Hydrochemistry of the Upper Floridan Aquifer, Florida

By Brian G. Katz

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PLATES
[Plates are in back pocket]

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CONVERSION FACTORS, VERTICAL DATUM, ACRONYMS, AND CHEMICAL TERMS

Multiply	By	To obtain
billion gallons (Ggal)	3,785,000	cubic meter
cubic foot per day per square foot times foot of aquifer thickness $[(ft^3/d)/ft^2]ft$	10.76	cubic meter per day per square meter times meter of aquifer thickness
foot (ft)	0.3048	meter
million gallons per day (Mgal/d)	0.04381	cubic meters per second

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Acronyms used in report

ACDES	=	Alachua County Department of Environmental Services
CBE	=	Charge-balance error
DS	=	Dissolved solids
FDER	=	Florida Department of Environmental Regulation
FGWQMN	=	Florida Ground-Water Quality Monitoring Network
milliequivalent per liter	=	meq/L
millimole per liter	=	mmol/L
RASA	=	Regional Aquifer Systems Analysis program
SI	=	Saturation index
TOC	=	Total organic carbon
USGS	=	U.S. Geological Survey
WATEQF	=	U.S. Geological Survey equilibrium speciation computer program for natural waters (Fortran IV) version

Chemical terms

Symbol	Ion
Ca^{2+}	Calcium
HCO_3^-	Bicarbonate
Mg^{2+}	Magnesium
Na^+	Sodium
K^+	Potassium
Cl^-	Chloride
SO_4^{2-}	Sulfate

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ABSTRACT

The major-ion composition of water in the Upper Floridan aquifer is affected predominantly by mineral equilibria and mixing of freshwater with sea water. Areal and vertical variations in major-ion chemistry are described using chemical analyses of water from 787 wells completed in the Upper Floridan aquifer. These analyses originated from two intensive regional studies of the hydrogeology and water chemistry of the Floridan aquifer system: the Florida Ground-Water Quality Monitoring Network Program and the U.S. Geological Survey Regional Aquifer Systems Analysis study on the Floridan aquifer system.

The Upper Floridan aquifer is composed of a thick sequence of limestone and dolomite of Tertiary age. Major minerals in the aquifer are calcite and dolomite. In some local areas, gypsum may be present in sufficient amounts to influence water chemistry. The degree of confinement has a profound influence on the major-ion chemistry.

The concentrations of most major ions and dissolved solids show an increase in concentration with depth and with the degree of confinement in the aquifer. Unconfined areas of the aquifer typically receive recharge water that contains low concentrations of major ions from rainfall and leakage from the overlying surficial aquifer system. In confined parts of the aquifer, such as in southern Florida, an increase in concentration of major ions with depth is related to mixing of freshwater with residual seawater.

Water from 58 percent of the wells completed in the aquifer is either the calcium-bicarbonate (46 percent) or the calcium-magnesium-bicarbonate (12 percent) hydrochemical facies. Calcite dissolution reactions in freshwater areas of the aquifer over most of the State account for the predominance of calcium bicarbonate hydrochemical facies, and this controlling process is reflected by low dissolved solids (less than 250 milligrams per liter) in these areas. A calcium-magnesium-bicarbonate hydrochemical facies is produced where dissolution of dolomite and magnesium-rich clay minerals adds significant amounts of magnesium to the water. Where substantial gypsum and pyrite dissolution occurs, sulfate is added to the ground water and the following hydrochemical facies are produced: calcium-magnesium-bicarbonate-sulfate (4 percent of the wells), calcium-magnesium-sulfate (3 percent), and calcium-sulfate (1 percent). Areas where these hydrochemical facies occur include northeast Florida, southwest Florida, and several locations in west-central Florida. In certain areas of the State where vertical or lateral mixing of seawater with freshwater occurs, three hydrochemical facies are noted: mixed-bicarbonate (5 percent), mixed (14 percent), and sodium-chloride (12 percent).

INTRODUCTION

The Floridan aquifer system in Florida is one of the most productive sources of ground water in the United States. In 1987, more than 2.5 Ggal of water were pumped from the aquifer system daily, with 690 Mgal/d being withdrawn for public supply (Marella, 1990). The Floridan aquifer system is also a major source of supply for agricultural, industrial, and rural uses. The aquifer system consists of as much as 3,500 ft of limestone and dolomite beds that are hydraulically interconnected to some degree (U.S. Geological Survey, 1985). The porous nature of the limestone and its proximity to the surface in some areas, coupled with rapid population growth in Florida, result in a ground-water resource that is highly susceptible to contamination.

In response to concern about the vulnerability to contamination of the Floridan aquifer system and other aquifer systems in the State, the Florida Legislature passed the Water Quality Assurance Act in 1983, which required the Florida Department of Environmental Regulation (FDER) to establish a statewide ground-water quality monitoring network. To develop and manage this network, a cooperative program was established involving FDER, the five water management districts in Florida, the U.S. Geological Survey (USGS), and other interested agencies. The main goals of the program, which has become known as the Florida Ground-Water Quality Monitoring Network Program (FGWQMN), are to (1) develop a network that will provide a continuing assessment of the water quality in the aquifer systems of Florida, (2) delineate regional changes in water-quality urbanization, agricultural use, industrialization, and other land-use changes through time, and (3) provide information to State and local agencies on the water quality of

these aquifer systems so the susceptibility of these systems to contamination can be assessed in managing water and land use.

In 1987, the USGS began a cooperative study with FDER to characterize the aqueous geochemistry of the major aquifer systems using data generated from the FGWQMN. The specific goals of the study were to delineate hydrochemical zones that define areas of similar water chemistry, to describe the major geochemical processes controlling the observed water quality, and to evaluate the design of the network for long-term monitoring of water quality for these aquifer systems.

Purpose and Scope

The purpose of this report is twofold: (1) to regionally characterize the major-ion chemistry of water from the Upper Floridan aquifer in Florida, and (2) to describe the principal geochemical processes that influence the major-ion chemistry of water from the aquifer.

'This report contains information on water quality and well characteristics collected as part of the FGWQMN Program and selected information collected and compiled during the USGS Regional Aquifer-System Analysis (RASA) study completed in 1987 of the Floridan aquifer system. This report combines the water chemistry information collected from these two studies and presents a regional hydrochemical analysis of major ions in the Upper Floridan aquifer.

The application of the concept of "hydrochemical facies" is commonly used to characterize the dominant-ion chemistry of ground water in a region (Back, 1960). As noted by Back (1966), the dominant-ion chemistry is controlled by geochemical and hydrologic processes occurring within an aquifer system. Hydrochemical facies are generally calculated by converting each cation and anion concentration in milligrams per liter to milliequivalents per liter (by dividing the ion concentration in milligrams per liter by its molecular weight and multiplying by its ionic charge). The relative proportion of each cation or anion to the sum of cations or anions is then calculated. In this report, a cation or anion is considered dominant when its relative proportion to the sum of cations or anions is greater than or equal to 60 percent. If the proportion of the sum of any two cations or two anions is equal to or greater than 80 percent, they are considered dominant. Water is designated as having a "mixed" hydrochemical facies if one anion or cation does not constitute more than 60 percent of the total equivalents of cations or anions, or any two cations or anions contribute less than 80 percent of the total equivalence of cations or anions. In a mixed hydrochemical facies, nearly equal proportions of all major ions are present. This classification of hydrochemical facies is a modification of the graphical presentation of dominant water types shown in Davis and DeWeist (1966).

Previous Reports

An inclusive bibliography of studies of the geohydrology and geochemistry of the Floridan aquifer system in Florida, Georgia, Alabama, and South Carolina is presented in USGS Professional Paper 1403. It consists of a series of nine chapters: A, summary (Johnston and Bush, 1988); B, hydrogeologic framework (Miller, 1986); C, hydraulics and regional flow (Bush and Johnston, 1988); D, hydrology of the Floridan in southeast Georgia and northeast Florida (Krause and Randolph, 1989); E, hydrology of the Floridan in east-central Florida (Tibbals, 1990); F, hydrology of the Floridan in west-central Florida (Ryder, 1985); G, hydrogeology of the Floridan in south Florida (Meyer, 1989); and H, hydrogeology of the Floridan in the Florida Panhandle and southwest Georgia (Maslia and Hayes, 1988). The geochemistry of the Floridan aquifer system is described by Sprinkle (1989) in chapter I, which includes lists of key papers that discuss aspects of the geochemistry of the Floridan aquifer system based on studies conducted in the 1960's through the mid-1980's. An inclusive bibliography of studies of the Floridan aquifer system published prior to 1965 is presented in Stringfield (1966).

Acknowledgments

HYDROGEOLOGIC SETTING

This section of the report summarizes the key hydrogeologic factors that affect the major-ion chemistry of water from the Upper Floridan aquifer on a regional, rather than local, scale. The factors highlighted in this report include hydrogeologic characteristics, mineralogy of the aquifer matrix, thickness and integrity of overlying confining units, and flow-system characteristics, such as recharge-discharge relations. For more detailed information on recharge to and discharge from the Floridan aquifer system and the geologic framework, mineralogy, and hydrology, the reader is referred to Stringfield (1966) and to USGS Professional Paper 1403. The areal extent of the entire Floridan aquifer system described in that USGS Professional Paper is shown in figure 1 of this report.
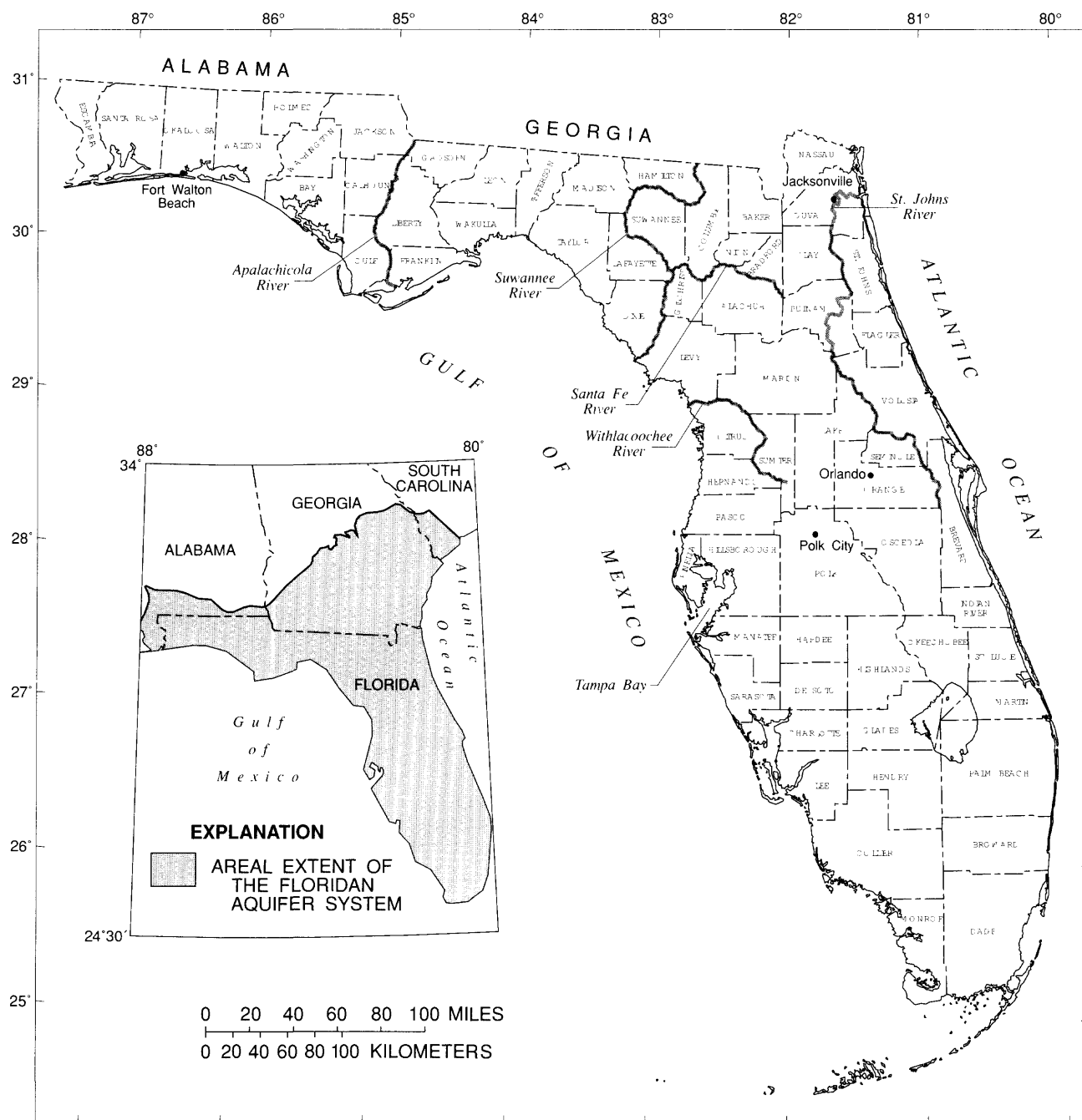
Figure 1. Areal extent of the Floridan aquifer system showing approximate updip limit, and counties and other locations in Florida.

General Hydrogeology

The Floridan aquifer system is composed predominantly of limestone and dolomite of Tertiary age ranging from late Paleocene to early Miocene. The system generally consists of the following geologic formations, from oldest to youngest: Oldsmar Formation, Avon Park Formation, Ocala Limestone, Suwannee Limestone, Tampa Limestone, and the lower part of the Hawthorn Formation where it contains permeable limestone beds that are hydraulically connected to the older limestone units. The permeability of these formations is generally one to several orders of magnitude greater than that of the rocks bounding the system above and below. Miller (1986)

places the top of the aquifer system at the top of highly permeable carbonate rocks that are hydraulically connected. The base of the system is formed by poorly permeable clastic rocks (locally calcareous) that separate the limestones of the Floridan aquifer system from deeper clastic units (Miller, 1986). This hydrologic definition for the top and base of the aquifer means that the boundaries of the aquifer system may occur within a stratigraphic unit, rather than at the top or bottom of the unit. The Floridan aquifer system ranges in thickness from about 100 ft near the Florida-Alabama border to about 3,500 ft in west-central Florida. The part of the aquifer system that contains freshwater is reported to have a maximum thickness of about 2,000 ft. Miller (1986) divides the Floridan aquifer system into three units: the Upper Floridan aquifer, the Middle confining unit, and the Lower Floridan aquifer. The Upper Floridan aquifer is separated from the Lower Floridan aquifer by less permeable beds of highly variable properties that Miller (1986) has termed the middle confining unit. Few supply wells penetrate beyond the Upper Floridan aquifer because it is so productive and because much of the Lower Floridan aquifer contains saline water.

Where the Upper Floridan aquifer is not at land surface, it is overlain by a varying sequence of sand, clay, marl, limestone, and dolomite that ranges in thickness from a few feet in parts of west-central and north-central Florida to hundreds of feet in south-central Florida, northeast Florida, and in the westernmost part of Panhandle Florida. Over much of Florida, deposits of sand and clay overlie the Upper Floridan aquifer. The sand generally forms a surficial aquifer system recharged by rainfall. In areas where thick deposits of clay and marl exist between the surficial aquifer system and the Upper Floridan aquifer, the movement of water from the surficial to the Upper Floridan is restricted, and the water in the Upper Floridan is confined. Areas where the Upper Floridan aquifer is unconfined, semiconfined, and confined are shown in figure 2. Water in the Upper Floridan is confined to some degree over much of the State, except where the aquifer crops out at or near the surface, and as a result is unconfined. Sinkholes and fractures are common in the unconfined and semiconfined areas (fig. 2) and may provide a hydraulic connection between the land surface and the Upper Floridan aquifer. In the semiconfined and confined areas of the State, the upper confining unit (Miller, 1986) is generally the Hawthorn Formation of Miocene age. This unit consists of interbedded sand and clay that is locally phosphatic and contains carbonate beds, which in southwest Florida form aquifers that are used locally for water supply (Ryder, 1985; Scott, 1988; and Meyer, 1989).

Mineralogy of Aquifer Matrix

The minerals that constitute the Upper Floridan aquifer matrix in large part determine the chemistry of the water that is in direct contact with these minerals. Sprinkle (1989) describes the matrix of the Floridan aquifer system as being composed predominantly of calcite and dolomite.

Also present are minor amounts of gypsum, apatite, glauconite, quartz, clay minerals (kaolinite and smectites), and trace amounts of metallic oxides and sulfides. In some local areas, measurable amounts of peat exist as thin layers (0.04 to 0.2 inches) in the limestone (Sprinkle, 1989). The minerals that appreciably influence chemistry of major ions in water in the Upper Floridan aquifer are discussed in more detail.

The most abundant mineral in the aquifer matrix is calcite and its composition ranges from stoichiometric calcite ($CaCO_3$) to low magnesium calcite ($Ca_{0.96}Mg_{0.04}CO_3$) (Hanshaw and others, 1971). Low magnesium calcite is unstable relative to stoichiometric calcite, and as a result accounts for less than 0.1 percent by weight of the Floridan aquifer system limestones (Plummer, 1977). Sprinkle (1989) reports that the amount of dolomite in the aquifer matrix varies both areally and vertically within and between formations. Based on analysis of cores from test wells, dolomite accounted for about 8 percent of the rocks of the Upper Floridan aquifer from a site near Polk City, Polk County (fig. 1). The percentage of dolomite in rocks beneath the Upper Floridan aquifer is much higher, ranging from 9 to 95 percent (Sprinkle, 1989). The composition of dolomite in the Upper Floridan aquifer ranges in composition from stoichiometric dolomite ($CaMg(CO_3)_2$) to low-magnesium dolomite ($Ca_{1.12}Mg_{0.88}(CO_3)_2$) (Randazzo and Hickey, 1978, p. 1178). The solubility of dolomite is determined by its composition, with low-magnesium dolomite being less stable than stoichiometric dolomite (Cook, 1984). The origin of dolomite in the Upper Floridan aquifer is uncertain, and Sprinkle (1989) presents a review of key papers from the literature on this topic.

Gypsum ($CaSO_4·2H_2O$), although a minor mineral in the Upper Floridan aquifer, has important hydrochemical implications. The presence or absence of intergranular gypsum was used as an indicator to delineate confining units of the aquifer system (Miller, 1986). Sulfate produced from the dissolution of gypsum was used as a progress variable to study mass transfer reactions along flow paths in the Upper Floridan aquifer (Plummer and others, 1983).

The clay mineralogy of the Upper Floridan aquifer has not been studied in detail. Sprinkle (1989) reports that kaolinite and possibly montmorillonite were identified using X-ray diffraction on samples of cores from the Avon Park Formation in west-central Florida. Several studies have demonstrated the importance of ion-exchange reactions involving clay minerals in controlling the concentrations of major cations. The exchange of Ca^{2+} for $2Na^+$ has produced a sodium-bicarbonate water type in some regional aquifers (Foster, 1950; Thorstenson and others, 1979; and Chapelle and Knobel, 1983). The effect of ion-exchange reactions in controlling the chemistry of water in the western panhandle of Florida is discussed later in this report.
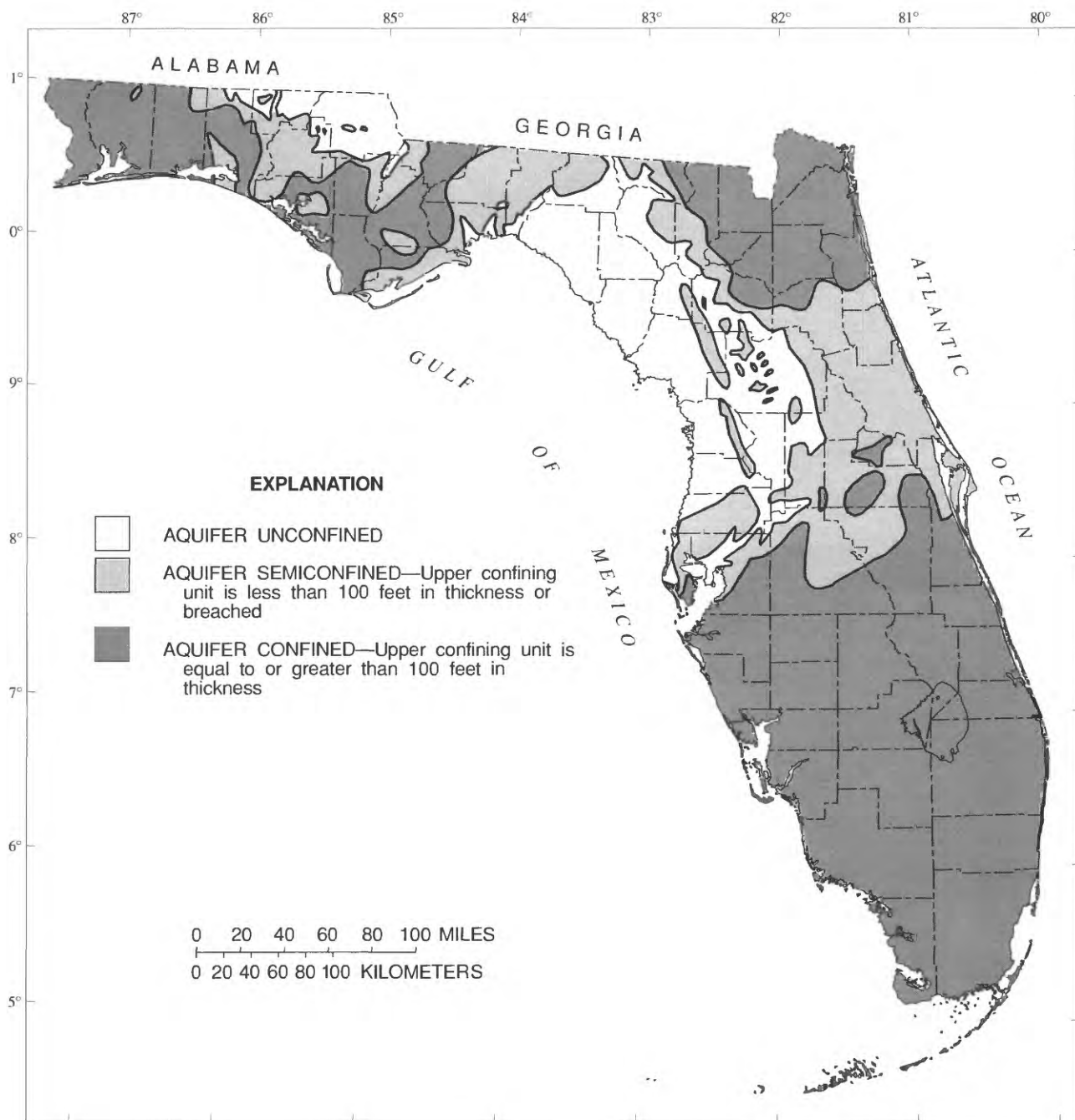
Figure 2. Confined, semiconfined, and unconfined areas of the Upper Floridan aquifer. (Modified from Miller, 1986.)

Flow-System Characteristics

The regional characteristics of the flow system in the Upper Floridan aquifer can be illustrated and summarized using a potentiometric-surface map (fig. 3). The contours on this map represent the potentiometric surface prior to extensive development of ground water in some areas of the State. Ground water flows from areas of high potential to areas of low potential. Areas of natural discharge of water from the aquifer generally occur in areas where both the potentiometric surface and the topography are low. These areas, which are indicated by depressions in the potentiometric surface, occur along stream channels or near springs. Bush and Johnston (1988) found that almost 90 percent of the natural discharge from the Upper Floridan aquifer is to rivers and springs. Aucott (1988) reported that areas of highest discharge include the north and central Gulf Coast; Tampa Bay; and the Suwannee, Withlacoochee, Santa Fe, St. Johns, and Apalachicola River Valleys (fig. 1).
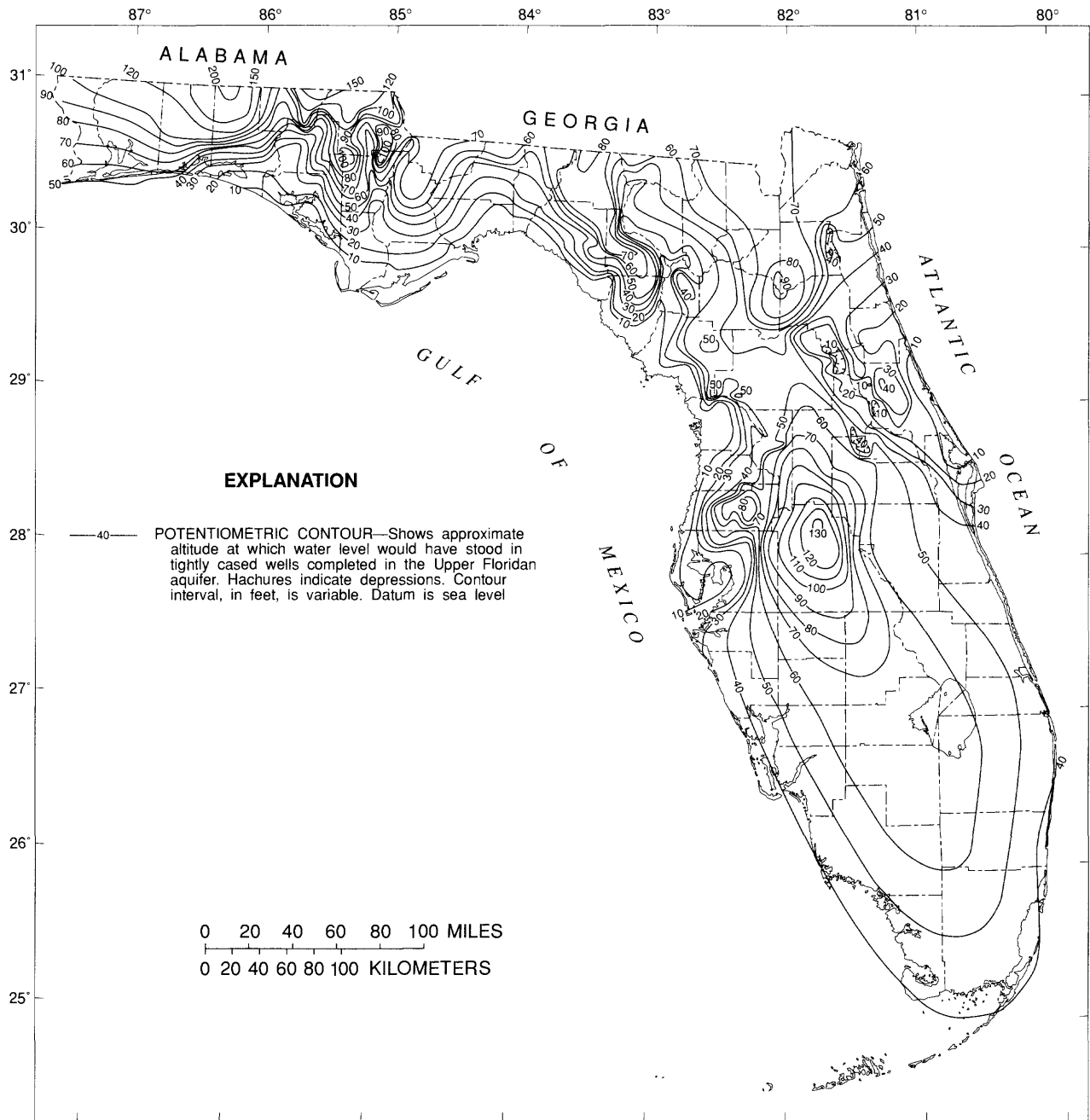
Figure 3. Estimated potentiometric surface of the Upper Floridan aquifer prior to development (Modified from Johnston and others, 1980.)

Generally, areas of recharge to the Upper Floridan aquifer are indicated by areas where the potentiometric surface and the topography are high. Areas of high recharge include the part of Polk County where the many sinkhole lakes serve as conduits for recharge, parts of Jackson and Washington Counties, and the De Land Ridge in west-central Volusia County (fig. 1) where the Upper Floridan aquifer is overlain by permeable deposits of sand (Aucott, 1988).

The actual amounts of recharge to and discharge from the Upper Floridan aquifer are directly related to the

thickness and integrity of the overlying confining unit(s) (Bush, 1982). In areas where the overlying material is thin, absent, breached, or is highly permeable (fig. 2), the movement of high amounts of water is likely. For example, the area extending from Levy County to Pasco County in the northwest-central part of the State (fig. 1) is one of large recharge (Swancar and Hutchinson, 1992). The confining material in this area is either thin or absent, and the head gradient is typically downward, providing optimal conditions for water to percolate rapidly into the Upper Floridan aquifer. In areas where the overlying

confining materials are thick and relatively impermeable, such as in southern Florida (fig. 2), the downward (recharge) or upward (discharge) movement of water through these materials is significantly impeded. Aucott (1988) presents a detailed map showing the areal distribution of recharge and discharge for the Upper Floridan aquifer in Florida. It is of interest to note that even though changes have occurred in recharge and discharge for the aquifer over large areas of the State as a result of development, these changes have not been regional in scale and have not altered the overall pattern of recharge and discharge (Aucott, 1988).

The transmissivity of the Upper Floridan aquifer ranges from approximately 1,000 to greater than 1,000,000 $[(ft^3/d)/ft^2]ft$ as a result of the wide variation in hydrogeologic conditions (Johnston and Bush, 1988). In the Florida Panhandle and southernmost Florida, low values of transmissivity occur where the aquifer is confined by thick sections of clay or low-permeability limestone. The transmissivities are generally the highest in the karst areas of central and northern Florida where the aquifer is partially confined or unconfined. An areal distribution of transmissivity of the Upper Floridan aquifer and a tabulation of data obtained from aquifer tests are presented in Bush and Johnston (1988).

The effects of confinement are clearly evident when ground-water fluxes are compared between confined and unconfined areas. Bush and Johnston (1988) subdivided the entire Floridan aquifer system into eight major ground-water areas (basins) bounded by flow lines (fig. 4). Within each area, ground-water discharge equals recharge, as simulated from a regional ground-water flow model (Bush, 1982). To illustrate the effect of confinement on discharge from the aquifer, areas V and VII are mostly confined and occupy about 30 percent of the area underlain by the aquifer (figs. 2 and 4). However, these two areas only contribute a small percentage of the total predevelopment discharge from the system (Bush and Johnston, 1988). In contrast, areas II, III, and IV are predominantly unconfined and contribute about 63 percent of the total predevelopment discharge; yet they occupy only about 20 percent of the land area where the aquifer system is present. Pumping has resulted in a substantial decline of water levels in several large areas of Florida, principally west-central Florida, the Fort Walton Beach area, the Jacksonville area and the Orlando area (fig. 1) (Healy, 1982). However, as noted in several recent reports, ground-water development has not greatly altered the overall regional pattern of recharge and discharge (Aucott, 1988; Johnston and Bush, 1988).

The relation between the degree of confinement and major-ion chemistry will be presented throughout this report. Previous studies have shown that the thickness of the confining unit and associated flow system characteristics can have a profound influence on the evolution of water chemistry along flow paths in the aquifer system (Back and Hanshaw, 1970; Plummer, 1977; Plummer and others, 1983; and Sprinkle, 1989).

HYDROCHEMISTRY

Methodology

The data used in this report consist of information collected and compiled during two intensive regional programs designed to study the hydrogeology and water chemistry of the Floridan aquifer system: the FGWQMN and the RASA. The approximately 800 wells selected for the FGWQMN by the Florida water management districts and the Alachua County Department of Environmental Services (ACDES) were designated specifically to characterize background water-quality conditions in the Upper Floridan aquifer; that is, these wells were chosen to avoid known areas of ground-water contamination. These data are currently available in computer files maintained by the FDER (Tim Glover, Florida Department of Environmental Regulation, written commun., 1990). The network consists of both existing and new monitoring wells installed for the aforementioned study. The criteria for selection of wells were based in part on site history, information on exact well location, and well-construction records (Humphreys and others, 1986). New wells were installed if existing wells meeting these criteria were not available in an area.

Detailed methods of collecting and analyzing water samples as part of the FGWQMN program are included in Quality Assurance Project Plans on file with FDER (Silkie Labbie, Florida Department of Environmental Regulation, written commun., 1990). In general, water-sample collection and analytical procedures were similar to standard USGS methods for sampling (Wood, 1976) and analysis (Fishman and Friedman, 1985). Commercial and water-management district laboratories followed a rigorous set of quality assurance measures that included the analysis of duplicate samples, laboratory and equipment blanks, and field blanks. Further, any analyses that exceeded a ±10 percent charge-balance error (CBE) were not included in the data analysis. Water analyses from 455 wells completed in the Upper Floridan aquifer met this CBE criterion. The locations of these wells are shown in figure 5. If multiple water samples were available for a given well, the median value for each major ion was computed from the analyses that met the CBE criterion.

The criteria for selection of wells used in the RASA study to describe the geochemistry of the Floridan aquifer system are given by Sprinkle (1989). Sprinkle's report contains water chemistry data for 601 wells completed in the Floridan aquifer system in Florida, Alabama, Georgia, and South Carolina. Data for major ions in water from the 332 wells used in this report were selected from a subset of Sprinkle's wells and are located in the Upper Floridan aquifer in Florida (fig. 6). Data for these wells are currently available in computer files maintained by the USGS (U.S. Geological Survey, 1974; 1975).
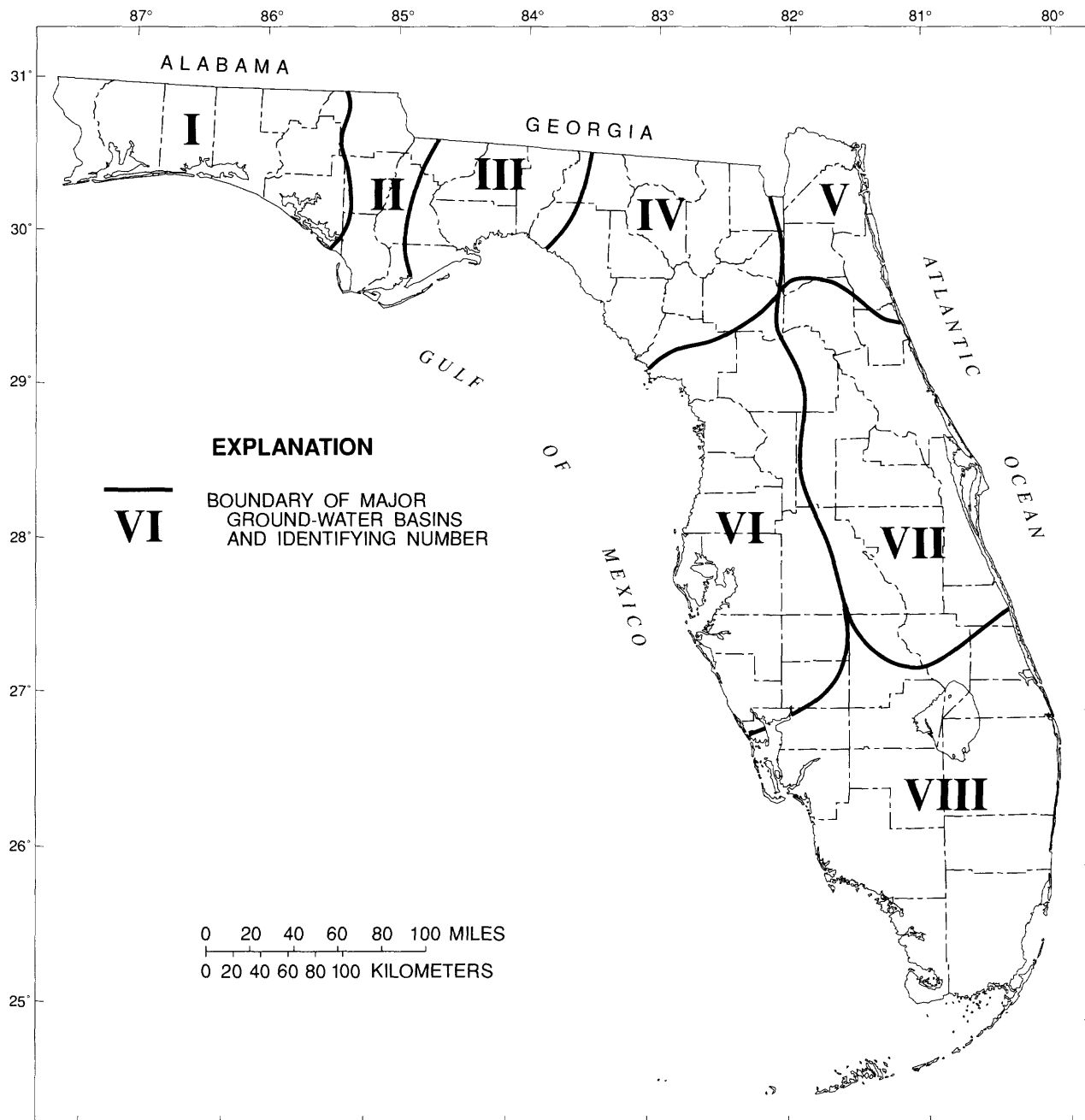
Figure 4. Major ground-water basins of the Upper Floridan aquifer. (From Bush and Johnston, 1988.)

For purposes of geochemical computations, it was assumed that all dissolved species are at equilibrium with one another. This assumption allows the use of computer-based thermodynamic models to calculate the distribution and activities of dissolved species (Nordstrom and others, 1979). The computer program WATEQF (Plummer and others, 1978) was used to calculate the chemical activity of each major ion in solution and the departure from equilibrium (saturation index or SI) of the water with respect to solid phases (minerals)

that may be dissolving or precipitating in the system. The SI of a particular mineral is defined as:

$$SI = \log (IAP/K_T)$$

where IAP is the ion activity product of the mineral-water reaction, and K_T is the thermodynamic equilibrium constant for the dissolution of the mineral, adjusted to the temperature of the given sample, T. The saturation index (SI) does not provide any information on the kinetics of dissolution or precipitation reactions. When SI is equal to 0, the mineral is in equilibrium with the aqueous phase.
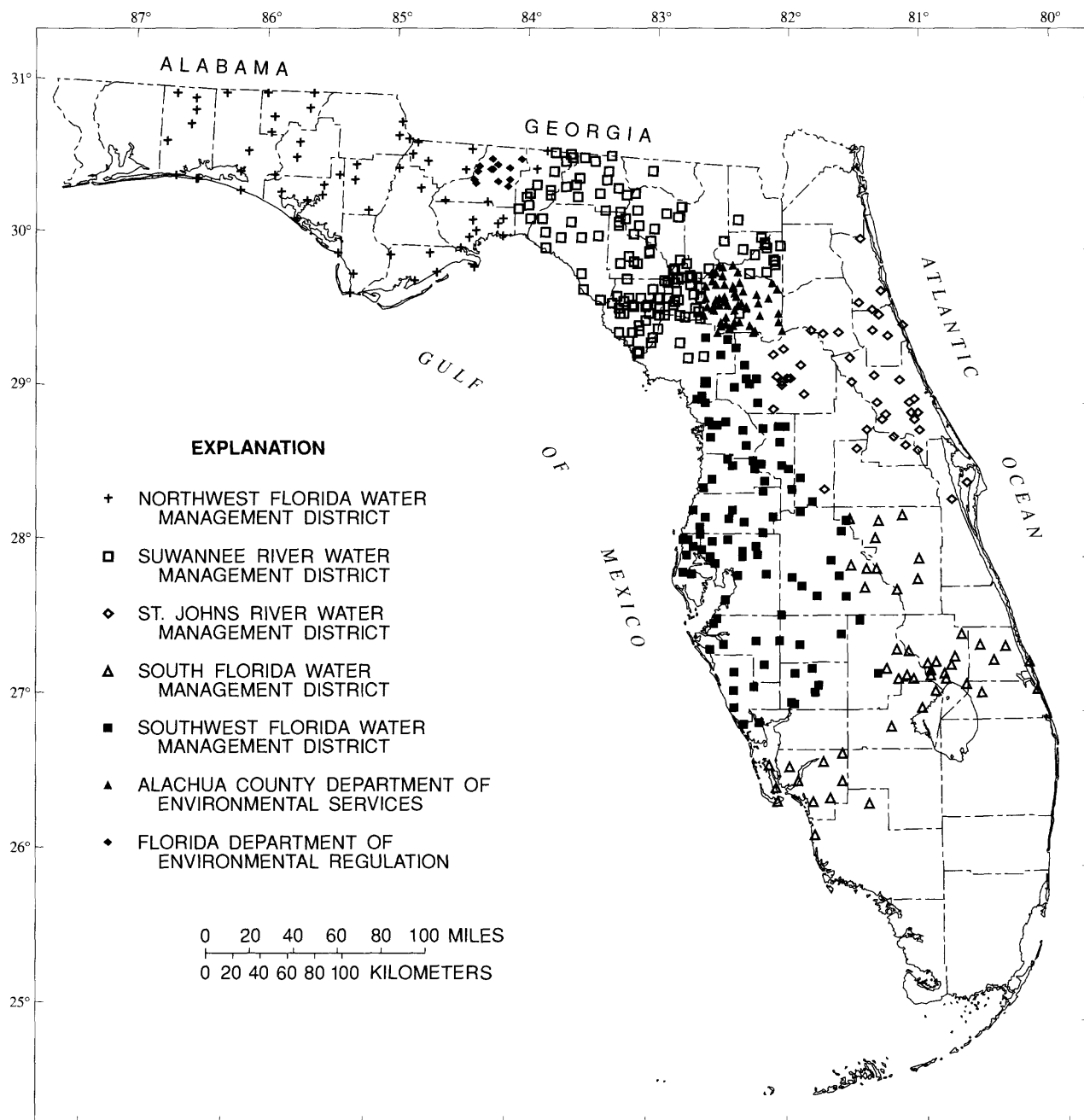
Figure 5. Location of wells completed in the Upper Floridan aquifer sampled by water management districts and county and state agencies.

When SI is less than 0, the water is undersaturated with respect to the mineral. That is, the mineral has thermodynamic potential to dissolve. When the SI is greater than 0, the water is supersaturated with respect to the mineral, which has the potential to precipitate from solution. Other factors may also determine if a mineral will precipitate and grow, such as nucleation energy, surface poisoning, and mineral surface topography (Drever, 1982).

Descriptive and nonparametric statistics are used in this report to summarize, by ground-water basin, concentrations of major ions (calcium, magnesium,

sodium, potassium, chloride, sulfate, and bicarbonate), dissolved solids, and temperature. Boxplots (graphical summaries) are used to compare the medians, the 25th and 75th percentiles, and probable outliers of selected characteristics among hydrogeologic groups (based on the degree of confinement of the aquifer in which the well is located). Nonparametric statistical techniques are used because the water-quality data generally are not normally nor lognormally distributed, and these techniques do not require equal variances and are not sensitive to outlying or inaccurate values (Iman and Conover, 1983).
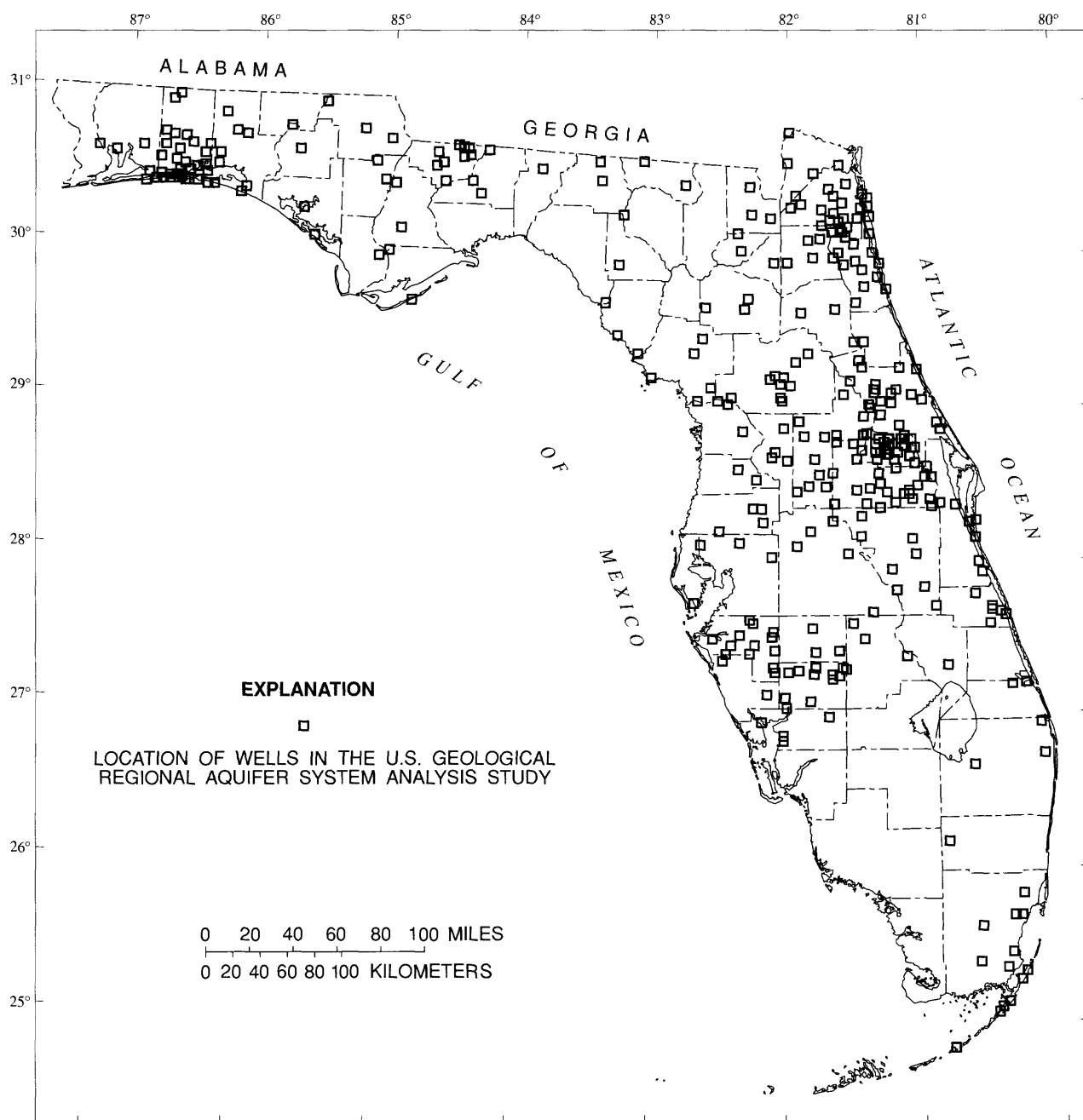
Figure 6. Location of wells selected from the Regional Aquifer Assessment Analysis of the Floridan aquifer systsem. (Modified from Sprinkle 1989.)

Hypothesis tests are used to determine if observed differences in constituent concentrations are due to random variability or statistically significant populations.

Spearman's Rho statistic is used to determine if the concentration of major ions is correlated with depth of well in each ground-water basin of the aquifer. This nonparametric statistic measures the strength of an increasing or decreasing relation between two variables (Iman and Conover, 1983). In this correlation method, all observations are given equal weight so that any extreme values will not have a disproportionate effect on the correlation. A positive or negative relation between a particular chemical constituent and well depth is considered significant at an alpha value, or level of significance, of 0.05.

To evaluate differences in chemical characteristics with the degree of confinement (unconfined, semiconfined, or confined conditions), data from the eight ground-water

basins are combined by geographic region. This was necessary because in some ground-water basins, there was an insufficient number of wells located in areas of unconfined, semiconfined, and confined conditions. The regional areas represent similar hydrogeologic conditions and are as follows: (1) wells located in ground-water basins I, II, and III are included in the Florida Panhandle region, (2) wells located in ground-water basins IV and V are included in the north Florida Peninsula region, and (3) wells located in ground-water basins VI, VII, and VIII are included in the south Florida Peninsula region. The Kruskall-Wallis test, which compares the mean rank of two or more independent groups, is used to test the null hypothesis that the concentrations of major ions and selected chemical characteristics are similar for unconfined, semiconfined, and confined conditions (groups) in each geographical region of the Upper Floridan aquifer (as is shown in a table later in the report). The alternative is that at least one of the groups in each geographical region has a different constituent concentration due to the degree of confinement. Differences between the mean rank of the groups are considered significant at an alpha level of 0.05. This value represents the maximum probability of rejecting the null hypothesis when it actually is true. If the probability (presented as p-value) is less than or equal to the alpha value, the null hypothesis is rejected. The use of these types of statistics are presented in more detail in Iman and Conover (1983) and Helsel and Ragone (1984).

Maps were prepared showing the areal distribution of major ions divided into concentration intervals. For comparison and continuity between this study and the RASA study (Sprinkle, 1989), the same concentration intervals are presented in this report that were delineated by Sprinkle. An additional map is included in this report that shows the vertical distribution of wells by depth interval in the Upper Floridan aquifer. This map is intended to provide the reader with an idea of how the differences in concentration of these ions are related to both the depth interval in the aquifer and the geographic location of the particular sampling site.

Statistical Summary of Selected Constituents, Temperature, and Depth of Wells Tapping the Aquifer

Descriptive statistics (number of observations, mean, standard deviation, median, minimum, and maximum) are presented in table 1 for major ions (Ca, Mg, Na, K, Cl, SO_4, HCO_3), temperature, depth of the well, and length of the open-bore interval. Data are grouped by ground-water basins (fig. 4). Summary statistics are also presented in table 1 for nitrate, phosphate, silica, total organic carbon, dissolved solids, and pH. However, no additional analyses of these data will be presented in this report.

In all ground-water basins with the exception of basin II, the wells included from the RASA study are substantially deeper than the wells from the FGWQMN. The two sets of data provide a large range in the depth of wells completed in the aquifer, which allows for a test of vertical variations in major-ion chemistry with depth. However, this difference in well depth between data sets also accounts for some changes in the areal distribution maps produced from this study and those generated by the RASA study (Sprinkle, 1989). These differences are highlighted in the following sections on major-ion chemistry.

To examine variations in water chemistry with depth in the aquifer, well depth and the length of the uncased well bore need to be known. Generally, wells in the Upper Floridan aquifer have a well bore (also referred to as the open interval) that is open to both low- and high-permeability zones below the bottom of a cased interval. The depth of the cased interval generally extends to the first rock layer that is encountered.

Water obtained during sampling under pumping conditions has migrated into the open interval from the highest permeability zone(s), where it has mixed with waters from other zones in the aquifer. The chemistry of water in the open interval has changed in response to possible changes in the temperature, ionic strength, pH, concentration (partial pressure) of dissolved gases, and redox potential. Most notable effects are the potential changes in the solubilities of minerals, such as calcite and dolomite. Sprinkle (1989) presents various scenarios that account for mixing in the open interval and its effect on water chemistry. He concluded that mixing can influence the carbonate equilibria in a water sample, which in some instances could produce oversaturated mixtures and in other instances undersaturated mixtures (Wigley and Plummer, 1976).

Depth information is available for most wells included in this study and is presented for selected intervals on plate 1. Unfortunately, information on the length of the open interval is available for less than 50 percent of the wells. However, in all ground-water basins with the exception of number V (fig. 4, northeast Florida), there is a significant positive relation between the length of the open interval and well depth (table 2). To evaluate chemical stratification with depth in the aquifer, depth of a well is chosen as the independent variable. It is important to emphasize that the exact depth of the zone contributing the largest quantity of water to the open interval in most wells is not known. In a general way, the temperature of the water may provide some information regarding the principal contributing zone because the water temperature typically increases with depth below land surface. For example, in four of the ground-water basins (I, II, VI, and VII) temperature increased significantly with well depth, indicating that in these basins, water being sampled in the deeper wells originates from deeper zones within the aquifer (table 2).

Table 1. Summary statistics for major ions, selected chemical constituents, temperature in water from wells; depth and length of open interval for wells completed in the Upper Floridan aquifer, by ground-water basin

[Concentrations are expressed in milligrams per liter, except as noted]

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum

Ground-water basin I

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum
Calcium	74	20.8	15.8	21.0	1.00	78.0
Magnesium	74	7.38	6.04	6.15	.28	31.0
Sodium	74	63.4	81.7	14.3	1.60	440.
Potassium	74	3.36	2.43	3.00	.100	9.85
Chloride	74	44.4	70.4	6.35	1.70	360.
Sulfate	74	6.91	8.61	5.60	.200	64.0
Bicarbonate	74	184.	90.3	169.	11.0	650.
Nitrate, as NO_3	32	2.42	2.18	1.50	.230	9.00
Phosphate, as PO_4	8	.083	.055	.086	.010	.153
Silica, as SiO_2	52	13.2	2.85	13.0	7.40	21.0
Total organic carbon	35	7.08	5.37	5.55	1.00	22.9
Dissolved solids	73	258.	184.	190.	4.00	1120.
pH (units)	74	7.84	.418	7.80	6.80	8.80
Temperature, °C	65	23.3	2.35	22.5	17.0	30.
Open interval, feet	29	123.	91.4	100.	20.0	383.
Well depth, feet	74	553.	263.	548.	114.	1,140.

Ground-water basin II

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum
Calcium	22	72.3	162.	31.5	9.20	790.
Magnesium	22	59.1	183.	11.5	.75	870.
Sodium	22	337.	1,466.	7.85	1.50	6,900.
Potassium	22	13.2	32.0	1.95	.20	150.
Chloride	22	620.	2,766.	7.45	1.90	13,000.
Sulfate	22	160.	518.	8.05	.20	2,400.
Bicarbonate	22	194.	84.6	162.	50.0	366.
Nitrate, as NO_3	17	1.15	1.16	.870	.0	4.30
Phosphate, as PO_4	5	.033	.068	.00	.0	.153
Silica, as SiO_2	9	15.4	6.67	16.0	7.30	30.0
Total organic carbon	17	5.01	4.01	3.91	.100	16.0
Dissolved solids	20	312.	344.	190.	110.	1,590.
pH (units)	22	7.51	.422	7.54	6.55	8.20
Temperature, °C	21	23.4	1.85	23.0	21.0	27.9
Open interval, feet	13	99.2	61.5	90.0	20.0	214.
Well depth, feet	22	337.	151.	303.	101.	612.

Ground-water basin III

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum
Calcium	68	58.1	61.5	40.5	10.0	480.
Magnesium	68	21.1	58.5	8.80	.31	430.
Sodium	68	76.6	394.	4.90	.840	3,200.
Potassium	68	5.39	17.6	.985	.170	130.
Chloride	68	121.	637.	6.15	2.30	5,200.
Sulfate	68	83.0	358.	5.50	.600	2,200.
Bicarbonate	68	174.	87.8	159.	29.3	549.
Nitrate, as NO_3	52	.812	1.62	.180	.010	11.0
Phosphate, as PO_4	40	.159	.201	.040	.010	1.07
Silica, as SiO_2	15	15.8	5.76	15.0	6.90	26.0
Total organic carbon	50	4.28	4.83	1.88	.0	20.0
Dissolved solids	65	318.	560.	180.	49.0	4,400.
pH (units)	68	7.17	.632	7.23	5.70	8.10
Temperature, °C	64	22.2	1.23	22.0	20.0	28.0
Open interval, feet	56	73.0	68.2	38.5	.0	306.
Well depth, feet	68	254.	219.	203.	.0	960.

Table 1. Summary statistics for major ions, selected chemical constituents, temperature in water from wells; depth and length of open interval for wells completed in the Upper Floridan aquifer, by ground-water basin--Continued

[Concentrations are expressed in milligrams per liter, except as noted]

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum
			Ground-water basin IV			
Calcium	182	67.8	34.1	60.0	.630	300.
Magnesium	182	10.6	22.2	6.05	.020	290.
Sodium	182	20.2	163.	5.10	.200	2,200.
Potassium	182	1.42	5.40	.485	.060	66.0
Chloride	182	30.2	230.	7.40	2.60	3,100.
Sulfate	182	18.5	97.2	5.30	.500	1,300.
Bicarbonate	182	216.	79.3	204.	39.0	463.
Nitrate, as NO_3	174	.445	1.51	.050	.0	15.0
Phosphate, as PO_4	171	.221	.245	.153	.0	2.76
Silica, as SiO_2	19	16.0	9.74	19.0	2.10	32.0
Total organic carbon	128	4.71	6.40	1.90	.0	46.8
Dissolved solids	134	291.	750.	210.	72.0	8,800.
pH (units)	181	7.07	.750	7.10	5.25	11.4
Temperature, °C	134	22.7	1.44	23.0	20.0	28.0
Open interval, feet	158	37.9	62.1	20.0	.0	400.
Well depth, feet	179	152.3	184.	84.0	.0	905.
			Ground-water basin V			
Calcium	48	83.9	82.9	66.5	17.0	550.
Magnesium	48	44.4	49.7	30.5	6.30	260.
Sodium	48	129.	397.	16.0	2.80	2,200.
Potassium	48	5.12	9.52	2.55	.30	58.0
Chloride	48	237.	719.	18.25	2.70	3,500.
Sulfate	48	191.	175.	155.	.10	870.
Bicarbonate	48	158.	43.7	160.	31.7	345.
Nitrate, as NO_3	4	.012	.0095	.008	.0050	.025
Phosphate, as PO_4	3	.056	.0108	.055	.046	.068
Silica, as SiO_2	25	21.3	7.28	22.0	5.55	36.0
Total organic carbon	4	3.44	.829	3.82	2.20	3.93
Dissolved solids	16	1,095.	1,895.	396.	101.	7,080.
pH (units)	45	7.62	.261	7.6	6.60	8.00
Temperature, °C	40	23.0	3.97	23.5	2.50	29.5
Open interval, feet	4	211.	199.	162.	45.0	477.
Well depth, feet	48	627.	307.	645.	200.	2,026.
			Ground-water basin VI			
Calcium	167	94.7	96.1	69.5	3.20	639.
Magnesium	167	34.5	83.6	9.60	.120	905.
Sodium	167	139.	658.	8.70	1.80	7,450.
Potassium	167	4.44	13.1	1.20	.040	133.
Chloride	167	270.	1,316.	12.0	1.00	15,000.
Sulfate	167	178.	352.	23.0	.0	2150.
Bicarbonate	167	171.	68.6	160.	3.20	354.
Nitrate, as NO_3	107	.104	.407	.0036	.0	3.85
Phosphate, as PO_4	98	.363	.325	.302	.0	2.47
Silica, as SiO_2	63	17.6	9.47	15.0	3.80	49.0
Total organic carbon	104	18.6	14.6	16.5	.10	65.8
Dissolved solids	157	933.	2,911.	300.	43.0	34,500.
pH (units)	146	7.55	.543	7.45	4.90	10.7
Temperature, °C	148	25.4	2.39	25.0	21.0	32.5
Open interval, feet	99	176.	260.	56.0	.0	1,115.
Well depth, feet	163	545.	445.	385.	20.0	1,535.

Table 1. Summary statistics for major ions, selected chemical constituents, temperature in water from wells; depth and length of open interval for wells completed in the Upper Floridan aquifer, by ground-water basin--Continued

[Concentrations are expressed in milligrams per liter, except as noted]

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum

Ground-water basin VII

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum
Calcium	165	74.1	54.4	55.0	11.0	290.
Magnesium	165	33.9	50.3	11.0	1.00	290.
Sodium	165	218.	467.	27.5	2.80	2,963.
Potassium	165	7.52	15.4	1.8	.100	110.
Chloride	165	412.	839.	38.0	4.40	5,200.
Sulfate	165	83.9	153.	12.5	.0	900.
Bicarbonate	165	180.	73.4	165.	38.0	435.
Nitrate, as NO_3	70	.132	.712	.0088	.0	5.90
Phosphate, as PO_4	43	.152	.231	.061	.004	.969
Silica, as SiO_2	124	15.0	8.18	12.5	1.50	61.0
Total organic carbon	60	5.53	6.49453	3.08	.0	26.6
Dissolved solids	136	926.	1,577.	332.	63.0	10,500.
pH (units)	154	7.59	.427	7.60	6.28	9.50
Temperature, °C	131	23.9	1.34	24.0	21.0	29.0
Open interval, feet	54	239.	320.	105.	.0	1,600.
Well depth, feet	159	394.	290.	340.	.0	1,600.

Ground-water basin VIII

Variable	Number of observations	Mean	Standard deviation	Median	Minimum	Maximum
Calcium	61	111.	96.8	86.0	24.0	540.
Magnesium	61	167.	296.	85.5	3.97	1,700.
Sodium	61	1,251.	2,420.	531.	6.40	12,000.
Potassium	61	51.4	97.3	21.0	.85	430.
Chloride	61	2,187.	4,240.	939.	12.5	20,000.
Sulfate	61	446.	533.	310.	1.00	2,800.
Bicarbonate	61	165.	55.7	162.	32.7	350.
Nitrate, as NO_3	39	.034	.086	.004	.004	.390
Phosphate, as PO_4	39	.012	.023	.0045	.004	.144
Silica, as SiO_2	59	15.7	6.58	15.5	3.30	38.8
Total organic carbon	46	2.45	3.19	1.80	.0	19.0
Dissolved solids	61	4,487.	7,919.	110.	108.	36,600.
pH (units)	60	7.53	.475	7.52	6.40	9.50
Temperature, °C	59	26.2	2.30	26.0	20.0	35.5
Open interval, feet	31	522.	361.	380.	3.00	1,500.
Well depth, feet	58	1,184.	623.	1,096.	433.	3,575.

In ground-water basins III, IV, V, and VIII, there is no significant relation between temperature of the water and depth of the well tapping the aquifer (table 2). This finding indicates that water mixes in the open interval from different permeable zones in the aquifer. Another possibility is that some shallow wells may be located in areas of discharge in the aquifer and they may receive warmer water from zones in the aquifer that are deeper than the bottom of their open interval zone. When data from ground-water basins are grouped by geographical area and the degree of confinement is included, the temperature of the water is closely related to the well depth. From a comparison of figures 7 and 8, it is evident that well depth increases as the degree of confinement increases from unconfined to confined conditions in all three geographical areas of the State, with the median temperature showing an increase in the confined areas.

The following sections of the report describe for each major ion the areal and vertical variations in concentration throughout the Upper Floridan aquifer, geochemical processes that control the concentrations of major ions in the aquifer, and the effect of the degree of confinement.

Calcium

The principal sources of calcium ion (Ca^{2+}) in water from the Upper Floridan aquifer are the dissolution of calcite, dolomite, and gypsum. The mixing of seawater with freshwater in some parts of the aquifer also contributes to high concentrations of Ca^{2+}. Ca^{2+} can be removed from aquifer water by precipitation of calcite (Plummer and others, 1983) and ion-exchange reactions involving Na^+ and Ca^{2+} on clays (Sprinkle, 1989).

Table 2. Spearman correlation coefficients of major ions and selected characteristics that vary significantly (0.05 alpha level) with well depth, by ground-water basin

[Minus sign indicates inverse correlation with depth; NS signifies no significant relation]

Number of observations	Ground-water basin							
	I	II	III	IV	V	VI	VII	VIII
	74	22	68	179	48	163	159	58
Calcium	-0.723	NS	-0.345	-0.510	-0.345	0.229	-0.15	0.302
Magnesium	-.223	.458	.317	.257	-.330	.606	NS	.293
Sodium	.767	.688	NS	.155	-.329	.368	-.164	.270
Potassium	.740	.605	.319	.264	-.474	.436	NS	NS
Chloride	.632	.536	NS	NS	-.321	.329	-.156	.288
Sulfate	.255	.525	.262	NS	-.379	.488	NS	.338
Bicarbonate	.735	.442	-.327	-.323	NS	NS	NS	NS
Dissolved solids	.583	.471	NS	-.261	NS	.359	NS	.315
pH	.673	NS	.745	.412	NS	.267	NS	.352
Temperature	.420	.684	NS	NS	NS	.672	.541	NS
Open-hole interval	.663	.757	.818	.574	NS	.721	.921	.776

Concentrations of Ca^{2+} in water from the aquifer range from less than 10 mg/L in northwest peninsular Florida (ground-water basin IV) to more than 640 mg/L in deep zones of the aquifer in southwestern Florida, where gypsum is likely dissolving (Sprinkle, 1989). Two large areas where concentrations of Ca^{2+} in ground water are less than 20 mg/L occur in the western Florida Panhandle and in southeastern Polk County and north-central Highlands County (pl. 2). Small isolated areas of Ca^{2+} concentrations less than 20 mg/L in ground water are also present throughout the northern two-thirds of the State (pl. 2). These areas were not delineated on the map of Ca^{2+} concentrations in water from the Floridan aquifer system prepared by Sprinkle (1989). The addition of wells

EXPLANATION

◊ / x Detached "x" or diamond indicate value farther than 1.5 or 3.0 times respectively, the interquartile range

— Whisker indicates extent of data values to a distance 1.5 times interquartile range

— 75th percentile
— 50th percentile
— 25th percentile

C   CONFINED

SC SEMICONFINED

UF UNCONFINED

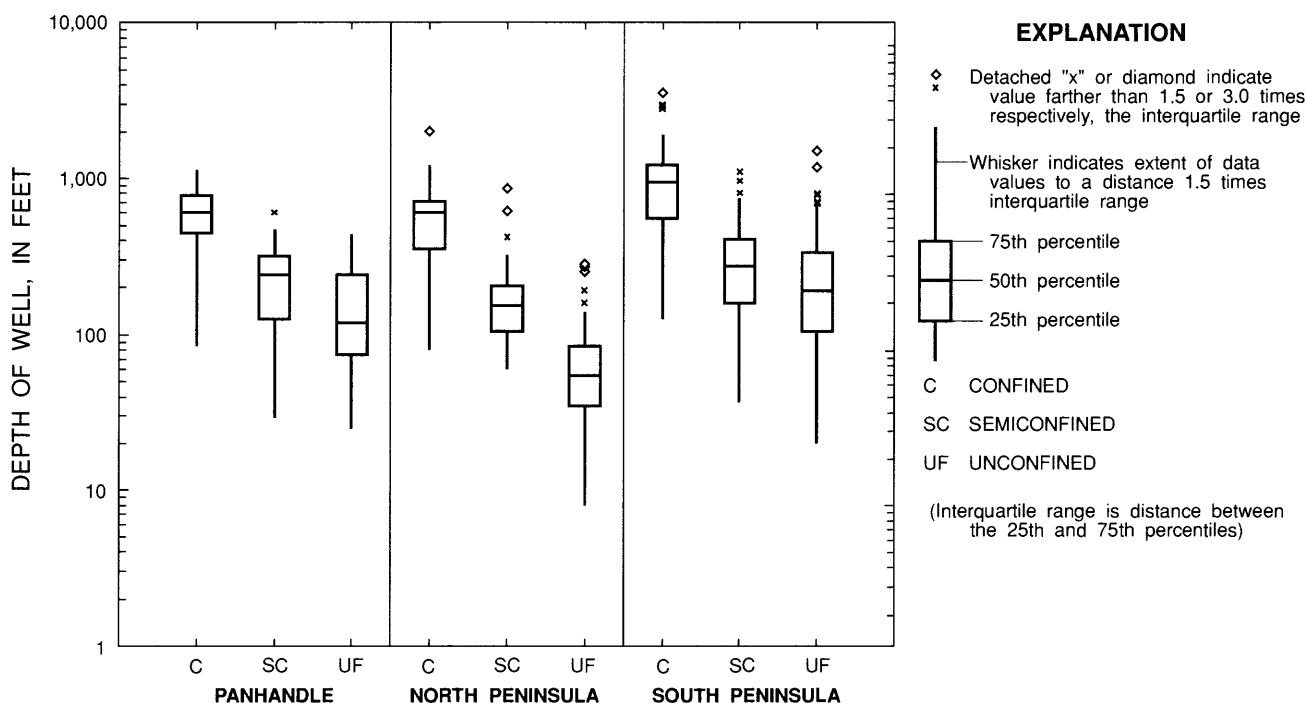(Interquartile range is distance between the 25th and 75th percentiles)

Figure 7. Graphical summary of the depth of wells completed in the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

from the FGWQMN that are generally not as deep as those included in the RASA study (Sprinkle, 1989) may account for some of these differences.

The concentration of Ca^{2+} in water from the aquifer appears to be chemically stratified with depth in ground-water basins VI and VIII, where Ca^{2+} concentrations increase significantly with depth (table 2). The positive relation between Ca^{2+} and depth corresponds to significant increases in the concentrations of chloride and dissolved solids. This indicates that the higher concentrations of Ca^{2+} with depth result primarily from seawater (either present day or remnant) mixing with freshwater in the aquifer. In contrast, Ca^{2+} concentrations show a significant decrease with depth in ground-water basins I, III, IV, V, and VII (table 2). In basins I and III in the Florida Panhandle, deeper wells are generally located the farthest distance downgradient along ground-water flow paths. As a result of ion-exchange reactions with clay minerals, Ca^{2+} concentrations decrease with increasing distance downgradient with a corresponding increase in Na^+ concentrations (Sprinkle, 1989). In ground-water basins V and VII, the observed decrease in Ca^{2+} concentration with depth is most likely related to the geographic location of shallow and deep wells (pl. 1). In these basins, shallower wells are generally located near the coast where Ca^{2+} concentrations are high because of mixing of freshwater and seawater in the aquifer. The deeper wells tend to be located in areas not affected by mixing of seawater. Thus, based on the location of shallow and deep wells, an apparent decrease in Ca^{2+} concentrations in water from these wells is observed with increasing depth in the aquifer.

Another complicating factor in ground-water basin VII is that relatively shallow wells are present in the St. Johns River Valley. High dissolved solids are present in this area as a result of mixing of freshwater with remnant seawater in the Upper Floridan aquifer (Frazee and McClaugherty, 1979). The location of wells in ground-water basin IV may be a controlling factor; however, it does not appear to be as obvious a control as in basins V and VII.

The concentration of Ca^{2+} is controlled throughout most of the Upper Floridan aquifer by reaction with calcite. The SI with respect to calcite were computed by WATEQF for water analyses from the 787 wells in the Upper Floridan aquifer (fig. 9). These calculations were based on field measurements of temperature and pH, and field and laboratory measurements of alkalinity (HCO_3^-). Sprinkle (1989) considered that a calculated SI in the range of -0.2 to +0.2 was an indication of saturation with respect to calcite. In this report, calculated SI values in the range of -0.5 to +0.5 are assumed to indicate saturation with respect to calcite because of the uncertainties in the measurement of alkalinity in the field and laboratory, the potential for error in measurement of field pH of as much as ±0.2 unit, and the possibility of loss of CO_2 from the sample during the sampling process or in transport to the laboratory. Plummer and others (1990) accepted an uncertainty in the SI for dolomite of ±0.5.
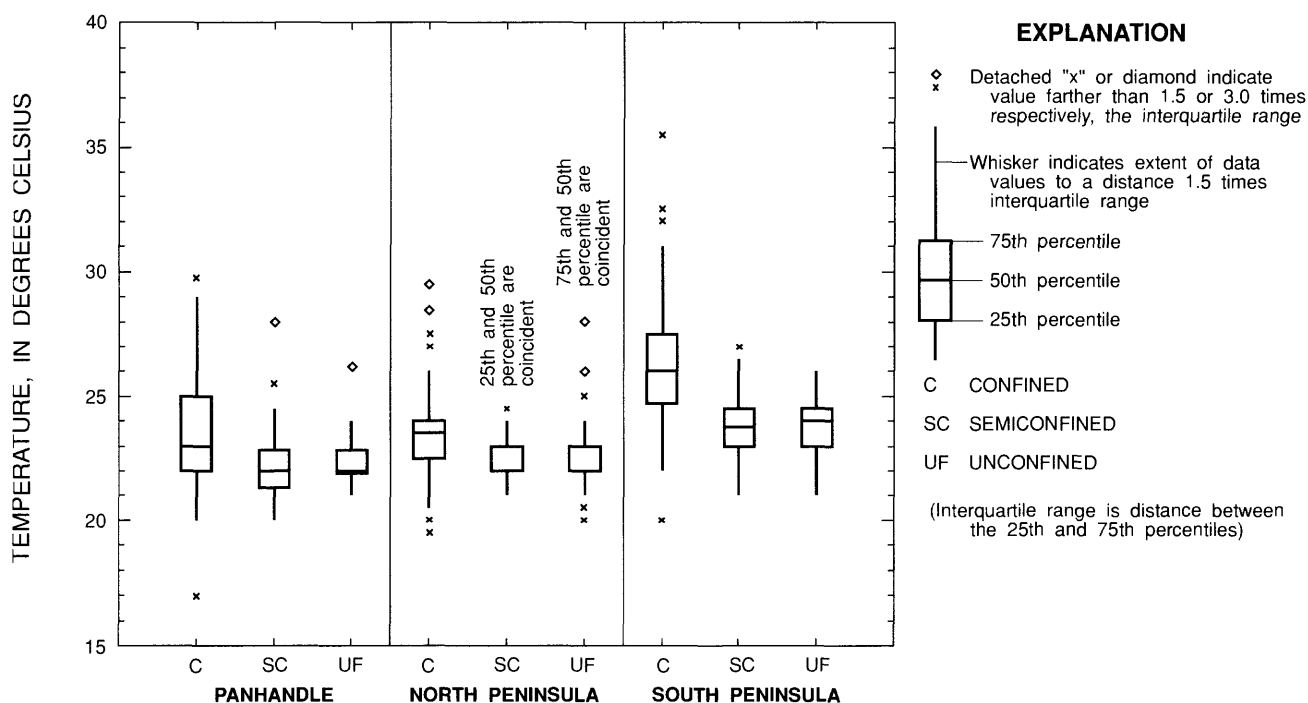

Figure 8. Graphical summary of the temperature of water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.
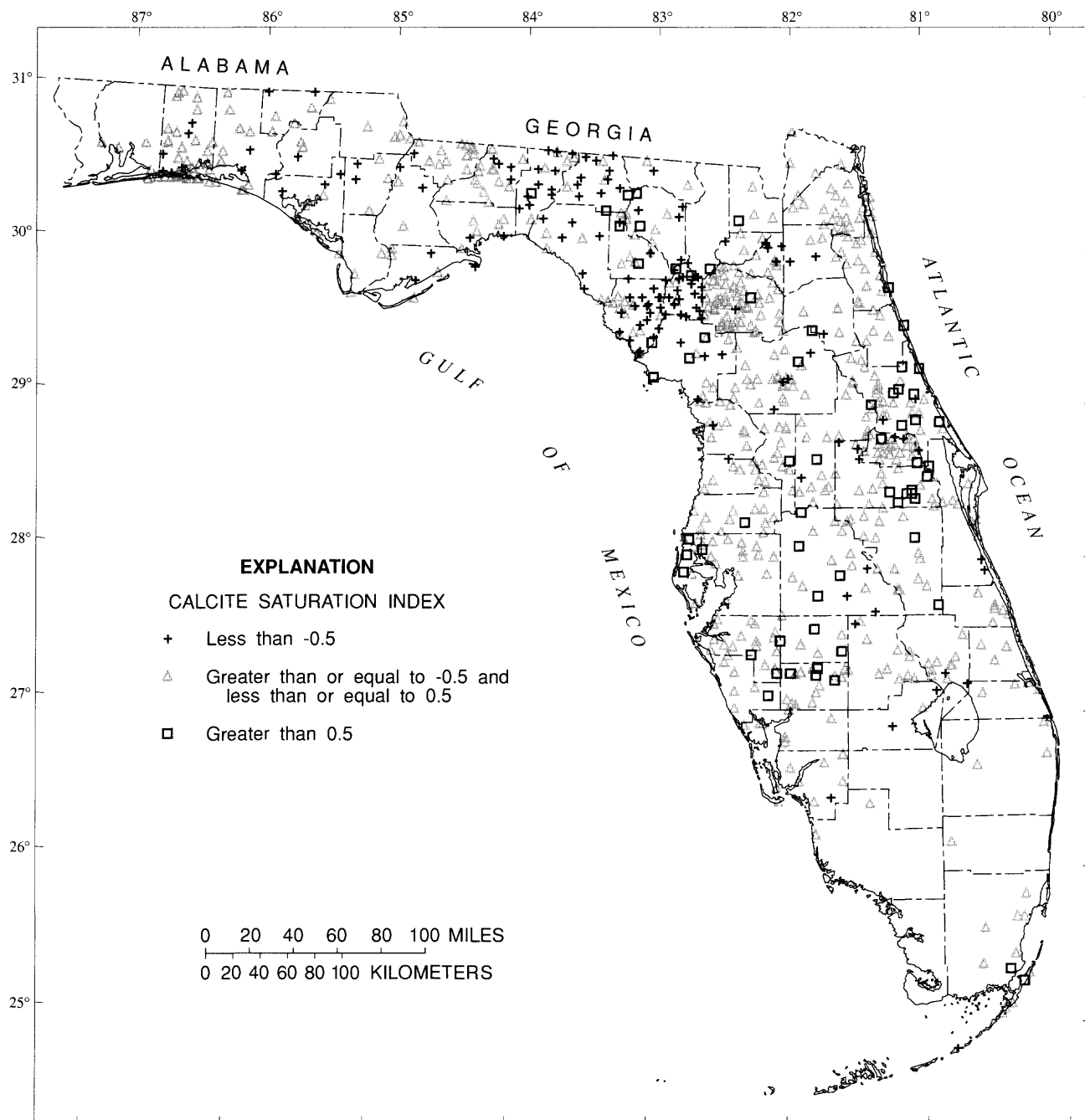
Figure 9. Calcite saturation index for water from the Upper Floridan aquifer.

It is evident from figure 9 that most of the water from the Upper Floridan aquifer is near or at saturation with respect to calcite. In recharge areas and where the aquifer is unconfined or semiconfined (such as in ground water basins III and IV) water from the aquifer is typically undersaturated with respect to calcite. In these areas, large amounts of rainfall or leakage from the overlying surficial aquifer system recharge the aquifer fairly rapidly not allowing sufficient contact time for the water to become saturated with respect to calcite (Lawrence and Upchurch, 1982). The water from the aquifer appears to be slightly undersaturated with respect to calcite in many locations in the Florida Panhandle. This apparent undersaturation may be related to local ion-exchange reactions that result in a reduction in the concentration of Ca^{2+} and causes the ground water to be undersaturated with respect to calcite. Sprinkle (1989) presents an alternative hypothesis that underlying sand aquifers in Cretaceous and Tertiary rocks may be discharging dilute sodium-bicarbonate water into the Upper Floridan aquifer.

Water from the aquifer that is oversaturated with respect to calcite (fig. 9) occurs in areas where the dissolved-solids concentrations are high (pl. 9, greater than 500 mg/L), predominantly in coastal areas, and in

areas where residual seawater in the aquifer is believed to be present (southern Florida and the St. Johns River Valley). In these areas, mixing of a calcium-bicarbonate freshwater with 10 percent or more seawater results in a mixture that is oversaturated with respect to calcite (Plummer, 1975). Upward leakage of waters that have dissolved gypsum from deeper parts of the Floridan aquifer system or Hawthorn Formation (S.B. Upchurch, University of South Florida, written commun., 1991) may occur in coastal areas. The water is calculated to be oversaturated with respect to calcite because of the common ion effect (Sprinkle, 1989). In many parts of the State, especially in southern Florida, deep wells may tap many zones of high permeability that could contain calcium-sulfate water. As a result of water from different zones mixing in the borehole, the sampled water, which is a mixture, would be oversaturated with respect to calcite, but water in each separate zone of the aquifer may not be oversaturated.

The degree of confinement of the Upper Floridan aquifer may have an important effect on the concentration of Ca^{2+} (fig. 10). In the north Florida Peninsula, the median Ca^{2+} concentration is higher in water from unconfined areas than in semiconfined and confined areas of the aquifer (fig. 10). Corresponding higher calculated partial pressures of carbon dioxide using WATEQF are also observed in the unconfined area (fig. 11). Large amounts of water charged with CO_2 recharge the aquifer in unconfined areas and have the potential to dissolve substantial amounts of calcite (Drever, 1982). However, near coastal areas, the higher concentration of Ca^{2+} in unconfined

areas is most likely related to seawater mixing. Theoretical mixing calculations with seawater and ground water at saturation with respect to calcite have shown that, even though higher amounts of calcite are dissolved in these coastal areas, the higher Ca^{2+} concentrations result from the mixing of seawater with ground water and not from the dissolution of calcite (Sprinkle, 1989). The median calcite SI (fig. 12) supports this conclusion, as the water in unconfined parts of the aquifer is slightly undersaturated with respect to calcite and the dissolution of calcite is thermodynamically favorable. In semiconfined and confined parts of the aquifer in the north Florida Peninsula, the median calcite SI is near zero indicating that calcite is controlling the concentrations of Ca^{2+} in water from the aquifer.

In south Florida, water from deep wells in the confined parts of the aquifer contain higher median Ca^{2+} concentrations than in unconfined and semiconfined areas of the aquifer (fig. 10). The median calcite saturation index for water from confined parts of the aquifer is greater than zero, indicating that the water is supersaturated with respect to calcite (fig. 12). As mentioned previously, dissolution of gypsum in the deep parts of the aquifer is likely and may contribute substantial amounts of Ca^{2+} to the water.

In the Florida Panhandle, median Ca^{2+} concentrations in water from confined parts of the aquifer are significantly lower than in unconfined areas (fig. 10; table 3). The aquifer in this part of the State contains large quantities of clays. Cation-exchange reactions, where $2Na^+$ are exchanging for Ca^{2+} in water from the aquifer,

Figure 10. Graphical summary of the concentration of calcium in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

may be responsible for the low Ca^{2+} concentrations and the elevated Na^+ concentrations. Also, any contribution to the aquifer from freshwater recharge would be minimized because of the large thickness of the confining unit. The median calcite SI is slightly less than zero (-0.2 to -0.3) (fig. 12), although possibly within the range of calcite saturation. High bicarbonate concentrations are present in the aquifer and, as a result, relatively high calcite SI are maintained. Some possible explanations for high bicarbonate concentrations in the aquifer are discussed in a later section.

Figure 11. Graphical summary of the calculated partial pressure of carbon dioxide in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

Figure 12. Graphical summary of the calcite saturation index for water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

Table 3. Comparison of mean ranks of major ions and other selected variables by degree of confinement (unconfined, semiconfined, and fully confined) in each of three geographical regions as determined by Kruskall-Wallis tests

[S, a significant difference among the degrees of confinement; NS, no significant difference among the degrees of confinement]

Constituent or characteristic	Geographical region		
	Panhandle peninsula	North peninsula	South
Calcium	S	S	S
Magnesium	NS	S	S
Sodium	S	S	S
Potassium	S	S	S
Chloride	NS	S	S
Sulfate	NS	S	S
Bicarbonate	S	S	NS
Dissolved solids	S	NS	S
Calcite saturation index	S	S	NS
Dolomite saturation index	S	S	S
Partial pressure CO_2, atmospheres	S	S	S
pH	S	S	NS
Temperature °C	S	S	S
Open interval, feet	S	S	S
Well depth, feet	S	S	S

Magnesium

The two principal sources for magnesium ion (Mg^{2+}) in the Upper Floridan aquifer are the dissolution of dolomite ($CaMg(CO_3)_2$) and mixing of freshwater with seawater. Another source of Mg^{2+} to the Upper Floridan aquifer is from the overlying Hawthorn Formation. Lawrence and Upchurch (1982) found that leaching of magnesium-rich clay minerals and dolomite contributed Mg^{2+} to water in the Upper Floridan aquifer in areas of north-central Florida. Where brackish or saline water is present in the aquifer, Mg^{2+} concentrations may approach the seawater concentration of 1,320 mg/L and exceed the associated concentrations of Ca^{2+}. Mg^{2+} concentrations in water from the aquifer range from less than 1 mg/L in some areas to more than 1,000 mg/L in coastal areas and in other areas where seawater or remnant seawater exists in the aquifer, such as in the valley of the St. Johns River and in southern Florida (pl. 3). In much of the aquifer, the concentrations of Mg^{2+} are less than 12 mg/L (0.5 mmol/L). This area of low Mg^{2+} concentrations is much larger than the area of similar Mg^{2+} concentrations delineated by Sprinkle (1989). This difference is most likely because the wells in the RASA study are substantially deeper over most of the State than wells from the FGWQMN. Deeper wells tend to produce water with higher Mg^{2+} concentrations (Sprinkle, 1989).

The concentration of Mg^{2+} is stratified with depth in the aquifer. Mg^{2+} concentrations increase significantly with well depth in ground-water basins II, III, IV, VI, and VIII and decrease significantly with depth in basins I and V (table 2). The decrease in Mg^{2+} concentration with well depth in Panhandle Florida (ground-water basin I) is most likely caused by ion-exchange reactions, analogous to cation-exchange involving Ca^{2+} and $2Na^+$. The chemical reaction is

$$Mg^{2+} + 2Na^+\text{-}EX = Mg^{2+}\text{-}EX + 2Na^+ ,$$
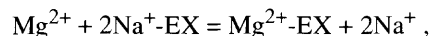
where EX represents the exchanger (clays or other minerals). Deeper wells in the aquifer are generally farther downgradient along ground-water flow paths and have the lowest Mg^{2+} concentrations and the highest Na^+ concentrations (Sprinkle, 1989). The decrease in Mg^{2+} concentration in water with depth in ground-water basin V is probably a function of geographical location of wells, with deeper wells farther inland with lower Mg^{2+} concentrations and shallower wells near coastal areas where Mg^{2+} concentrations are higher because of mixing of freshwater and seawater.

Water from confined areas in the Florida Peninsula have much higher Mg^{2+} concentrations than water from unconfined or semiconfined areas (fig. 13). This relation is most likely the result of deeper wells in confined areas of the State producing water with higher concentrations of Mg^{2+} than water from shallower wells in unconfined or semiconfined areas with lower concentrations. Lawrence and Upchurch (1982) have found that the concentration of Mg^{2+} in water from the aquifer in the north-central part of the State is related to the thickness of the overlying Hawthorn Formation, which contributes Mg^{2+} from the leaching of Mg-rich clay minerals and dolomite (Scott, 1988). In the panhandle, the effect of ion-exchange reactions is most likely responsible for the lower median concentration of Mg^{2+} in the confined area compared with concentrations in unconfined areas.

Mg^{2+} can be added to solution when magnesium-calcite dissolves and pure calcite precipitates because the low-magnesian form of the mineral is thermodynamically more stable (Plummer and MacKenzie, 1974). Dolomite dissolution (dedolomitization) could also result in an increase of Mg^{2+} concentrations in the Upper Floridan aquifer (Back and others, 1983). A map of dolomite SI was prepared from water analyses from the 787 wells in the aquifer (fig. 14). In large areas of the aquifer, the water is below saturation with respect to dolomite; however, in other areas of the State, water from the aquifer is probably at saturation or over-saturated with respect to dolomite (fig. 14). These areas are generally located in coastal areas of eastern and southwestern Florida, the St. Johns River Valley, and in the southern part of the State.

Sprinkle (1989) presented the following factors that may account for SI values greater than zero for dolomite in the aquifer: errors in the laboratory analysis (account for apparent oversaturation), mixing of waters from different
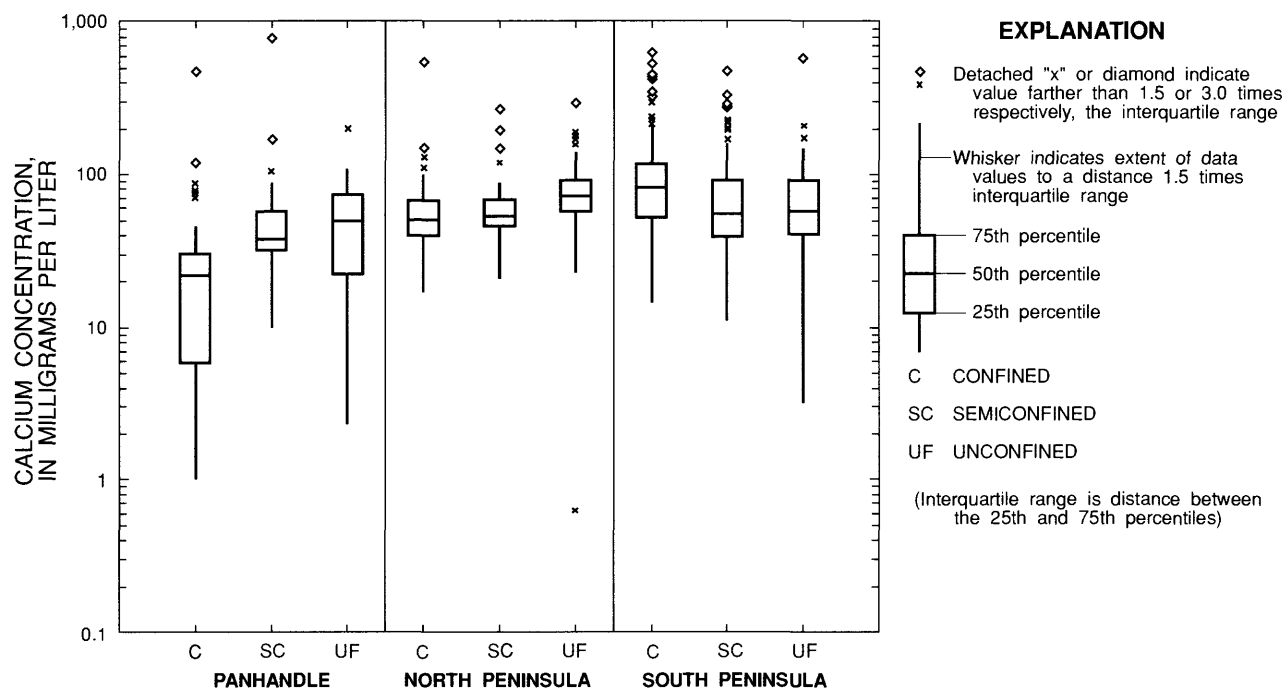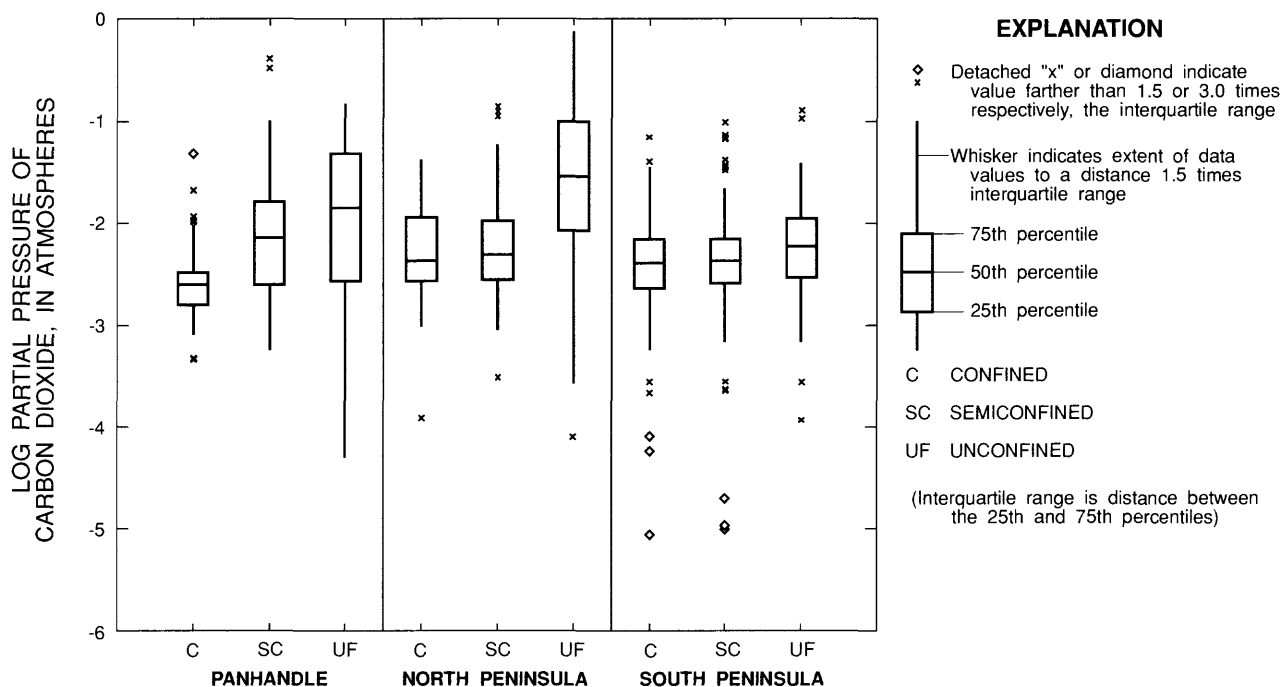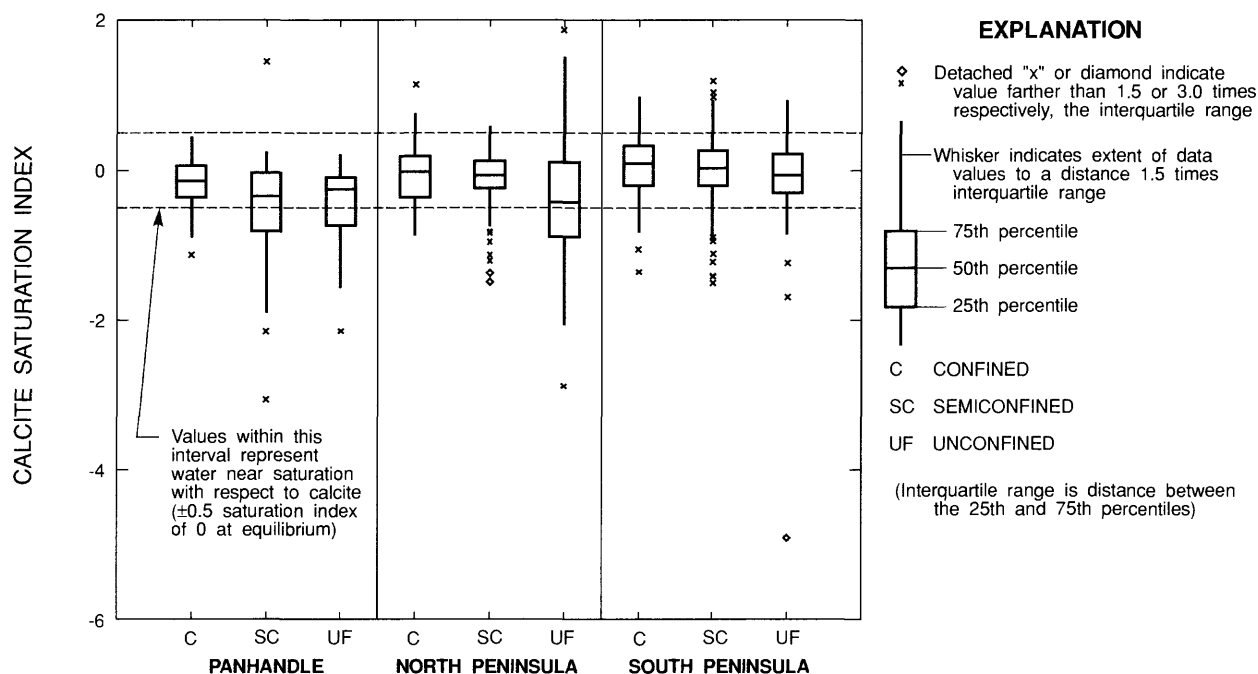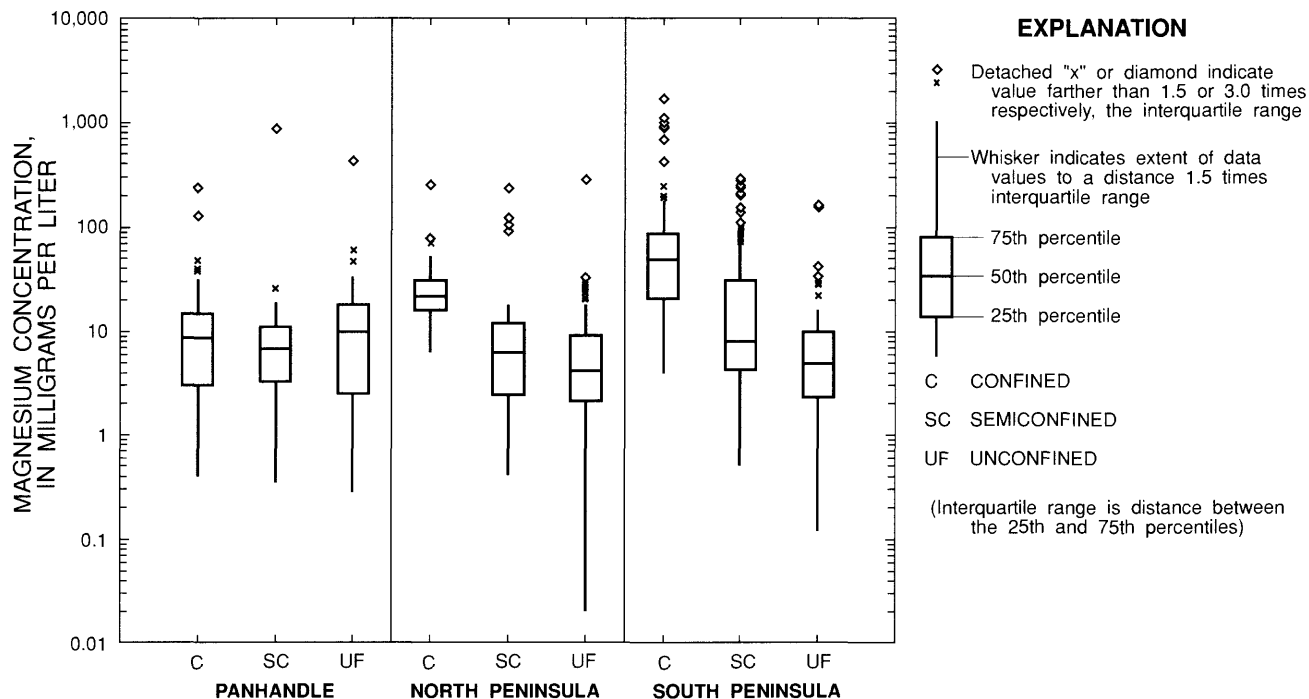
Figure 13. Graphical summary of the concentration of magnesium in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

zones in the aquifer in the open interval of the well, dissolution of nonstoichiometric dolomite that is more soluble, and kinetic effects that prevent the precipitation of dolomite from solution. When data are grouped by the degree of confinement and geographical region, it is apparent that in confined areas of the panhandle and the north Florida Peninsula and in all parts of the aquifer in the south Florida Peninsula, the median SI for dolomite is very close to zero. This may indicate that dolomite saturation is controlling the concentrations of Mg^{2+} in some parts of the Upper Floridan aquifer (fig. 15).

To help distinguish between Mg^{2+} from mineral dissolution processes and seawater mixing reactions, measured Mg^{2+} concentrations in ground water are plotted against Mg^{2+} concentrations that would result from the nonreactive mixing of different volumes of seawater with distilled water. A straight line representing theoretical seawater dilution is also plotted. Points to the right of this line indicate sources other than seawater are contributing Mg^{2+} to solution. An example of such a plot using data from ground-water basin VIII is provided in figure 16. To calculate the theoretical Mg^{2+} concentration, first the Mg:Cl ratio in seawater is calculated to be 0.0974 based on the magnesium and chloride concentrations in seawater, 55.1 mmol/L and 566 mmol/L (Nordstrom and others, 1979). To calculate the theoretical Mg^{2+} concentration for a particular sample, it is assumed that the Cl⁻ concentration in the sample results only from seawater mixing. This measured Cl⁻ concentration is then multiplied by the Mg:Cl ratio in seawater to obtain the maximum expected (calculated) concentration of Mg^{2+} in the ground water at that site, assuming all Mg^{2+} came

from seawater. Water from wells in ground-water basins I through IV are enriched in Mg^{2+} relative to the seawater dilution line shown in figure 16. In basin I, however, any Mg^{2+} contributed from ion-exchange reactions would plot above the seawater dilution line and is not distinguishable from Mg^{2+} from mineral dissolution reactions. Water from wells in basin V are predominantly enriched in Mg^{2+}; however, some sites do plot near the seawater dilution line. Approximately one-fourth of the water from wells in basins VI and VII plot on or near the mixing line. Approximately three-fourths of the water from wells in basin VIII plot on the seawater mixing line, which corroborates the fact that seawater is the source for the high salinity in the aquifer in southern Florida.

Sodium and Potassium

The concentrations of sodium (Na⁺) and potassium (K ⁺) in water from the Upper Floridan aquifer vary greatly with location and depth in the aquifer. The lowest concentrations of Na⁺ (0.20 mg/L) and K⁺ (0.06 mg/L) are found in ground-water basin IV, an area where significant recharge from rainfall occurs. Basin IV also contains the shallowest wells (pl. 1) of any basin and most of the aquifer is unconfined in this area. The low concentrations of Na⁺ and K⁺ in ground water are very similar to concentrations of these ions in rainfall, which are typically about 1 mg/L and 0.2 mg/L, respectively (Sprinkle, 1989, table 1). In areas where remnant seawater is present in the Upper Floridan aquifer (ground-water basin VIII and St. Johns River Valley) and in coastal mixing zones, the concentrations of Na⁺ and K⁺ approximate their concentrations in seawater, 11,000 and 400 mg/L, respectively.

Over most of the State, Na$^+$ concentrations are less than 23 mg/L (1.0 mmol/L) (pl. 4) and K$^+$ concentrations are less than 5 mg/L (0.1 mmol/L) (pl. 5). These low concentrations in ground water result from the low concentrations of these ions in rainfall and to the trace amounts of Na$^+$ and K$^+$ in principal minerals in the aquifer (Sprinkle, 1989). In fact, with the addition of many shallow wells from the FGWQMN there is a much larger area of the State with these low concentrations of Na $^+$ and K$^+$ in water from the aquifer than in the maps prepared by Sprinkle (1989). The main difference between the maps prepared in this study (pls. 4 and 5) and the ones prepared

by Sprinkle is most evident along the Gulf Coast of Florida where isolated well sites are shown producing water with elevated Na $^+$ and K$^+$ concentrations (pls. 4 and 5) as opposed to the broad bands of elevated concentrations of these ions shown on Sprinkle's maps.

In the panhandle region of Florida (ground-water basins I, II, and III), Na$^+$ and K$^+$ concentrations increase significantly with depth in the aquifer, indicating a chemical stratification with depth (table 2). This increase with depth is also apparent from a comparison of the median concentrations of Na$^+$ (fig. 17) and K$^+$ (fig. 18) with the degree of confinement. The median concentrations of
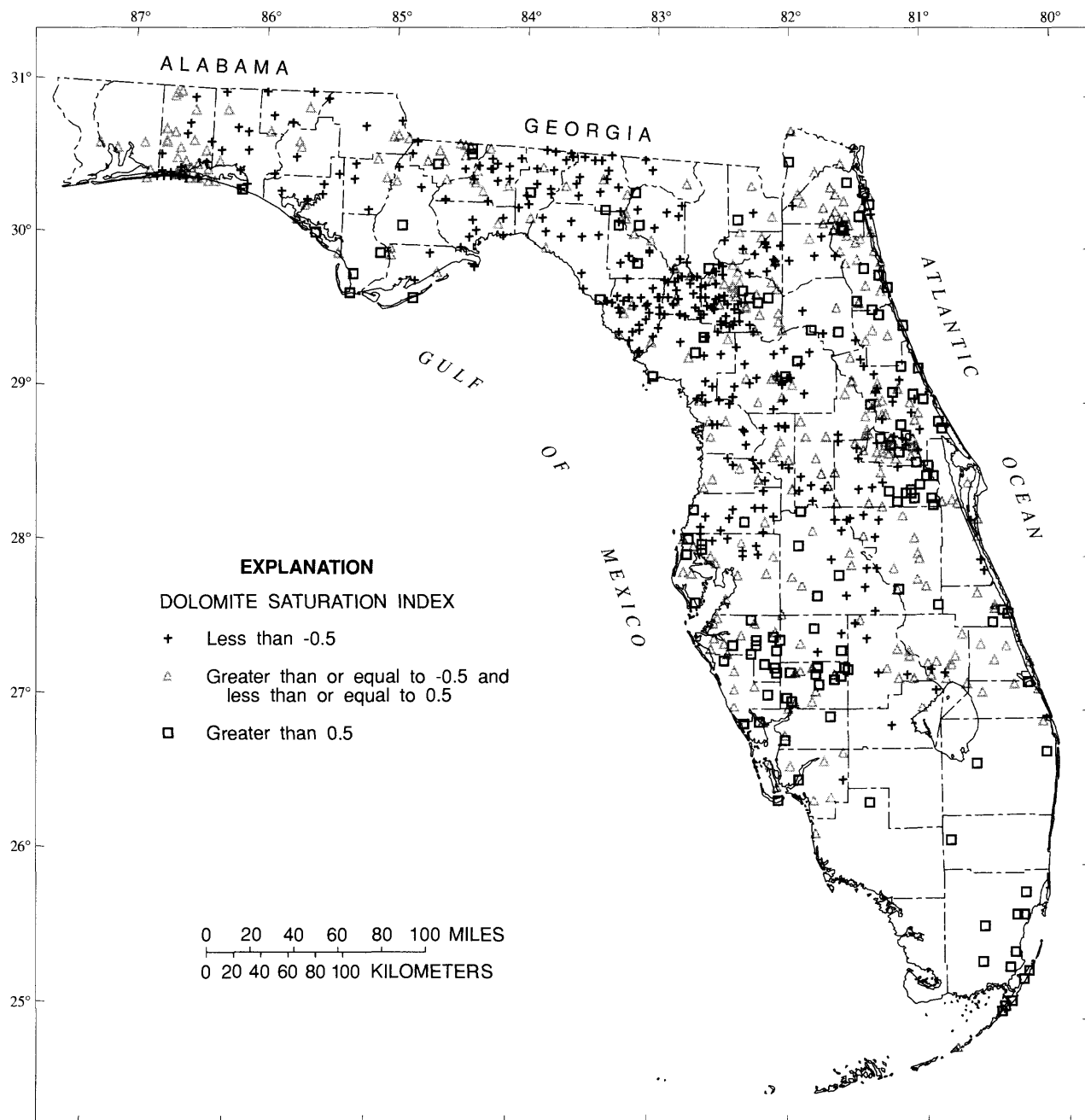

Figure 14. Dolomite saturation index for water from the Upper Floridan aquifer.

EXPLANATION

◇ Detached "x" or diamond indicate
x   value farther than 1.5 or 3.0 times
     respectively, the interquartile range

— Whisker indicates extent of data
     values to a distance 1.5 times
     interquartile range

75th percentile
50th percentile
25th percentile

C   CONFINED
SC SEMICONFINED
UF UNCONFINED

(Interquartile range is distance between
the 25th and 75th percentiles)

Values within this
interval represent
water near saturation
with respect to dolomite
(±0.5 saturation index
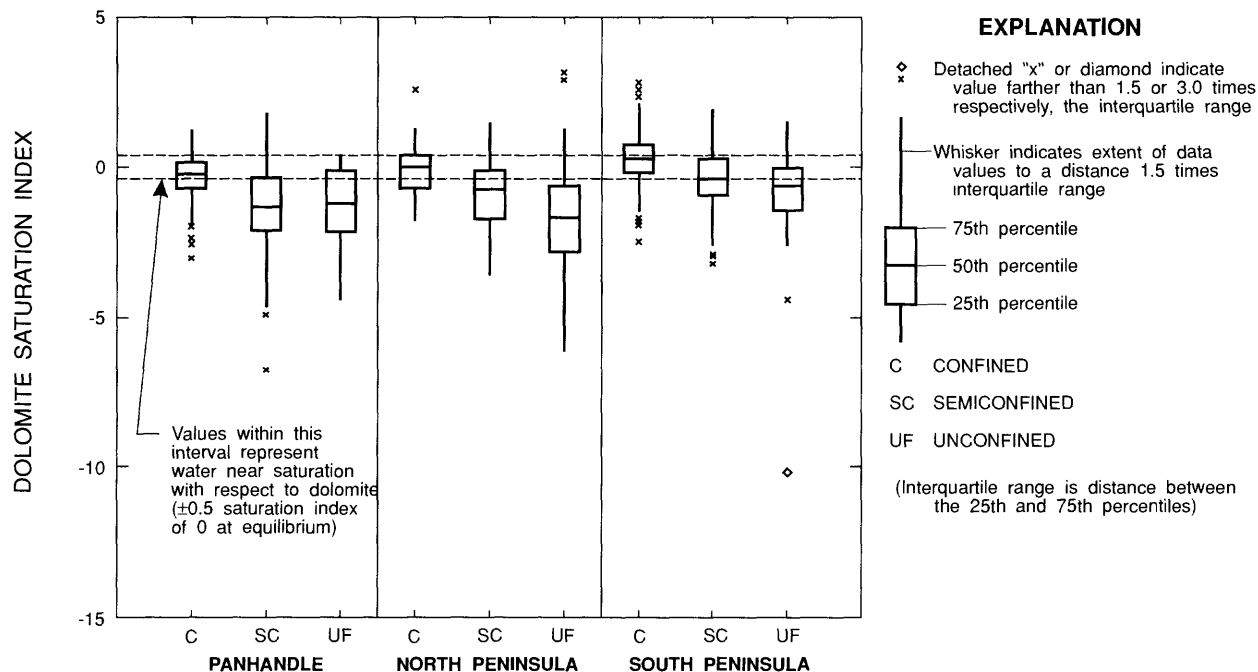of 0 at equilibrium)

Figure 15. Graphical summary of the dolomite saturation index for water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

these ions in water from the shallower wells in unconfined areas of this region are significantly lower than the concentrations of these ions in water from deeper wells located in confined parts of the aquifer (figs. 16 and 17). The increase in Na^+ and K^+ concentrations with a corresponding decrease in Ca^{2+} concentrations in downgradient locations in the aquifer indicates that ion-exchange reactions are controlling the observed concentrations of these ions.

The relation between Na^+ and K^+ with depth for peninsular Florida is not as consistent as in the panhandle. In ground-water basins IV, VI, and VIII, Na^+ is positively correlated with depth, whereas in ground-water basins V and VII, it is inversely correlated with depth (table 2). Potassium also is positively correlated with depth in ground-water basins IV and VI, but there is no significant correlation between K^+ and depth in ground-water basins VII and VIII.

The highest concentrations of Na^+ and K^+ in ground water appear to be related to remnant seawater in the aquifer. This is further supported by the high Cl^- concentrations in areas such as the St. Johns River Valley and in Gadsden County (Pascale and Wagner, 1981). These areas are discussed in more detail in the following section.

Chloride

The principal source of chloride (Cl^-) in water from the Upper Floridan aquifer is seawater, especially in areas of high Cl^- concentration. Natural salts of Cl^- (evaporite minerals) are not present in the aquifer material (Sprinkle,

1989). The upper limit of Cl^- concentration recommended as a secondary drinking water standard for public water supplies in Florida is 250 mg/L (Florida Department of Environmental Regulation, 1985). Over most of the State, the Cl^- concentration in the Upper Floridan is less than 250 mg/L (pl. 6). Cl^- concentrations in the Upper Floridan aquifer are generally less than 50 mg/L in recharge areas of the State, because recharge water (rainfall) is generally low in Cl^- concentrations (Hendry and Brezonik, 1980;
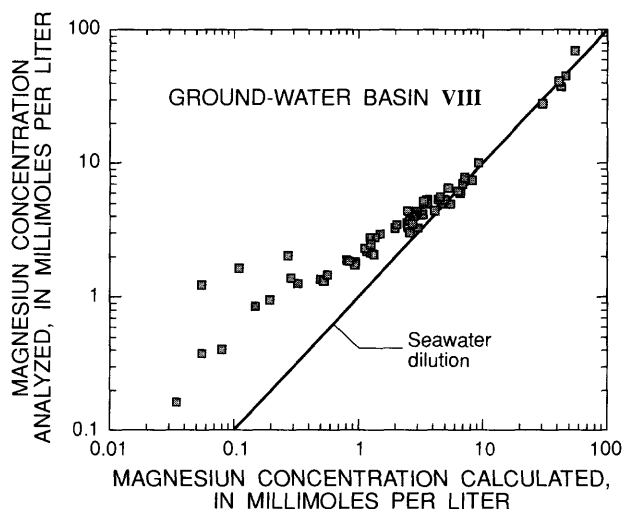

Figure 16. Relation between analyzed and calculated magnesium concentration in water from the Upper Floridan aquifer for ground-water basin VIII.

Irwin and Kirkland, 1980). In coastal areas, especially in southwest and southeast Florida, water from the aquifer contains Cl⁻ concentrations as high as 19,500 mg/L, which is the concentration in seawater.

Cl⁻ concentration in water increases significantly with total well depth in ground-water basins I, II, VI, and VIII, but decreases significantly with depth in the aquifer in ground-water basins V and VI (table 2). In basins III and IV, no significant relation between the concentration of Cl⁻ in

ground water and depth in the aquifer is observed. When ground-water basins are grouped by geographical region, a pattern of chemical stratification in the aquifer is more apparent, especially in the south peninsula. In all three regions, median Cl⁻ concentrations in water in unconfined and semiconfined parts of the aquifer, which generally comes from shallow wells, are substantially lower than median concentrations in confined parts of the aquifer (fig. 19).

Figure 17. Graphical summary of the concentration of sodium in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

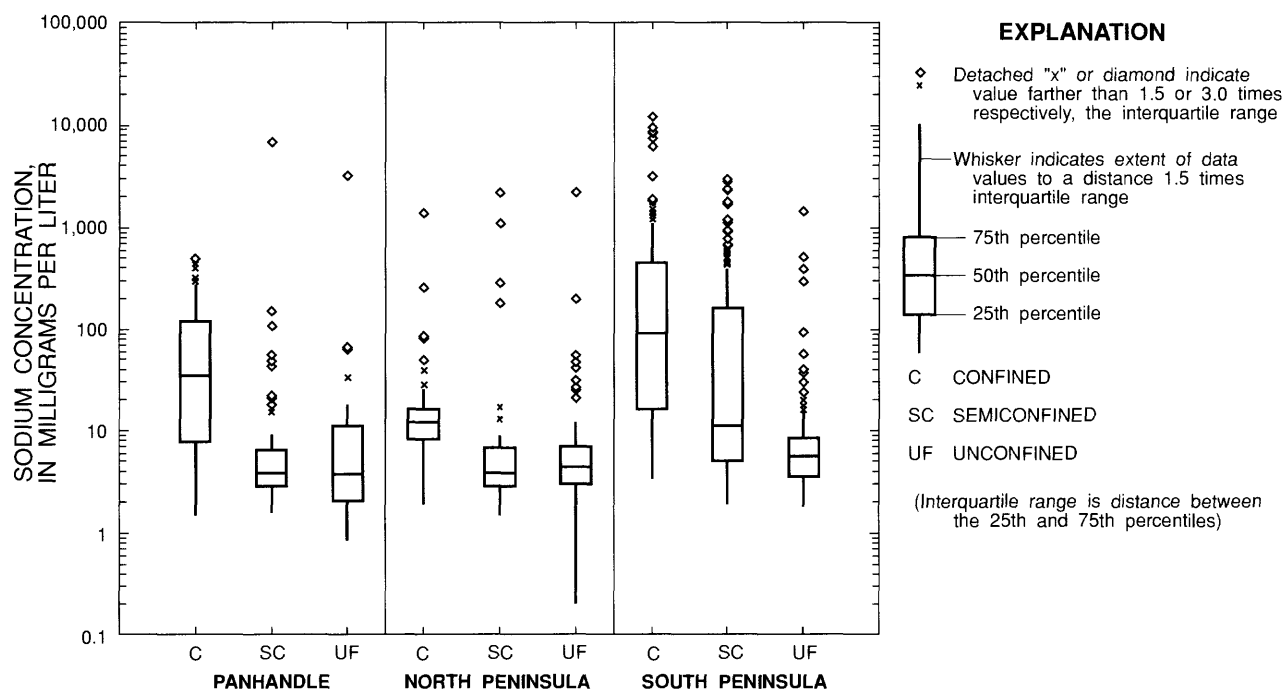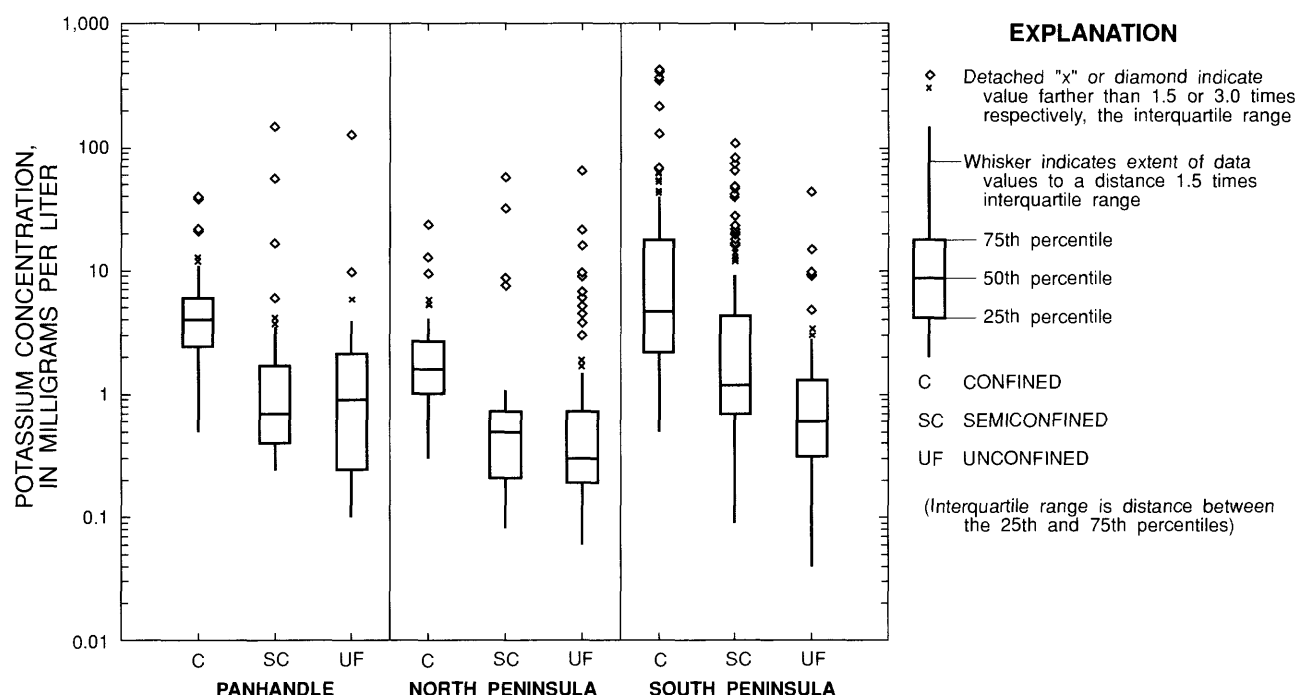

Figure 18. Graphical summary of the concentration of potassium in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.
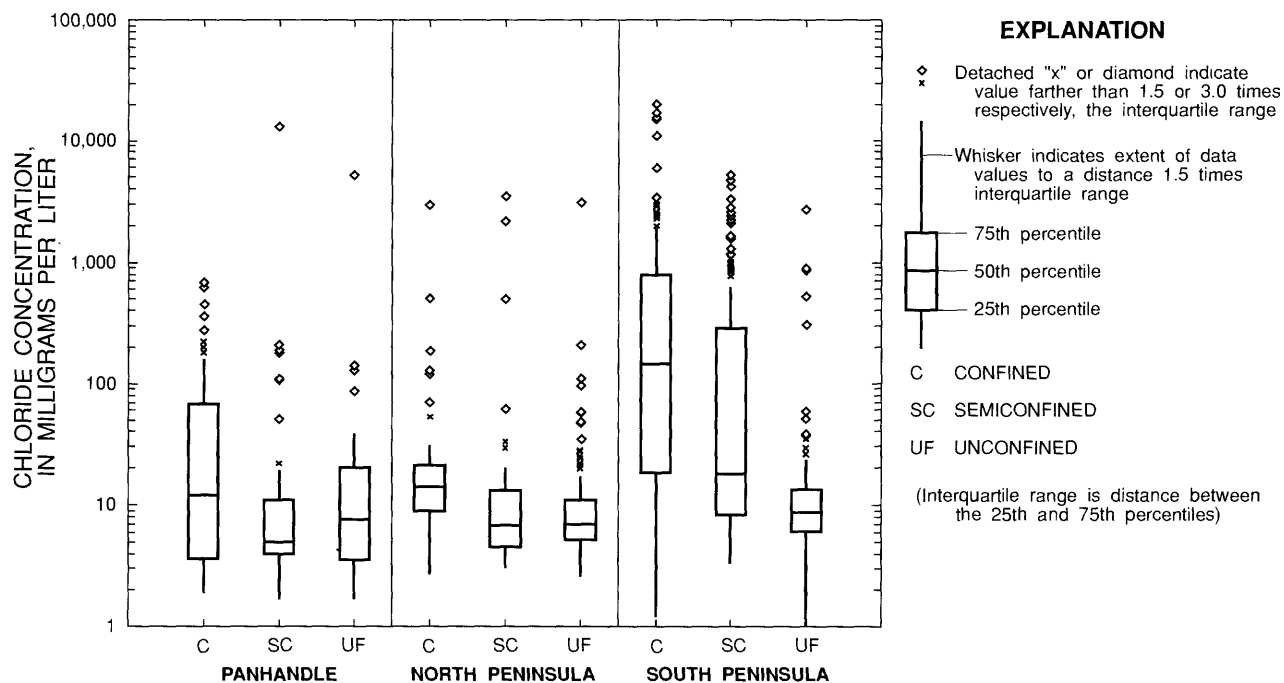
Figure 19. Graphical summary of the concentration of chloride in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

As observed with the concentrations of Na^+ and K^+ in ground water, the addition of the many shallow wells from the FGWQMN results in low concentrations of Cl^- in water from the aquifer in a much larger area of the State than those shown in the maps prepared by Sprinkle (1989). The main difference between the Cl^- map prepared in this study (pl. 6) and the one prepared by Sprinkle is most evident along the Gulf Coast of Florida where only isolated wells are shown producing water with elevated Cl^- concentrations (pl. 6) as opposed to the broad bands of elevated concentrations of Cl^- shown on Sprinkle's map. There is, however, a close similarity between the areal distribution of Cl^- shown on plate 6 with Sprinkle's (1989, fig. 22) map of Cl^- concentrations in water from the upper 200 ft of the aquifer system. This similarity results from addition of wells from the FGWQMN that produce water from shallower zones than most of the wells included in the map prepared by Sprinkle (1989). The upper 200 ft of the aquifer generally consist of Ocala Limestone or Suwannee Limestone. These formations are highly permeable and generally contain water with Cl^- concentrations less than 250 mg/L. Sprinkle (1989) concluded that wells along the Gulf Coast and in southern Florida that penetrate more than 100 ft will yield water with Cl^- concentrations greater than 250 mg/L.

In addition to coastal areas, high Cl^- concentrations (greater than 250 mg/L) are evident in two other areas of the State: along the St. Johns River Valley, and in southern Florida (pl. 6). The high chloride concentrations along the St. Johns River may be the result of the inability of the present fresh-water flow system to flush out the remnant seawater that entered the aquifer system during high stands of the sea in past

geologic time (Tibbals, 1990). Leve (1983) attributed the high Cl^- concentrations in the St. Johns River Valley to fault zones in northeastern Florida where deeper brackish water rises because of higher heads in the Lower Floridan aquifer. However, Miller (1986) found that the faults mapped in the St. Johns River Valley influence only the Upper Floridan aquifer and do not extend into the deeper aquifer system. Toth and others (1989) also suggest that connate seawater is responsible for the high Cl^- concentrations in the Upper Floridan aquifer in the Wekiva River basin (Orange, Lake, and Seminole Counties).

Apparently, the time of year that a well is sampled has an effect on the concentration of Cl^- in water from the aquifer in the St. Johns River Valley. Rutledge (1985) found that seasonal fluctuations in Cl^- concentrations were large; the maximum Cl^- concentration was more than twice the minimum over the period of record. Increases in chloride concentrations in water from public-supply wells occurred predominantly during dry seasons (December to March) when water withdrawals are high and water levels are low.

The elevated concentrations of Cl^- in water from the aquifer in southern Florida have been described in detail in many previous studies that are summarized in Sprinkle (1989). In that part of the State, simulations of the steady-state aquifer system have shown that ground-water circulation is very slow. As a result, the flushing of remnant seawater has not occurred. Meyer (1989) reports that freshwater and saline water zones are intermingled depending upon the permeability of these zones. Cl^- concentrations are higher in the low permeability zones than in the high permeability zones. As a result, the residual saline water is removed from the most permeable zones, and not necessarily the most shallow zones of the aquifer.
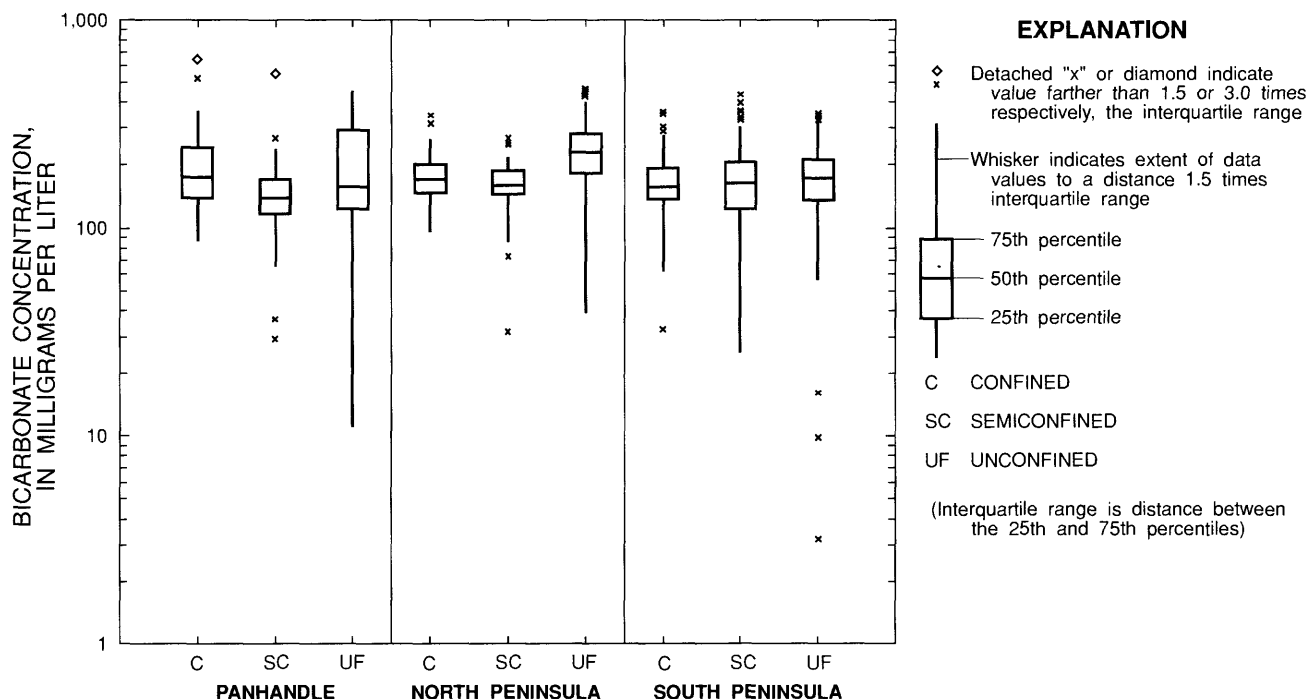
Figure 20. Graphical summary of the concentration of bicarbonate in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

Bicarbonate

Sources of bicarbonate (HCO_3^-) in water from the Upper Floridan aquifer include (1) the equilibration of CO_2 in recharge water that passes through the unsaturated zone and the soil zone, (2) dissolution of calcite and dolomite, and (3) oxidation of organic material by microorganisms, particularly organisms involved in sulfate reduction reactions. The concentration of HCO_3^- in water from the Upper Floridan aquifer ranges from 3.2 mg/L in recharge areas in the northwest part of the Florida Peninsula (ground-water basin VI) to more than 650 mg/L in the western panhandle of Florida (ground-water basin I) (pl. 7). Areas of low HCO_3^- concentrations (61-121 mg/L) are more prevalent on plate 7 than in the map of HCO_3^- concentrations delineated by Sprinkle (1989). This difference may result from the wells in the RASA study being significantly deeper over most of the State than wells from the FGWQMN.

Throughout most of the State, HCO_3^- concentrations have a fairly narrow range, generally from 122 to 224 mg/L (2.0-4.0 mmol/L). HCO_3^- concentrations in water show a significant increase with total depth in ground-water basins I and II, a significant decrease with total depth in basins III and IV, and no significant relation with total depth in basins V, VI, VII, and VIII (table 2). The similarity in HCO_3^- distribution is also evident when the ground-water basins are grouped into the three geographical regions of the State (fig. 20). No significant differences in the concentration of HCO_3^- are observed among the unconfined, semiconfined, and confined parts of the aquifer in the south Florida Peninsula (table 3).

It is evident that the calculated partial pressure of CO_2

is substantially higher in unconfined areas in all three geographical regions (fig. 11). One might expect that because CO_2 partial pressure is higher in unconfined areas, the HCO_3^- concentration should also be correspondingly higher in these areas. However, several other processes that will be discussed can contribute or remove HCO_3^- from water in these areas.

The highest concentrations of HCO_3^- are observed in the Upper Floridan aquifer in the western Florida Panhandle (pl. 7). Two explanations have been offered for these elevated HCO_3^- concentrations. The HCO_3^- concentrations may have been increased by microbial oxidation of organic matter and sulfate reduction (Sprinkle, 1989), as is indicated by the reaction: $SO_4^{2-} + 2CH_2 O = H_2 S + 2HCO_3$. Measurable amounts of hydrogen sulfide (HS^-) have been observed; however, the upgradient concentrations of sulfate are less than 20 mg/L, which indicates that sulfate reduction may not be a major source of CO_2 to ground water in this area. It is possible that substantial sulfate reduction may have occurred in the past because sulfate-rich water is not occurring in present-day flow conditions (Sprinkle, 1989). Another limitation to this process occurring is that little organic matter is present locally in the Upper Floridan aquifer in the western panhandle of Florida.

Another explanation for the generation of elevated HCO_3^- concentrations in water from the aquifer involves ion exchange and calcite dissolution. The water may become locally undersaturated with respect to calcite because cation-exchange reactions are lowering the concentration of Ca^{2+} and calcite may dissolve to reestablish saturation. Calcite is slightly undersaturated in

water from this area (fig. 9). This process appears to be supported by a limited amount of isotopic data for ^{13}C. However, additional measurements of carbon-13 and sulfur-34 isotopic data need to be collected to properly evaluate if dissolution of calcite or sulfate reduction is causing elevated HCO_3^- concentrations in the deeper ground water in this area (Sprinkle, 1989).

Other areas of high HCO_3^- concentrations occur along the Gulf Coast of Florida and in east-central Florida. Where seawater and freshwater mix in the aquifer along the Gulf Coast, some dissolution of limestone occurs with a corresponding increase of HCO_3^- concentrations. Wigley and Plummer (1976) report that there is a tendency for carbonate minerals to be undersaturated when the ionic strength of a solution is changed by mixing freshwater with seawater. However, Sprinkle (1989) found that only about 0.3 mmol (less than 20 mg/L) of HCO_3^- could be added to ground water by dissolution of calcite during mixing before equilibrium is reestablished. This amount is well below that needed to account for the almost 100 mg/L increase in HCO_3^- for coastal wells compared to HCO_3^- concentrations in water samples from wells farther inland.

Another possible explanation for higher HCO_3^- concentrations along the Gulf Coast may be related to the presence of high concentrations of organic carbon in water that recharges the ground water, especially in ground-water basins II, III, and IV. Sprinkle (1989) suggests that organic acids may be generated from the leaching of organic litter accumulated in hardwood and pine forests in these areas. These organic acids could be present in ground water at locally high concentrations and therefore may have been included in the analysis for HCO_3^- (alkalinity titration). Spearman's Rho (correlation coefficient) statistic is used to determine if a relation exists between HCO_3^- concentration and measured total organic carbon (TOC) concentration in ground water in this area. A significant positive relation (0.05 alpha level) is observed for HCO_3^- and TOC in water from wells located in ground-water basins III and IV, indicating that the presence of organic acids may result in a positive error in the HCO_3^- concentration determined in the laboratory. Supporting this explanation is the observation that excess anions, calculated from the charge-balance error (previously mentioned in the methods section) show a significant positive relation with TOC in ground-water basin III. The cation-anion imbalance apparently results from unmeasured cations, possibly ammonium, strontium, and iron. Sprinkle (1989) suggests that significant biochemical activity would have to occur in the aquifer to produce these high concentrations of ammonium and iron. However, the identification and quantification of these biochemical processes cannot be determined at this time. Organic carbon may become oxidized in ground water to form carbon dioxide which could also result in elevated concentrations of HCO_3^-.

The high HCO_3^- concentrations in east-central Florida are most likely related to the local recharge area in western Volusia County (Tibbals, 1990). Sprinkle (1989) reports that in this area the confining unit overlying the Upper Floridan aquifer is thin and composed of calcareous sands. High HCO_3^- concentrations are produced from the dissolution of calcite and dolomite because high amounts of recharge water react with these minerals in a system partly open to carbon dioxide. Mixing reactions with residual seawater may cause a further increase in HCO_3^- concentrations, as reported by Phelps and Rohrer (1987) for a nearby study area in northeast Seminole County. HCO_3^- may also be added to the ground water as the result of sulfate reduction, which has been reported to occur locally (Sprinkle, 1989). Water in some coastal wells is supersaturated with respect to calcite and dolomite, and the local decrease in HCO_3^- concentration may be the result of precipitation of calcite and dolomite (Sprinkle, 1989).

Comparison of maps showing the areal distribution of HCO_3^- and Ca^{2+} concentration (pls. 2 and 7) indicates that the solubility of calcite controls both the concentration of HCO_3^- and Ca^{2+} in freshwater from the aquifer. Dedolomitization reactions mentioned in the section on magnesium also have some effect on the HCO_3^- concentration in ground water. The overall effect of this reaction is a net increase in the concentration of HCO_3^- to solution (Plummer and others, 1983). Sprinkle (1989) suggests, however, that the net increase of HCO_3^- concentration from this reaction is small because gypsum is generally not present in substantial amounts throughout the aquifer. In some parts of the State, such as in northeast and west-central Florida, the dedolomitization reaction may be important in increasing the HCO_3^- concentration because sulfate concentration is higher than would be expected from seawater dilution and dissolution of gypsum may be locally important (Sprinkle, 1989).

Sulfate

The principal sources of sulfate (SO_4^{2-}) in water from the Upper Floridan aquifer are the dissolution of the mineral gypsum and mixing of seawater with freshwater. Two other sources of SO_4^{2-}, identified in recharge areas of the Upper Floridan aquifer, are oceanic aerosols and the atmospheric oxidation of sulfides (Rye and others, 1981). Pyrite oxidation in the overlying Hawthorn Formation may also contribute SO_4^{2-} to the aquifer in some areas where vertical movement of water occurs from the confining unit to the Upper Floridan aquifer (S.B. Upchurch, University of South Florida, written commun., 1991). The upper limit of SO_4^{2-} concentration recommended as a secondary drinking water standard for public water supplies in Florida is 250 mg/L (Florida Department of Environmental Regulation, 1985). The SO_4^{2-} concentration in the aquifer is less than 250 mg/L over most of the State, (pl. 8). SO_4^{2-} concentrations in the aquifer range

from less than 1.0 mg/L to the seawater concentration of 2,750 mg/L. High concentrations of SO_4^{2-} occur in freshwater that is in contact with gypsum, even though the aquifer material contains only a few percent of the mineral (Sprinkle, 1989). Areas of low SO_4^{2-} concentrations (less than 50 mg/L) are more prevalent on plate 8 than on the map of SO_4^{2-} concentrations delineated by Sprinkle (1989). This difference is most likely related to the wells in the RASA study being significantly deeper over most of the State than wells from the FGWQMN. Water from deeper wells tends to contain higher SO_4^{2-} concentration than water from shallow wells. The main difference between the SO_4^{2-} map prepared in this study (pl. 8) and the one prepared by Sprinkle is most evident along the Gulf Coast of Florida where isolated well sites are shown producing water with elevated SO_4^{2-} concentrations (pl. 8) as opposed to the broad bands of elevated concentrations of SO_4^{2-} shown on Sprinkle's map.

SO_4^{2-} concentrations in ground water increase significantly with depth in ground-water basins I, II, III, VI, and VIII and decrease significantly with depth in basin V (table 2). The increase in concentration with depth is most likely related to deeper wells producing increased salinity water that is relatively high in SO_4^{2-} concentration. As mentioned in previous sections, the decrease in SO_4^{2-} concentration with depth in northeast Florida (basin V) is most likely related to the geographic location of shallow and deep wells (pl. 1). In these basins, shallower wells are generally near the coast where SO_4^{2-} concentrations are high because of mixing of freshwater

and seawater in the aquifer. The deeper wells tend to be in areas not affected by mixing of seawater. Thus, based on the location of shallow and deep wells, an apparent decrease in SO_4^{2-} concentrations in water from these wells is observed with increasing depth in the aquifer. The presence of SO_4^{2-} as the major ion in water from some of the shallow coastal wells may also be related to dissolution of gypsum (Frazee and McClaugherty, 1979). Reduction of SO_4^{2-} by microorganisms may also be important locally, as Tibbals (1990) reports the presence of hydrogen sulfide in water from some wells in this area.

When ground-water basins are grouped by geographical region, chemical stratification of SO_4^{2-} in the aquifer is more apparent. In the north and south regions of the Florida Peninsula, median SO_4^{2-} concentrations in water from typically shallow wells in unconfined and semiconfined parts of the aquifer are substantially lower than median concentrations in confined parts of the aquifer (fig. 21). In the panhandle, there is no significant difference in SO_4^{2-} concentrations among the different confinement conditions. In this area, as mentioned previously in the section on HCO_3^-, SO_4^{2-} reduction may be occurring or has occurred that would account for a decrease in SO_4^{2-} concentration and a corresponding increase in HCO_3^- concentration in the confined part of the aquifer (Sprinkle, 1989). Reduced sulfur species (hydrogen sulfide) have been detected in the water from this part of the aquifer (Sprinkle, 1989).

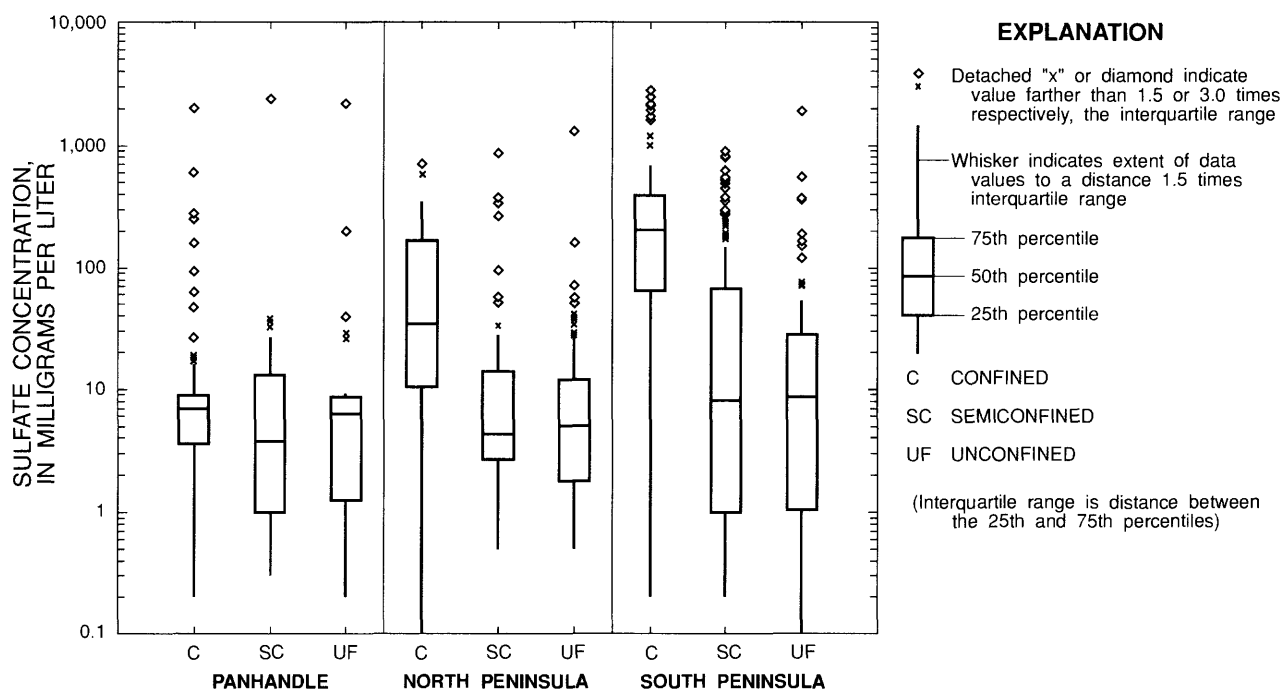To better understand the relative importance of the contribution of SO_4^{2-} from the two major sources,

Figure 21. Graphical summary of the concentration of sulfate in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

dissolution of gypsum and mixing of freshwater with seawater, the SO_4^{2-}:Cl^- concentration ratio (in equivalents) is plotted against the SO_4^{2-} concentration (in millimoles per liter) for each ground-water basin (fig. 22) (Rightmire and others, 1974).

The reference lines in figure 22 are the concentration relations between SO_4^{2-} and Cl^- that represent:

(1) the dissolution of gypsum in a dilute water from the Upper Floridan aquifer with the following concentrations of SO_4^{2-} (0.01 mmol/L; 1.0 mg/L) and Cl^- (0.065 mmol/L; 2.3 mg/L) and no subsequent SO_4^{2-} precipitation. This line is labeled "gypsum solution" and is obtained by hypothetically adding increments of SO_4^{2-} to the dilute ground water and plotting the resulting SO_4^{2-} and Cl^- concentrations (fig. 22), and

(2) the mixing of seawater with dilute ground water, also with no SO_4^{2-} lost from solution. This line is labeled "mixing" and is determined by calculating the total dissolved SO_4^{2-} and Cl^- concentrations obtained by mixing the dilute ground water with seawater, using volume increments of seawater from 1 to 100 percent (fig. 22). Even though the mixing is linear, the mixing line is curved because of the logarithmic scale.

The intersection of the two lines would be displaced to the left if the composition of rainfall is used as the freshwater end member and to the right if water containing higher concentrations of SO_4^{2-} and Cl^- is used as the freshwater end member. The slope of the gypsum dissolution line would remain the same; however, the line would be shifted to the right or left depending upon the composition of the freshwater end member. The seawater mixing line (curve) would show increasing curvature with increasing SO_4^{2-} concentrations of the freshwater end member. An example of a mixing line with a high degree of curvature is presented by Steinkampf (1982) for a study area in southwest Florida.

Ground water from all eight basins (fig. 22) shows evidence of both gypsum solution and mixing of seawater with dilute ground water. In ground-water basins V and VI, SO_4^{2-}:Cl^- ratios increase almost uniformly from that of fresh, dilute ground water, although the starting composition should be shifted toward the right (higher initial SO_4^{2-} concentrations). These data suggest that SO_4^{2-} in water from the Upper Floridan aquifer in these basins may originate predominantly from gypsum dissolution. Water from wells in basins V and VI contains high SO_4^{2-} concentrations relative to Cl^- and HCO_3^- and dissolution of gypsum in these areas has been previously reported as an important source of SO_4^{2-} in ground water (Frazee and McClaugherty, 1979; Sprinkle, 1989). SO_4^{2-} in water from the aquifer in ground-water basins I, II, III, IV, VII, and VIII originates from a combination of the two sources, and it is difficult to distinguish the relative importance of either source.

It is significant to note that the importance of two additional reactions involving the transformation and production of SO_4^{2-} cannot be discerned from these diagrams (fig. 22). First, reduction of SO_4^{2-} to HS^- may account for values below the seawater mixing line (fig. 22). Second, the oxidation of pyrite in the overlying Hawthorn Formation may contribute SO_4^{2-} to water in the Upper Floridan aquifer that would plot in between the lines on figure 22 representing gypsum solution and mixing with seawater.

Dissolved Solids

The two predominant sources for dissolved solids (DS) in water from the Upper Floridan aquifer are mineral dissolution reactions and mixing of freshwater with seawater. DS concentrations range from less than 10 mg/L in some unconfined (recharge) areas to more than 30,000 mg/L along the coasts (pl. 9). The concentration of DS increases significantly with depth in the aquifer in ground-water basins I, II, VI, and VIII; decreases significantly with depth in basin IV, and shows no relation with depth in basins III and VII (table 2). In basin IV, shallow wells (pl. 1) tend to be located near the Gulf Coast where higher concentrations of DS are found in ground water as a result of freshwater mixing with seawater; whereas deeper wells farther inland are located in recharge areas of the aquifer and mineral dissolution reactions maintain low concentrations of DS in the ground water. In basins V and VII, the typical location of shallow wells near the coast and deeper wells inland may result in a situation where DS shows no relation with total depth in the aquifer.

It is evident that the areal distribution of DS (pl. 9) closely matches the areal distribution of Cl^- concentrations (pl. 6) in water from the aquifer. In areas where mixing with seawater has occurred, Cl^- concentration is the major component of DS. The DS concentration is less than 250 mg/L for most of the State. In coastal areas and in areas where remnant seawater is present, the Upper Floridan aquifer contains wells with DS concentrations greater than 1,000 mg/L. As observed with the concentrations of Cl^- in ground water, the addition of the many shallow wells from the FGWQMN results in low concentrations of DS in water from the aquifer in a much larger area of the State than those shown in the map prepared by Sprinkle (1989). The main difference between the DS map prepared in this study (pl. 9) and the one prepared by Sprinkle (1989) is most evident along the Gulf Coast of Florida where isolated well sites are shown producing water with elevated DS concentrations (pl. 9) as opposed to the broad bands of elevated concentrations of DS shown on Sprinkle's map. In some coastal wells, the DS concentrations approach that of seawater, approximately 36,000 mg/L. Sprinkle (1989) found that shallow wells in coastal areas and in south-central Florida may yield water with concentrations of DS less than 500 mg/L. However, wells completed in zones greater than 100 feet deep will most likely produce more mineralized water.
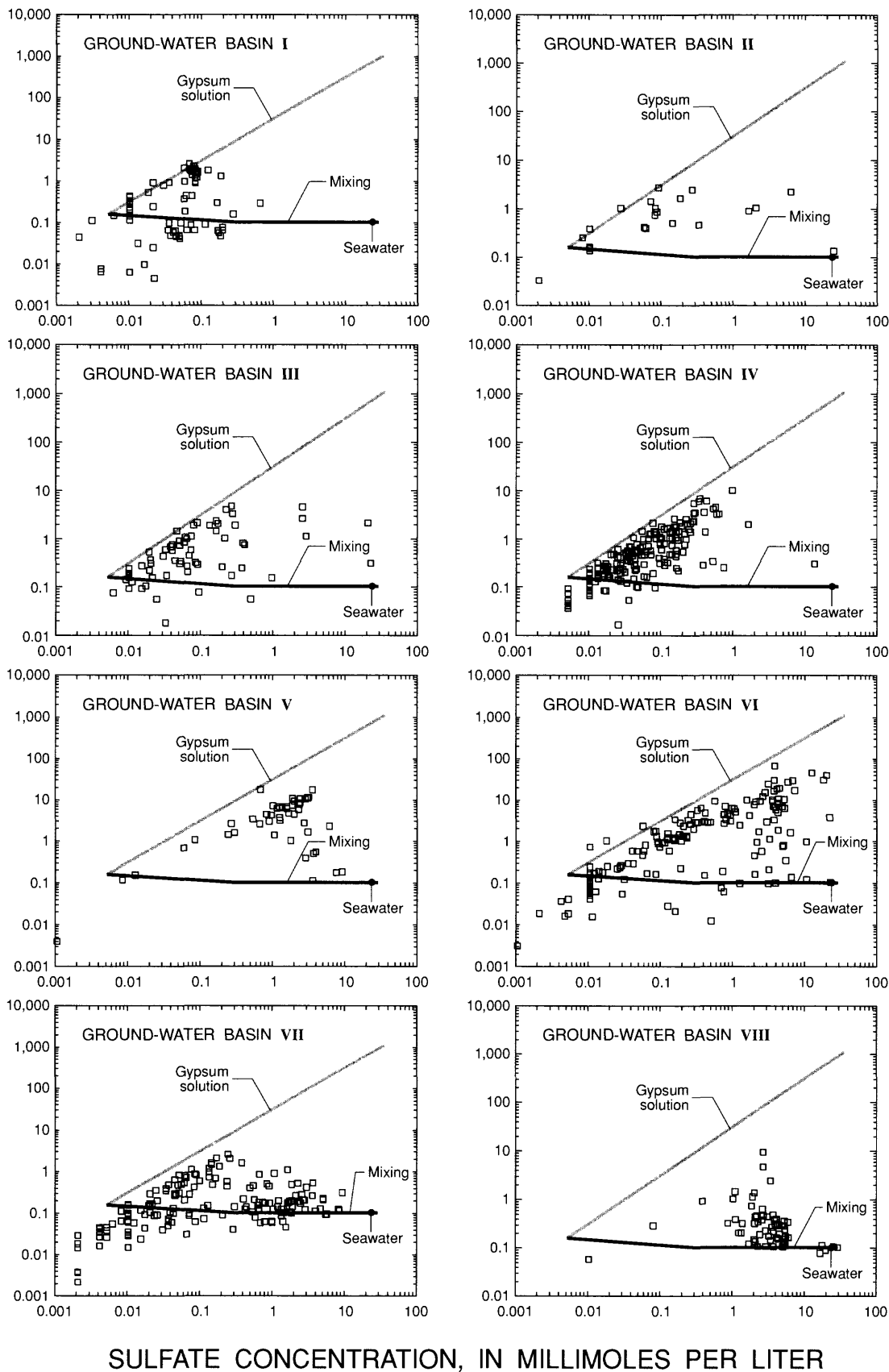
Figure 22. Relation of sulfate-to-chloride ratios (SO_4:Cl) to sulfate concentrations in water from the Upper Floridan aquifer for the major ground-wataer basins. (Modified from Rightmire and others, 1974.)
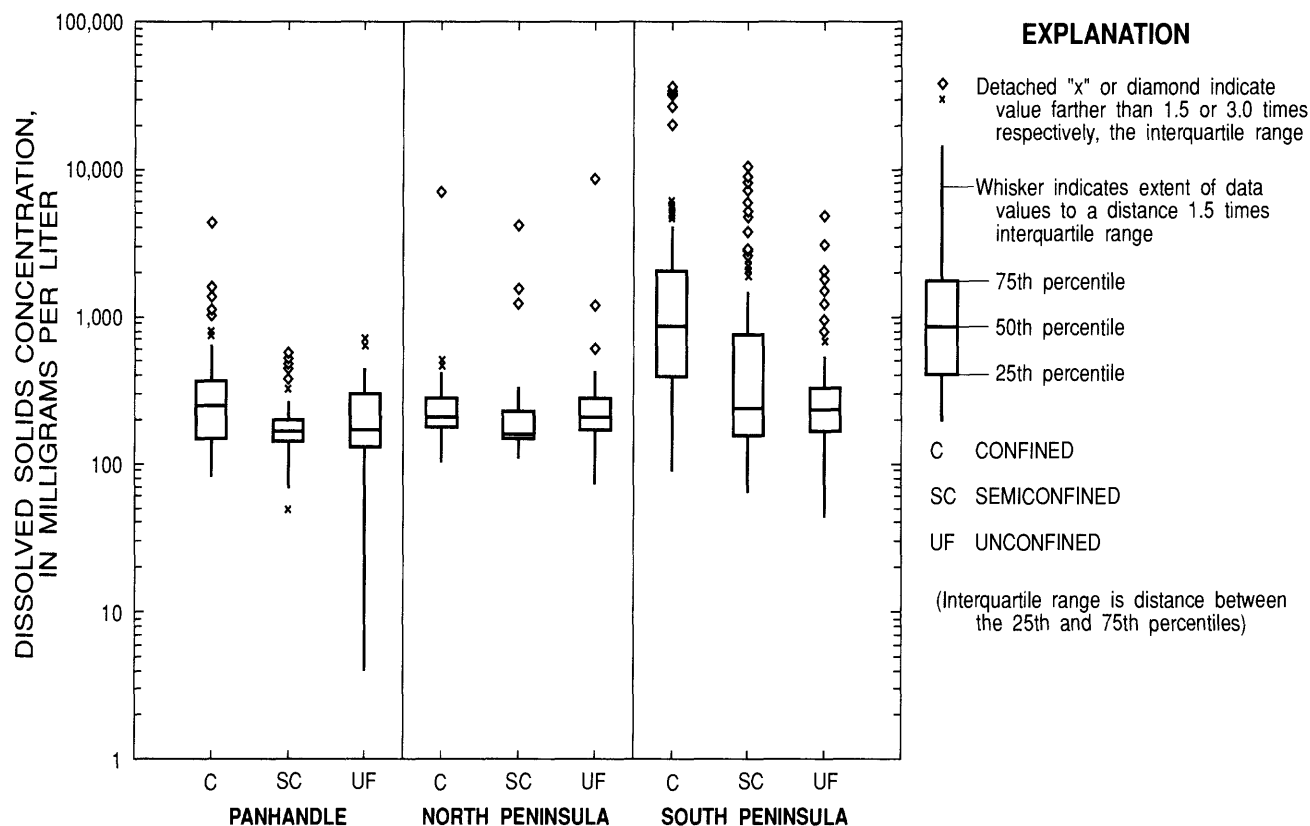
Figure 23. Graphical summary of the concentration of dissolved solids in water from the Upper Floridan aquifer in unconfined, semiconfined, and confined areas for three regions in Florida.

When ground-water basins are grouped by geographical region and the data are separated by degree of confinement (fig. 23), chemical stratification of DS is readily apparent in the southern peninsula and the panhandle region of the State. In the north Florida Peninsula region the median concentrations of DS are almost identical in water from the aquifer under unconfined, semiconfined, and confined conditions. This finding is probably related to the relatively low median Cl⁻ concentrations in water from the aquifer under the various confinement conditions (fig. 18).

The concentration of dissolved solids in ground water is controlled by two major processes. Throughout most of the State (except in coastal areas), the DS concentration in ground water generally is below 500 mg/L due to the effects of equilibrium with respect to calcite and dolomite. The generally low quantities of gypsum (a highly soluble mineral) present in the aquifer also restrict the DS concentration from exceeding 500 mg/L in most areas. Seawater mixing with freshwater most likely elevates the concentration of DS above 500 mg/L.

One anomalous area worth noting is where the DS concentration is high but Cl⁻ concentration is less than 250 mg/L. This area, in northeast Florida has undergone major development, and as a result large head declines in ground water from predevelopment levels have been noted (Bush and Johnston, 1988). A number of recent

studies (Leve, 1983; Brown, 1984) indicate that highly mineralized water from the Lower Floridan aquifer accounts for the increase in DS concentration in the Upper Floridan aquifer in this area.

Hydrochemical Facies and Geochemical Processes

The hydrochemical facies showing the dominant cation(s) and anion(s) in water from the Upper Floridan aquifer are delineated on plate 10. Water from 58 percent of the wells in the aquifer is either the Ca-HCO₃ (46 percent) or the Ca-Mg-HCO₃ (12 percent) hydrochemical facies. Calcite dissolution reactions in the aquifer over most of the State account for the Ca-HCO₃ hydrochemical facies and evidence for this controlling process is the low DS (less than 500 mg/L). A Ca-Mg-HCO₃ hydrochemical facies is produced where dissolution of dolomite (or dedolomitization) adds relatively large amounts of Mg²⁺ to the water. Where substantial gypsum dissolution occurs, SO₄²⁻ is added to the ground water and the following hydrochemical facies are produced: Ca-Mg-HCO₃ -SO₄ (4 percent of the wells), Ca-Mg-SO₄ (3 percent), and Ca-SO₄ (1 percent). Areas where these hydrochemical facies occur include northeast Florida, southwest Florida, and several locations in

west-central Florida (pl. 10). In northeast Florida, Sprinkle (1989) reports that upconing of mineralized water along fault zones may account for these observed hydrochemical facies.

In areas of the State where vertical or lateral mixing of seawater with freshwater occurs, three hydrochemical facies are noted: mixed-HCO_3 (5 percent), mixed (14 percent), and Na-Cl (12 percent). In vertical mixing zones, Sprinkle (1989) reports that the water chemistry changes from a Ca-Mg-HCO_3 type with low DS at or near the top of the zone to a Na-Cl hydrochemical facies (high DS) near the bottom of the zone. The hydrochemical facies in these zones depends on the thickness of the zone of transition. Pumping wells near coastal areas may also induce the landward movement of seawater, resulting in mixed- or Na-Cl hydrochemical facies. The amount of seawater mixing is dependent upon the depth of the well, the location of the transition zone, and the rate of pumping. As noted previously, there are a number of shallow wells near coastal areas that yield freshwater with DS of less than 250 mg/L (pl. 9).

Mixing of ground water with seawater (remnant) has occurred in parts of the State that are not near coastal areas. In the St. Johns River Valley and in Gadsden County, mixed-HCO_3 and Na-Cl hydrochemical facies result from mixing. In southern Florida, residual saline water is present in the Upper Floridan aquifer, with DS concentrations greater than 1,000 mg/L. Na-Cl hydrochemical facies are dominant in this area.

The distribution of hydrochemical facies in the Upper Floridan aquifer is closely related to the flow system characteristics. In a generalized manner, the residence time of water in the aquifer and the distance of travel through the aquifer can be approximated by rates of recharge to and discharge from the aquifer (Bush and Johnston, 1988). When the locations of wells in the aquifer are classified according to ranges in rates of annual recharge and discharge (Aucott, 1988), distinct relations are observed between recharge and discharge areas and predominant hydrochemical facies. Water typically has short residence times and correspondingly short ground-water flow paths in the high-rate recharge areas (greater than 10 in/yr) and in the high-rate discharge areas (greater than 5 in/yr). Bush and Johnston (1988) report that the proximity of high-rate recharge to high-rate discharge areas is indicative of a well-developed shallow flow system (highly transmissive) in the unconfined and semiconfined parts of the Upper Floridan aquifer. The water in these parts of the aquifer typically has low DS concentrations and Ca-HCO_3 hydrochemical facies predominate, with 85 and 65 percent of all hydrochemical facies in high-rate recharge and high-rate discharge areas, respectively (fig. 24). The relatively low DS are constrained by the partial pressures of carbon dioxide, which are generally highest in the unconfined and semiconfined areas (fig. 11), and by the solubility of calcite (figs. 9 and 12) and dolomite (figs. 14 and 15).
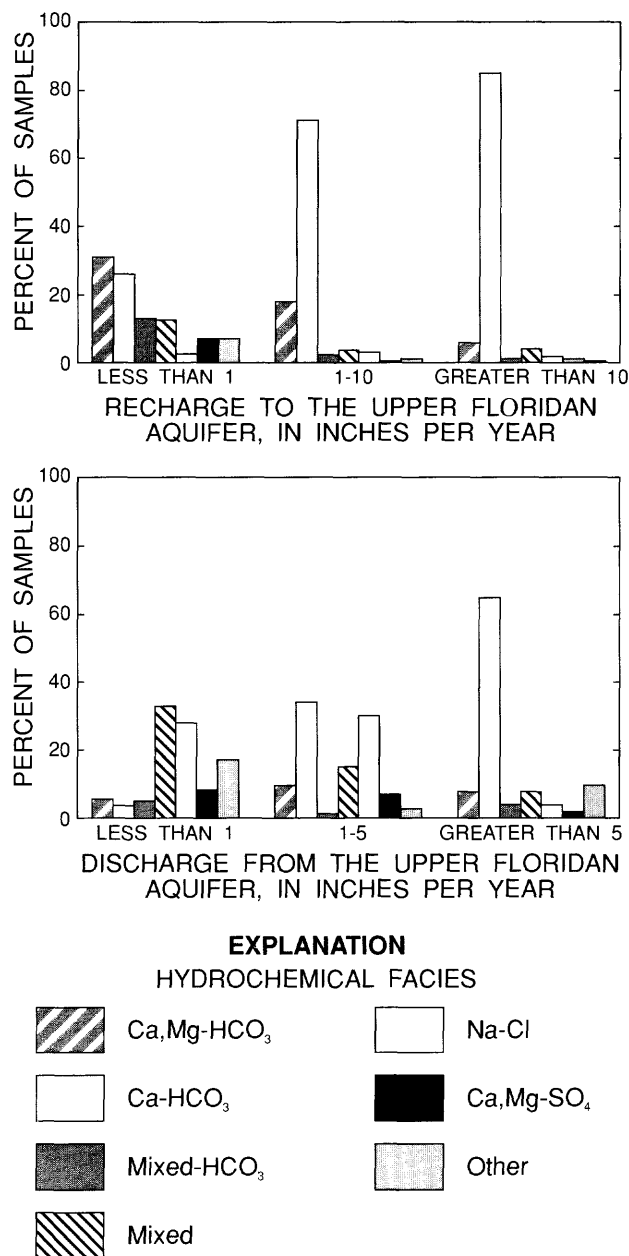
Figure 24. Distribution of hydrochemical facies by rate of recharge to and discharge from the Upper Floridan aquifer in Florida.

It is important to note that the water chemistry can be highly variable in areas where the aquifer is unconfined and has generally low DS, (for example in ground-water basins III, IV, and VI). Different hydrochemical facies can occur as a result of variable residence times for water in different zones of the aquifer and recharge water with variable composition from overlying aquifer systems or direct infiltration of rainfall. Hydrochemical processes in these unconfined areas of the Upper Floridan aquifer are not well understood and their effect on the chemical composition of water in the shallow part of the aquifer need further study.

As the residence time of water increases in the aquifer and presumably the length of the ground-water flow paths also increases, the DS concentrations increase and other hydrochemical facies besides $Ca-HCO_3$ appear in higher percentages (fig. 24) than those found in areas of lower rates of recharge to and discharge from the Upper Floridan aquifer. For example, in areas of moderate recharge to the aquifer (1-10 in/yr), $Ca-HCO_3$ is still dominant at 71 percent of all hydrochemical facies; however, $Ca,Mg-HCO_3$ has increased to 18 percent and Na-Cl has increased to 3 percent of all hydrochemical facies (table 4). In areas of moderate rates of discharge from the aquifer (1-5 in/yr), $Ca-HCO_3$ is now only 34 percent of all hydrochemical facies, whereas Na-Cl and mixed hydrochemical facies are now 30 and 15 percent, respectively (table 4). This high percentage of Na-Cl and mixed hydrochemical facies indicate that mixing of ground water (with calcium and bicarbonate as the predominant ions) with seawater may be occurring and the water chemistry is evolving toward the composition of seawater. These areas, which are characterized by higher DS concentrations than in areas of high-rate recharge and discharge, have flow systems that are less active because of the high degree of confinement of the aquifer (Bush and Johnston, 1988).

Table 4. Percentages of hydrochemical facies and number of wells grouped by rate of recharge to and discharge from the Upper Floridan aquifer

[<, less than; >, more than; --, no data]

	Recharge (inches per year)			Discharge (inches per year)		
	<1	1-10	>10	<1	1-5	>5
Number of wells	112	163	170	217	73	52
Hydrochemical facies:						
$Ca-HCO_3$	26	71	85	3.7	34	65
$Ca,Mg-HCO_3$	31	18	5.9	5.5	9.6	7.7
$Mixed-HCO_3$	13	2.5	1.2	5.1	1.4	3.9
$Ca,Mg-HCO_3,SO_4$	3.6	0.6	--	8.8	--	--
$Ca,Mg-SO_4$	7.2	0.6	1.2	7.6	6.9	1.9
Mixed	13	3.7	4.1	33	15	8
Na-Cl	2.7	3.1	1.8	28	30	3.9
Other	3.5	0.5	0.8	8.3	3.1	9.6

In areas of the State where recharge to and discharge from the Upper Floridan aquifer are very low (less than 1 in/yr), ground-water flow is very sluggish and DS concentrations are extremely high, for example in ground-water basin VIII (table 1). The thick confining unit in these areas limits the diffuse upward leakage and also restricts recharge.

The predominant hydrochemical facies in low-rate recharge areas (fig. 24) is $Ca,Mg-HCO_3$ (31 percent); however, there are several other important hydrochemical facies as indicated by the following percentages: $Ca-HCO_3$ (26), $mixed-HCO_3$ (13), mixed (13), $Ca,Mg-SO_4$ (7), and Na-Cl (3). In low-rate discharge areas (fig. 24), the predominant hydrochemical facies is mixed (33 percent), but other hydrochemical facies are present at increased percentages: Na-Cl (28), other (17), $Ca,Mg-SO_4$ (8), $Ca,Mg-HCO_3$ (6), $Ca-HCO_3$ (4), and $mixed-HCO_3$ (5).

The relation between dominant ions in water from the Upper Floridan aquifer and rates of recharge and discharge is also evident from a trilinear diagram of median concentrations of major ions in ground water from each recharge or discharge subgroup (fig. 25). Calcium and bicarbonate are the dominant ions in all recharge areas and in high rate discharge areas. As the rate of discharge from the aquifer decreases, no dominant chemical species are observed (fig. 25).

The chemical evolution of the composition of ground water from the predominant $Ca-HCO_3$ and $Ca,Mg-HCO_3$ hydrochemical facies in recharge areas to mixed and Na-Cl hydrochemical facies in discharge areas has been observed and reported for many regional ground-water basins throughout the world. Chebotarev (1955) concluded that the chemical composition of ground water tends to evolve toward the composition of seawater, based on more than 10,000 chemical analyses of ground-water samples from Australia. Domenico (1972) relates the chemical evolution of ground water from recharge to discharge areas by depth zones in large sedimentary basins. Traveltime and ground-water flow distance tended to increase from the upper zone of shallow depths to the lower zone of deeper wells.

For a more detailed discussion of the major geochemical processes along specific ground-water flow paths in the entire Floridan aquifer system, the reader is referred to Sprinkle (1989). His report summarizes results from the many previous studies involving mass-transfer simulations to determine geochemical processes controlling the chemical composition of water along ground-water flow paths. Sprinkle (1989) also develops models of plausible reactions along three ground-water flow paths in the Upper Floridan aquifer in Florida using mass-balance and mass-transfer techniques. These models describe and quantify the major geochemical processes occurring in the aquifer: (1) dissolution of calcite, dolomite, and gypsum toward equilibrium; (2) mixing of freshwater in the aquifer with seawater or recharge water; (3) ion-exchange reactions, involving Na^+ exchanging with Ca^{2+}; and (4) microbial reactions involving the reduction of SO_4^{2-} and the production of HCO_3^-.

EXPLANATION

RECHARGE, IN INCHES PER YEAR

□   Less than 1 (204)

△   1 to 10 (175)

○   Greater than 10 (164)

DISCHARGE, IN INCHES PER YEAR

■   Less than 1 (827)

▲   1 to 5 (358)

●   Greater than 5 (269)

NOTE: Number in parentheses is dissolved solids concentration, in milligrams per liter
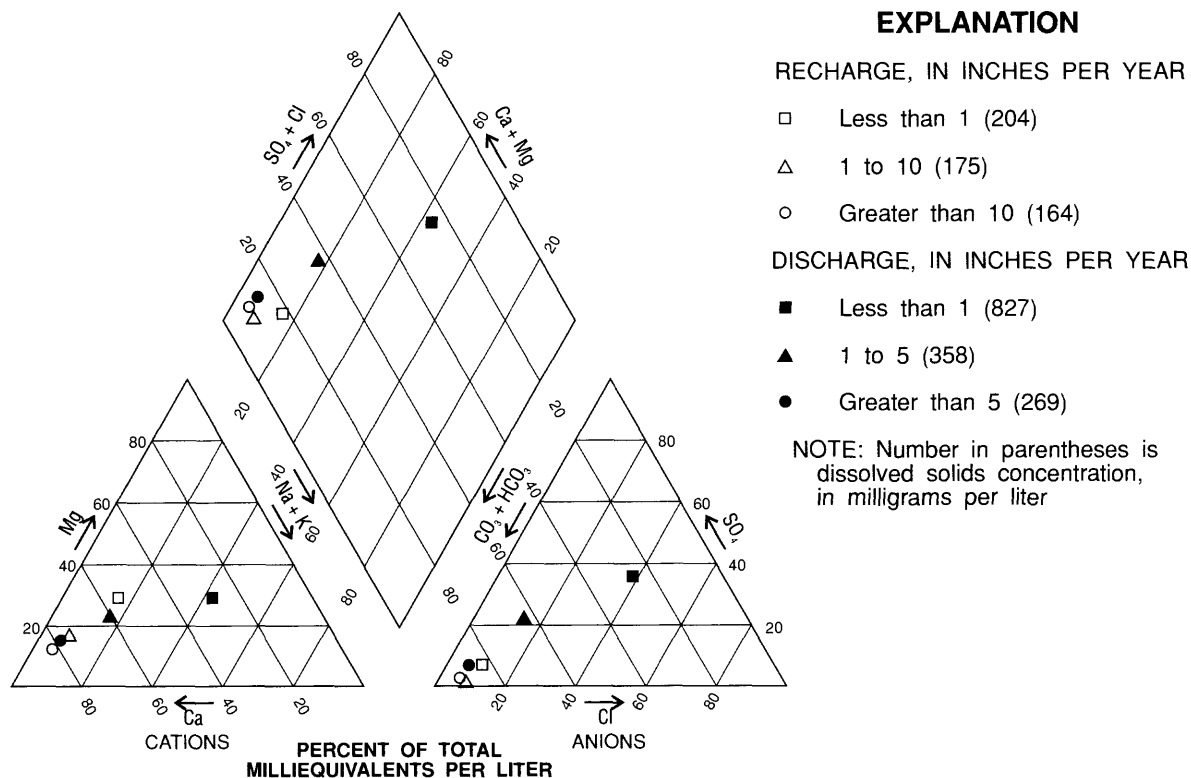
Figure 25. Diagram showing the median major-ion chemistry of ground water from areas represented by different rates of recharge to and dischrge from the Upper Floridan aquifer.

SUMMARY AND CONCLUSIONS

The Upper Floridan aquifer in Florida is one of the most productive sources of ground water in the United States. More than 2.5 Ggal of water are pumped from the aquifer daily, with 690 Mgal/d being withdrawn for public supply. The Upper Floridan aquifer is also a major source of supply for agricultural, industrial, and rural uses. The Upper Floridan aquifer system consists of limestone and dolomite beds of Tertiary age that are hydraulically interconnected to some degree and as much as 3,500-feet thick. The porous nature of the limestone and its proximity to the surface in some areas, coupled with rapid population growth in Florida, result in a ground-water resource that is highly susceptible to contamination.

The actual amounts of recharge to and discharge from the Upper Floridan aquifer are directly related to the thickness and integrity of the overlying confining unit(s). In areas where the confining material is either thin or absent, such as the north-central Florida Peninsula, the vertically downward head gradients provide optimal conditions for water to percolate rapidly into the Upper Floridan aquifer, although not all areas where the confining unit is absent are recharge areas. In areas where the overlying confining materials are thick and relatively impermeable, such as in southern Florida, the downward

(recharge) or upward (discharge) movement of water through these materials is significantly impeded. The degree of confinement has a profound influence on the chemistry of water in the aquifer system. In areas where the aquifer is overlain by a thick confining unit, a closed-system evolution of the ground water occurs. There is also the potential for remnant seawater in these areas to persist because of the inability of the freshwater to flush out this residual saline water.

The data used in this report consist of information collected and compiled during two regional programs designed to study the hydrogeology and water chemistry of the Floridan aquifer system: the Florida Ground-Water Quality Monitoring Network (FGWQMN) and the Regional Aquifer Systems Analysis (RASA). After screening of chemical analyses, a subset of major-ion data in water from 455 wells was selected from the approximately 800 wells completed in the Upper Floridan aquifer in the FGWQMN Program. These data were combined with major-ion data in water from a subset of 332 wells from the RASA study. The wells included in the RASA study generally were deeper than the wells described in the FGWQMN. The large range in depths of wells allowed some evaluation of chemical stratification of major ions

with depth in the aquifer. However, the typically long open interval for deep wells complicates the interpretation because mixing of water from different depth zones commonly occurs within the borehole.

Most major ions showed an increase in concentration with depth in most areas when the data were grouped by the degree of confinement in the aquifer. The deeper wells in confined areas of the aquifer generally yield water with higher concentrations of major ions and DS than water from shallower wells in unconfined areas. Recharge in unconfined areas of the Upper Floridan commonly occurs with water that contains low concentrations of major ions (from rainfall and leakage from the overlying surficial aquifer system). In confined areas of the south Florida Peninsula, an increase in concentration of major ions with depth is related to mixing of freshwater with residual seawater.

Water from 58 percent of the wells completed in the aquifer is either the $Ca-HCO_3$ (46 percent) or the $Ca-Mg-HCO_3$ (12 percent) hydrochemical facies. Calcite dissolution reactions in freshwater areas of the aquifer over most of the State account for the predominance of $Ca-HCO_3$ hydrochemical facies, and this controlling process is reflected by low DS (less than 250 mg/L) in these areas. A $Ca-Mg-HCO_3$ hydrochemical facies is produced where dissolution of dolomite (or dedolomitization reactions) adds Mg^{2+} to the water. Leaching of magnesium-rich clay minerals and dolomite in the overlying Hawthorn Formation may also contribute Mg^{2+} to water entering the Upper Floridan aquifer in recharge areas of north-central Florida. Where substantial gypsum dissolution occurs or oxidation of sulfide minerals, SO_4^{2-} is added to the ground water and the following hydrochemical facies are produced: $Ca-Mg-HCO_3-SO_4$ (4 percent), $Ca-Mg-SO_4$ (3 percent), and $Ca-SO_4$ (1 percent). Areas where these hydrochemical facies occur include northeast Florida, southwest Florida, and several locations in west-central Florida.

In parts of the State where vertical or lateral mixing of seawater with freshwater occurs, three hydrochemical facies are noted: mixed-HCO_3 (5 percent of the wells), mixed (14 percent), and Na-Cl (12 percent). In vertical mixing zones, it has been reported that the water chemistry changes from a $Ca-Mg-HCO_3$ type with low DS at or near the top of the zone to a Na-Cl hydrochemical facies (high DS) near the bottom of the zone. The type of hydrochemical facies in these zones depends on the thickness of the zone of transition. Pumping wells near coastal areas may also induce the landward movement of seawater, resulting in mixed or Na-Cl hydrochemical facies. The amount of seawater mixing is dependent upon the depth of the well, the location of the transition zone, and the rate of pumping.

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