

Major-Ion and Selected Trace-Metal Chemistry of the Biscayne Aquifer, Southeast Florida

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 91-4009

Prepared in cooperation with the

FLORIDA DEPARTMENT OF ENVIRONMENTAL REGULATION



Tallahassee, Florida

1991

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ABBREVIATIONS AND CONVERSION FACTORS

The inch-pound units used in this report may be converted to metric (International System) units by the following factors.

Multiply inch-pound unit	By	To obtain metric unit
inch (in.)	25.4	millimeter (mm)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
foot squared per day (ft ² /d)	0.09290	meter squared per day (m ² /d)

ADDITIONAL ABBREVIATIONS

mg/L = milligram per liter

µg/L = microgram per liter

µm = micrometer

mv = millivolts

SI = saturation index

TOC = total organic carbon

PVC = polyvinyl chloride

BCEQCB = Broward County Environmental Quality Control Board

DERM = Metropolitan Dade County Deartment of Environmental Resources Management

FDER = Florida Deartment of Environmental Regulation

FGWQMN = Florida Deartment of Environmental Regulation
Ground Water Quality Monitoring Network Program

QAPP = Quality Assurance Project Plans

SFWMD = South Florida Water Management District

USEPA = U.S. Environmental Protection Agency

USGS = U.S. Geological Survey

WATSTORE = Water-Data Storage and Retrieval System

Major-Ion and Selected Trace-Metal Chemistry of the Biscayne Aquifer, Southeast Florida

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Abstract

The major-ion and selected trace-metal chemistry of the Biscayne aquifer was characterized as part of the Florida Ground-Water Quality Monitoring Network Program, a multiagency cooperative effort concerned with delineating baseline water quality for major aquifer systems in the State. The Biscayne aquifer is unconfined and serves as the sole source of drinking water for more than 3 million people in southeast Florida. The Biscayne aquifer consists of highly permeable interbedded limestone and sandstone of Pleistocene and Pliocene age underlying most of Dade and Broward Counties and parts of Palm Beach and Monroe Counties. The high permeability is largely caused by extensive carbonate dissolution.

Water sampled from 189 wells tapping the Biscayne aquifer was predominantly a calcium-bicarbonate type with some mixed types occurring in coastal areas and near major canals. Major-ion chemistry is areally uniform throughout the aquifer. According to nonparametric statistical tests of major ions and dissolved solids, the concentrations of calcium, sodium, bicarbonate, and dissolved solids increased significantly with well depth (0.05 significance level), probably a result of less circulation at depth. Potassium and nitrate concentrations decreased significantly with depth. Although the source of recharge to the aquifer varies seasonally, there was no statistical difference in the concentration of major ions in paired water samples from 27 shallow wells collected during wet and dry seasons.

Median concentrations for barium, chromium, copper, lead, and manganese were below maximum or secondary maximum contaminant levels set by the U.S. Environmental Protection Agency. The median iron concentration only slightly exceeded the secondary maximum contaminant level. The concentration of barium was significantly related (0.05 significance level) to calcium and bicarbonate concentration. No distinct areal pattern or vertical distribution of the selected trace metals was evident in water from the Biscayne aquifer. Sources for trace metals found in water from the Biscayne aquifer may include local contamination, well-construction techniques, canal-aquifer interactions, and natural occurrence in area soils and rock.

INTRODUCTION

The Biscayne aquifer underlies almost all of Dade and Broward Counties and parts of Palm Beach and Monroe Counties (fig. 1). The unconfined aquifer is composed of highly permeable interbedded limestone and sandstone. The high permeability is caused largely by extensive carbonate dissolution. The U.S. Environmental Protection Agency (USEPA) has designated the aquifer as a "sole source aquifer" because it is the principal source of drinking water for more than 3 million people in southeast Florida.

In 1983, the State of Florida passed the Water Quality Assurance Act. This act mandated the Florida Department of Environmental Regulation (FDER) to establish a statewide ground-water quality monitoring network program. One of the main objectives of this program is to delineate baseline concentrations of water-quality constituents for the major aquifer systems throughout the State. These findings will provide a reference for comparison with future ground-water conditions. More information on this program is presented by the Florida Department of Environmental Regulation (1990) and Katz and Choquette (1991).

The U.S. Geological Survey (USGS) began a cooperative study with FDER (in 1987) to characterize the ground-water chemistry of the major aquifer systems in the State. The water-quality and hydrologic data generated by the statewide monitoring network are being used to: (1) delineate hydrochemical zones that define areas of similar water chemistry, (2) describe the major geochemical processes controlling the observed water quality, and (3) evaluate the design of the ambient network for long-term monitoring of water quality for the aquifer systems.

Purpose and Scope

This report describes the major-ion and trace-metal chemistry of the Biscayne aquifer. Data are presented to define the areal, vertical, and seasonal water-quality distribution of the major ions throughout the aquifer and to characterize the areal and vertical distribution of and factors controlling the concentration of trace metals throughout the

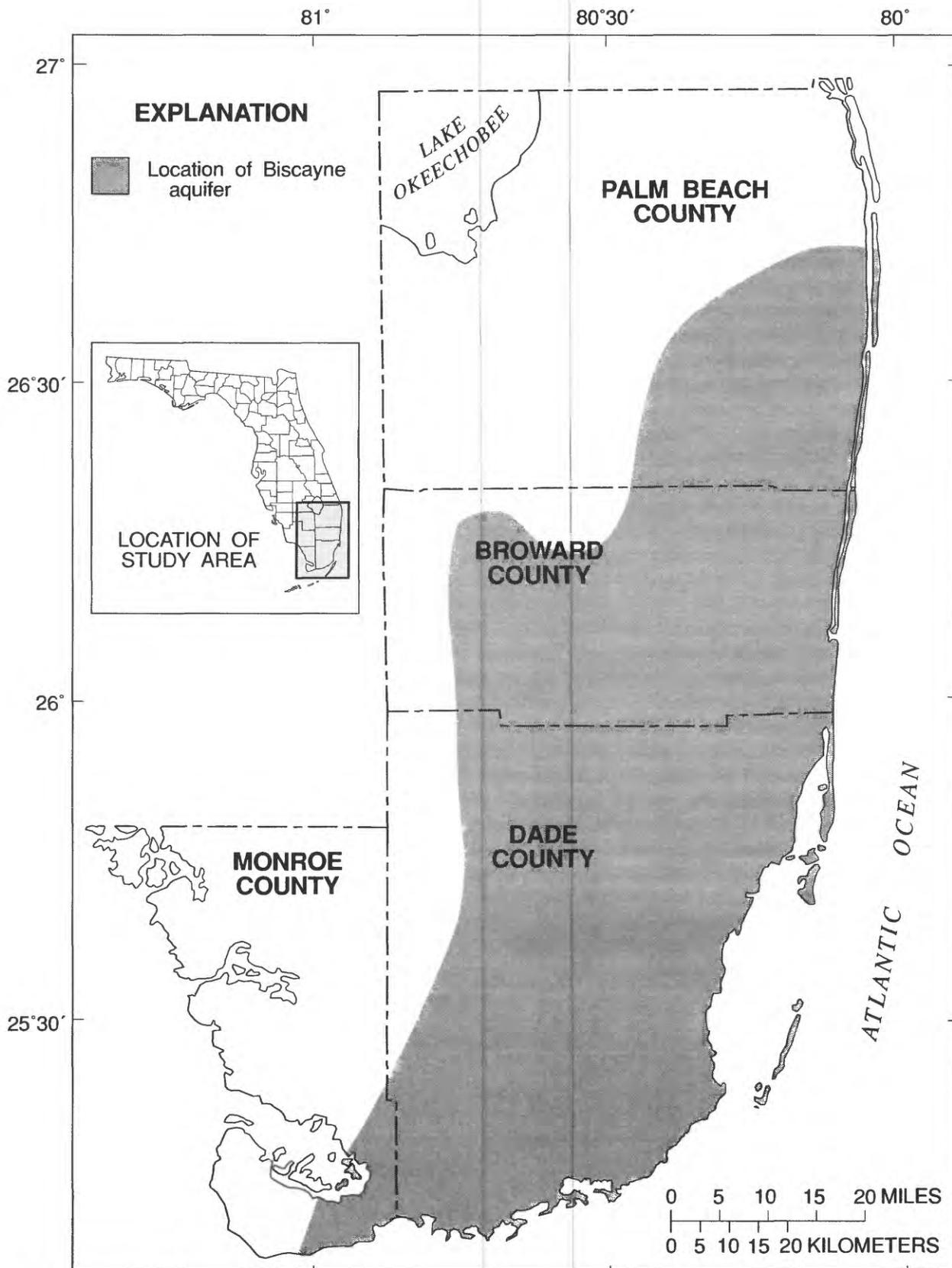


Figure 1. Location and extent of the Biscayne aquifer.

aquifer. This report presents data from two sources. The South Florida Water Management District (SFWMD) provided data that were collected as part of the State of Florida's Department of Environmental Regulation Ground Water Quality Monitoring Network Program and will be referred to as the FGWQMN data set. These data were collected from August 1984 through January 1989. Additional data were also retrieved from the USGS National Water-Data Storage and Retrieval System (WATSTORE) data base and will be referred to as the USGS data set. Most of these data were collected from October 1975 through September 1989 as part of numerous hydrologic investigations conducted by the USGS.

Previous Investigations

The Biscayne aquifer has been the subject of many past and present geologic, hydrologic, and water-quality investigations. Some of the most notable and relevant to this investigation are included below.

The earliest and most comprehensive report on the Biscayne aquifer was prepared by Parker and others (1955). The report provided information on the geology, occurrence and movement of ground water, water quality, and saltwater intrusion. Schroeder and others (1958) presented geologic sections for Dade and Broward Counties and a contour map of the base of the Biscayne aquifer. Klein and others (1975) provided an overview of water resources in south Florida, including sections on the Biscayne aquifer, saltwater intrusion, and the effects of pumping on water levels. Canal-aquifer interaction, recharge and discharge, ground-water withdrawals, and vulnerability to contamination were described by Klein and Hull (1978).

Recent reports on the surficial aquifer systems in Broward and Dade Counties include in-depth investigations of geology by Causaras (1985, 1987); chemical characteristics of water by Howie (1987) and Sonntag (1987); and hydrogeology, aquifer characteristics, and ground-water flow by Fish (1988) and Fish and Stewart (USGS, written commun., 1990).

Hydrogeology of the Biscayne Aquifer

Differences of opinion exist in the description of the areal extent and depth of the Biscayne aquifer. Previous descriptions of the Biscayne aquifer (Klein and others, 1975; Klein and Hull, 1978; Klein and Causaras, 1982) have recently been modified. The more recent description by Fish (1988, p. 20) follows:

The Biscayne aquifer is redefined herein as that part of the surficial aquifer system in southeast Florida comprised (from land surface downward) of the Pamlico Sand, Miami Oolite, Anastasia Formation,

Key Largo Limestone, and Fort Thompson Formation, all of Pleistocene age, and contiguous highly permeable beds of the Tamiami Formation of Pliocene age where at least 10 feet of the section is very highly permeable (a horizontal hydraulic conductivity of about 1,000 ft/d or more). If there are contiguous highly permeable limestone or calcareous sandstone beds of the Tamiami Formation, the lower boundary is the transition from these beds to subjacent sands or clayey sands. Where the contiguous beds of the Tamiami Formation do not have sufficiently high permeability, the base of highly permeable limestone or sandstone in the Fort Thompson Formation, Anastasia Formation, or Key Largo Limestone is the base of the Biscayne aquifer.

The Biscayne aquifer is wedge-shaped and ranges from 20-feet thick on the western edge, increasing to more than 300 feet in parts of coastal Broward and Palm Beach Counties (Klein and Causaras, 1982, Fish, 1988, p. 61). The aquifer lithology becomes more sandy and less permeable in southeast Palm Beach County (Klein and Hull, 1978, p. 3). Most of Dade County lies within an area of high transmissivity (greater than 300,000 ft²/d (feet squared per day)) and some values exceed 1,000,000 ft²/d in central and southeastern parts of the county (J.E. Fish and Mark Stewart, USGS, written commun., 1990). Recent aquifer tests in Broward County show an average transmissivity of about 375,000 ft²/d and individual values exceed 800,000 ft²/d in some areas (Fish, 1988, p. 31). Transmissivity values have been estimated from specific capacity values for the zone of higher secondary permeability in eastern Palm Beach County and range from 1,000 ft²/d to 100,000 ft²/d (Swayze and Miller, 1984, p. 20).

Average annual rainfall in southeast Florida ranges from 58 to 64 inches (Klein and Hull, 1978, p. 15). About 75 percent of the total annual precipitation generally falls during the wet season, June through October (Klein and others, 1975, p. 22). Recharge to the aquifer is primarily from rainfall and averages 37 to 38 inches annually (Schroeder and others, 1958, p. 37; Fish, 1988, p. 66). Water is impounded in conservation areas in the western and central parts of Dade, Broward, and Palm Beach Counties for water-supply use and to maintain sufficient water levels in the numerous canals to deter saltwater encroachment during the dry season (fig. 2). During that time, recharge to the aquifer occurs as seepage from these conservation areas and canals. The return flow of water used for irrigation and urban runoff also contributes recharge to the aquifer. Discharge from the Biscayne aquifer occurs as evapotranspiration (20 in/yr (inches per year)), ground-water flow to canals and the sea (15.5 in/yr), and, to a lesser extent, by pumping. Although pumpage is only a small part of the total discharge, its effects are amplified because withdrawals are greatest during the dry season when recharge is smallest. Pumping of ground water accounts for approximately 2.5 in/yr in eastern Broward County (Fish,

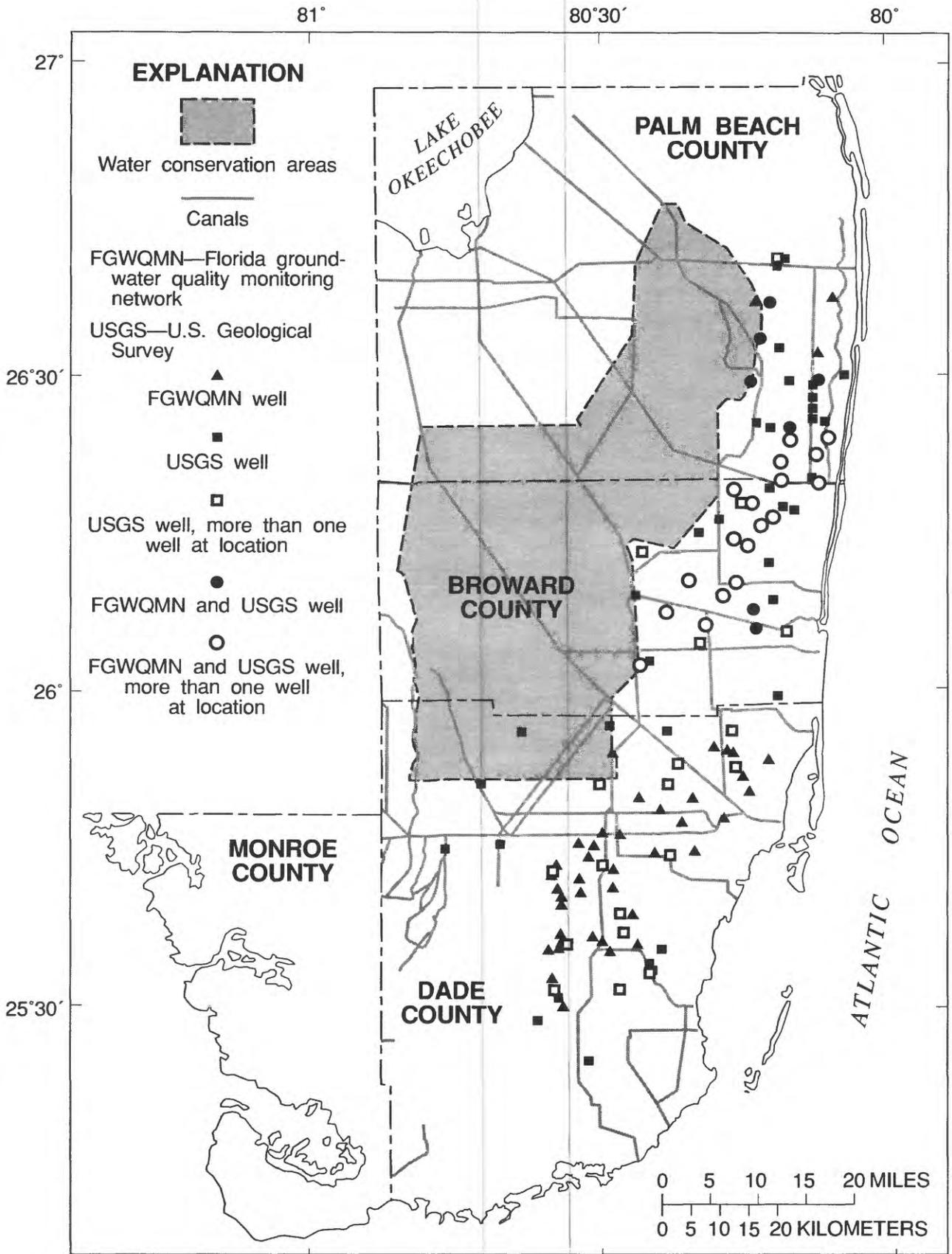


Figure 2. Location of canals, conservation areas, and wells.

1988, p. 67) and 3.7 in/yr in Dade County (J.E. Fish and Mark Stewart, USGS, written commun., 1990).

Ground-water flow patterns in southeast Florida have been substantially altered since the onset of development in the early 1900's (Schroeder and others, 1958). Prior to development, wet-season flow direction was outward in all directions from a ground-water divide that developed beneath the Atlantic Coastal Ridge (fig. 3). This included a deep, downward, and westward component toward The Everglades that gradually turned southward toward the Gulf of Mexico and the Atlantic Ocean (fig. 3). Today, with the effective lowering of ground-water levels beneath the Atlantic Coastal Ridge and altered recharge patterns, ground water flows southward and eastward toward the sea. On a much smaller scale, local ground-water flow patterns have been altered by well fields, canals, and conservation areas.

Canals have been effective in lowering ground-water levels in southeast Florida and have changed the distances that ground water flows before being discharged (Klein and Hull, 1978; Fish, 1988). Although it is known that the water in the canals and in the aquifer are interrelated hydraulically, this relation is not well documented in the literature. Therefore, chemical relations between these two components are not very well understood. Generally, ground water moves toward the canals during the wet season and away from the canals during the dry season. However, it is not always known whether canals act as fully penetrating boundaries that divide the aquifer into individual flow cells or as partially penetrating boundaries (Fish, 1988).

Saltwater intrusion has long been a concern in southeast Florida (Parker and others, 1955; Schroeder and others, 1958; Klein and others, 1975; Klein and Hull, 1978; Klein and Waller, 1985). After canal construction and prior to the inclusion of control structures, seawater was free to flow inland through the canals and infiltrate into the aquifer during times of lowered water levels. The inclusion of the canal control structures combined with the impoundment of water in the conservation areas (to maintain water levels) have stabilized the saltwater-freshwater interface near the coast and at the entrances to major canals (Klein and Hull, 1978; Klein and Causaras, 1982). Klein and Hull (1978) show the extent of saltwater intrusion in 1975. The figure given in Klein and Hull (1978) has been updated using recent average chloride concentrations in water from wells completed in the base of the Biscayne aquifer (fig. 4). These data were retrieved from WATSTORE for the period October 1975 through May 1990.

Sources of Water-Quality Data

Data were obtained from two sources. The first data set consisted of water analyses collected as part of the FGWQMN for the Biscayne aquifer. The wells selected for this sampling program were designated specifically to

characterize baseline conditions and, therefore, wells were not eliminated from the data set on the basis of location. Water samples were collected and analyzed by the SFWMD, Metropolitan Dade County Department of Environmental Resources Management (DERM), and Broward County Environmental Quality Control Board (BCEQCB). An additional contract laboratory was also used for sample analyses.

The second set of water analyses were retrieved from the USGS data base, WATSTORE. Only analyses containing values for all of the following dissolved constituents were considered: calcium, magnesium, sodium, potassium, bicarbonate, chloride, and sulfate. Because this data base contains information from various hydrologic investigations, including contamination studies, the analytical data were edited to eliminate data for wells with anomalously high concentrations that were suspected or known to represent contamination. Also, data were deleted for wells that were known to be part of contamination monitoring studies or that were not located within the Biscayne aquifer (Klein and Causaras, 1982; Fish, 1988; J.E. Fish and Mark Stewart, USGS, written commun., 1990).

Both data sets were screened for analytical error by means of computing charge balance error. Only analyses having a charge balance error of 10 percent or less were included for evaluation. Some wells were common to both data sets. When multiple analyses existed for a well, median values for each constituent were computed for each well. The FGWQMN and USGS data were combined because statistical comparison of individual constituents for the two data sets showed no significant difference (0.05 significance level) with the exception of the bicarbonate ion. This difference could be the result of bicarbonate values measured in the laboratory for the FGWQMN data set as opposed to values measured in the field for the USGS data set. Typically, field values of bicarbonate will be higher than laboratory values because bicarbonate may be removed from solution if calcium carbonate precipitates between the time of collection and of analysis. The combined data base contained major-ion chemistry of water from 189 wells.

Trace-element data collected for the FGWQMN program were analyzed by four laboratories using different analytical methods. This resulted in differing detection limits. Water samples from 181 wells were analyzed for one or more of the following: arsenic, barium, cadmium, chromium, copper, cyanide, iron, lead, manganese, mercury, nickel, selenium, silver, and zinc. Further discussion includes only trace metals for which 50 percent or more of the analyses were above detection limit: barium, chromium, copper, iron, lead, and manganese. USGS data for these six metals from 55 wells were combined with the FGWQMN data, resulting in a final data set that includes samples from 236 wells. Because of the different detection limits reported by the laboratories and multiple analyses for some wells, only the most recent analyses were used in geochemical and statistical analyses.

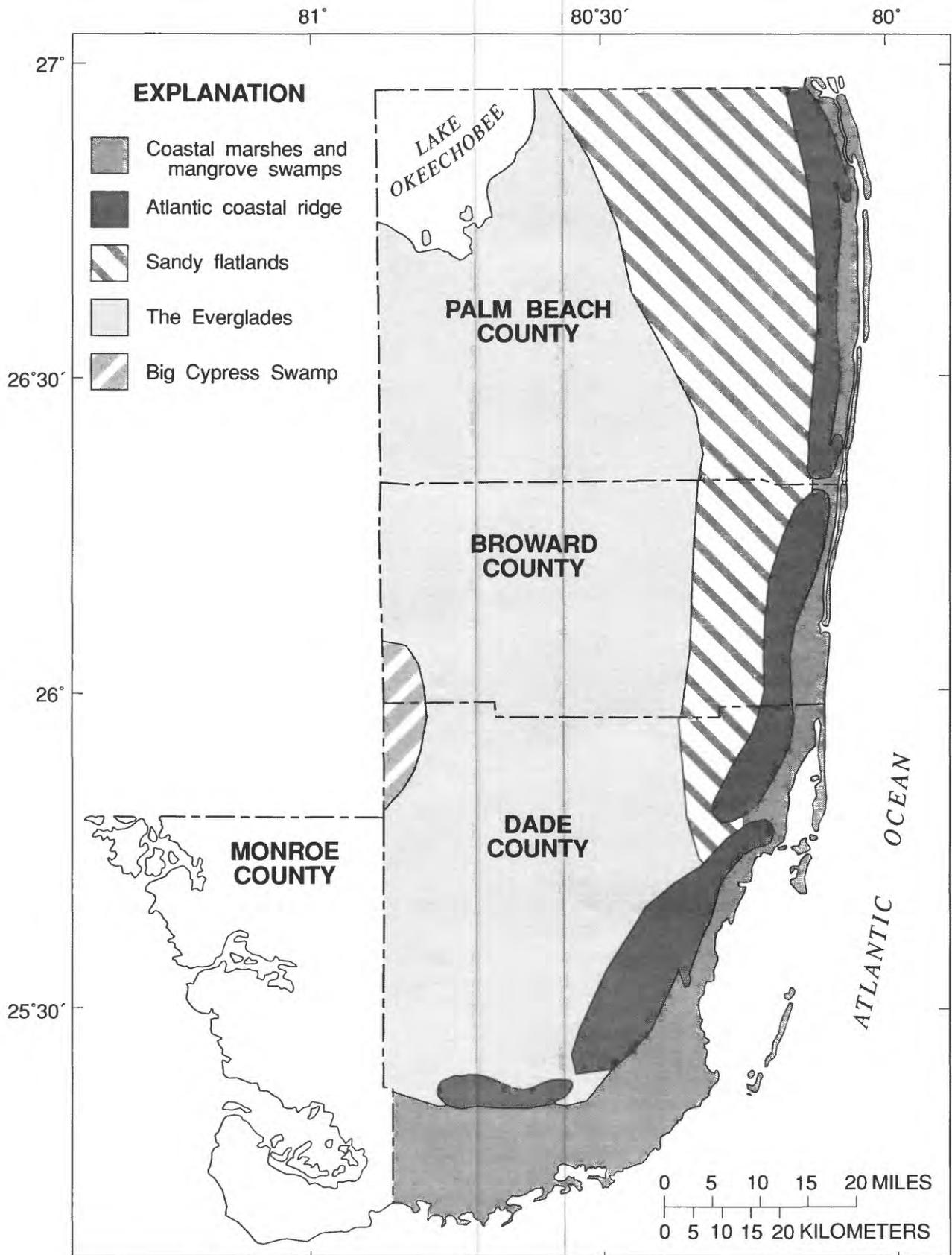


Figure 3. Physiographic features of the study area prior to development.

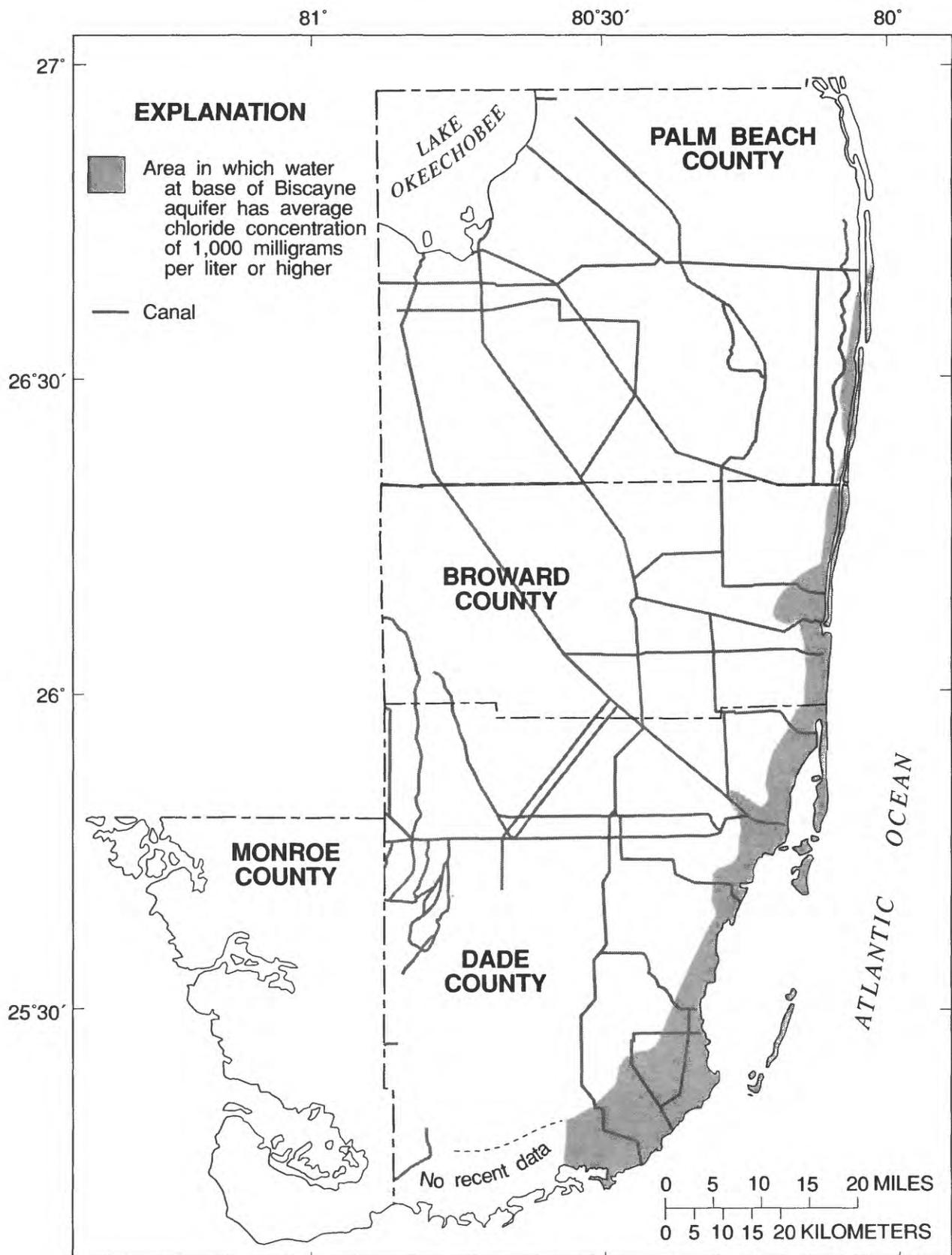


Figure 4. Inland extent of saltwater intrusion in the Biscayne aquifer, October 1975 through May 1990.

Water-quality data for selected canals in southeast Florida were retrieved from WATSTORE. Data from 23 locations for 17 canals were used for comparison with ground-water quality data for both the major ions and the trace metals.

Methods

Detailed sample collection and analytical methods performed by the laboratories for the FGWQMN program are included in the Quality Assurance Project Plans (QAPP) on file with the FDER for Metropolitan Dade County Department of Environmental Resources Management (1987), and Post, Buckley, Schuh & Jernigan, Inc. (1987), Broward County Environmental Quality Control Board (1988), and the South Florida Water Management District (1990). Analytical methods for the major ions were the same for all laboratories, but differed for the metals. Quality assurance practices included routine split replicates, known field spikes, field blanks, equipment blanks, and standard reference samples.

Standard USGS procedures were followed during sample collection (Wood, 1976) and sample analysis (Fishman and Friedman, 1985; Wershaw and others, 1987) for the data retrieved from WATSTORE. Quality assurance included the previously mentioned practices.

Nonparametric statistical methods were used to analyze the major-ion data because at least one constituent was neither normally nor log normally distributed. The one exception is the use of a parametric paired t-test. This test was used to compare seasonal differences. The differences between the major-ion median values for each season for the wells with paired data were computed and tested for normality. Even though the data for each constituent by season were not normally distributed, the seasonal differences (wet season median value minus the dry season median value) were normally distributed. The trace-element data contained some metal concentrations reported only as below the analytical detection limit (censored data). Also, because several laboratories were involved with different analytical procedures, the data also contained multiple detection limits (multiply censored data). Descriptive statistics were estimated using the log normal probability plot method for multiple detection limits (Helsel and Cohn, 1988). This method was used because it is robust, efficient, and is less sensitive to departures from log normality. Relations between trace metals and various factors were determined using a linear regression model that estimates the model parameter using a maximum likelihood estimation procedure referred to as TOBIT (T.A. Cohn, USGS, written commun., 1990).

MAJOR-ION CHEMISTRY

Major-ion chemistry can be used as a general indicator of water quality and to help identify some of the physical-chemical processes that affect the composition of natural waters. It also provides a means to assess regional differences in water quality as well as changes in quality with time. A statistical summary of the concentration of selected chemical constituents, dissolved solids, and total organic carbon (TOC), are presented in table 1. In all cases, the mean concentration exceeds the median concentration. This indicates that high concentrations are influencing the mean and that the median is a better estimate of central tendency. Large standard deviations and differences between the mean and median values usually indicate that the data are not from a normal distribution. The hypothesis that the data were from a normal distribution was tested using the Shapiro-Wilk statistic (SAS Institute, Inc., 1988). The results indicated departure from normality for most of the constituents. Therefore, for consistency, nonparametric procedures were used for all the statistical analyses.

Table 1. Statistical summary of the concentration of selected chemical constituents and characteristics in water from wells tapping the Biscayne aquifer

[All concentration values are in milligrams per liter; pH, is in standard units; < = less than; °C = degrees Celsius]

Con- stituent or charac- teristic	Sample size	Median	Mean	Stand- ard devia- tion	Mini- mum	Maxi- mum
Calcium, dissolved	189	92	94	25	27	190
Magnesium, dissolved	189	3.7	5.3	4.9	.9	53
Sodium, dissolved	189	22	29	42	2.8	530
Potassium, dissolved	189	1.8	2.7	2.6	.23	16
Chloride, dissolved	189	36	49	77	5.0	980
Bicarbonate	189	272	283	74	66	610
Nitrate	153	.13	1.5	1.0	<.04	32
Sulfate, dissolved	189	17	22	23	.1	160
pH	160	7.13	7.11	.25	6.35	7.80
Dissolved solids, residue at 180 °C	189	350	379	166	111	2,130
Total organic carbon	127	14	17	15	.8	74

Areal Distribution

Hydrochemical facies were determined for each well using a classification based on percentage of equivalents per million (Davis and DeWiest, 1966). In order for a water type to be classified by a single cation, it must have at least 60 percent of the total cation equivalents per million, likewise for the dominant anion. The explanation of dominant water types, the basis of the facies presented in this study, is more easily seen in figure 5. A mixed facies occurs when there is no dominant water type.

The dominant water type is a calcium-bicarbonate with 84 percent of the analyses falling in this category. The predominance of this water type reflects the control of calcite solubility on the chemistry of the ground water. Calcium-sodium-bicarbonate is the next dominant hydrochemical facies (9 percent of the analyses). Calcium-mixed anion, mixed, and mixed cation-chloride facies make up the remaining 7 percent. Samples from one well near the coast exhibit a sodium-chloride facies. Most of the samples exhibiting facies other than calcium-bicarbonate are from

wells near the coast, adjacent to canals or conservation areas, or near well fields.

Stiff diagrams are commonly used to show similarities and differences in the major-ion composition of water (Hem, 1985). The chemical composition of water from selected wells is depicted in figure 6 for a north-south transect in the Biscayne aquifer. Spatial variation of hydrochemical facies is not apparent in the water of the Biscayne aquifer because of the predominance of calcium-bicarbonate water type and lack of specific areal pattern for the other water types. This result is expected because of the dominant calcium-carbonate composition of the Biscayne aquifer material.

Vertical Distribution

Variations in water quality within the Biscayne aquifer may occur not only areally but also with depth. Correlation analysis can be used to test the hypothesis that there is a relation between depth in the aquifer and the concentration of major ions, dissolved solids, and TOC. Correlation analysis

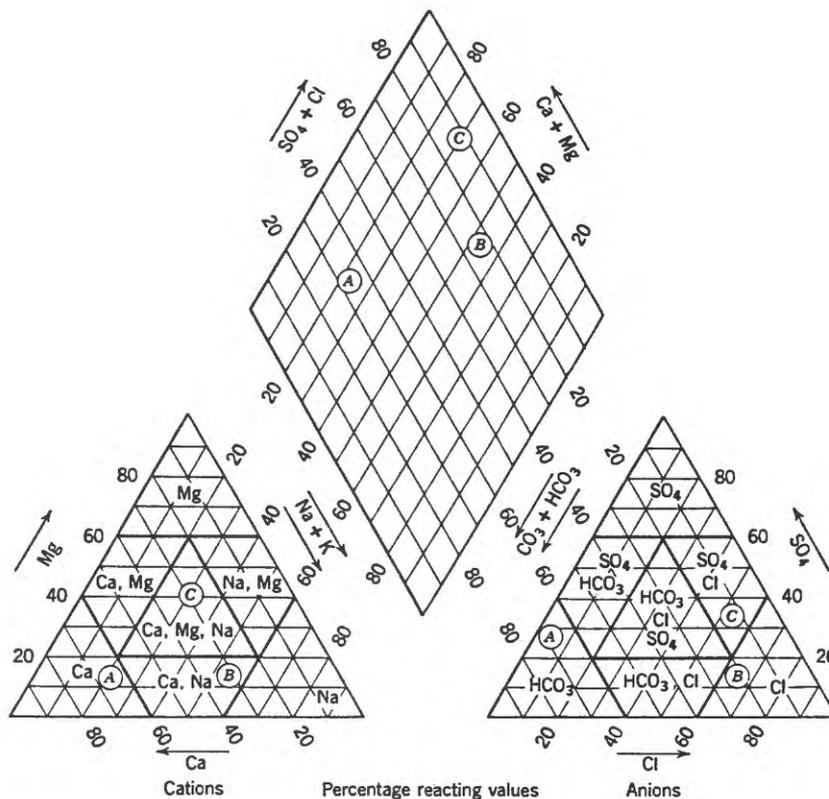


Figure 5. Water classification based on the percentage of equivalents per million. Point A represents calcium bicarbonate water; point B, calcium, sodium, chloride water; point C, sodium, calcium, magnesium, chloride, sulfate water. (Figure reprinted, with permission, from *Hydrogeology* by Stanley N. Davis and Roger J.M. DeWiest, p. 119, copyright © 1966 by John Wiley & Sons, Inc.)

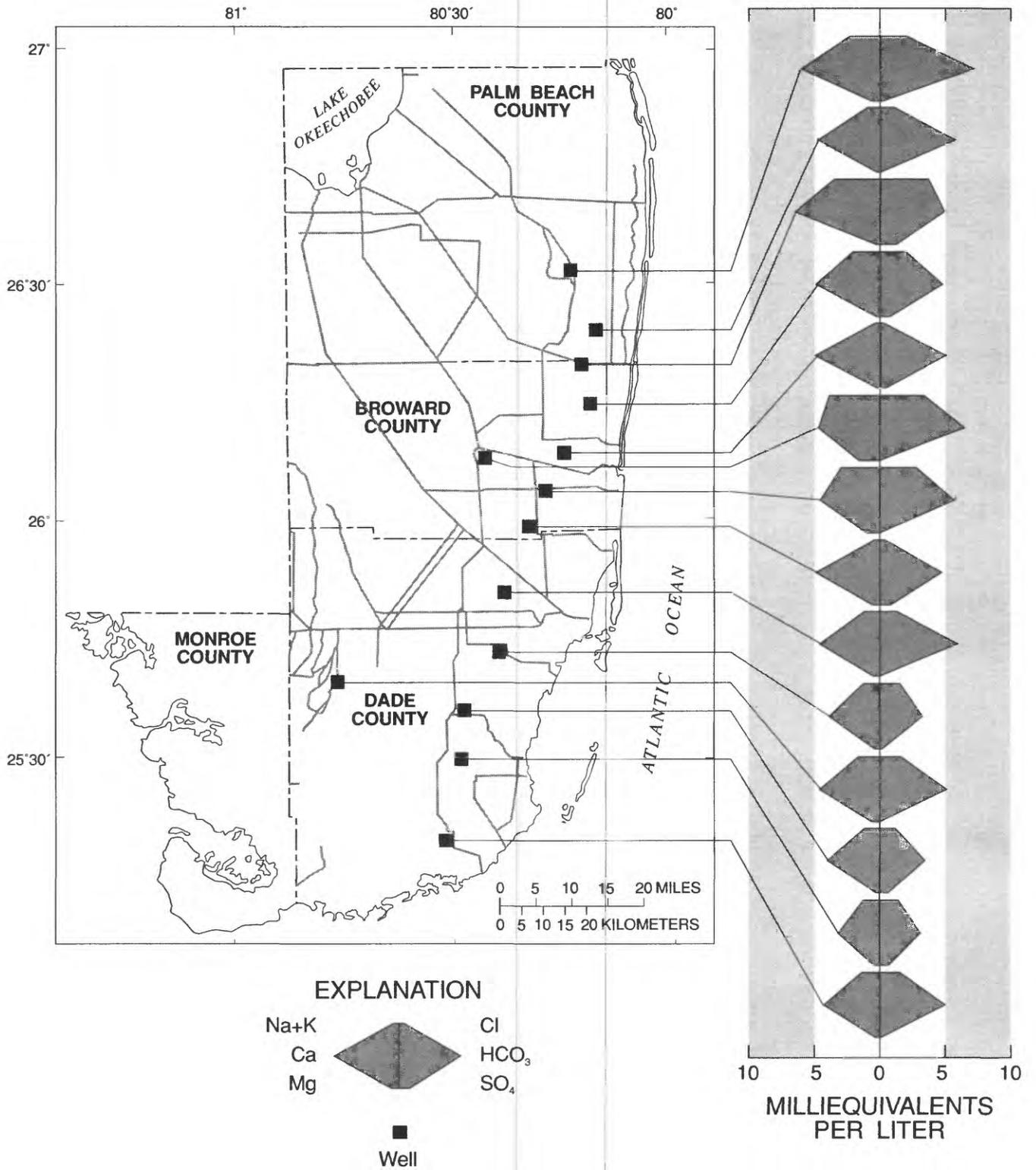


Figure 6. Major-ion composition of water samples from selected wells tapping the Biscayne aquifer.

measures the strength of a linear relation between two variables. Spearman's rank order correlation (SAS Institute, Inc., 1988), a nonparametric test that uses the ranks of the data, was used to determine if there is a linear relation between depth in the aquifer and major-ion chemistry. The results for each constituent are presented in table 2. For this analysis, correlations were considered statistically significant for probability values (p-values) less than or equal to 0.05. P-values are the probability of incorrectly rejecting the null hypothesis, that states there is no correlation. In other words, the probability that the observed correlation occurs solely as a result of chance. The concentrations of nitrate and potassium showed a significant decrease with depth whereas the concentrations of calcium, sodium, bicarbonate, and dissolved solids showed a significant increase with depth. At the 0.05 significance level, chloride and TOC did not show a significant relation with depth; however, because the p-values are only slightly greater than 0.05 (table 2), there is a possible correlation.

Table 2. Results of Spearman correlation analysis for relation between well depth and selected chemical constituents and characteristics in water from wells tapping the Biscayne aquifer

[Significance of p-value equal or less than 0.05; < = less than; °C = degrees Celsius]

Constituent or characteristic	Correlation coefficient	P-value
Calcium, dissolved	0.29	<0.001
Magnesium, dissolved	-.06	.388
Sodium, dissolved	.14	.048
Potassium, dissolved	-.17	.022
Chloride, dissolved	-.14	.058
Bicarbonate	.32	<.001
Nitrate	-.21	.011
Sulfate	.08	.251
Dissolved solids, residue at 180 °C	.29	<.001
Total organic carbon	.18	.058

Ground-water circulation has been altered by the canals and conservation areas, which effectively have eliminated the wet-season water-table mound below the Atlantic Coastal Ridge (Fish, 1988). Presently, year-round flow patterns are similar to those of predevelopment dry-season flow (slow circulation with depth) with the exception of local variations due to canal recharge and pumping. The increase in concentrations of calcium and bicarbonate with depth may result from this slower circulation of water that permits a longer contact time between the ground water and the predominant mineral, calcite, in the limestone. Calcite is important in controlling the concentrations of calcium and bicarbonate until equilibrium is reached because the mineral dissolves or precipitates in response to changes in concentration of these two ions. It is assumed that calcite will continue to dissolve as long as it is in contact with ground water that is undersaturated with respect to this mineral. The computer

program WATEQF (Plummer and others, 1978) was used to calculate the saturation index (SI) for calcite. The computed value for the calcite SI was slightly less than zero, suggesting that calcite has a thermodynamic potential to dissolve in this system. The increase in sodium and dissolved solids concentration with depth also indicates that less exchange or mixing occurs with depth between the deeper water and younger recharge water containing lower concentrations of these ions.

Seasonal Distribution

The predominant mechanism for recharging the Biscayne aquifer is different during the wet season (June-October) and dry season (November-May). Precipitation is the dominant source of recharge in the wet season, whereas infiltration of water from canals and conservation areas is the dominant source in the dry season. A paired t-test was used to test for the effect of seasonal differences in recharge on the chemistry in the shallow part of the aquifer. A parametric test was used because, even though the data were not normally distributed, the differences between the paired data were normal (SAS Institute, Inc., 1988). Eighty-five wells had water samples taken during both seasons. Twenty-seven of those wells were less than 30-feet deep. The test was restricted to the 27 shallow wells because they are more likely to be influenced by differences in chemistry of the recharge water. Each constituent was tested for significant differences among analyses in the wet season and dry season. The results are presented in table 3. For this analysis, differences were considered statistically significant for p-values less than or equal to 0.05. No significant difference was detected between chemical analyses of ground water taken during the wet season and the dry season.

Table 3. Results of paired t-test for seasonal differences in the concentration of selected constituents and characteristics in water from wells less than 30 feet in depth in the Biscayne aquifer

[Significance of p-value equal or less than 0.05; — = not enough data to evaluate; °C = degrees Celsius]

Constituent or characteristic	P—value
Calcium, dissolved	0.176
Magnesium, dissolved	.728
Sodium, dissolved	.445
Potassium, dissolved	.382
Chloride, dissolved	.579
Bicarbonate	.085
Nitrate	—
Sulfate	.579
Dissolved solids, residue at 180 °C	.582
Total organic carbon	.483

The median, mean, standard deviation, and range of concentration for selected chemical constituents, dissolved solids, and TOC for water from 15 to 17 canal locations in southeast Florida are presented in table 4. To test the hypothesis that there was no difference between the shallow ground-water quality and that of the canal water, the Wilcoxon rank sum test was used. This is a nonparametric test that uses the ranks of the data to compare the means. The concentrations for calcium and sulfate are significantly lower and the concentrations for magnesium, sodium, potassium, chloride, and dissolved solids are significantly higher (0.05 significance level) in canal water than their corresponding concentrations in ground water (table 1). This suggests that although the chemistry of the canal water differs from that of the aquifer, the chemistry of the water recharged to the aquifer from the canals probably has little, if any, influence on the chemistry of the shallow ground water. Dilution may likely mask the effect of canal recharge on the chemistry of the shallow ground water. The samples for this study were not collected specifically to evaluate canal-aquifer interactions, therefore, possible local effects on ground-water chemistry resulting from recharge of water from canals may not be apparent.

SELECTED TRACE-ELEMENT CHEMISTRY

The mobility and fate of certain trace metals in ground water that is used for public water supply is a matter of great concern because of possible adverse effects on human health. In the Biscayne aquifer, detectable dissolved concentrations for barium, chromium, copper, iron, lead, and manganese were found in 50 percent or more of the analyses. The term "dissolved" is operationally defined as those metals in a water sample that pass through a 0.45 μm (micrometer) membrane filter (Fishman and Friedman, 1985). The median, mean, standard deviation, and range of dissolved concentrations in water from wells tapping the Biscayne aquifer are presented in table 5. These descriptive statistics were estimated using a probability plotting procedure that incorporates multiple detection limits (Helsel and Cohn, 1988). Also included in table 5 are the maximum contaminant levels or secondary maximum contaminant levels allowed for these six metals as regulated under the Safe Drinking Water Act of 1986 (U.S. Environmental Protection Agency, 1988a, 1988b, 1989). Drinking water standards for the State of Florida are identical to those of the Federal Government. The median concentrations for all metals with the exception of iron were lower than either the maximum contaminant levels or the secondary maximum contaminant levels. Furthermore, the maximum concentrations for barium and copper were also below the maximum contaminant levels set by USEPA (table 5).

Table 4. Statistical summary of the concentration of selected chemical constituents and characteristics in water from canals in southeast Florida

[All concentration values are in milligrams per liter; pH is in standard units; Data are from the U.S. Geological Survey WATSTORE data base; °C = degrees Celsius]

Con-stituent or charac-teristic	Sample size	Median	Mean	Stand-ard devia-tion	Mini-mum	Maxi-mum
Calcium, dissolved	17	84	84	7.5	74	100
Magnesium, dissolved	17	8.8	10	6.4	2.9	32
Sodium, dissolved	17	49	50	22	23	120
Potassium, dissolved	17	2.5	2.8	1.4	1.2	6.6
Chloride, dissolved	17	78	82	38	36	190
Bicarbonate	17	276	283	45	224	415
Nitrate	16	.04	.06	.06	.01	.19
Sulfate, dissolved	17	14	19	16	4.3	53
pH	17	7.62	7.57	.15	7.27	7.85
Dissolved solids, residue at 180 °C	17	422	440	116	323	818
Total organic carbon	15	21	22	9.4	5.0	46

Areal Distribution

No distinct areal pattern was evident for selected trace-element concentrations in water from the Biscayne aquifer. Generally, iron and manganese concentrations were high (53 percent and 6 percent, respectively, exceeded secondary maximum contaminant levels) throughout the aquifer. Parker and others (1955, p. 731) reported that the concentration of iron in the Biscayne aquifer ranges between 1,000 $\mu\text{g/L}$ (micrograms per liter) and 4,000 $\mu\text{g/L}$, and in some areas exceeds 4,000 $\mu\text{g/L}$. Iron concentrations for samples taken for recent studies in Dade and Broward Counties ranged from less than 10 $\mu\text{g/L}$ to 9,800 $\mu\text{g/L}$ and varied widely, both areally and with depth (Howie, 1987; Sonntag, 1987).

Vertical Distribution

A regression analysis, which uses maximum likelihood estimation procedures to estimate the regression parameters, referred to as TOBIT (T.A. Cohn, USGS, written commun., 1990), was used to test for a relation between trace-element concentration and total depth of a well. The procedure provides estimates of the parameters of a simple linear model when the trace-element data are censored at multiple detection limits. The slope of the regression line indicates the

Table 5. Statistical summary of the concentration of selected metals in water from wells tapping the Biscayne aquifer

[All units in micrograms per liter; only values that were above detection limit are included; USEPA = U.S. Environmental Protection Agency; MCL = maximum contaminant level; SMCL = secondary maximum contaminant level; BDL = below detection limit]

Constituent	Sample size	Median	Mean	Standard deviation	Minimum	Maximum	USEPA drinking water regulations (MCL or SMCL)
Barium, dissolved	165	24	36	38	BDL	300	¹ 1,000
Chromium, dissolved	208	1.0	3.4	8.5	BDL	90	¹ 50
Copper, dissolved	172	.7	2.2	4.3	BDL	31	² 1,000
Iron, dissolved	182	312	1,027	2,119	BDL	21,000	² 300
Lead, dissolved	200	3	10	44	BDL	604	¹ 50
Manganese, dissolved	211	14	19	19	BDL	150	² 50

¹Maximum contaminant level (MCL): Enforceable, health-based regulation that is to be set as close to the maximum contaminant level goal as is feasible. The definition of feasible means the use of best technology, treatment techniques, and other means that the Administrator of USEPA finds, after examination for efficacy under field conditions and not solely under laboratory conditions, are generally available (taking cost into consideration).

²Secondary maximum contaminant level (SMCL): Contaminants that affect the esthetic quality of drinking water. At high concentrations or values, health implications as well as esthetic degradation may also exist. SMCLs are not federally enforceable but are intended as guidelines for the States.

relation (positive or negative) between the two variables, metal concentration and well depth. Results for the relation between selected trace metals and depth in the aquifer are presented in table 6. For this analysis, p-values less than or equal to 0.05 were considered statistically significant. There was no significant relation between the concentration of any of the six trace metals and well depth in water from wells tapping the Biscayne aquifer.

Table 6. Results of regression analyses for relation between well depth and selected metals in water from wells tapping the Biscayne aquifer

[Significance of p-value equal or less than 0.05]

Constituent	P-value
Barium, dissolved	0.855
Chromium, dissolved	.508
Copper, dissolved	.861
Iron, dissolved	.338
Lead, dissolved	.331
Manganese, dissolved	.723

Factors Affecting the Concentration of Selected Trace Metals

The sources of barium, chromium, copper, iron, lead, and manganese found in water from the Biscayne aquifer are either natural (mineral weathering) or are influenced by man. There are no reported analyses available for these trace

metals in the Biscayne aquifer material (limestone). However, Hem (1985) lists the following typical concentrations (parts per million, milligrams per kilogram) of these elements in limestone: barium, 30; chromium, 7.1; copper, 4.4; iron, 8,190; lead, 16; and manganese, 842. Therefore, one would expect that chemical weathering of the limestone would yield naturally low concentrations of barium, chromium, copper, and lead to water that is in contact with the rock. Recharge water to the Biscayne aquifer may contain elevated concentrations of iron and manganese as a result of leaching of these metals from overlying soils (Estes, 1987). Concentrations of chromium, copper, and lead above background levels may result from local contaminant sources (such as industrial uses of these metals and agricultural activities), well construction techniques (type of casing material, composition of drilling fluids), or burning of fossil fuels (Leckie and James, 1974).

The presence of these six trace metals in ground water is related to the solubility of minerals and coordinative compounds of these metal ions (Leckie and James, 1974). Important parameters controlling the behavior of these trace metals in water from the Biscayne aquifer are pH, the redox conditions in different parts of the aquifer, the type and concentration of complexing inorganic and organic ligands and chelating agents, and the oxidation state of the mineral components.

In an effort to gain some insight regarding the important hydrochemical processes or parameters controlling the behavior of these metals in water from the Biscayne aquifer, two methods were used. The first method involved

calculating the distribution of aqueous species at equilibrium for barium, iron, and manganese using the computer program WATEQF (Plummer and others, 1978). Lack of thermodynamic data precluded the calculation of the distribution of aqueous species of chromium, copper, and lead. The second method involves the use of statistical techniques to determine if any relation exists between the six trace metals and the following variables: pH, and the concentrations of total organic carbon, calcium, bicarbonate, and sulfate. In addition, a comparison is made of the concentration of selected metals among different types of casing material used in the construction of the well.

The concentration and distribution of aqueous species of iron and manganese are dependent upon redox (Eh) and pH conditions. Variations in the redox condition can change the oxidation state of iron and manganese, and can change the species or ligands available for complexing or chelating with these two metals. Measurements of Eh in water from selected wells tapping the Biscayne aquifer ranged from -250 to +150 mv (millivolts) (Jeff Herr, South Florida Water Management District, written commun., 1990). The pH ranged from 6.30 to 7.30 for water collected from these same wells. The pE values calculated using WATEQF range from -4.24 to +2.54. By definition, $pE = -\log [e^-]$ and is analogous to the expression for pH involving hydrogen-ion activity. The redox conditions for these calculated pE values in the aquifer range from a reducing (anoxic) environment to transitional (slightly oxidized) environment (Leckie and James, 1974). Using the median composition of water from the Biscayne aquifer (tables 1 and 5) and the range of Eh and pH values measured, the predominant species of iron and manganese were calculated using WATEQF. Over the range of Eh and pH measurements, Fe^{2+} and Mn^{2+} are the predominant species. For the higher pH and pE waters, $Fe(OH)_2^+$ constitutes only about 2 percent of the total iron in solution. Under these conditions, the concentration of iron may be controlled

by the solubility of amorphous $Fe(OH)_3$, whose saturation index calculated using WATEQF is +1.1. Hem (1985) reports that the occurrence of iron concentrations from 1 to 10 mg/L (milligrams per liter) are common in ground water with a pH between 6.0 and 8.0 and sufficiently reducing conditions. For water with a pH of 7.3 and Eh values from -250 to 150 mv, $MnHCO_3^+$ constitutes about 14 percent of the total manganese in solution. At this higher pH, rhodochrosite ($MnCO_3$) may control the concentration of manganese in solution, suggested from its SI of -1.7.

The description of the behavior of iron and manganese in ground water using equilibrium considerations alone may be somewhat misleading. One reason is that sorption and ion-exchange processes are neglected in a thermodynamic model such as WATEQF. Another reason involves the nature of the sampling technique. Many particulate metal hydrous oxides, such as iron and manganese, are small enough to pass through a 0.45- μm filter. These oxides are known to sorb other trace metals (Hem, 1985). When the filtered sample is acidified, the particulates and the sorbed metals have the potential to dissolve, releasing not only the scavenged trace metals but also increasing the "dissolved" iron and manganese concentrations.

To test for a relation between the six metals and selected chemical variables, TOBIT was used to estimate regression parameters for a linear model that incorporates the multiply censored data (multiple detection limits) for these metals (T.A. Cohn, USGS, written commun., 1990). The concentration of each trace metal was log transformed prior to input to the regression models. The procedure provides the p-values that a significant relation exists between a particular metal and an independent variable. The significance level, which describes the probability of falsely detecting a relation between variables, was chosen to be 0.05. The results of the TOBIT procedure for the selected trace metals and chemical variables are presented in table 7.

Table 7. Results of regression analyses for relation between factors affecting metal concentrations and selected metals in water from wells tapping the Biscayne aquifer

[Significance of p-value equal or less than 0.05; + = positive relation; - = negative relation]

Constituent	Factors affecting metal concentration				
	Calcium (p-value)	Bicarbonate (p-value)	pH (p-value)	Total organic carbon (p-value)	Sulfate (p-value)
Barium, dissolved	<0.001 (+)	<0.001 (+)	0.002 (+)	0.135	0.129
Chromium, dissolved	.503	.075	.008 (+)	.787	.121
Copper, dissolved	.544	.174	.010 (-)	.365	.664
Iron, dissolved	.116	.018 (+)	.003 (+)	.094	.343
Lead, dissolved	.681	.013 (-)	.067	.002 (+)	.070
Manganese, dissolved	.982	.986	.103	.727	.849

Some of the following significant relations between selected metals and chemical variables are worth mentioning. The concentration of barium showed a significant positive relation with increasing pH and increasing concentrations of calcium and bicarbonate (table 7). Barium has been shown to be incorporated in calcite during coprecipitation reactions (Pingitore, 1986). This relation corresponds to the increase in the concentration of calcium and bicarbonate (alkalinity) with depth in the aquifer and suggests that in areas where ground-water flow is slow, calcium, bicarbonate, and barium are brought into solution by the dissolution of calcite. There is less exchange of water in these zones and as a result, the concentrations of these ions are higher than in areas where there is rapid exchange of water. Based on speciation calculations using WATEQF, over the range of pH values (6.3-7.3) measured in water for the aquifer, barium exists as Ba^{2+} .

Lead was the only trace metal whose concentration showed a significant positive relation with TOC (table 7). Stumm and Morgan (1981) report that lead shows a moderate affinity to form complexes with organic anions such as acetate, citrate, and phthalate. Assuming that TOC in some way represents the concentration of organic compounds that could chelate with a particular trace metal, then it is somewhat surprising that copper did not show a similar relation. It has been reported that the distribution of copper species is affected markedly by the formation of organic complexes (Stumm and Morgan, 1981).

The concentration of chromium in water for the aquifer shows a significant positive relation with pH (table 7). Chromium most likely occurs as the anionic species CrO_4^{2-} in aerobic freshwater (Stumm and Morgan, 1981) and, as a result, an increase in pH would not favor the formation of hydroxide complexes. The distribution of chromium species would also be affected by the redox condition of the water; however, information is lacking to properly evaluate this factor.

The association of barium, chromium, copper, and lead with hydrous oxides of iron and manganese has been demonstrated in a number of studies (Hem, 1976, 1977, 1980; Ku and others, 1978). Unfortunately, because multiple detection limits exist for iron and manganese as well as the other trace metals, the TOBIT procedure could not be used to evaluate a relation between the concentrations of iron or manganese and barium, chromium, copper, and lead. However, scatter plots (not presented) of detectable concentrations of barium, chromium, copper, lead, and manganese as opposed to the concentration of iron suggest that a positive relation may exist.

The type of casing material used in well construction may have an influence on the concentration of the selected trace metals in water samples from the aquifer. Previous studies have shown that certain types of casing material may release metallic contaminants into well water through leaching or corrosion (Miller, 1988). Another study (Cooper, 1986) found evidence for rapid adsorption of copper and lead from ground water on black iron casing material. Sufficient data exist for the comparison of median concentrations of the selected metals and three types of casing material for wells tapping the Biscayne aquifer: black iron, polyvinyl chloride (PVC), and stainless steel. Median concentrations, interquartile range (75th percentile concentration minus 25th percentile concentration), number of analyses, and percent of analyses below detection limits for each casing type are listed in table 8. The number of analyses for each metal for the different casing types is variable because there are missing analytical values in addition to concentrations below detection limit. It is important to note that the median concentrations for iron and manganese are nearly identical for black iron and PVC casing materials, although the interquartile range is higher for black iron than for PVC casing type. This suggests that iron is not being introduced to the water sample from most black iron cased wells. The lowest iron concentrations are observed for water from the wells with stainless steel

Table 8. Statistical summary of concentrations of selected trace metals in water from the Biscayne aquifer by the type of casing material

[N, sample size; IQR = interquartile range; concentration values are in micrograms per liter; PVC, polyvinyl chloride; percent of analyses below detection limit is indicated by parentheses]

Casing type	Barium			Chromium			Copper			Iron			Lead			Manganese		
	N	Me-dian	IQR ¹	N	Me-dian	IQR	N	Me-dian	IQR	N	Me-dian	IQR	N	Me-dian	IQR	N	Me-dian	IQR
Black iron	38	18.8 (34)	10.1	75	1.1 (35)	3.5	70	1.1 (39)	2.0	47	300 (30)	927	75	4.6 (17)	8.7	70	20.9 (0)	29.1
PVC	54	40.2 (30)	36.2	63	0.9 (56)	3.3	63	0.8 (68)	1.7	54	312 (22)	468	63	1.4 (49)	5.3	55	11.9 (20)	12.7
Steel	23	17.6 (8.7)	20.5	23	0.3 (78)	0.5	23	0.4 (70)	1.0	17	7.7 (82)	34.8	23	5.2 (26)	9.0	23	8.8 (4)	11.9

¹Interquartile range (IQR) - the difference between the 75th percentile and the 25th percentile.

casing. The median concentration of lead is highest for the stainless steel casing type, possibly indicating that leaching of lead from the casing material may be occurring. A comparison of median concentrations of chromium and copper for the different types of casing material cannot be made because of the high percentage of concentrations below the reported detection limits. These limited results indicate that with the exception of lead, there does not appear to be any relation between the type of casing material and the concentration of the selected trace metals in water from the Biscayne aquifer.

The high concentrations observed for chromium, copper, iron, lead, and manganese in water from the aquifer (maximum values in table 5) may be related to very local conditions, possibly the result of localized contaminant sources. In some areas, water from canals may introduce trace metals into the aquifer. Median, mean, standard deviation, and range of concentrations for barium, chromium, copper, iron, lead, and manganese in water taken from several canals in the study area during 1975-90 are listed in table 9. Median trace metal concentrations in water from canals (table 9) are higher than corresponding median trace metal concentrations in water from the aquifer (table 5). However, given the limited information on the hydrologic interaction between canal water and water in the aquifer, it is not possible at this time to determine if the occurrence of trace metals in the aquifer is directly influenced by canal water.

Table 9. Statistical summary of the concentration of selected metals in water from canals in southeast Florida, 1975-90

[All concentration values are in micrograms per liter; data are from U.S. Geological Survey WATSTORE data base]

Con-stituent	Sample size	Me-dian	Mean	Stand-ard divia-tion	Mini-mum	Maxi-mum
Barium, dissolved	46	36	44	23	5	100
Chromium, dissolved	20	3	6.2	8.7	1	40
Copper, dissolved	66	3	6.1	13	1	80
Iron, dissolved	83	100	143	167	4	1,240
Lead, dissolved	64	7	11	14	1	72
Manganese, dissolved	50	6	8.8	8.6	1	41

SUMMARY AND CONCLUSIONS

The major-ion and selected trace-element chemistry of the Biscayne aquifer was characterized from ground-water quality data collected from the Florida Ground-Water Monitoring Network Program. This network was established as part of a multiagency cooperative study delineating back-ground water quality for the major aquifer systems through-

out the State. The Biscayne aquifer, the principal source of drinking water in southeast Florida, is a wedge-shaped, unconfined, highly permeable limestone and sandstone aquifer. Transmissivity is very high, generally greater than 300,000 ft²/d but exceeds 1,000,000 ft²/d in some areas. Recharge to the aquifer occurs primarily from precipitation during June through October and infiltration from canal and conservation areas during November through May. Predevelopment flow patterns have been altered dramatically due to the numerous canals, well fields, water management practices, and water conservation areas.

Water sampled from 189 wells in the Biscayne aquifer was typically of a calcium-bicarbonate type. Other water types that were found less commonly included calcium-mixed anion, mixed cation-bicarbonate, and mixed. Water from one well exhibited a sodium-chloride water type. Water types other than calcium-bicarbonate occurred primarily where they were influenced by proximity to the coast, canals, or well fields.

Nonparametric (Spearman's rank order correlation) and parametric (paired t-test) statistical techniques were used to test for vertical and seasonal differences in ground-water chemistry, respectively. There was a significant decrease in potassium and nitrate concentrations with increasing well depth whereas calcium, sodium, bicarbonate, and dissolved solids concentrations in water increased significantly with well depth. Slower circulation at depth (greater residence time) may cause an increase in the concentration of these constituents. Major-ion concentration in analyses from 27 shallow wells (less than 30 feet deep) did not change significantly (0.05 significance level) with season.

Barium, chromium, copper, iron, lead, and manganese were detected in water from the aquifer in 50 percent or more of the analyses. The trace metals were analyzed by four separate laboratories, and, as a result, detection limits varied because of different analytical methods and laboratory practices. The median concentrations for each trace metal, except iron, were below the maximum contaminant levels or secondary maximum contaminant levels set by the U.S. Environmental Protection Agency.

No distinct areal pattern was evident for the concentration of any of the selected trace metals in water from the Biscayne aquifer. Also, no significant relation was observed for any of the trace metals with depth in the aquifer. Concentrations of iron above the secondary maximum contaminant level were observed in samples from wells at many locations throughout the entire aquifer, both areally and vertically. High iron concentrations in water from the Biscayne aquifer have also been reported by previous studies. Iron and manganese occur naturally in the aquifer as a result of chemical weathering of the limestone aquifer material and from recharge water that percolates through overlying soils that contain large amounts of extractable iron and manganese. The concentration of barium in the ground water is significantly related to the concentrations of calcium and

bicarbonate. This suggests that barium, a component of limestone, may be brought into solution when the rock dissolves during contact with ground water. The occurrence of lead, chromium, and copper in water from the aquifer may be related to localized sources of contamination (such as industrial or agricultural uses of these metals) or through canal-aquifer interactions.

Numerous canals in the study area may introduce trace metals into the aquifer. Median values for barium, chromium, copper, and lead for samples from canals in the study area are slightly higher than the corresponding median values for samples collected from the Biscayne aquifer. Because of limited information on canal-aquifer interactions, it is not possible at this time to determine to what extent trace-element concentrations in the aquifer are influenced by canal water recharge. Other possible sources for high trace-element concentrations in the aquifer are local contamination sources, well construction methods and materials, and natural dissolution of minerals with variable pH and redox conditions in the aquifer.

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