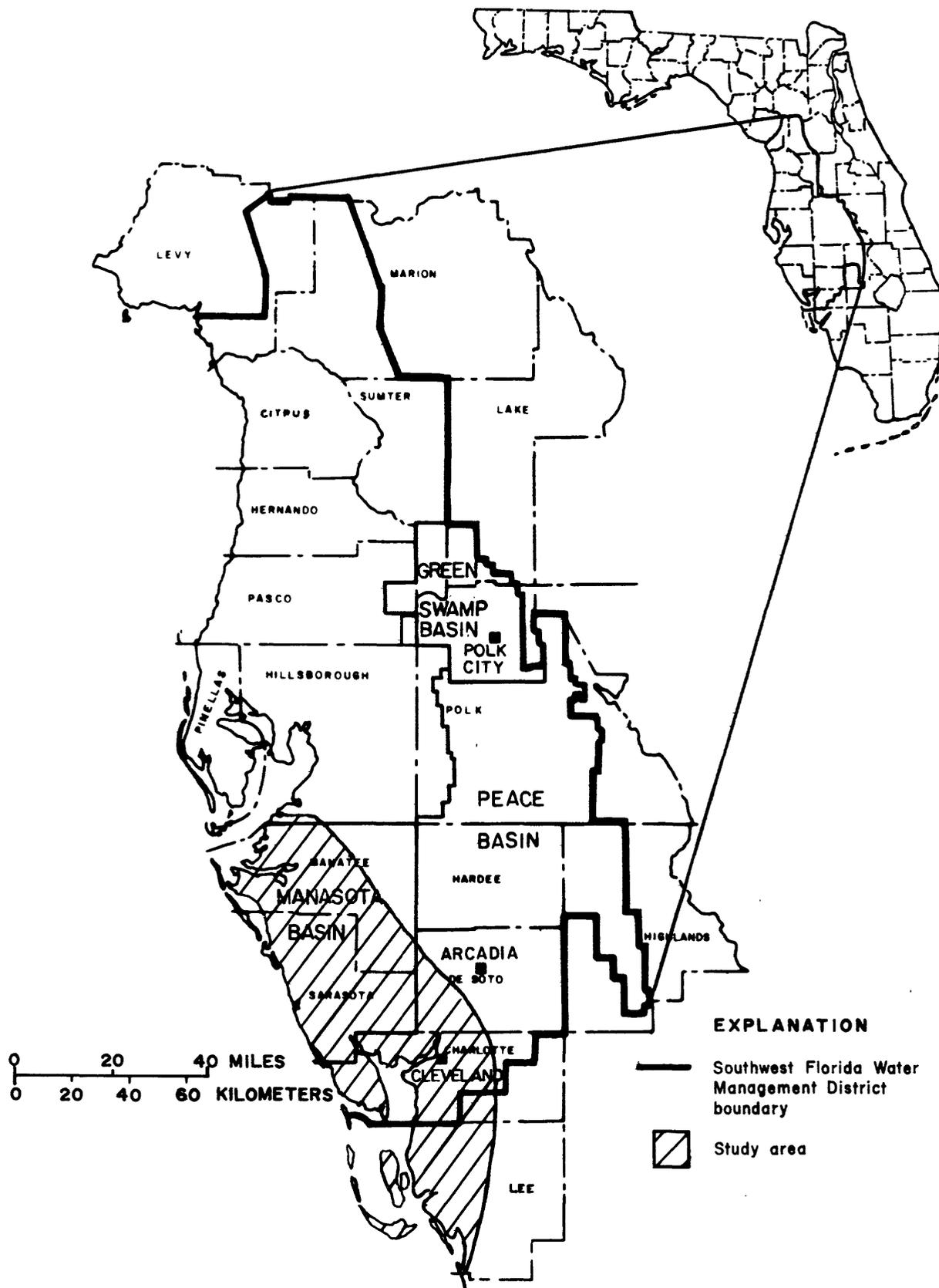


Figure 1.--Location of the study area.

Table 1.--Population and housing units April 1, 1970, and April 1, 1980

[From University of Florida, 1981]

County	Population			Housing units		
	April 1 (census)		Percent change	April 1 (census)		Percent change
	1980	1970		1980	1970	
Charlotte	59,115	27,559	114.5	35,180	13,752	155.8
De Soto	19,039	13,060	45.8	7,458	4,095	82.1
Lee	205,266	105,216	95.1	111,013	43,511	155.1
Manatee	148,442	97,115	52.9	83,586	42,841	95.1
Sarasota	<u>202,251</u>	<u>120,413</u>	<u>68.0</u>	<u>113,355</u>	<u>56,242</u>	<u>101.5</u>
Total	643,113	363,363	74.5	350,592	160,441	118.5

Any water-management plan for the study area is complicated by a poorly understood, broad, complex zone of saline ground waters. These waters constitute a large, manageable, and exploitable resource that, in some locales, is used for public supply after reverse-osmosis treatment. In other areas, the saline ground waters are mixed with waters of better quality and used following conventional treatment. Development of other water sources, storage and transport facilities, and treatment techniques will determine the extent to which saline waters will be utilized. Optimal utilization will require an understanding of the origins and distributions of the constituents in these waters and the rationale for their presence. This information will form a basis from which estimates can be made of the probability and magnitude of possible adverse effects on ground-water quality caused by future resource development.

Recognizing the need for comprehensive information about these waters of variable quality, the U.S. Geological Survey, in cooperation with the Southwest Florida Water Management District, investigated their character and distribution in the Manasota and lower Peace Basins (fig. 1). This report presents the results of the study. Principal objectives were to: (1) develop a better understanding of areal water-quality variations, and (2) relate the information developed to the extant concepts of the areal geohydrologic system. A decision was made in the planning phase of the study to focus investigative efforts on the Floridan aquifer. This decision was based on the following: (1) there was little water-quality data available from individual aquifers other than from the Floridan aquifer; (2) the Floridan aquifer, as a whole, is consistently the most permeable part of any vertical section in the study area; (3) many, if not most, wells withdraw from units in or hydraulically connected to the Floridan aquifer; and (4) the study period, October 1979-September 1981 (2 years) was insufficient to investigate the chemical character and distribution of individual and interrelated waters in all aquifers present.

Saline water is defined by the U.S. Geological Survey (Krieger and others, 1957, p. 5) as having a dissolved solids (residue, 180°C) concentration greater than 1,000 milligrams per liter (mg/L). The dissolved materials in ground water have several possible sources: (1) precipitation and recharge waters, (2) connate waters or residual seawater, and (3) the rock in which the water is stored and through which it has passed. The extent and diversity of the saline waters are products of the nature of the geohydrologic system and the regional geohydrologic history--sea-level fluctuations, the extent of dilution of connate waters, the rates and amounts of recharge, and the reactivity of aquifer materials.

Values listed in this report are in inch-pound units. Multiply the inch-pound value by the appropriate conversion factor to obtain a metric equivalent.

<u>Inch-pound unit</u>	<u>Conversion factor</u>	<u>Metric unit</u>
inch (in)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi ²)	2.590	square kilometer (km ²)
million gallons per day (Mgal/d)	0.0438	cubic meters per second (m ³ /s)

Chemical concentrations are given in millimoles per liter, micromoles per liter, milligrams per liter, and moles per kilogram of water (molal). Molar concentration units can be converted to mass concentration units by multiplying the molar value by the gram formula weight of the appropriate specie (table 2). See the following example:

$$\begin{array}{r}
 1.636 \text{ millimoles of Cl}^- \text{ per liter at site 16} \\
 \times 35.453 \text{ milligrams of Cl}^- \text{ per millimole (from table 2)} \\
 \hline
 58.00 \text{ milligrams of Cl}^- \text{ per liter}
 \end{array}$$

Elevations in this report are all referenced to the National Geodetic Vertical Datum of 1929 (NGVD of 1929). This datum was derived from average sea-level elevation data for many years of record at 26 tide stations along the Atlantic, Pacific, and Gulf of Mexico coasts, and was formerly called mean sea level. In this report, NGVD of 1929 is referred to as sea level.

Table 2.--Gram formula weights of selected dissolved species

<u>Dissolved specie</u>	<u>Gram formula weight (milligrams/millimole)</u>
Bromide (Br)	79.904
Calcium (Ca)	40.08
Chloride (Cl)	35.453
Fluoride (F)	18.9984
Iron (Fe)	55.847
Bicarbonate (HCO ₃)	61.0173
Potassium (K)	39.102
Magnesium (Mg)	24.312
Manganese (Mn)	54.938
Sodium (Na)	22.9898
Silica (SiO ₂)	60.0843
Sulfate (SO ₄)	96.0616
Strontium (Sr)	87.62

PREVIOUS INVESTIGATIONS

The hydrogeochemistry of the study area has not been examined in detail. There are, however, numerous reports on adjacent areas that discuss chemical evolution of water in the regional flow system (Hanshaw and others, 1965; Back and others, 1966; Back and Hanshaw, 1970 and 1971; Rightmire and Hanshaw, 1973; Hanshaw and Back, 1974; Wigley, 1975; Plummer and Wigley, 1976; Plummer, 1977; and Plummer and Back, 1980). These studies dealt primarily with the central part of peninsular Florida, roughly from as far north as Ocala to as far south as Cleveland. Most of the studies, however, were restricted to the ground-water flow path between Polk City and Arcadia (fig. 1) and discuss the processes active in the evolution of observed dissolved specie distributions. The studies are a significant source of Floridan aquifer geochemical data and served as a guide for this study.

PHYSICAL SETTING

Physiography

The coastal sections of the Manasota and lower Peace Basins encompass about 2,085 mi² in Charlotte, De Soto, Lee, Manatee, and Sarasota Counties. Most of this area lies in the Gulf Coastal Lowlands (White, 1970), an area of coastal terraces, swamps, lagoons, and barrier islands. The origins and

distribution of these features are the product of areal geology, depositional history, sea-level fluctuations, drainage development, and the availability of sand-sized material for beach formation; these are discussed in detail by Cooke (1945), Vernon (1951), and Parker and others (1955). The northeast part of the study area encompasses the westernmost and southwesternmost parts of the De Soto Plain and Polk Upland, respectively (White, 1970). The base of the De Soto Plain is about 30 feet above sea level. Land surface grades gently to the southwest. Altitudes range from about 135 feet in the Polk Upland in north-central Manatee County to sea level along the coast and estuaries. About 85 percent of the study area is below 50 feet in altitude.

Climate

The climate of the study area is subtropical, with warm, wet summers and mild, relatively dry winters. The wet season is typically June through September, when approximately 60 percent of the mean annual rainfall occurs. It is characterized by hot days (above 35°C) and numerous thunderstorms with accompanying heavy rainfall. Extremely intense rainfall events are usually associated with tropical disturbances that occasionally move through the area. The mean annual (1941-70) precipitation is about 53 inches, and the mean annual temperature (1941-70) is about 23°C.

Geohydrology

Peninsular Florida is the aerial exposure of the Floridan Plateau (fig. 2). The plateau is underlain by a thick sequence of sediments that overlies an igneous-metamorphic basement. Sediment thickness in the study area ranges from about 1.8 miles to more than 3.5 miles (Kohout, 1965, p. 251), increasing in thickness to the south and southwest. The freshwater-flow system comprises roughly the top 1,500 feet of material. The system units can be loosely grouped into the surficial aquifer, intermediate aquifers and confining beds, the Floridan aquifer (as described by Parker and others, 1955, p. 199), and the lower confining bed. The geohydrologic framework is shown in table 3.

The uppermost deposits are essentially sands, underlain by sediments of variable composition, structure, occurrence, and associated water quality. These upper sediments comprise the surficial aquifer and are predominantly fine and clayey sands, with shell beds and limestones significant in some locales. The surficial deposits range in thickness from about 65 to 200 feet.

A Miocene to Pleistocene interval of confining beds and intermediate aquifers separates the surficial aquifer and the Floridan aquifer. This interval is a 230- to 600-foot thick heterogeneous mixture of limestones, dolomites, marls, clays, and sands. The intermediate aquifers are frequently tapped for domestic, irrigation, and some municipal water supplies in the study area, particularly in Charlotte, Lee, and Sarasota Counties. The Verna well field in northeast Sarasota County (fig. 4) withdraws about half of its total pumpage from the intermediate aquifers and the remainder from the Floridan aquifer (P. D. Ryder, oral commun., 1981). Hydraulic continuity between the underlying Floridan aquifer and the overlying surficial aquifer is occasionally facilitated by facies variation in this

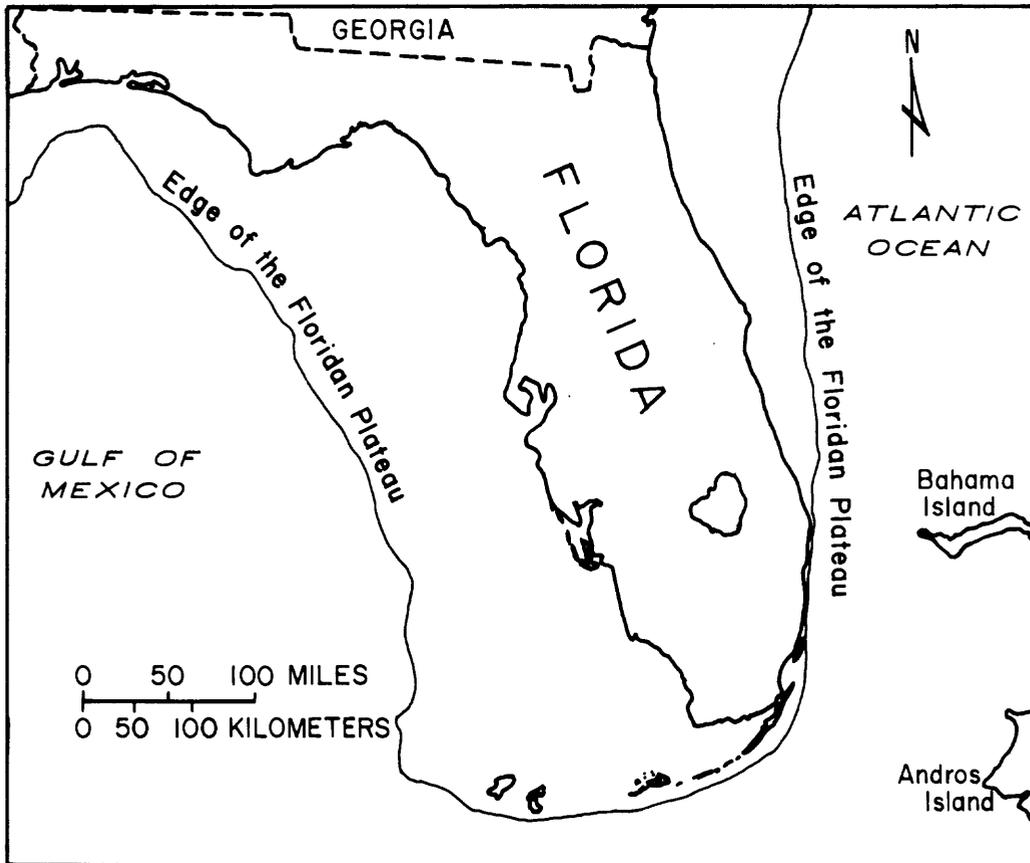


Figure 2.--Location of the Floridan Plateau.

Table 3.--Geohydrologic framework

[Modified from Wilson and Gerhart, 1980]

Series		Formation	Geohydrologic unit
Holocene		Surficial deposits	Surficial aquifer
Pleistocene		-----	-----
Pliocene		Undifferentiated deposits ¹	Intermediate aquifers and confining beds
Miocene	Middle	Hawthorn Formation	-----
	Lower	Tampa Limestone	
Oligocene		Suwannee Limestone	Floridan aquifer
Eocene	Upper	Ocala Limestone	
	Middle	Avon Park Limestone	
		Lake City Limestone	
			Lower confining bed

¹ Includes all or part of Caloosahatchee Marl, Bone Valley Formation, and Tamiami Formation.

sequence, sinkholes, and improperly constructed wells. Where permeable zones in the basal part of the interval are hydraulically connected with the Floridan aquifer, they are considered a part of the Floridan aquifer.

The principal water-bearing unit in southwest Florida is a thick sequence of massively bedded, Eocene-to-Miocene carbonate rocks referred to in Florida as the Floridan aquifer. Drill cuttings, cores, and geophysical logs are essentially the sole sources of stratigraphic, lithologic, and structural information about the aquifer, as there is no outcrop in the study area. The aquifer top is not stratigraphically continuous, as inferred in the discussion of the overlying, less-permeable beds. This is due to facies changes, generally from limestone or dolomite to clay, and irregularities of the karst topography of the buried limestone surface.

An ubiquitous feature of the lower part of the Floridan aquifer in the study area is a porous, highly permeable dolomitic interval of the Avon Park Limestone (middle Eocene). This interval is the most productive water-bearing zone in the section. The top of the interval was mapped by Wolansky and others (1980) within the Southwest Florida Water Management District. In this study, wells not completed into the dolomitic zone are considered to sample only the upper part of the Floridan aquifer.

The lower confining bed begins in that section of the Lake City Limestone (middle Eocene) where intergranular gypsum or anhydrite is vertically persistent. Few data exist as to the characteristics of this interval in the study area, as there is little commercial incentive to drill into it.

Use of the Floridan aquifer is somewhat restricted in roughly the southern half of the study area because of relatively poor water quality. South of central Sarasota County, untreated water from the Floridan aquifer is used almost solely for agricultural and industrial supplies. Municipal use requires extensive treatment, commonly reverse osmosis, as noted in the introductory section.

The predevelopment ground-water flow pattern in the Floridan aquifer can be inferred from the potentiometric surface map in figure 3. The map represents the best estimate of the configuration of the Floridan aquifer potentiometric surface before ground-water withdrawals began. The predevelopment surface map is presented for two reasons: (1) it facilitates a general understanding of regional ground-water flow, and (2) it agreed with the observed distributions of significant dissolved constituents. The flow lines illustrate the general directions of ground-water flow. It will be shown later that selected dissolved constituents increase in the same directions.

Direct recharge to the Floridan aquifer occurs primarily northeast of the study area in the Green Swamp Basin and Highlands Ridge area of the Peace Basin (fig. 1). There is some recharge from vertical leakage within the study area where the altitude of the water-table in the surficial aquifer is higher than the potentiometric surface of the Floridan aquifer. Calculations using data presented by Wilson and Gerhart (1980) and Ryder (1981) yield average maximum annual recharge rates from leakage ranging from 0.55 to 2 inches per year per unit area. The maximum occurs in the vicinity of the Verna well field in the northeast part of the study area

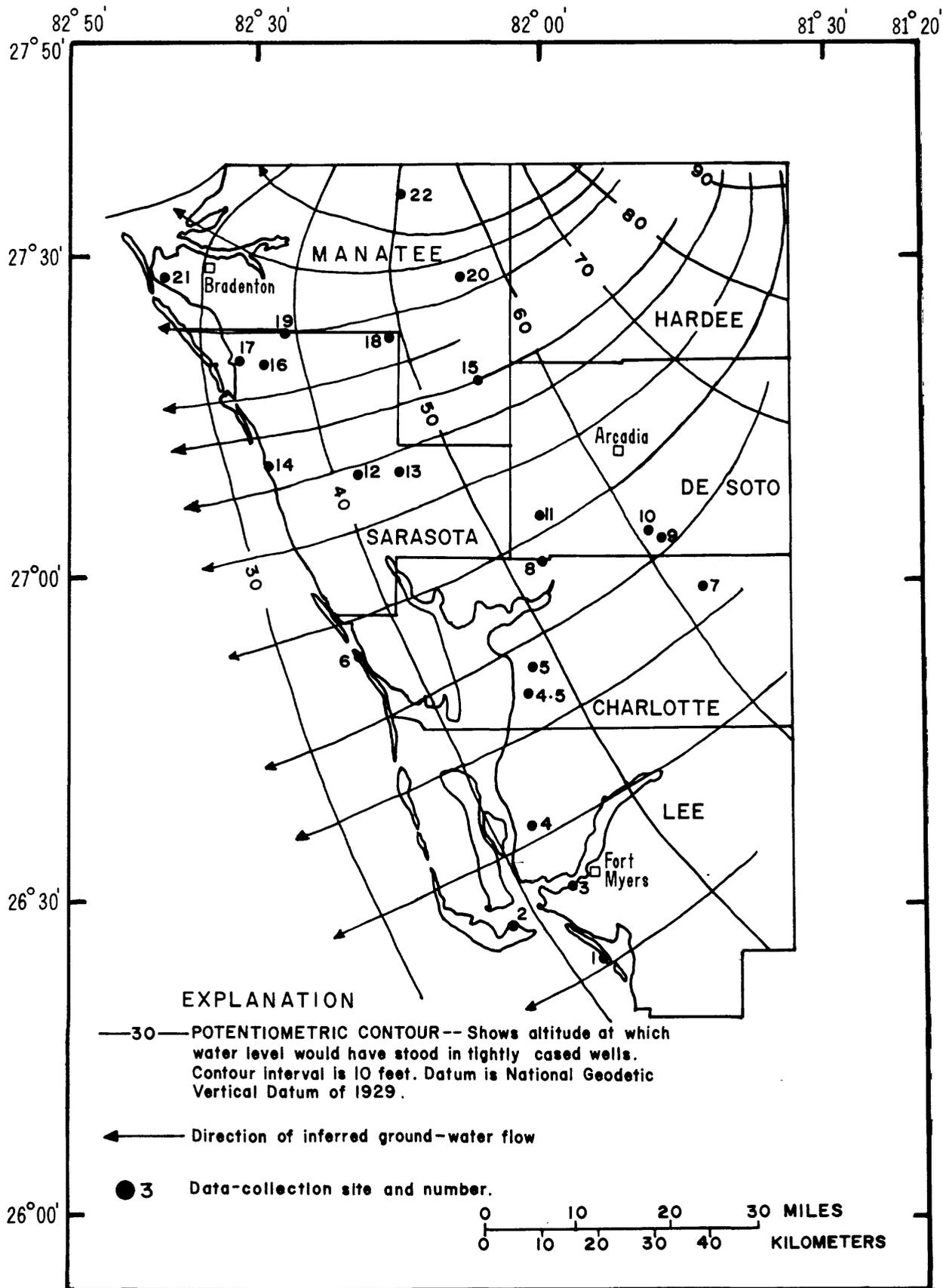


Figure 3.--Predevelopment potentiometric surface of and inferred flow pattern in the Floridan aquifer in southwest-central Florida and location of data-collection sites.

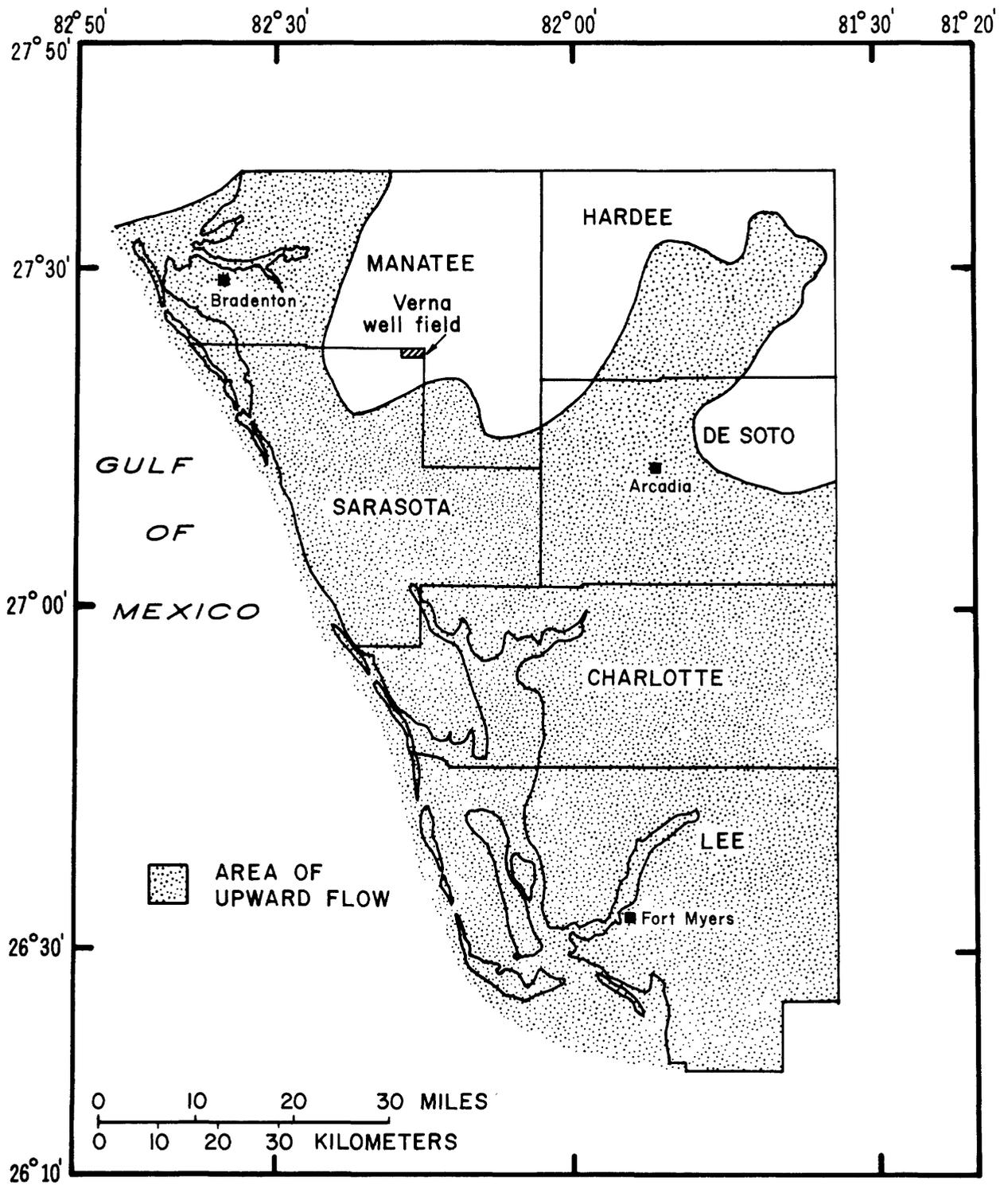


Figure 4.--Estimated area of predevelopment upward flow from the Floridan aquifer.

(fig. 4), where the water-table altitude and the intermediate aquifer potentiometric surface are higher than the Floridan aquifer potentiometric surface. Where this relation is reversed, natural discharge from the Floridan aquifer is upward to streams, springs, and overlying aquifers (fig. 4) upgradient from the freshwater-saltwater interface.

Ground-water withdrawals in 1980 for the five counties in the study area are listed in table 4. Irrigation was the largest water-use category and accounted for 79.7 percent of the estimated average daily pumpage rate of about 250 Mgal/d. Public supply and rural usage accounted for 11.4 percent and 6.5 percent, respectively.

Table 4.--Estimated average daily ground-water withdrawals in 1980 in Charlotte, De Soto, Lee, Manatee, and Sarasota Counties

[Data from Duerr and Trommer, 1981, and S. D. Leach, oral commun., 1981]
 [Withdrawals, by usage category (million gallons per day)]

County	Public	Rural	Irrigation	Industrial
Charlotte	0.00	1.24	22.49	0.00
De Soto	.71	2.15	33.30	.53
Lee	16.82	6.21	39.31	4.08
Manatee	.00	5.08	64.92	.19
Sarasota	<u>11.07</u>	<u>1.59</u>	<u>20.38</u>	<u>.10</u>
Total	28.60	16.27	180.40	4.90

WATER CHEMISTRY

Data Collection

Water samples and field water-quality data were collected during July-November 1980 at 23 well sites (fig. 3, table 5). All but three wells (4.5, 6, and 7) are known to be completed in and open only to intervals in the Floridan aquifer based on geologic and geophysical logs; well construction data; conversations with well drillers, private consultants, and previous investigators; and a map of the top of the Floridan aquifer (Buono and Rutledge, 1978).

Table 5.--Data-collection sites

Data site number	Owner or name	Location (latitude N longitude W seq. no.)	Depth in feet well/casing
1	Bay Beach Golf Club	262435N815351W01	950/740
2	The Dunes - deep	262734N820315W01	896/700
3	The Landings - deep	263301N815520W01	1,200/600
4	Pine Island Water Assoc. no. 1	263818N820204W02	850/625
4.5	Tony Leto/Hot Springs	264923N820137W01	1,900/648
5	Old Facefull	265124N820124W01	1,454/ ¹
6	Palm Island Beach	265314N822002W01	450/421
7	Golden Groves, Bermont	265842N814148W01	² /600
8	ROMP 10 - Deep	270152N820028W01	917/595
9	J. R. Aborgia	270332N814733W01	1,211/685
10	Roper Groves	270442N814943W01	1,189/640
11	General Development - deep test	270554N820036W01	1,411/1,326
12	ROMP 19/WAM-1	270959N822030W01	425/405
13	EAM-1	271021N821516W01	420/400
14	Southbay Utilities - deep	271035N822859W01	710/493
15	Edgeville - deep	271832N820648W01	600/487
16	Bobby Jones Golf Club - no. 1	272036N822846W01	1,000/440
17	Sarasota Injection Monitor - no. 2	272053N823202W02	1,500/1,108
18	Verna Pr. 27	272256N821635W01	1,000/620
19	Charles Schmidt Dairy	272312N822104W01	1,490/620
20	Old Myakka - deep	272735N820834W01	560/514
21	Manatee Fruit Co. - glad. field	272738N823847W01	511/415
22	H & G Farms - no. 1	273531N821505W01	1,160/480

¹ Plugged at 1,200 feet.

² Plugged at 800 feet.

Site 4.5 was a water-supply well for an adjacent exploratory oil well. The casing was removed from the abandoned oil test well during World War II, and several plugs were set at successive depths. Shortly thereafter, site 4.5 began to discharge about 4 Mgal/d of warm, saline water (F. A. Kohout, oral commun., 1981) that probably is not entirely from the Floridan aquifer. Site 6 is marginally deep and may not be open to the Floridan aquifer. Water-level data are needed to better establish the water source. Site 7 was initially drilled to a depth of 1,310 feet with 715 feet of casing. The resultant water quality was unsatisfactory and the well was plugged back to a depth of 800 feet. Explosives were then detonated at a depth of about 600 feet to complete the well (Horace Sutcliffe, Jr., oral commun., 1981; Ken Kennard, oral commun., 1981). Uncertainty as to the resultant completion interval and postdetonation well integrity raises doubt as to whether the well samples only the Floridan aquifer.

Sites 11, 17, 19, and 22 are completed in the highly permeable middle Eocene dolomitic zone, but only site 11 samples the dolomitic interval exclusively. Site 18 was drilled into the middle Eocene, based on geophysical logs in a report on the Verna well field (Sutcliffe and Buono, 1979, p. 13). A map of the top of the dolomitic zone (Wolansky and others, 1980), however, indicates that this well bottoms out about 110 feet above the zone top. The remaining wells sample varying intervals of the aquifer above the middle Eocene.

Unaerated samples were collected from each well for field and laboratory analyses. Water temperature, specific conductance, pH, and bicarbonate ion concentration were determined at each site at the time of collection. Samples were collected after temperature, specific conductance, and pH in the produced stream from the well had stabilized as indicated by three consecutive, identical (within the limits of determinative capability) measurements. Filtered samples were obtained using a 0.1 micrometer in-line membrane filter. Analytic results and physical characteristics are presented in table 6.

Chemical Characteristics

The sampled waters varied widely in dissolved solids (residue at 180°C) concentrations and in the relative concentrations of individual species. The waters ranged from fresh in the northeast to very saline in the southwest. This trend coincides with regional geologic dip and holds true for all of the essentially nonreactive dissolved constituents, temperature, and specific conductance. Water temperature and dissolved species concentrations also increase with depth in the aquifer.

Water from site 20 in Manatee county, farthest upgradient and in the upper part of the Floridan aquifer, is a calcium magnesium bicarbonate sulfate type that has evolved from recharge area waters by means of dolomite $[\text{CaMg}(\text{CO}_3)_2]$ and gypsum $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$ solution with simultaneous low-magnesian calcite (CaCO_3) precipitation (Plummer, 1977). The waters from sites 1 through 6 are farthest downgradient from the recharge area and are moderately to very saline sodium magnesium chloride types that are similar in ionic proportions to seawater. The intermediate waters grade between these two end-member types.

Table 6.--Field data and results of analyses

[Data site numbers correspond with figure 3. Samples collected July-November 1980.
Concentrations are in millimoles per liter, except as indicated]

Data site number	Temperature (°C)	pH field (units)	Sodium	Potassium	Magnesium	Calcium	Strontium	Manganese ¹	Iron ¹	Bicarbonate	Fluoride	Chloride	Bromide	Sulfate	Silica	Residue, 180°C ²	Spec. cond., 25°C field (µmho cm ⁻¹)
1	28.8	7.38	29.58	0.72	6.17	4.75	0.29	0.18	1.25	2.72	0.07	39.49	0.066	4.89	0.27	3,160	5,310
2	29.6	7.31	82.65	1.28	11.11	5.74	.40	.18	13.43	3.11	.07	110	.200	4.37	.32	7,660	11,650
3	29.7	7.42	24.79	.69	4.52	3.00	.23	.00	.72	2.95	.07	31	.040	3.33	.33	2,730	4,280
4	28.4	7.41	21.75	.59	4.11	2.50	.23	.18	2.86	3.28	.06	27.14	.079	2.91	.32	2,390	3,730
4.5	35.3	7.14	382.78	9.21	45.25	11.0	.25	.55	13.79	2.20	.04	423	.288	22.90	.17	32,700	39,500
5	28.9	7.36	26.10	.46	4.94	4.00	.40	.00	.90	2.36	.05	36.67	.055	3.23	.32	2,910	4,250
6	28.5	7.18	104.39	1.25	13.98	10.24	.65	.36	15.76	2.84	.05	135.4	.011	6.66	.30	10,200	13,800
7	32.2	7.78	24.36	.43	4.94	4.50	.50	.36	6.09	1.87	.04	33.85	.080	5.20	.23	2,670	4,120
8	27.0	7.59	4.35	.19	2.51	2.50	.19	.36	2.15	2.46	.10	4.51	.014	4.27	.35	1,040	1,385
9	28.4	7.62	2.48	.08	1.48	1.80	.22	.18	1.25	2.79	.05	3.10	---	1.67	.38	600	920
10	31.2	7.41	5.65	.10	1.89	2.25	.49	.18	.54	2.95	.04	8.74	.018	1.98	.37	1,030	1,520
11	30.7	7.39	4.00	.12	2.34	2.75	.31	.36	3.94	3.44	.08	5.64	.010	3.23	.42	1,090	1,420
12	26.3	7.22	1.35	.13	3.41	5.00	.16	.00	.18	2.79	.09	.82	.004	8.12	.45	1,400	1,600
13	25.8	7.28	1.09	.08	2.71	3.50	.19	.00	.00	3.23	.09	.93	.004	5.20	.40	1,010	1,260
14	26.7	7.10	5.65	.17	6.99	11.49	.16	.55	8.95	2.79	.11	7.90	.018	18.74	.40	3,240	3,390
15	26.2	7.43	.70	.08	1.81	2.00	.13	.91	11.28	3.61	.09	.48	.004	2.19	.47	597	770
16	27.7	7.39	1.30	.13	2.96	4.25	.26	.00	1.07	3.43	.11	1.64	.004	5.20	.52	990	1,245
17	26.1	7.51	21.75	.36	8.64	9.74	.23	1.09	28.65	1.25	.06	31.03	.014	13.53	.42	3,920	5,600
18	29.4	7.20	.61	.07	3.13	4.50	.16	.18	1.79	3.11	.06	.54	---	6.56	.43	1,140	1,700
19	28.5	7.24	19.14	.87	8.23	8.24	---	.55	3.58	2.56	.15	11.56	.041	21.86	.82	4,010	4,200
20	25.2	7.70	.48	.04	.86	1.37	---	.55	2.69	3.10	.04	.39	.003	1.02	.35	366	500
21	25.2	7.21	3.04	.17	2.39	3.00	.09	.00	.90	4.42	.11	5.64	.015	1.87	.75	900	1,310
22	29.0	7.30	.43	.05	1.73	3.50	.13	.00	.54	3.05	.06	.48	.010	4.37	.33	864	1,040

¹ Concentration in micromoles per liter.

² Concentration in milligrams per liter.

The gradation in water types is illustrated in the plot of major cation and anion equivalent concentration percentages on the tri-linear diagram in figure 5. The data illustrate evolution of ground-water quality in a carbonate geohydrologic system. Site 20 in figure 5 is representative of Floridan aquifer water near the study area inflow boundary. As this water moves downgradient, it systematically reacts with aquifer minerals, relative magnesium and sulfate concentrations increase, and the water gradually evolves to a composition typified by site 12. Farther downgradient, this water mixes with more saline water, as evinced by an increasing chloride percentage, evolving toward a marine-like water.

FACTORS INFLUENCING GROUND-WATER CHEMISTRY

The chemical composition of waters in the Floridan aquifer result from physical mixing and chemical interactions between water and aquifer materials. These systematic interactions encompass sedimentary diagenetic reactions and mass transfer. They combine with depositional history and structural activity to produce the hydrologic properties that determine the ability of the aquifer to store and transmit water.

Permeability

The permeability distribution in the Floridan aquifer is nonuniform, as it has resulted from a combination of factors that act nonuniformly in carbonate depositional systems. Interconnected joints and fractures facilitate the flow of relatively large volumes of water at relatively high velocities. This flow enhances dissolution of aquifer material, amplifying channeling effects and essentially localizing permeability. Bedding planes, or analogous laminar structures, and faults are also potential sites of preferential flow and subsequent dissolution. The extent of horizontal and vertical interconnection between such features controls the large-scale or areal permeability distribution.

Development of small-scale permeability due to the evolution of mineral assemblages is a dynamic process in the history of a flow system in a carbonate aquifer. It essentially entails a reduction of initial porosity with a simultaneous permeability increase. Aragonite (CaCO_3) and magnesian calcites are the dominant minerals in recently deposited marine carbonate sediments. Aragonite is a calcium carbonate mineral with a different crystal structure than calcite. It is more soluble than calcite, and as the sediments are initially flushed of saline interstitial fluids, aragonite inverts to calcite. This process, together with the recrystallization of adjacent original calcite to a calcite with a lower magnesium concentration, results in increased mineral grain size and grain cementation. As grains enlarge, initially existing small pores are "concentrated" in larger intergranular spaces, and permeability is increased. The chemical environment also becomes increasingly conducive to dolomitization, or dolomite precipitation, as native marine waters are flushed from the sediments (Folk and Land, 1975, p. 64-65). Dolomitization can either increase or decrease porosity and permeability (Hanshaw and Back, 1979, p. 302).

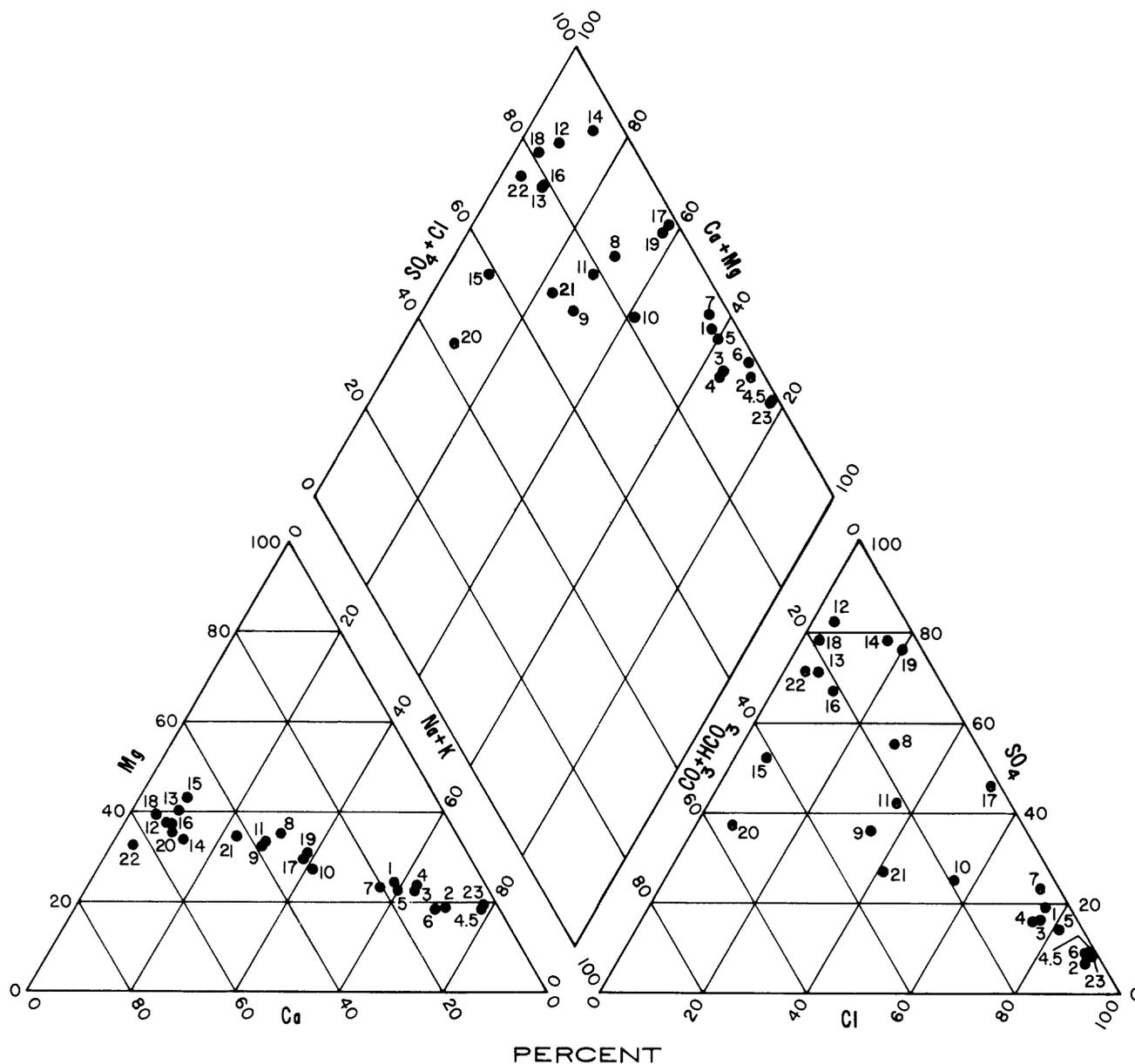


Figure 5.--Trilinear plot of major cation and anion equivalent percentage concentrations. Site 23 is seawater (from Goldberg, 1963, p. 4-5).

Much of the Tertiary dolomite in peninsular Florida could have been deposited or formed in a brackish depositional environment (Hanshaw and Back, 1971, p. 147).

Lateral compositional variations within the geologic units account for variations in permeability, as demonstrated by wells at sites 12 and 13. The wells were constructed nearly identically (table 5; Geraghty and Miller, Inc., 1981, p. A-5, A-8) and are 5.4 miles apart, roughly along a flow line (fig. 3). Lithologic logs and water-level data from site 12 (Geraghty and Miller, Inc., 1981, p. 24, B4-B12) indicate that about 148 feet of interbedded clays and limestones isolate the sampled interval in the Floridan aquifer from the deepest intermediate aquifer. The same interval at site 13 contains little clay and is more permeable, facilitating hydraulic continuity between the completion interval and the overlying intermediate aquifer.

The chloride concentrations in the intermediate and upper Floridan aquifers at site 12 are about 2 and 0.82 millimoles per liter, respectively (Geraghty and Miller, Inc., 1981, p. D9; table 4). The higher chloride concentration in the intermediate aquifer, combined with the higher permeability of the intervening interval at site 13, explains the higher chloride concentration noted in the Floridan aquifer at site 13. The water in the entire permeable section at site 13 appears to be well mixed, based on water-quality data collected during drilling (Geraghty and Miller, Inc., 1981, p. D9, D14), as there is little chloride concentration variation with depth in the interval.

Mixing

The permeable nature of the Floridan aquifer facilitates mixing of different water types within the aquifer. The scale and efficiency of mixing depend on pore geometry and permeability distribution. Macroscopic features, such as interconnected solution channels and cavities developed along bedding planes, fractures, and joints, are the most significant flow paths in the Floridan aquifer. These channels and cavities facilitate nonuniform deep invasion of native waters, resulting in a broad transition zone between upgradient fresh and downgradient saline waters.

The effectiveness of mixing and the resulting water-quality gradation are illustrated in a comparison of observed bromide and chloride concentrations with seawater dilution values (fig. 6). The straight line in figure 6 shows the bromide and chloride concentrations that would result if seawater were increasingly diluted. These ions are essentially nonreactive in all of the waters sampled and are indicators of the extent of fluid mixing. The analytic data follow the dilution trend to a chloride concentration of about 2.5 millimoles per liter (mmol/L). Sites with lower concentrations are the youngest and freshest waters sampled. The data for site 16 plot closer to the line than the other freshwater sites because of its higher chloride concentration. This site is a golf course irrigation well that samples roughly the upper half of the aquifer through a 560-foot open-hole completion interval. It was drilled and completed to within about 150 feet of the highly permeable dolomitic zone. The dolomite zone in the vicinity of site 16 contains moderately saline water as indicated by data for sites

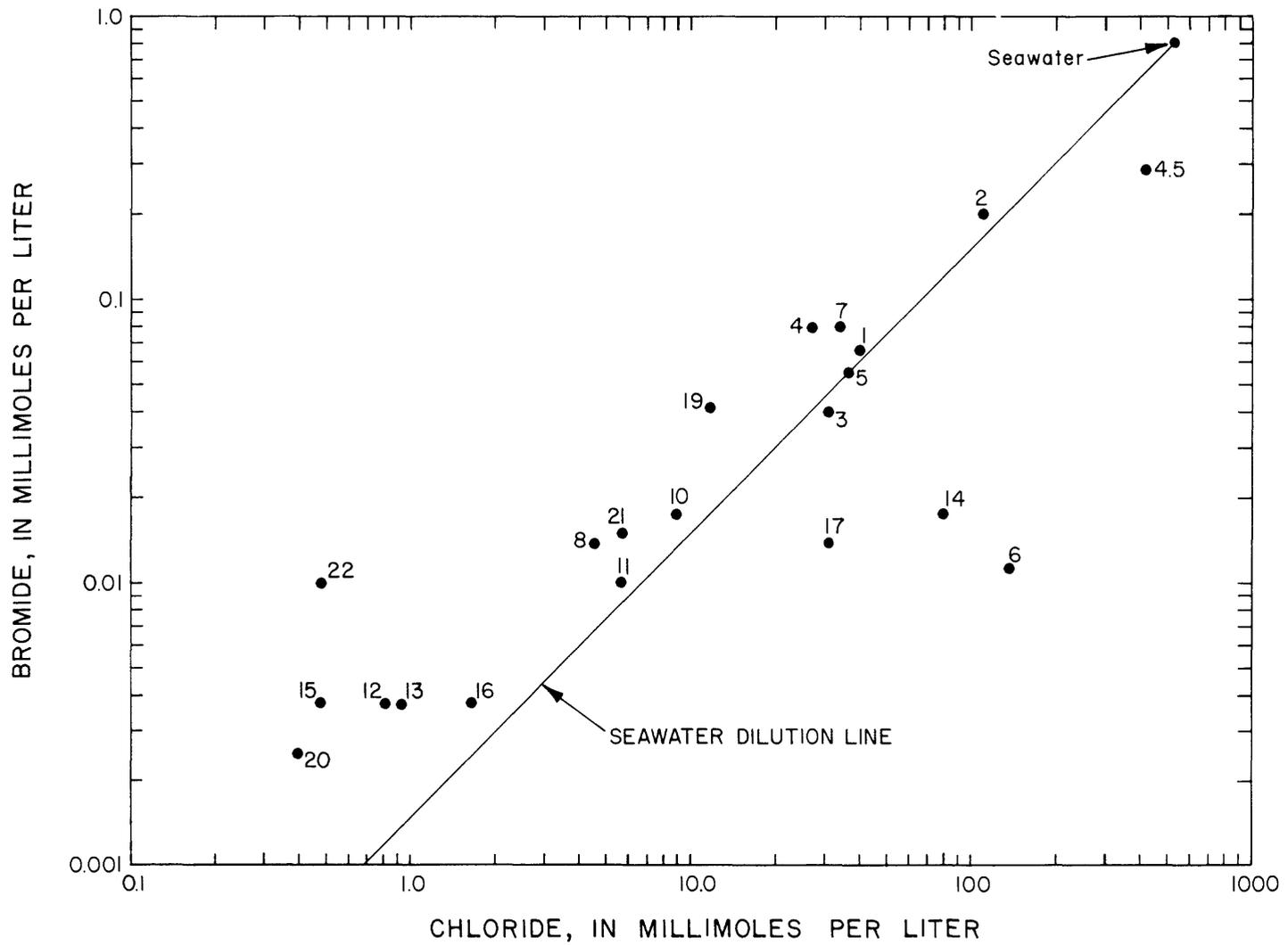


Figure 6.--Bromide concentration versus chloride concentration.

17 and 19 (table 6). Site 16 is heavily used about 9 months each year and conceivably induces some upward flow from the more saline dolomitic zone. This flow could account for the observed chloride concentration if it contributes 5 to 10 percent of the well discharge. The data for this site were collected during the period of heavy pumpage.

Mixing is a significant control on ground-water quality only in the extreme coastal part and the southern half of the study area. This is illustrated by comparing the relations between specific electrical conductance and dissolved solids and between conductance and dissolved chloride (fig. 7a, b). Figure 7a shows that the conductances of sampled waters increase with increasing dissolved solids concentrations. The relation approximates a straight line and seems to indicate that all waters sampled are essentially the products of simple mixing.

The lines on figure 7b are conductance-chloride relations for seawater dilutions and sodium chloride solutions. The sodium chloride solutions are an approximation of seawater (Horne, 1969, p. 56-57) and are presented because they include lower chloride concentrations than the available seawater dilution data. This figure shows that sites with chloride concentrations greater than about 2.5 mmol/L roughly follow these dilution lines, the deviation increasing with decreasing chloride concentration. This indicates that the concentrations of nonreactive dissolved species, such as chloride and bromide, are an approximate measure of the percentage of marine-like water present in a sample. Those samples with less than 2.5 mmol/L of chloride do not closely follow the dilution trends. These are relatively fresh, upgradient sites, which are essentially free of any marine-like component, and their compositions are largely controlled by other processes.

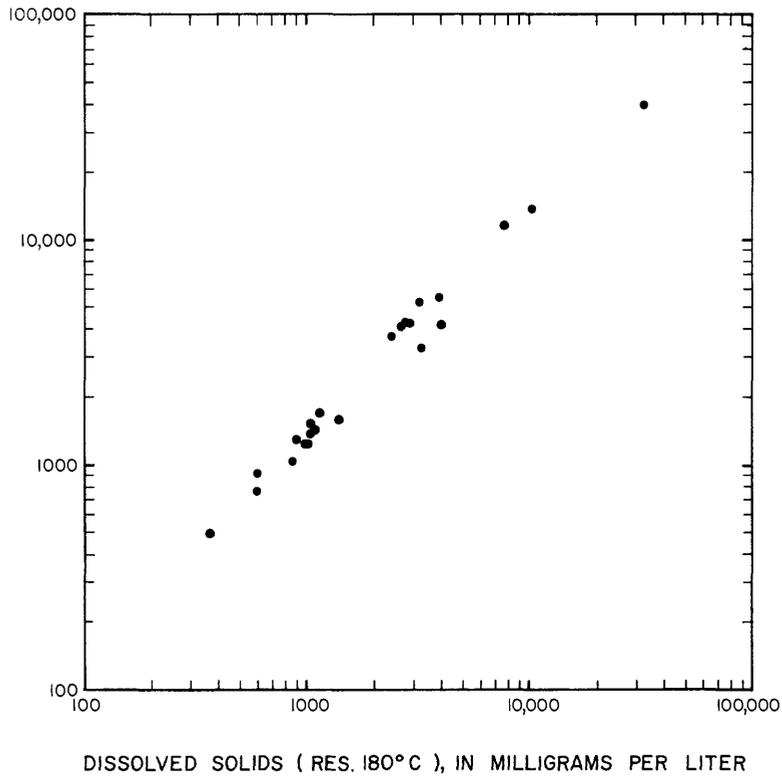
Geochemistry

Mineral solution and precipitation, ion sorption and desorption, and oxidation-reduction reactions are the most significant natural controls on the suites of dissolved materials in ground-water systems. Solution and precipitation are the primary, large-scale diagenetic processes in the evolution of Floridan aquifer water quality as evinced by the concentration distributions of selected dissolved species.

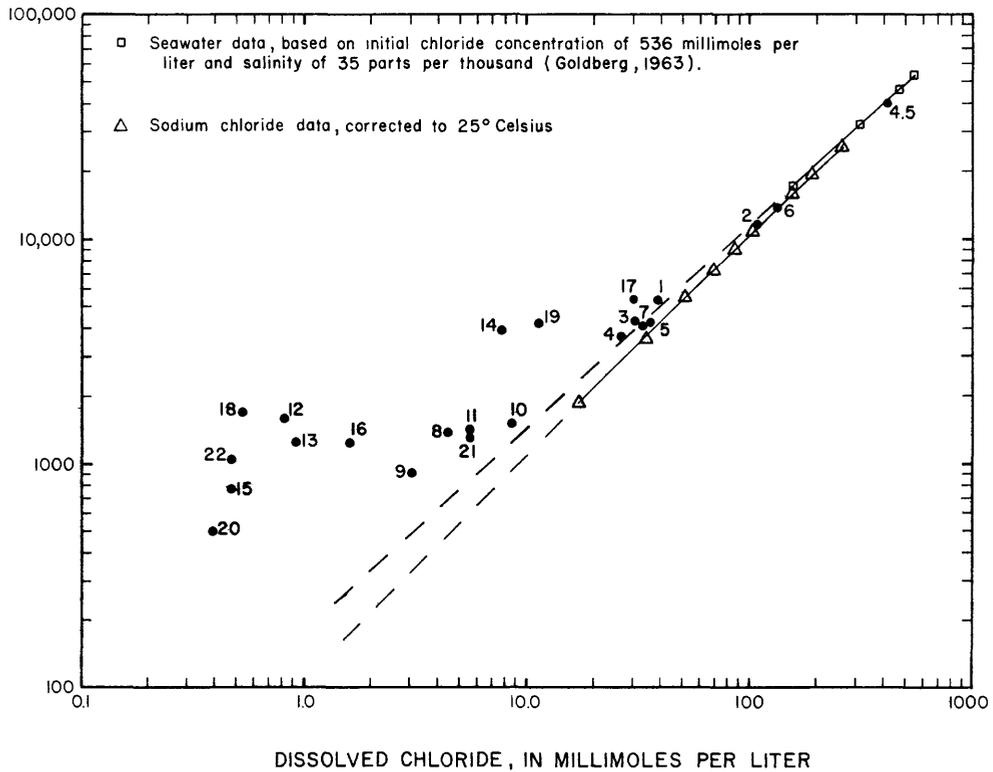
Dolomite, gypsum, calcite (the rhombohedral crystal form of calcium carbonate), and aragonite (the orthorhombic form) are major mineral sources and sinks for many of the dissolved species in the Floridan aquifer. The extent to which they affect dissolved concentrations depends on individual mineral solubility, as simply explained below.

All minerals dissolve, to some extent, in ground water. The amount of a particular mineral that can be dissolved depends largely on its elemental composition and crystal structure. This tendency to dissolve is referred to as mineral solubility. The greater the mineral solubility, the greater the input of the individual mineral components to the ground water by mineral dissolution; the lower the solubility, the greater the tendency for mineral components to be removed from solution by mineral precipitation.

SPECIFIC CONDUCTANCE, IN MICROMHOS PER CENTIMETER AT 25° CELSIUS



A. SPECIFIC CONDUCTANCE VERSUS DISSOLVED SOLIDS.



B. SPECIFIC CONDUCTANCE VERSUS DISSOLVED CHLORIDE.

Figure 7.--Specific conductance versus dissolved solids and chloride concentrations. (Seawater data from Goldberg, 1963, p. 4-5; sodium chloride solution data from Weast, 1978.)

The concentration of a specific ion in ground water depends on the minerals with which the water is or has been in contact, the respective mineral solubilities, the composition of the influx and the waters in place, and the flow rate through the aquifer.

Only finite amounts of minerals can be dissolved or precipitated by a finite ground-water volume. The dynamic nature of the flow system, however, enables the transport or alteration of huge amounts of aquifer material on a geologic time scale. When a dissolved concentration limit is reached, mineral solution continues, although the dissolved concentration does not increase. The limit is maintained because the rate at which dissolved material is added to solution (mineral solution) is equaled by the rate at which it is removed (mineral precipitation). This condition is known as chemical equilibrium. The ultimate concentration of a specific dissolved specie is determined essentially by: (1) the solubility of the least soluble mineral present of which it is a component and (2) the concentrations of other dissolved species. This limitation can be observed in figure 8, a plot of dissolved calcium and magnesium concentrations versus dissolved chloride. The calcium and magnesium values fall within a narrow concentration range, compared to that of chloride, and do not approximate a dilution trend, as shown in figure 6. A similar data distribution is shown by other dissolved species (table 6) that react appreciably in solution and are present in aquifer minerals, including bicarbonate, fluoride, sulfate, iron, manganese, strontium, and silica.

As noted in the discussion of permeability, a large part of initially deposited carbonate sediment is aragonite. Its orthorhombic crystal structure is more open than the rhombohedral calcite framework and accommodates positive ions with radii equal to or greater than that of calcium (table 7). Aragonite commonly contains a significant amount of strontium, which can substitute readily for calcium in the crystal framework. As aragonite inverts to calcite, the inability of the calcite framework to accommodate strontium explains the general strontium concentration increase observed downgradient from the recharge area. Celestite (SrSO_4) solution possibly contributes to observed strontium concentrations, but mineralogic data to support this thesis or to quantify any possible contribution could not be found.

Table 7.--Crystal ionic radii of selected elements

Ion	Crystal radius (A°)	
Ba ²⁺	1.34	} Fit into orthorhombic
Sr ²⁺	1.12	
Ca ²⁺	.99	} structure
Mn ²⁺	.80	
Fe ²⁺	.74	} Fit into rhombohedral
Mg ²⁺	.66	

Calcite recrystallization is contemporaneous with aragonite inversion. The varying magnesium concentration in the calcite originally deposited is higher than that in the recrystallized calcite because the low-magnesian form of the mineral is thermodynamically more stable (Plummer and Mackenzie, 1974, p. 79). The excluded magnesium ions remain in solution, increasing the ground-water magnesium concentration. Dolomite solution, dedolomitization, is also a means by which magnesium concentrations can increase. The result of these effects can be seen in the data distribution in figure 9. This figure is a plot of observed ground-water magnesium concentrations versus magnesium concentrations that would derive from nonreactive dilution of seawater with distilled water. For example, the magnesium and chloride concentrations in seawater are about 55.5 mmol/L and 536 mmol/L, respectively. These concentrations yield a Mg/Cl ratio of 0.104. The magnesium and chloride concentrations at site 4 were 4.11 mmol/L and 27.14 mmol/L, respectively, and yield a ratio of 0.15. Assuming that the chloride concentration at site 4 resulted solely from seawater dilution, the maximum magnesium concentration that could be expected is 2.81 mmol/L ($= 27.14 \times 55.5 \div 536$). This is significantly less than the analyzed value from site 4. Figure 9 shows that all but two sites (2 and 6) were enriched in magnesium, relative to a simple seawater dilution with site 4.5 being only slightly enriched. The exceptions are moderately to very saline waters that probably owe most of their compositional traits to mixing.

Gypsum is commonly found in parts of the Floridan aquifer. Plummer (1977) concluded that it plays a significant role in the evolution of ground-water quality. Its influence is illustrated in figure 10, a plot of sulfate chloride equivalent concentration ratio versus the sulfate concentration in millimoles per liter. The lines in figure 10 are the concentration relations between sulfate and chloride that would result from: (1) gypsum dissolution in ground water from site 20, with no subsequent sulfate precipitation--line labeled "gypsum solution" and (2) mixing seawater with water from site 20, again with no sulfate lost from solution--line labeled "mixing."

The mixing relation shown was determined by calculating the sulfate and chloride concentrations obtained by hypothetically diluting seawater (with water from site 20) from 100 percent to 0.5 percent seawater. This is a linear dilution; the resulting line in figure 10 is curved because of the logarithmic scale. A similar curve, displaced to the left, would result if rainfall in the vicinity of the recharge area was used as the fresh end member (fig. 10). The dissolution relation was derived by hypothetically adding increments of sulfate to site 20 water, then calculating and plotting the sulfate chloride ratio versus the sulfate concentration.

The data from sites 12, 13, 15, 18, and 22 are near the solution line. Their sulfate chloride ratios increase almost uniformly from that of site 20, suggesting that the dissolved sulfate in the ground water at these sites comes largely from gypsum in the aquifer. The remainder of the sites are mixtures of sulfate derived mostly from gypsum solution, with a marine-like contributor becoming more significant as a seawater chloride concentration is approached. These conclusions agree with the findings of Pearson and Rightmire (1980).

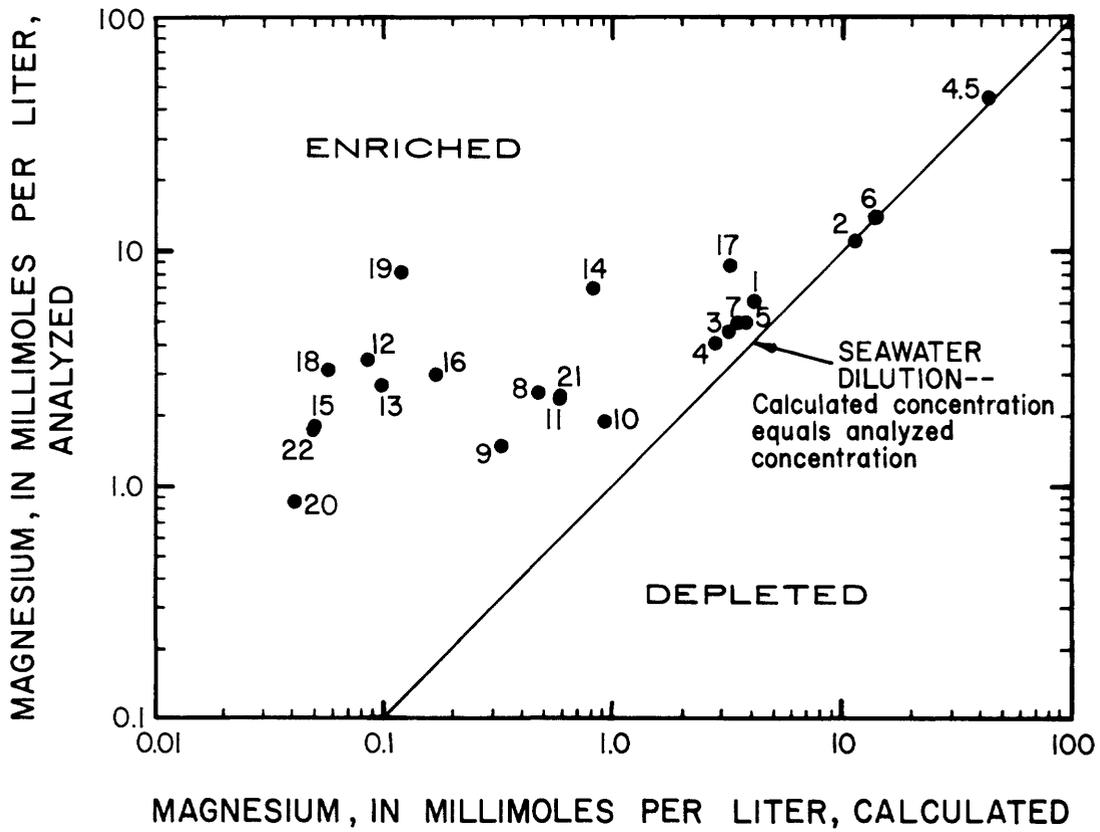


Figure 9.--Analyzed versus calculated magnesium concentrations.

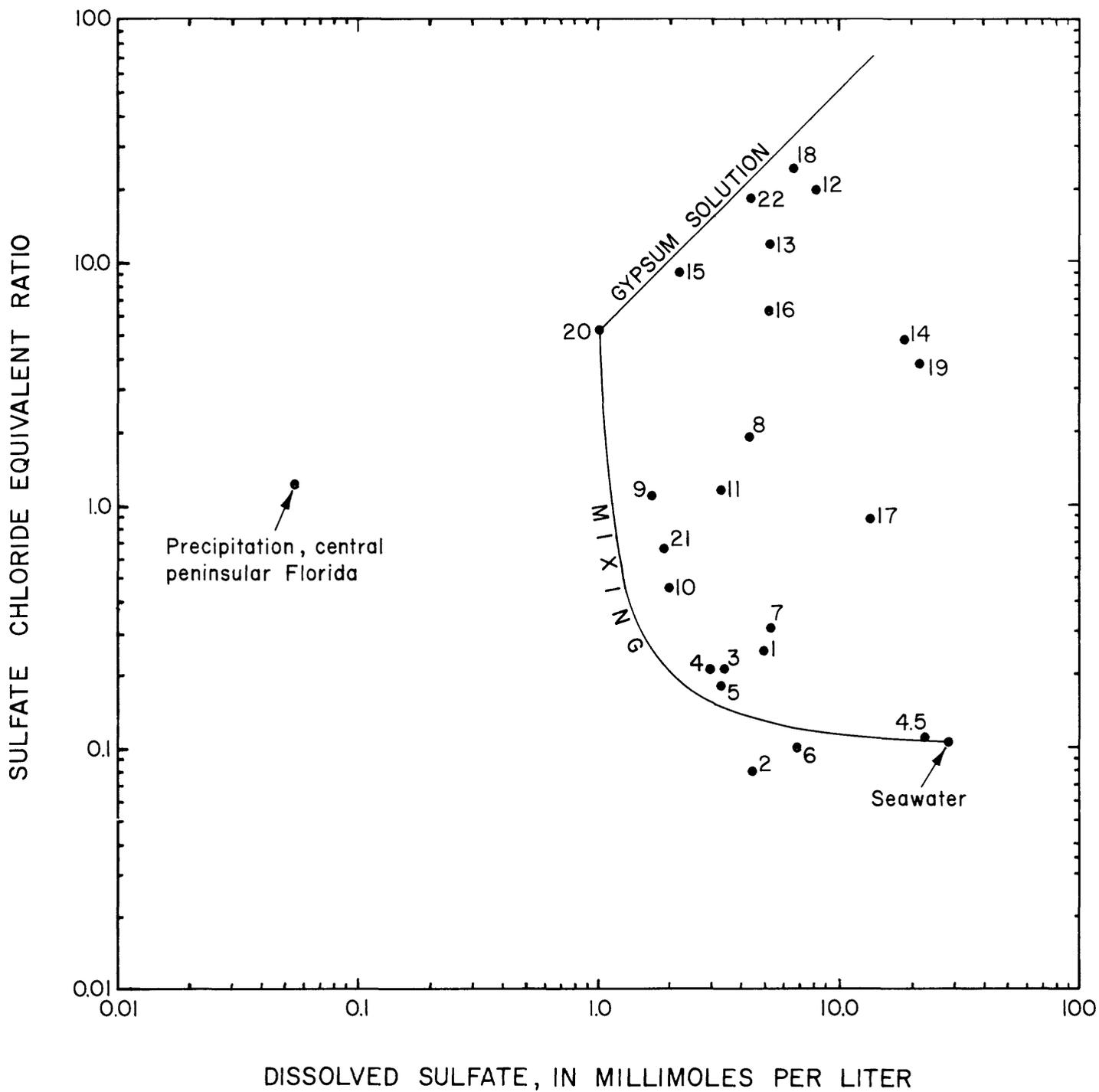


Figure 10.--Sulfate chloride equivalent concentration ratio versus sulfate concentration. (Seawater data are from Goldberg, 1963, p. 4-5. Precipitation data are from Irwin and Kirkland, 1980, p. 63.)

Figure 11 shows the areal dissolved sulfate distribution in the upper part of the Floridan aquifer, July-November 1980. A conspicuous feature is the anomalously high concentration in northeast Sarasota County in the vicinity of the Verna well field. This is based on data from site 18, which is in the well field at a land-surface elevation of 85 feet. This well was initially drilled to about 1,106 feet below sea level, then plugged to 916 feet (Sutcliffe and Buono, 1979, p. 19, 21). The top of the dolomite zone at this site is about 1,030 feet below sea level (Wolansky and others, 1980). The sulfate data, therefore, suggest two possible situations or a combination thereof: (1) the plug is leaking; or (2) there is significant hydraulic continuity between the completion interval, 535 to 916 feet below sea level, and the top of the dolomite zone, 114 feet below. If the plug is sound, then the well or well field may be inducing significant vertical flow of more saline water from the deeper permeable interval to the upper part of the aquifer. Seaburn and Robertson, Inc., (1980, fig. 32., p. 125) also reported higher sulfate concentrations in this area. Their data, however, were not from wells that sampled the Floridan aquifer exclusively.

Comparison of the sulfate distribution (fig. 11) with the chloride distribution in the upper part of the aquifer (fig. 12) demonstrates that both show concentration increases in the general direction of ground-water flow (fig. 3). There is a significant difference between the two in the northwestern part of the study area. The sulfate concentration at site 21 is sufficiently low (table 6) to cause the area with less than 250-mg/L to intersect rather than parallel the coastline. This feature occurs solely because of the lack of contradictory data collected in this study and may not be real. Peek (1958) reported sulfate concentrations between about 400 and 700 mg/L in the upper part of the Floridan aquifer in the vicinity of site 21. His chloride data agree with the findings of this study, whereas the dissolved solids data he reported are as much as about 1.5 times that found in 1980. His wells did not sample the Floridan aquifer exclusively.

The sulfate value from site 21 appears low for a water at that position in the flow system and so near the coast. There are several possible explanations. The analytic data could be in error, but this is not likely, as the analysis is chemically balanced. Additionally, chemical equilibrium calculations yield reasonable results. Peek (1958) reported sulfate values ranging from 100 to 1,710 mg/L for wells located near the coast that sampled the intermediate aquifers. Corresponding chloride data from these wells do not support the possibility that the well casing is leaking fresher water from this interval into the sampled zone. Further, the site operator indicated that the study analytical data reflect water-quality data collected periodically since 1974. Downward movement of freshwater is also unlikely, as Ryder (1981) shows from 100 to 200+ feet of confining material overlying the Floridan aquifer in this area. This inconsistent sulfate concentration will be explained only after additional data have been collected.

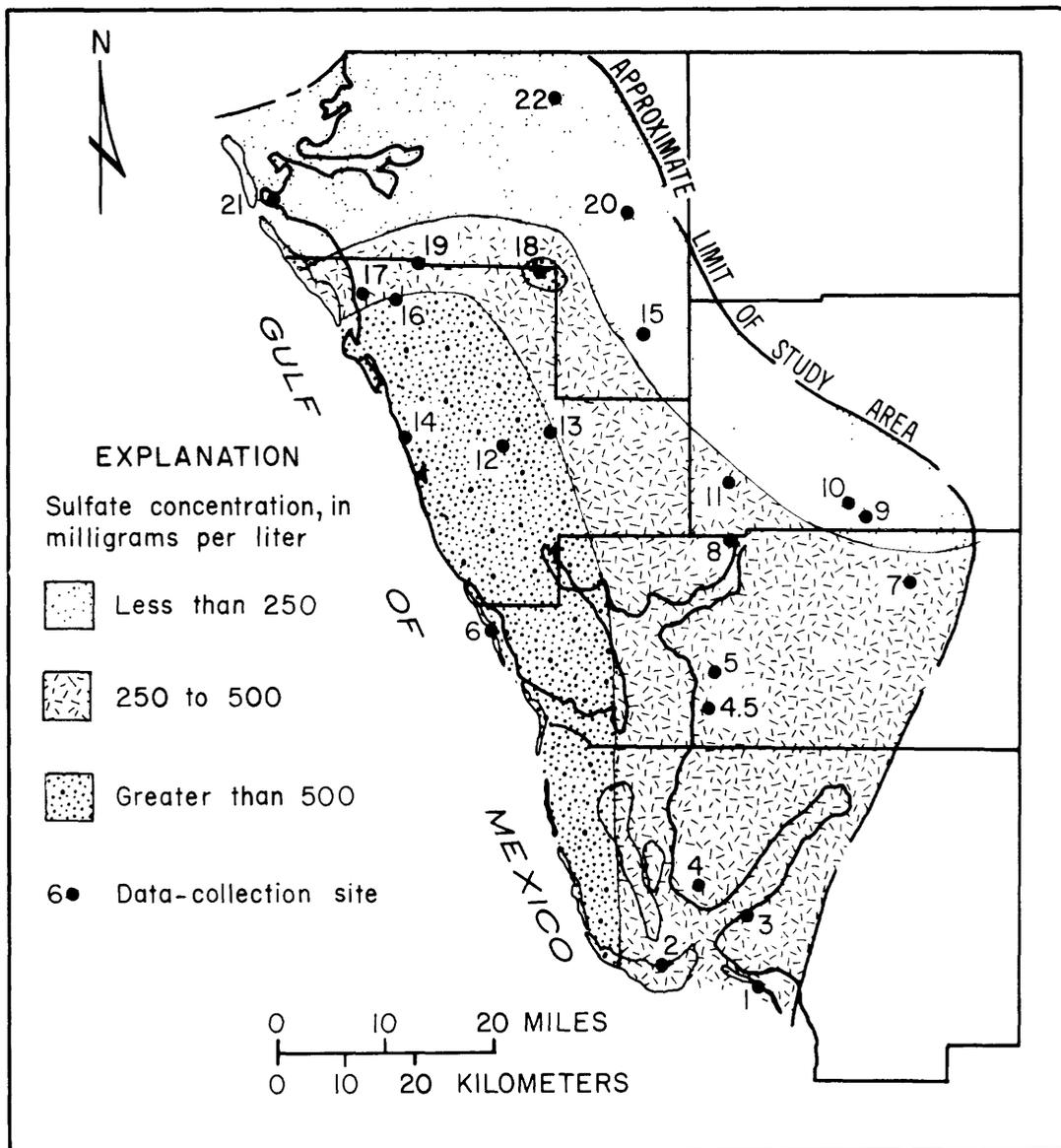


Figure 11.--Estimated dissolved sulfate distribution in the upper part of the Floridan aquifer, July-November 1980.

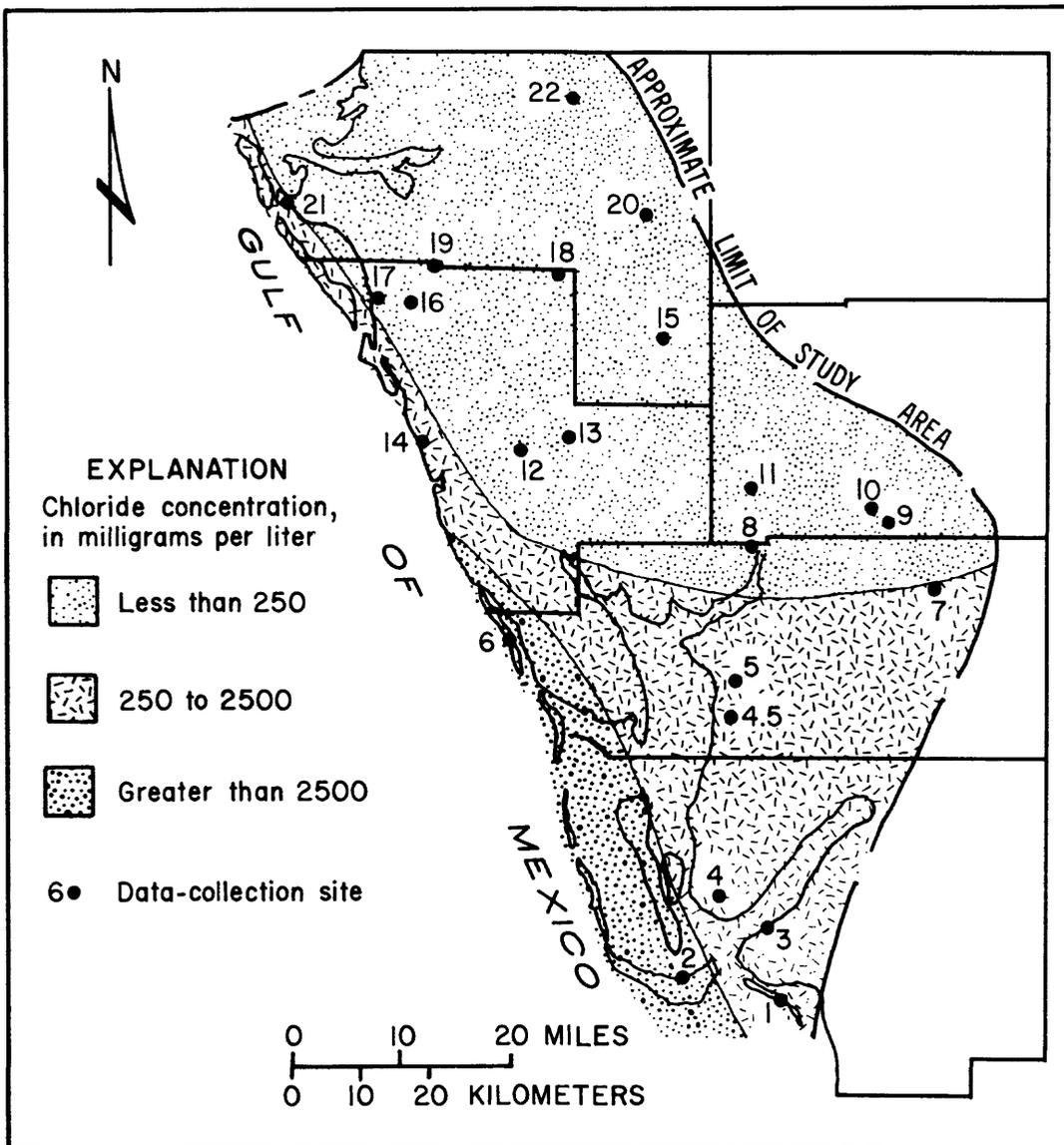


Figure 12.--Estimated dissolved chloride distribution in the upper part of the Floridan aquifer, July–November 1980.

Figure 13 shows the estimated distribution of dissolved solids in the upper part of the Floridan aquifer, July-November 1980. This distribution further suggests the possibility of upward movement of poorer quality water in the vicinity of the Verna well field. It also conveys an understanding of the general flow pattern in the aquifer--that of flow towards the south and west that has been gradually improving ground-water quality farther and farther downgradient in the aquifer since the last period of marine inundation. The general agreement between predevelopment flow and dissolved constituent distributions, together with data analyses discussed, indicate that, except possibly for the Verna area, ground-water development has not yet had a discernible regional effect on water quality in the study area.

The hypothesis of no induced regional effects on ground-water quality is based solely on the results of this study, but does not preclude the possibility of future development-induced changes. The situation at the Verna well field must be considered in any future management planning for selected areas of the Southwest Florida Water Management District. This report discusses water-quality variations in one such region. The entire coastal zone is another area of concern, as water in the Floridan aquifer in this region grades from potable to very saline in relatively short distances along lines normal to the coast. This transition occurs, in some areas, over less than 5 miles (K. W. Causseaux, oral commun., 1981). The potential for degradation in ground-water quality in such areas warrants future study.

SUMMARY

Water-quality data from a broad zone of saline ground waters in coastal southwest Florida were interpreted to provide an understanding of the Floridan aquifer geohydrologic system and geochemical processes operating in it. Wells completed exclusively in the Floridan aquifer were carefully sampled. The areal distributions and variations of the chemical and physical characteristics of the ground water indicate that past and present aquifer mineralogy, lithology, and permeability distribution are the most significant factors in the evolution of the saline waters.

Dispersive mixing of distinct end-member waters in the aquifer results in the observed distributions of the relatively nonreactive, and to some extent reactive, dissolved species. The upper part of the Floridan aquifer in the more upgradient areas contains a fresh, calcium magnesium bicarbonate sulfate type water. The deeper, more permeable, dolomitic zone in the same vicinity contains a similar fresh water with higher calcium, magnesium, and sulfate concentrations. The downgradient end member is a very saline, sodium magnesium chloride type water that is similar to seawater. Waters intermediate in the flow system are combinations of the end members that have reacted with aquifer minerals. Comparison of seawater dilution data with observed data can be used to estimate the extent of mixing in the Floridan aquifer.

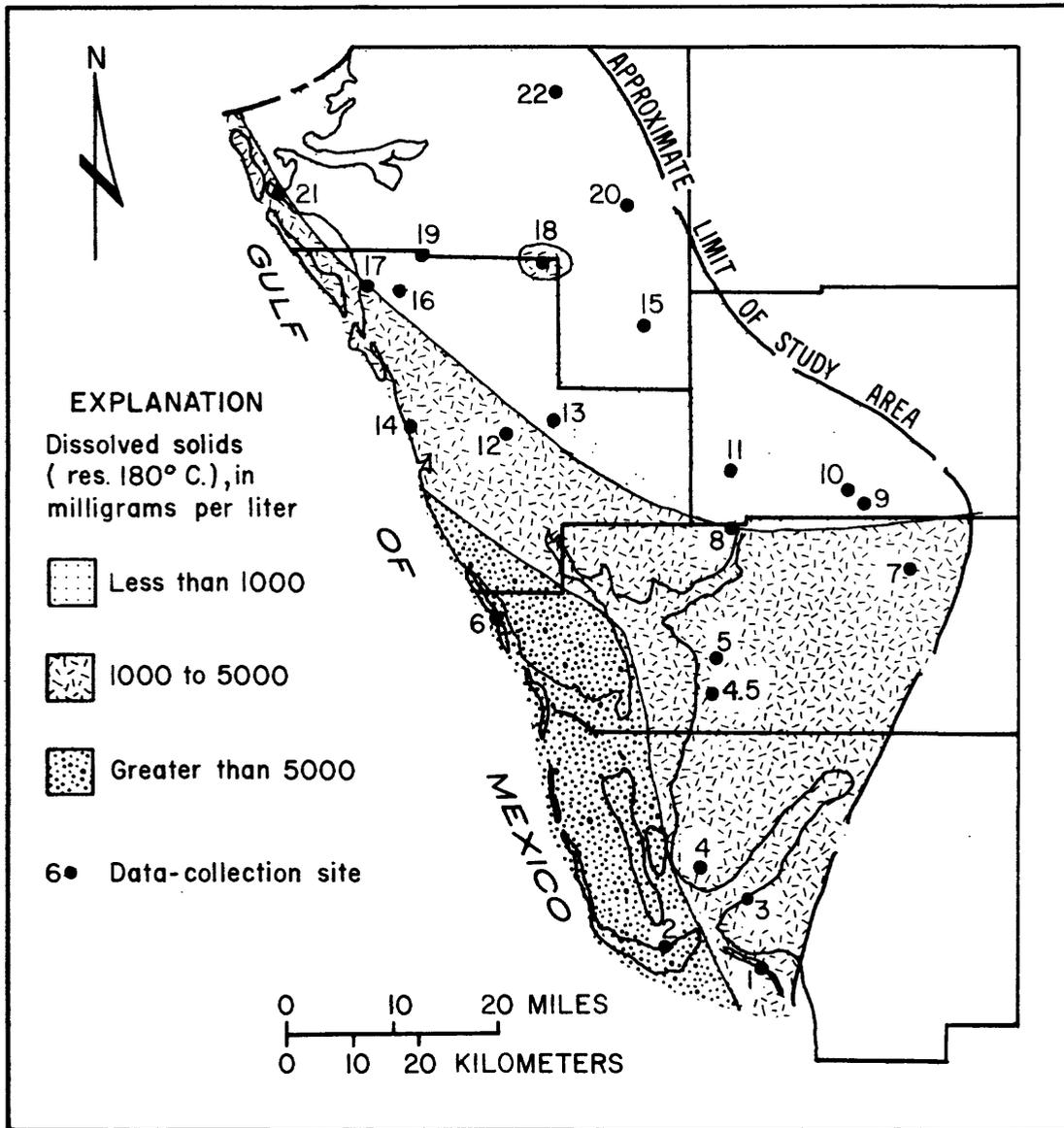


Figure 13.--Estimated distribution of dissolved solids (residue at 180°C) in the upper part of the Floridan aquifer, July–November 1980.

Diagenetic processes, including aragonite inversion, calcite recrystallization, and dedolomitization, have resulted in relative and absolute magnesium and strontium concentration increases. Gypsum solution and marine-like water dilution account for the observed dissolved sulfate distribution. The effect of gypsum solution is more pronounced in the fresher, upgradient waters.

An examination of the areal distribution of dissolved chloride, sulfate, and dissolved solids concentrations, relative to the ground-water flow system, indicates some potential for water-quality degradation by vertical flow from the dolomitic zone to the upper part of the aquifer. This could be occurring in the vicinity of the Verna well field.

This conceptual understanding of the origins and distribution of dissolved materials in the Floridan aquifer in coastal southwest Florida is a fundamental part of the knowledge needed to develop an areal ground-water management plan. It is part of the requisite basis from which estimates can be made of the potential for development-induced perturbations in the geohydrologic system.

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