

# Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

By CRAIG L. SPRINKLE

REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

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tion). As discussed in a number of hydrology texts (for example, Freeze and Cherry, 1979, p. 109–111), dissolution of limestone (and development of secondary permeability) is enhanced in ground-water systems open to a large (infinite) source of CO<sub>2</sub> gas. A secondary effect of confinement is reduction in the rate of flushing of salty water from the system. Confinement may also allow changes in oxidation-reduction potential to develop owing to isolation of the ground water from atmospheric oxygen. Confinement can also protect the ground-water resource by reducing the amount of surface contaminants that reach the system.

The hydraulic effects of confinement on the system are clearly seen when areas of confinement (fig. 11) are compared with principal areas of recharge and discharge. A map of recharge and discharge areas of the Upper Floridan was developed (Bush and Johnston, 1988, pl. 11) from simulation of the steady-state predevelopment flow system; the map is reproduced in figure 12. Thick confinement in southeastern Georgia and in southern Florida extend the discharge zone (area of diffuse upward leakage, fig. 12) over thousands of square miles; in contrast, discharge zones in unconfined areas along the Gulf Coast of Florida are narrow, extending over a few hundreds of square miles. More dramatic effects of confinement are seen when ground-water fluxes are compared between confined and unconfined areas. Bush and Johnston (1988, fig. 22) subdivided the aquifer system into major ground-water areas bounded by flow lines, so that within each area, ground-water discharge equals recharge in the steady-state condition. The total simulated discharge from the Floridan aquifer system prior to development was approximately 21,700 cubic feet per second (ft<sup>3</sup>/s) (fig. 13). Simulation showed that approximately 90 percent of this discharge occurred as springflow or discharge to streams in areas where the upper confining unit is thin or absent. By comparing figures 11 and 13, the effects of confinement on ground-water flow activity in different ground-water areas may be seen. For example, areas II, III, and IV are mostly unconfined, occupy about one-fifth of the land area where the Floridan aquifer system is present, and together account for about 63 percent of the total predevelopment discharge. Areas V and VII are mostly confined and occupy about half of the area underlain by the Floridan, yet they contribute only about 13 percent of the total predevelopment discharge from the system. Pumpage from the Floridan aquifer system of about 3 billion gallons per day (gal/d) (early 1980's) represents about 17 percent of total discharge (Bush and Johnston, 1988). This pumpage has resulted in water-level declines of more than 10 ft in three large areas—western panhandle Florida, west-central Florida, and along the Atlantic Coast from Jacksonville to north of Savannah (Bush and

Johnston, 1988, pl. 6). Nonetheless, ground-water development has not greatly altered the fact that most of the discharge from the Upper Floridan aquifer is to springs and streams.

This brief characterization of the flow system is sufficient for the following discussion of aquifer geochemistry; for more detailed descriptions of both the aquifer system and models developed to simulate its ground-water flow, the reader is referred to Bush (1982), Krause (1982), Ryder (1982), Tibbals (1981), and chapters C, D, E, F, and H of Professional Paper 1403 (Bush and Johnston, 1988; Krause and Randolph, 1989; Tibbals, in press; Ryder, 1986; Maslia and Hayes, 1988).

## DESCRIPTION OF GROUND-WATER CHEMISTRY

### METHODOLOGY

The majority of the data used in this investigation are from previous analyses of water samples from wells and springs in the Floridan aquifer system. These data were obtained during the period 1950 to 1982 as part of areal hydrologic studies by the U.S. Geological Survey in cooperation with Federal, State, and local governmental agencies and are currently available in computer files maintained by the Geological Survey (U.S. Geological Survey, 1974, 1975). Chemical data from springs were used primarily to obtain a better understanding of the hydrogeochemistry of the Upper Floridan where it is unconfined. Chemical data from springs were also used to supplement the well data to obtain a better regional description of selected constituents. Wells with chemical data were selected on the basis of (1) depth of well penetration into the Upper or Lower Floridan aquifer, (2) areal coverage of the entire Floridan aquifer system, and (3) relatively complete chemical data in computer storage. After a preliminary review of about 52,000 water analyses from more than 7,000 wells and about 250 springs in Alabama, Florida, Georgia, and South Carolina, a subset of 601 analyses (representing 601 wells) was chosen to characterize the major ion chemistry of the Upper Floridan aquifer. Of these 601 wells, 404 are open to more than half the total thickness of the Upper Floridan at the well and none penetrate below the base of the aquifer. Very few chemical data from wells in the Lower Floridan aquifer were available for this study. Owing to the scarcity of chemical and hydrologic data from the Lower Floridan, this report emphasizes geochemical properties and processes in the Upper Floridan aquifer. Discussion of the hydrogeochemistry of the Lower Floridan aquifer is limited to maps showing distribution of chloride and concentrations of dissolved solids.

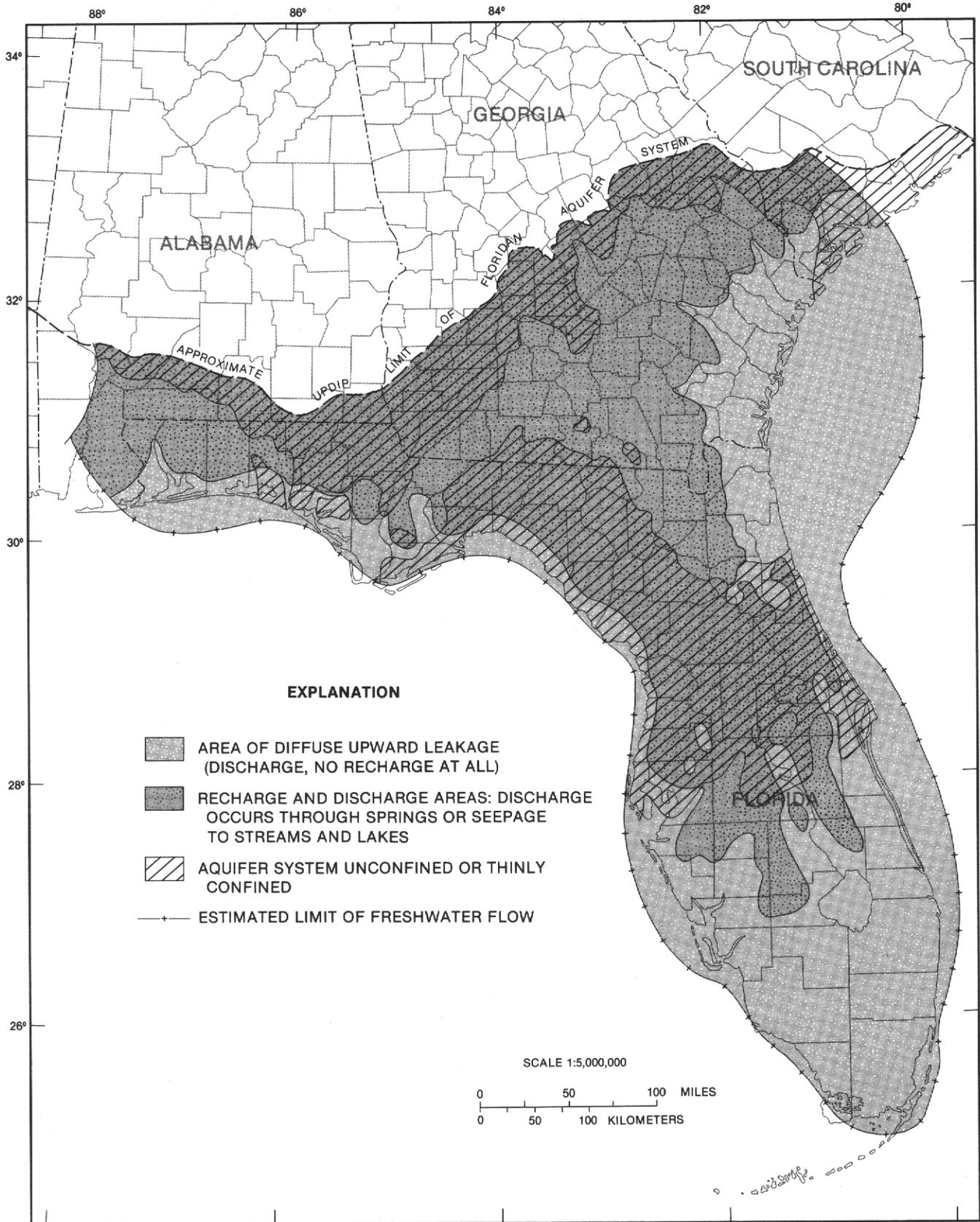


FIGURE 12.—Areas of discharge from and recharge to the Upper Floridan aquifer. (From Bush and Johnston, 1988.)

REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

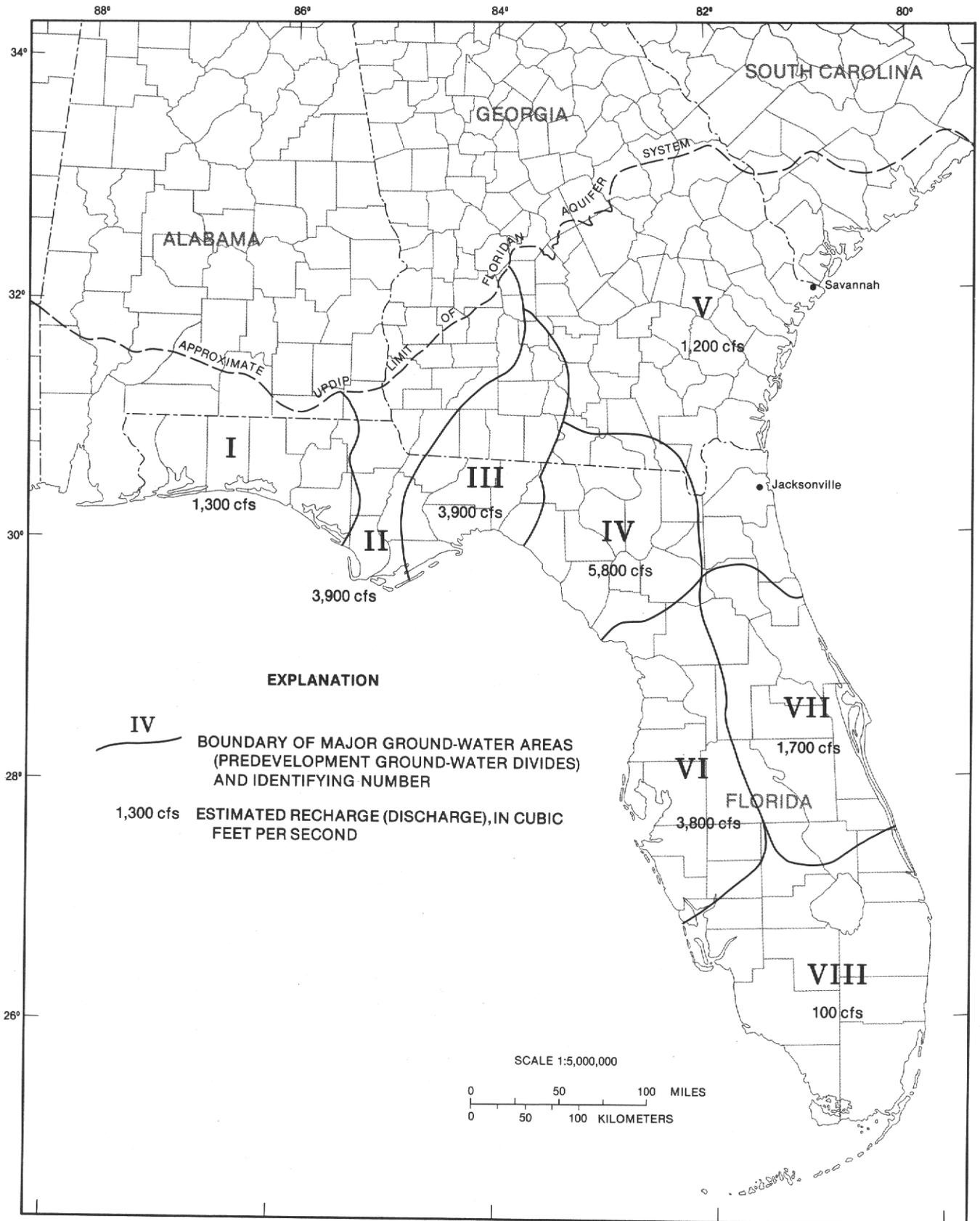


FIGURE 13.—Estimated predevelopment discharge from major ground-water areas of the Upper Floridan aquifer. (From Bush and Johnston, 1988.)

Methods for collecting and analyzing water samples have changed considerably during the period 1950 to 1982; therefore, comparing old and new chemical analyses of water samples requires some caution. Early techniques for collecting and analyzing common chemical constituents and trace metals emphasized collection of clear samples and acidification of trace metal samples with acetic acid (Rainwater and Thatcher, 1960). After about 1970, samples were routinely passed through a 0.45-micrometer ( $\mu\text{m}$ ) filter and acidified in the field with nitric acid to pH 2.0 in order to preserve cations in solution (Brown and others, 1970; Skougstad and others, 1979). Nutrient samples, when collected, were filtered and preserved by chilling to 4 °C for "dissolved" species; unfiltered water samples were chilled to 4 °C for "total" nutrient species. Field measurements of temperature and specific conductance were routinely made throughout the 32-year (yr) period; field measurements of pH and alkalinity were routinely performed by the Geological Survey in Florida and Georgia after about 1970. Because of the need for accurate pH and alkalinity determinations for making mineral saturation calculations (Back, 1963; Barnes, 1964), only analyses of water samples collected after 1970 were used for mineral equilibria calculations during this study. The stable isotope data presented in this paper were obtained by the techniques of Epstein and Mayeda (1953), Bigeleisen and others (1952), McKinney and others (1950), and Gleason and others (1969). The  $^{14}\text{C}$  data reported were obtained by methods described by Thatcher and others (1977, p. 17-22). Trace organic chemicals were analyzed by methods described by Goerlitz and Brown (1972) and Wershaw and others (1987).

Most of the analyses used in this study were originally reported in units of milligrams per liter (mg/L) or micrograms per liter ( $\mu\text{g/L}$ ). For ease of comparison with other studies and with regulatory criteria, the majority of figures and tables in this report present chemical data in these units. For geochemical calculations, however, the molal unit (moles of a substance per kilogram of water) is more appropriate. The conversion from milligrams per liter to millimolal (mmolal) is made by applying the following equation:

$$\text{Substance A (mmolal)} = \frac{\text{concentration of A (mg/L)}}{\text{formula wt. of A (mg/mmol)} \times \text{solution density (kg}_s\text{/L)} \times [1 - (\text{dissolved solids (ppm)} \times 10^{-6})] \text{ (kgH}_2\text{O/kg}_s\text{)}}$$

Note that dissolved solids measured in milligrams per liter is approximately equal to dissolved solids expressed as parts per million in dilute solutions (solutions with density approximately 1.000 and containing dissolved solids less than 5,000 mg/L).

Chemical analyses by themselves reveal little about processes that change the chemical character of ground water as it moves through the Floridan aquifer system. One of the principal methods of interpreting natural ground-water geochemistry is to assume that all dissolved species are at equilibrium. This assumption permits the use of thermodynamic models of aqueous solutions to calculate the distribution of dissolved species, a technique adopted for this study. A wide variety of computer-based models is available to calculate distributions and activities of dissolved species (Nordstrom and others, 1979). Once the species activities are calculated, the saturation state of the solution (that is, ground water) with respect to minerals and gases can be tested. Additional computations can also be made that quantitatively predict the evolution of an initial solution into a final solution by mixing and reaction with other solutions, gases, or solids (Helgeson and others, 1970; Plummer and Back, 1980; Plummer and others, 1983).

The aqueous model used during this study is contained in a computer program called WATEQF (Plummer and others, 1978). Except as noted in the following text and in tables 9, 10, and 11, the same values of equilibrium constants, ion-pairing constants, reaction enthalpies, and temperature-dependent analytical expressions for equilibrium constants of the aqueous species listed in WATEQF (Plummer and others, 1978, table 1 and attachment A) were also used in this study. Activity coefficients were calculated for samples containing less than 1,000 mg/L dissolved solids by using the Debye-Huckel equation (Truesdell and Jones, 1974, p. 240-241); otherwise, the Davies equation (Plummer and others, 1978, p. 5) was used. WATEQF calculates both activities of aqueous species and departure from equilibrium (saturation index, or S.I.) for many solid phases (minerals) and gases that might be in contact with the aqueous phase. The S.I. is expressed as

$$\text{S.I.} = \log (\text{IAP}/K_T)$$

where

IAP=ion activity product of the components of the solid or gaseous phase, and

$K_T$ =solid or gaseous phase solubility equilibrium product at the specified temperature.

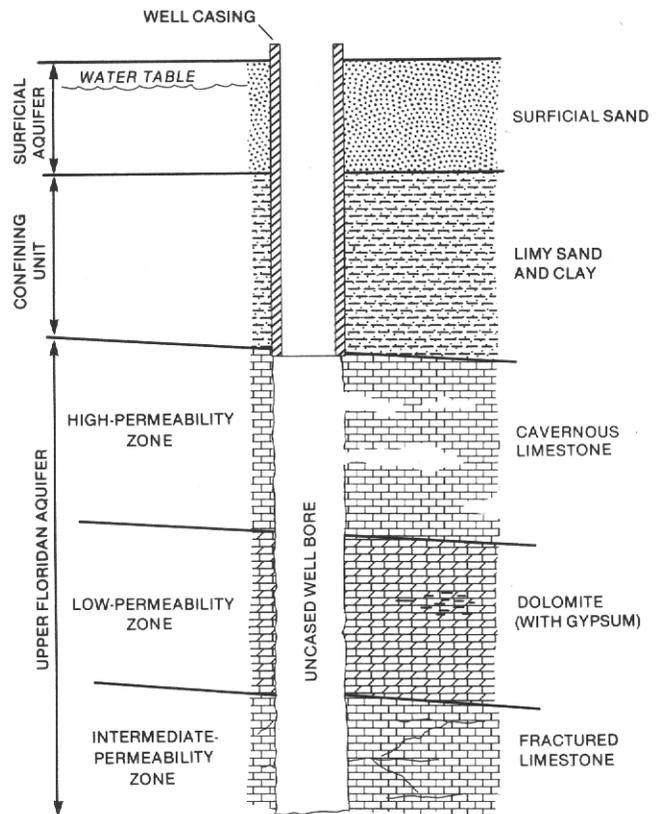
When S.I. is equal to 0, the solid or gaseous phase is in equilibrium with the aqueous phase. When S.I. is less than 0, the solid or gaseous phase is undersaturated, that is, the phase has thermodynamic potential to dissolve. When S.I. is greater than 0, the solid or gaseous phase is supersaturated, and the phase has the potential to exsolve by precipitation or volatilization. If present in the aquifer system, minerals probably are dissolving when negative saturation indices are calculated,

although the dissolution rates may be exceedingly slow. However, a potential to precipitate when S.I. is greater than 0 does not by itself cause minerals to form in the aquifer; there are other factors such as mineral surface topography, surface poisoning, and nucleation energy that may inhibit the formation and growth of a mineral (Drever, 1982, p. 116–124).

Description of the regional geochemistry required interpretation of both chemical and hydrologic data, because of ground-water mixing that affects water samples collected from wells or springs. Springflow is related to hydraulic heads within each permeable zone that contributes springflow and to amounts of recharge that occur throughout the spring's catchment area. Thus, a seasonal and year-to-year variation in the "mix" at the spring outlet is possible. This variation has not been directly observed during this study, but records of water analyses from, for example, Rainbow and Silver Springs in Marion County, Fla. (Rosenau and others, 1977, p. 269–281), show both seasonal and long-term variation, especially in sulfate and hardness. Osmond and others (1974) used uranium isotopes to separate the various shallow- and deep-flow contributions to Rainbow and Silver Springs; their methods, however, were not adopted for this study.

Samples from wells are also affected by mixing of ground water among permeable zones, because practically all the wells drilled into the Floridan aquifer system are open-bore wells (shown schematically in fig. 14). An open-bore well effectively "short circuits" the natural variations in vertical permeability, so that very small changes in head with depth are sufficient to cause flow within the bore. The important features of typical wells in the Upper Floridan aquifer are as follows: (1) the well casing generally extends only to the first rock layer encountered; (2) the well bore is open to both high- and low-permeability zones below the bottom of the casing; (3) under nonpumping conditions, water may migrate freely within the bore among zones of different hydraulic heads; and (4) under pumping conditions, the greatest amount of water is produced from zones that have the greatest horizontal permeability, regardless of static heads. These features produce a variety of possible "mixing scenarios" (table 5) for the water produced from a well. When a well in the Floridan aquifer system encounters saline water at depth, water-density effects will also affect the "mix" in pumped samples (Kohout and Hoy, 1963).

Mixing that occurs within the well bore (or spring) affects interpretation of the aquifer geochemistry by (1) modifying solution temperatures, (2) changing environmental isotope ratios, (3) changing the water's ionic strength, (4) changing net partial pressures of dissolved gases, and (5) altering solution pH and Eh. The latter



Diagrammatic, not drawn to scale.

FIGURE 14.—Typical well constructed in the Upper Floridan aquifer.

three effects are potentially significant in affecting solubilities of minerals, especially of calcite and dolomite. Many papers have been written discussing the effects of mixing on carbonate equilibria (Bogli, 1964; Ernst, 1964; Thrailkill, 1968; Runnells, 1969; Hanshaw and others, 1971; Badiozamani, 1974; Plummer, 1975; Wigley and Plummer, 1976; Hanor, 1978; Back and others, 1979). The essence of these papers is that when two waters of different  $\text{CO}_2$  partial pressure ( $P_{\text{CO}_2}$ ) or ionic strength are mixed, the molalities and activities of ions and species in the final mixture are not linearly related to the end-member values.

Wigley and Plummer (1976) discussed five factors affecting the nonlinear behavior of ion activities in mixtures, of which three are the most important in affecting the carbonate equilibria within the Upper Floridan: (1) the algebraic effect, (2) the  $\Delta P_{\text{CO}_2}$  effect, and (3) the ionic strength effect. The algebraic effect describes the tendency of two dissimilar but carbonate-mineral-saturated solutions to produce oversaturated mixtures. In contrast, the  $\Delta P_{\text{CO}_2}$  effect describes the tendency of undersaturated mixtures to form from solutions with different initial  $P_{\text{CO}_2}$ ; if one end member contains much higher

TABLE 5.—Examples of mixing ground water within open-bore wells in the Floridan aquifer system

	a. Casing to top of Floridan aquifer system; heads decrease with depth	b. Casing to rock in overlying confining unit; heads decrease with depth	c. Casing to top of Floridan aquifer system; heads increase with depth	d. Casing to rock in overlying confining unit; heads increase with depth
Type I: Well idle for long time; pumping (or flowing) for short time prior to sampling	Water sample is from Floridan; water from shallowest permeable zone invades deeper zones; water sample is a mixture, may be chemically similar to water from shallowest highly permeable zone	Water sample is from confining unit and Floridan; water from confining unit invades deeper zones; water sample is mixture from Floridan and confining unit in unknown proportions	Water sample is from Floridan; water from deepest permeable zone invades shallower zones; water sample is a mixture, may be chemically similar to water in deepest highly permeable zone	Water sample is from confining unit and Floridan; water from deepest permeable zone invades shallower zones (including confining unit); water sample is a mixture, may be chemically similar to water in deepest permeable zone
Type II: Well pumped for sampling soon after drilling completed	Water sample is from Floridan; water from shallowest permeable zone beginning to invade deeper zones; water sample is a mixture from all permeable zones, dominated by most permeable zone	Water sample is from confining unit and Floridan; water from confining unit beginning to invade deeper zones; water sample is a mixture from all permeable zones, dominated by most permeable zone	Water sample is from Floridan; water from deepest permeable zone beginning to invade shallower zones; water sample is a mixture from all permeable zones, dominated by most permeable zone	Water sample is from confining unit and Floridan; water from deepest permeable zone beginning to invade shallower zones (including confining unit); water sample is a mixture from all permeable zones, dominated by most permeable zone
Type III: Well pumped (or flowing) "continuously" prior to sampling	Water sample is from Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone	Water sample is from confining unit and Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone	Water sample is from Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone	Water sample is from confining unit and Floridan; each permeable zone yields water to mix in bore depending on permeability; water sample is a mixture dominated by most permeable zone

$P_{CO_2}$ , the  $\Delta P_{CO_2}$  effect can overwhelm the algebraic effect. The third effect also describes a tendency for mixtures to become undersaturated, since the activities of ions in the mixture are nonlinearly related to the ionic strength of the mixture, even though the ionic strength of the mixture is related to the two end-member compositions.

Some effects of mixing water from different aquifer layers on the chemistry of samples from open-bore wells can be illustrated using theoretical mixtures of water samples collected from two deep wells in the Upper Floridan aquifer near Waycross, Ga. (Matthews and Krause, 1984). During this study, a pumping test was conducted on well TW-1 which penetrates the entire Floridan from 625 to 1,856 ft. Chemical analyses (table 6) indicate strong similarities between samples from TW-1 collected after pumping at 2,000 gallons per minute (gal/min) for nearly 48 hours and samples obtained from the same well during packer testing of permeable zones. One anomaly in the analytical results is the carbon-14 value for the pumping test sample. This sample also contained measurable tritium (3 tritium units), indicating some atmospheric contamination of the water sample.

Packer tests of selected intervals in TW-1 indicated that heads increased only a few tenths of a foot with depth (Matthews and Krause, 1984, p. 10). Matthews and Krause (1984, p. 11) also reported data from flow-meter surveys of TW-1 while pumping at a rate of about 1,900 gal/min. They calculated the following yields from different permeable zones:

Interval, feet below land surface	Yield, gallons per minute	Percentage of total flow
635-750	1,100	58
750-900	500	26
940-970	60	3
1,070-1,090	240	13
		100

Even though well TW-1 was not sampled until several months after completion, mixing of water between different zones was apparently minimized by lack of large head differences within the open interval and the comparatively low permeability of the rocks below 1,101 ft. Thus, the flow and chemical data are mutually consistent; they indicate that the water pumped from TW-1, which is 1,856 ft deep, comes almost entirely from the interval of about 635 to 1,101 ft.

TABLE 6.—Chemical analyses of water from wells in the Upper Floridan aquifer near Waycross, Ga.

[Molalities, saturation indices, ionic strengths, and log  $P_{CO_2}$  computed by WATEQF (Plummer and others, 1978). Dashes indicate constituent not analyzed. g/mL, grams per milliliter; PDB, Pee Dee belemnite; SMOW, Standard Mean Ocean Water; CDM, Canyon Diablo meteorite]

	Well and sample depth (feet below land surface)			
	TW-2 1,901 to 1,966	TW-1 packer set at 1,101; sample from 1,101 to 1,856	TW-1 packer set at 1,101; sample from 635 to 1,101	TW-1 pump test; well open from 635 to 1,856
Date of sample	05-08-81	06-08-81	06-09-81	06-17-81
Water temperature, °C	22.5	23.8	23.1	24.0
Field pH	8.09	7.16	8.10	7.74
Density, g/mL at 20 °C	1.023	1.004	0.999	0.999
Ionic strength	$5.41 \times 10^{-1}$	$9.75 \times 10^{-2}$	$6.60 \times 10^{-3}$	$6.64 \times 10^{-3}$
-Log $P_{CO_2}$	3.401	1.957	2.786	2.405
$^{14}C$ activity, percent modern	---	0	$4.3 \pm 0.6$	$16.5 \pm 1.5$
Concentration, in millimoles per kilogram water				
Calcium (Ca)	21.11	14.49	1.074	1.099
Magnesium (Mg)	28.58	15.24	0.741	0.741
Sodium (Na)	398.7	20.47	0.697	0.653
Potassium (K)	6.182	0.486	0.061	0.049
Aluminum (Al)	0.004	0.002	0.001	0
Iron (Fe)	0.032	0.017	0.036	<0.001
Manganese (Mn)	0.006	0.001	0.002	0
Strontium (Sr)	0.207	0.106	0.003	0.003
Silica (SiO <sub>2</sub> )	0.268	0.350	0.500	0.783
Field alkalinity, as CaCO <sub>3</sub>	1.650	3.501	3.682	3.722
Chloride (Cl)	397.7	19.20	0.424	0.395
Sulfate (SO <sub>4</sub> )	52.42	28.66	0.417	0.469
Fluoride (F)	0.302	0.416	0.032	0.026
Bromide (Br)	0.832	0.058	0.004	0.004
Sulfide (S)	0.025	0.033	0.026	---
Nitrite (NO <sub>2</sub> ) + nitrate (NO <sub>3</sub> ), as N	<0.001	<0.001	<0.001	---
Ammonia (NH <sub>4</sub> ) + organic nitrogen, as N	0.207	0.044	0.009	---
Orthophosphorus, as P	<0.001	<0.001	<0.001	---
Total phosphorus, as P	<0.001	<0.001	<0.001	---
Stable isotope ratios, in parts per thousand				
$^{13}C/^{12}C_{PDB}$	-4.7	-3.0	-12.1	-12.4
$^{18}O/^{16}O_{SMOW}$	-2.8	-3.3	-3.2	-3.1
$^2H/^1H_{SMOW}$	-14.5	-17.0	-15.5	-17.0
$^{34}S/^{32}S_{CDM}$	---	22.1	22.3	23.5
Saturation indices				
Calcite	0.72	0.25	0.58	0.26
Dolomite	1.73	0.68	1.11	0.47
Gypsum	-0.01	0.00	-2.14	-2.08

The samples from well TW-1 are typical of those collected from type II-c wells (table 5). Suppose, however, that the Waycross wells were resampled after 20 yr (type I-c well), or that the hydrologic conditions at the wells were different and that significant flow occurred between zones prior to the initial sampling. The chemistry of "samples" collected under various mixing conditions may be simulated using the chemical data in table 6 and the program PHREEQE (Parkhurst and others, 1980). Prior to mixing, PHREEQE was used to balance the net electrical charge of the chemical analyses given in table 6 by addition of  $K^+$  or  $Cl^-$ , so that upon mixing the

solution pH could be calculated by change in charge balance. Each analysis was also brought to calcite equilibrium by adding  $CO_2$ , which may have degassed from the water samples prior to field measurement of alkalinity and pH. The following changes were made to the analytical data shown in table 6:

Water sampling zone	Millimoles added			New solution		
	$K^+$	$Cl^-$	$CO_2$	pH	-log $P_{CO_2}$	Ionic strength
635-1,101	0.536	0	0.266	7.50	2.171	$6.9 \times 10^{-3}$
1,101-1,856	0	0.166	0.324	6.90	1.694	$9.76 \times 10^{-2}$
1,901-1,966	0.904	0	0.241	7.22	2.381	$5.42 \times 10^{-1}$

The large change in pH caused by bringing the samples to calcite equilibrium appears to indicate errors in the alkalinity and pH determinations made during sampling. The collection of samples from deep wells is probably best accomplished by a closed-system apparatus (Wood, 1976), but during testing of the Waycross wells these conditions were not always satisfied.

Assuming the Waycross wells were shut in for 20 yr prior to resampling, the slight head differences measured in the wells could produce "samples" having varying chemistries, as shown in figure 15A. If head relationships were different and heads decreased with depth, there would be no significant change in water chemistry from that measured in 1981 because the greatest permeability occurs in the upper part of the wells (635–1,101 ft). However, if the zone from 1,901 to 1,966 ft had higher hydraulic conductivity or much higher heads (or both), saline water could invade the shallower permeable zones. "Samples" from the Waycross wells might then be similar to the mixtures shown in figure 15B. Other situations could be simulated by varying the estimated amounts of water entering the well bore from different zones. These examples illustrate the potential effects of mixing in open-bore wells on chemistry of samples. Large differences in analytical results between samples taken years apart might be related to mixing rather than to changes in the regional or local flow system. The examples also illustrate the complexities of interpreting new "first-time" samples from old open-bore wells. For additional discussion of the effects of well construction and pumpage on water samples, the reader is referred to Claassen (1982).

The uncertainties introduced by mixing in open-bore wells can be decreased by sampling only those wells that have been pumped or have flowed almost continuously since being drilled (type III, table 5). These wells would yield water from the same highly permeable zone year after year. Collecting water samples from a network of "continuously" flowing municipal or irrigation wells will provide a regional view of the geochemistry of the aquifer system. This method was used in peninsular Florida by Back and Hanshaw (1970). However, in exchange for obtaining unmixed samples from highly productive zones, some deficiencies in this sampling scheme must be accepted, including the following: (1) municipal and irrigation wells tend to produce only good-quality water; thus poor-quality, saline, or briny zones that occur in the system may not be detected; (2) regionally, zones of high permeability are not always continuous, and the production zones tapped by widely separated wells may yield water that traveled by different flow paths at different rates; and (3) regionally, high-permeability zones most commonly occur in the Ocala Limestone, which is almost entirely calcite.

Deeper water-bearing zones (older rock units) may contain more dolomite, gypsum, apatite, peat, or other solid phases which can markedly influence the regional ground-water chemistry.

Whether or not mixing has affected ground-water samples, calculations of calcite and dolomite saturation indices are dependent on accurate measurements of pH and dissolved inorganic carbon species (alkalinity) (Back, 1963; Langmuir, 1971; Pearson and others, 1978). The "adjustments" of analyses discussed above indicate that the greatest change in calcite (or dolomite) saturation is made when CO<sub>2</sub> concentrations are changed. For example, the original water analysis from the 635–1,101-ft zone of the Waycross well had an S.I.<sub>calcite</sub> of +0.58 at a field pH of 8.10 (table 6). "Addition" of 0.266 mmol of CO<sub>2</sub> (per kilogram of H<sub>2</sub>O) brought the analysis to equilibrium with calcite at a pH of 7.50. One might question whether this amount of degassing would be observable in the field: using the ideal-gas law, the loss of 0.266 mmol of CO<sub>2</sub> per kilogram of H<sub>2</sub>O from a 50-mL sample (used to measure pH) represents 0.325 mL of pure CO<sub>2</sub> gas (at 25 °C and 1 atmosphere). Thus, even though nonstoichiometric phases may be reacting, most of the supersaturation of carbonate minerals calculated from historic water analyses from the Floridan aquifer system is probably the result of CO<sub>2</sub> outgassing and change from in situ alkalinity and pH.

## MAJOR CONSTITUENTS

### CALCIUM

Calcium is a principal component of the major minerals in the Floridan aquifer system and therefore is a major dissolved constituent in ground water in most of the region. Concentrations of calcium ion (Ca<sup>2+</sup>) in water from the Upper Floridan aquifer vary from less than 5 mg/L in western panhandle Florida to more than 570 mg/L in deep, gypsiferous zones in southwestern Florida (pl. 1). The concentration of Ca<sup>2+</sup> is controlled throughout most of the aquifer system by mineral saturation and (or) cation exchange. The important reactions are

