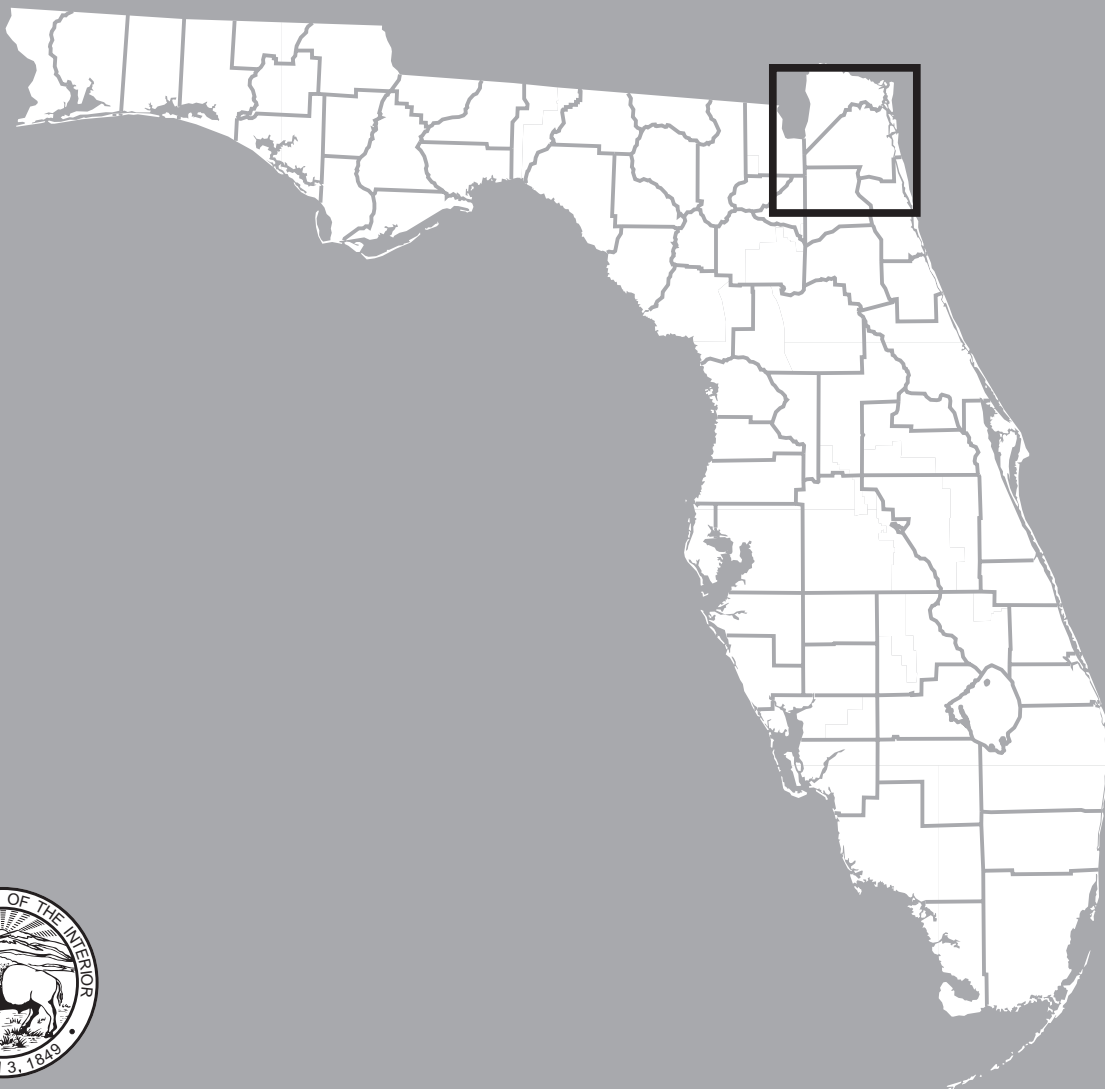


The Distribution of Bromide in Water in the Floridan Aquifer System, Duval County, Northeastern Florida

U.S. Geological Survey

Water-Resources Investigations Report 94-4154

Prepared in cooperation with the
City of Jacksonville, Florida



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By E.R. German *and* G.F. Taylor

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 94-4154

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Tallahassee, Florida
1995



U.S. DEPARTMENT OF THE INTERIOR

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U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, AND ACRONYMS

Multiply	By	To obtain
<u>Length</u>		
foot (ft)	0.3048	meter

Abbreviated water-quality units

BrO₃⁻ = bromate ion
HOBr = hypobromous acid
HOCl = hypochlorous acid
mg/L = milligrams per liter
O₃ = ozone
OBr⁻ = hypobromite ion

Acronyms

DBPs = disinfection by-products
MCL = maximum contaminant level
THM = trihalomethanes
USGS = U.S. Geological Survey

Symbols

< = less than
> = more than

The Distribution of Bromide in Water in the Floridan Aquifer System, Duval County, Northeastern Florida

By E.R. German *and* G.F. Taylor

ABSTRACT

Although Duval County, Florida, has ample ground-water resources for public supply, the potential exists for a problem with excessive disinfectant by-products. These disinfectant by-products result from the treatment of raw water containing low concentrations of bromide and naturally occurring organic compounds. Because of this potential problem, the relation of bromide concentrations to aquifer tapped, well location and depth, and chemical characteristics of water in the Floridan aquifer system underlying Duval County were studied to determine if these relations could be applied to delineate water with low-bromide concentrations for future supplies.

In 1992, water samples from 106 wells that tap the Floridan aquifer system were analyzed for bromide and major dissolved constituents. A comparison of bromide concentrations from the 1992 sampling with data from earlier studies (1979-80) indicates that higher bromide concentrations were detected during the earlier studies. The difference between the old and new data is probably because of a change in analytical methodology in the analysis of samples.

Bromide concentrations exceeded the detection limit (0.10 milligrams per liter) in water from 28 of the 106 wells (26 percent) sampled in 1992. The maximum concentration was 0.56 milligrams per liter. There were no relations between bromide and major dissolved constituents, well depth, or aquifer tapped that would be useful for determining bromide concentrations. Areal patterns of bromide occurrence are not clearly defined, but areas with relatively high bromide concentrations tend to be located in a

triangular area near the community of Sunbeam, Florida, and along the St. Johns River throughout Duval County.

INTRODUCTION

The city of Jacksonville, in Duval County, Florida, is a rapidly-growing area with an increasing need for potable water (fig. 1). Although water of good quality for public supply generally is available in the county, there is a potential for organic by-products to be produced in the finished water, resulting from the treatment of raw water. Known as DBPs (Disinfection By-Products), they result from chemical treatment of raw water containing low concentrations of naturally occurring organic compounds.

These by-products are of concern because many DBPs are known carcinogens, and others are suspected carcinogens. DBPs include trihalomethanes (THMs) and other products which commonly result from the treatment process in which raw water is disinfected with chlorine or ozone. Presently, water-quality standards are in effect only for total THM content. A maximum contaminant level (MCL) of 0.1 mg/L has been set by the Florida Department of Environmental Protection for total THM content in drinking water (Florida Dept. of State, 1993). The THMs included in this standard are bromodichloromethane, dibromochloromethane, tribromomethane (bromoform), and trichloromethane (chloroform).

As mandated by the 1986 Safe Drinking Water Act amendments, the U.S. Environmental Protection Agency currently is developing more strict standards for DBPs. In addition to lowering the present THM standard, the new regulations may include specific DBP compounds, including brominated species, making control of brominated DBPs an important aspect of water treatment.

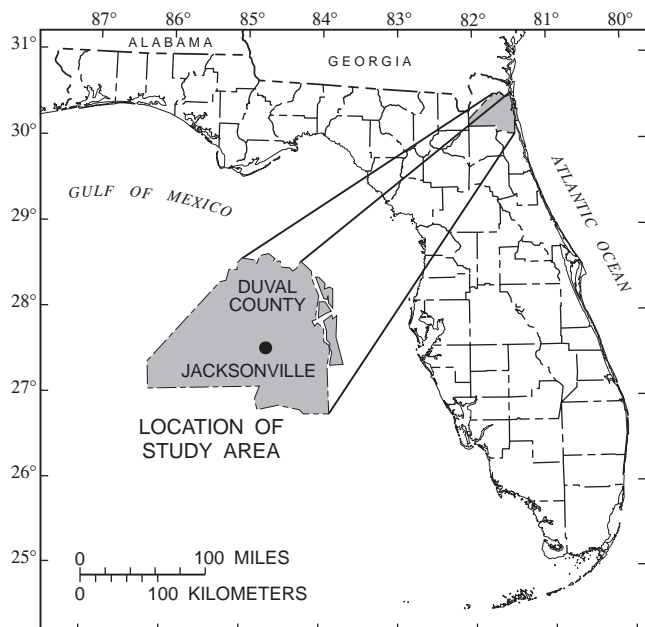


Figure 1. Location of the study area.

Because of the possibility of the formation of undesirable DBPs and the additional costs of removing them during water treatment, a knowledge of the distribution of bromide in waters of the Floridan aquifer system is desirable for resource management. Locations of future supply wells, for example, could then be selected to obtain water with minimum bromide concentrations. The distribution and concentrations of bromide in Duval County have not been documented, though historical data on bromide concentration are available as a result of past studies. However, the historical data are of limited usefulness because of possible bias in the method used to quantitatively determine bromide prior to 1984.

In 1992, the U.S. Geological Survey (USGS), in cooperation with the city of Jacksonville, sampled selected wells in Duval County for dissolved bromide, chloride, and other major constituents in an investigation to delineate the distribution of bromide in water in the Floridan aquifer system. The relation of bromide concentration to the aquifer tapped, well location and depth, and various chemical characteristics of water was studied to determine if these relations could be used to locate areas of relatively low-bromide concentrations.

Purpose and Scope

The purpose of this report is to describe the distribution of bromide in water in the Floridan aquifer system in Duval County, Fla. (fig. 1), and to present

the results of an investigation to determine relations between bromide concentration and selected variables. The description includes an evaluation of historical data to assess the reliability of the older data, because the historical bromide concentrations were determined using a different analytical method than the method used in 1992. Bromide concentrations are summarized by aquifer, and the areal distribution of bromide concentration is presented. The relation of bromide concentration to well depth and other more commonly determined water-quality characteristics are evaluated to determine if these relations could be used for estimating bromide concentration in water at locations that have some water-quality data, but no bromide data.

Water samples were collected from 106 wells tapping the Floridan aquifer system in Duval County during June-August of 1992. Wells were selected for sampling that would provide a wide and relatively uniform areal coverage and that would be representative of sampling a range of mineralization commonly encountered in potable supply wells. Bromide and chloride concentrations were determined in water samples from all wells; concentrations of major dissolved constituents were determined in samples from 86 of the wells. All references to bromide and major ions, except alkalinity, in the following sections refer to the dissolved concentrations.

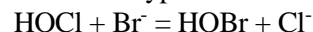
Background

Formation of brominated DBPs during routine drinking water treatment is the result of reactions of naturally occurring bromide ions in the water with chlorine or ozone. In the case of chlorination, the bromide ion (Br^-) is oxidized by hypochlorous acid (HOCl) to hypobromous acid (HOBr), which then may react with naturally occurring organic compounds to form bromoform and other brominated compounds. The reactions are as follows:

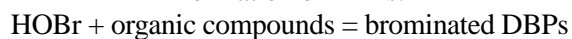
Chlorination of water:



Formation of hypobromous acid:

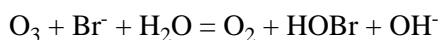


Formation of DBPs:

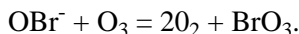


The use of ozone (O₃) for treating drinking water is becoming more prevalent as public utilities seek to minimize DBP formation with alternatives to chlorination. However, application of ozone is not without potential for formation of undesirable DBPs if the water contains trace levels of bromide. Ozone can oxidize bromide ions to hypobromous acid, leading to the formation of bromoform and other brominated compounds, as in chlorination. In addition, ozone can further react with the hypobromite ion (OBr⁻), formed by ionization of hypobromous acid, to yield the bromate ion (BrO₃⁻). The bromate ion is a possible carcinogen (Kurokawa and others, 1986). The reactions are as follows:

Formation of hypobromous acid:



Formation of bromate ion:



Bromide occurs naturally in low concentrations in water in the Floridan aquifer system, probably originating from seawater. The concentration of bromide in seawater is about 67 mg/L, and the concentration of chloride is about 19,000 mg/L (Hem, 1986), resulting in a mass ratio of about 0.0035. Various geochemical processes could result in the variation of bromide to chloride (and other ion) ratios in water in the Floridan aquifer system.

Methods of Investigation

Prior to sampling, all wells were purged by removing at least three casing volumes of water. If specific conductance, pH, or temperature of the purged water were still changing after three casing volumes had been removed, the well was further pumped (or allowed to discharge if free flowing) until these water-quality characteristics had stabilized or until five casing volumes of water had been removed. Sample bottles then were filled from the pump discharge. The points of sample withdrawal were as close to the wellhead as possible, and all samples were taken on the pump side of any pressure tanks or treatment points.

Samples for dissolved constituents were filtered through a 0.45-micron membrane filter and treated according to methods described in Fishman and

Friedman (1985). Samples for the determination of specific conductance and alkalinity were not filtered. All samples were analyzed in the USGS laboratory in Ocala, Fla.

HYDROGEOLOGY

Two aquifer systems are present in the study area. They are, in the order in which they would be penetrated by a well, the surficial aquifer system and the Floridan aquifer system. Separating the two aquifer systems are the clays, silts, and sands of the intermediate confining unit, which includes most of the Hawthorn Formation. The intermediate confining unit contains beds of lower permeability that confine the water in the Floridan aquifer system under artesian pressure. The Floridan aquifer system has three major water-bearing zones separated by less-permeable semiconfining units (Brown, 1984). All the geologic units in the study area yield some water to wells, but their water-bearing characteristics differ considerably. The major hydrogeologic units underlying the area, their stratigraphic equivalent, and their hydrologic properties are shown in figure 2.

The Floridan aquifer system, the principal source of ground water in northeastern Florida, underlies all of Florida and parts of Alabama, Georgia, and South Carolina. Most reports that describe the hydrogeology of northeastern Florida use the terms "Floridan aquifer" (Parker and others, 1955) or "the principal artesian aquifer" (Stringfield, 1966) to describe the water-bearing rocks herein referred to as the Floridan aquifer system. Miller (1986, p. B45) defined the Floridan aquifer system as a vertically continuous sequence of carbonate rocks of generally high permeability that are mostly of Tertiary age; the rocks are hydraulically connected in varying degrees, and their permeability generally is one or more orders of magnitude greater than that of rocks bounding the system above and below.

The Floridan aquifer system ranges from about 1,600 to 1,900 ft in thickness in the study area. The system is divided into two aquifers of relatively high permeability, referred to as the Upper Floridan and the Lower Floridan aquifers. In the study area, the Lower Floridan aquifer is further divided into two water-bearing zones. These aquifers are separated by a less permeable unit that restricts the vertical movement of water.

Series	Formation	Approximate thickness (feet)	Lithology	Hydrogeologic unit	Hydrologic properties	
Holocene to Upper Miocene	Undifferentiated surficial deposits	20-120	Discontinuous sand, clay, shell beds, and limestone	Surficial aquifer system	Sand, shell, limestone, and coquina deposits provide local water supplies.	
Miocene	Hawthorn Formation	100-500	Interbedded phosphatic sand, clay, limestone, and dolomite	Intermediate confining unit	Sand, shell, and carbonate deposits provide local limited water supplies. Low permeability clays serve as the principal confining beds for the Floridan aquifer system below.	
Eocene	Upper Ocala Limestone	100-350	Massive fossiliferous chalky to granular marine limestone	Floridan aquifer system	Upper Floridan aquifer	Principal source of ground water. High permeability overall. Water from some wells shows increasing salinity.
	Middle Avon Park Formation	700-1,100	Alternating beds of massive granular and chalky limestones, and dense dolomites		Middle semiconfining unit	Low permeability limestone and dolomite.
	Lower Oldsmar Formation	300-500			Lower Floridan aquifer	Upper zone
				Semiconfining unit		Low permeability limestone and dolomite.
					Fernandina permeable zone	High permeability salinity increases with depth.
Paleocene	Ceder Keys Formation	about 500	Uppermost appearance of evaporites; dense limestones	Sub-Floridan confining unit	Low permeability; contains highly saline water.	

Figure 2. Generalized geology and hydrogeology of Duval County, Florida (from Spechler, 1994).

The Upper Floridan aquifer in the study area corresponds to the Ocala Limestone and, in some areas, also includes the upper part of the Avon Park Formation. The top of the aquifer generally lies at greater depths in the northern part of the study area; the altitude at the top of the aquifer surface ranges from about 250 ft below sea level to more than 600 ft below sea level in several areas in central Duval County (Spechler, 1994).

The middle semiconfining unit separates the Upper and Lower Floridan aquifers and comprises beds of dense, relatively less-permeable limestone and dolomite of variable thickness and permeability. This unit generally is present in the upper part of the Avon Park Formation, and ranges in thickness from about 100 to 200 ft (Miller, 1986, p. B57).

Brown (1984, p. 15) recognized two major water-bearing zones within the Lower Floridan aquifer: the middle water-bearing zone and the lower water-bearing zone, referred to in this report as the upper zone of the Lower Floridan and the Fernandina

permeable zone, respectively (fig. 2). These zones are separated by another less permeable semiconfining unit.

In most of the study area, the upper zone of the Lower Floridan aquifer consists of approximately the lower two-thirds of the Avon Park Formation, which is composed of alternating beds of limestone and dolomite. Permeability in this zone is mostly related to secondary porosity developed along bedding planes, joints, and fractures. The unit is about 500 ft thick in the Jacksonville area and the top is about 950 to 1,400 ft below land surface (Krause and Randolph, 1989, p. 22). About half of the water pumped by large municipal and industrial wells in the Jacksonville area is from the upper zone of the Lower Floridan aquifer (Krause and Randolph, 1989, p. 22).

The Fernandina permeable zone is a high-permeability unit that lies at the base of the Floridan aquifer system in parts of southeastern Georgia and northeastern Florida (Miller, 1986, B70). Little is known about the extent or thickness of the Fernandina

permeable zone. Data from the few wells that have penetrated the zone in the study area indicate that the zone extends over the northern half of St. Johns and all of Duval and Nassau Counties. The thickness of the zone is estimated to be about 100 ft in the Jacksonville area.

BROMIDE DISTRIBUTION

Bromide concentrations and other water-quality data collected in June-August 1992 from the 106 wells in Duval County (fig. 3) are listed in the appendix. Well data also are listed in the appendix. In following sections of the report these data are summarized in three ways. Exploratory data analysis is used to describe the distribution of concentrations by aquifer. Correlation analysis and data plots are used to indicate the relation of bromide to other characteristics. Map-scale plots of bromide concentrations are used to depict areal patterns.

Comparison of Recent and Historical Bromide Data

Historical data (1979-80) on the concentration of dissolved bromide apparently are not comparable with recent data (1992) because of a change in 1984 in analytical methodology. The historical data have a tendency toward higher bromide concentrations, as indicated by a summary of bromide concentrations in water from 162 wells tapping the Floridan aquifer system in Duval County sampled in 1979-80 (fig. 4). The median of the historical bromide concentrations is 0.10 mg/L, whereas the median of the recent sampling of 106 wells in Duval County is <0.10 mg/L. The maximum concentration of the historical data was 2.3 mg/L, whereas the maximum of the recent data is 0.56 mg/L.

More specific evidence of the non-comparability of historical and recent bromide data is furnished by data for 35 wells that were sampled in 1979-80 and again in 1992 (fig. 4). Bromide concentrations were less than the detection limit in only 2 of the wells sampled in 1979-80 but were less than the detection limit in 21 of the 35 wells sampled in 1992. Of the 35 wells sampled twice, 27 had higher bromide concentrations in the earlier samples. The median concentration of the 1979-80 sampling was 0.20 mg/L, but <0.10 mg/L for the 1992 sampling.

It is not likely that bromide concentrations were lower in 1992 than prior to 1981, because there is no

reason to expect such a regional change. Further, other water-quality characteristics were nearly the same for both periods. For example, the median chloride concentration of water from 34 wells sampled both periods for chloride was 20 mg/L prior to 1981 and was 19 mg/L in 1992.

The reason for the differences in the bromide concentrations reported for the two periods probably is differences in the laboratory methods for sample analysis. Bromide concentrations in the water samples collected in 1979-80 were determined by the USGS laboratory in Atlanta, using the catalytic oxidation method (Skougstad and others, 1979, p. 329-330). This method is based on the catalytic effect of bromide on the oxidation of a known amount of iodide by potassium permanganate. The bromide concentrations in water samples collected in 1992 and presented in this report were determined by the USGS laboratory in Ocala, using a modification of the phenol-red method (American Public Health Association, 1992). In this method, bromide ions present in the water sample are oxidized to bromine, which then hydrolyzes to hypobromite. The hypobromite ion reacts with phenyl red to form a characteristically colored complex; the concentration then can be accurately determined with spectrophotometry. Determination of the reason for differences in concentrations reported by the two analytical methods is beyond the scope of this study. Further discussions of the distribution of bromide in this report are based only on the data collected in 1992.

The Frequency of Bromide Occurrence

In 1992, bromide concentration exceeded the detection limit (0.10 mg/L) in water from 28 of the 106 wells sampled (26 percent). The maximum concentration of bromide was 0.56 mg/L, and the median concentration was <0.10 (fig. 4).

A summary of the bromide concentrations by aquifer supplying water to the well indicates that 75 percent of the wells tapping only the Upper Floridan aquifer had bromide concentrations in water of about 0.13 mg/L or less, and more than 75 percent of the wells tapping both the Upper and Lower Floridan aquifers had concentrations in water less than 0.10 mg/L (fig. 5). The overall distribution of data indicates no difference in bromide concentration in water from wells tapping the Upper Floridan aquifer and water from wells tapping both the Upper and Lower Floridan aquifers. Six wells tap only the Lower Floridan aquifer, which is an insufficient number to assess aquifer-related differences in concentration.

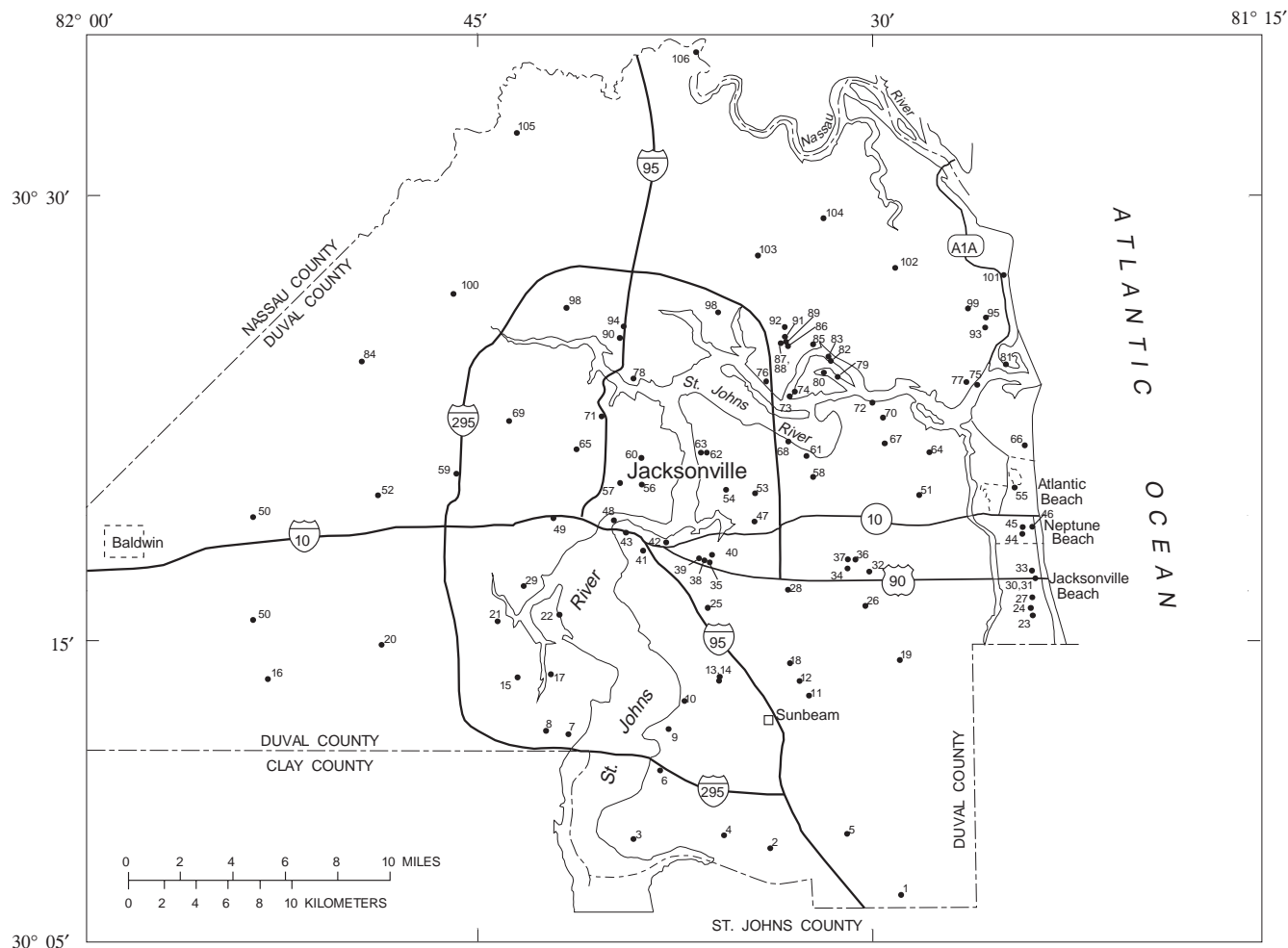


Figure 3. Location of wells that were sampled in 1992 for bromide concentrations, Duval County, Florida. (Map number is used to identify wells in the appendix.)

Relation of Bromide Concentration to Aquifer, Well Depth, and Chemical Characteristics

The single-variable relation of bromide concentration to well and casing depth, and to other chemical characteristics was investigated by applying the Spearman correlation analysis and by using graphical analysis. In the Spearman correlation analysis, data values (concentrations, well properties) are replaced with their ranks, with 1 representing the lowest concentration or value, and the total number of data values representing the highest concentration or value. The use of ranks, rather than raw data, makes the correlation procedure nonparametric, or unaffected by the distribution of the data.

Coefficients of determination and p-values for these coefficients were computed from the Spearman correlation analysis, and are given in table 1. The coefficients of determination indicate the fraction

of the variation in rank of the bromide concentration (the dependent variable) that is explained by the variation in rank of the other chemical characteristics or well properties (independent variables). The p-value is a probability representing the significance of the analysis, and is used to infer whether or not to reject the null hypothesis (no relation between bromide and the independent variable). In this report, the null hypothesis is rejected if the p-value is 0.05 or less, indicating that relations between bromide and the independent variable are considered to be real (statistically significant), rather than just due to chance.

The Spearman correlation analysis was done in two ways. First, all wells were used, even if bromide concentrations were undetectable. A mean rank was computed and used for all wells with undetectable bromide concentrations. The analysis then was repeated using only wells with detectable concentrations of bromide.

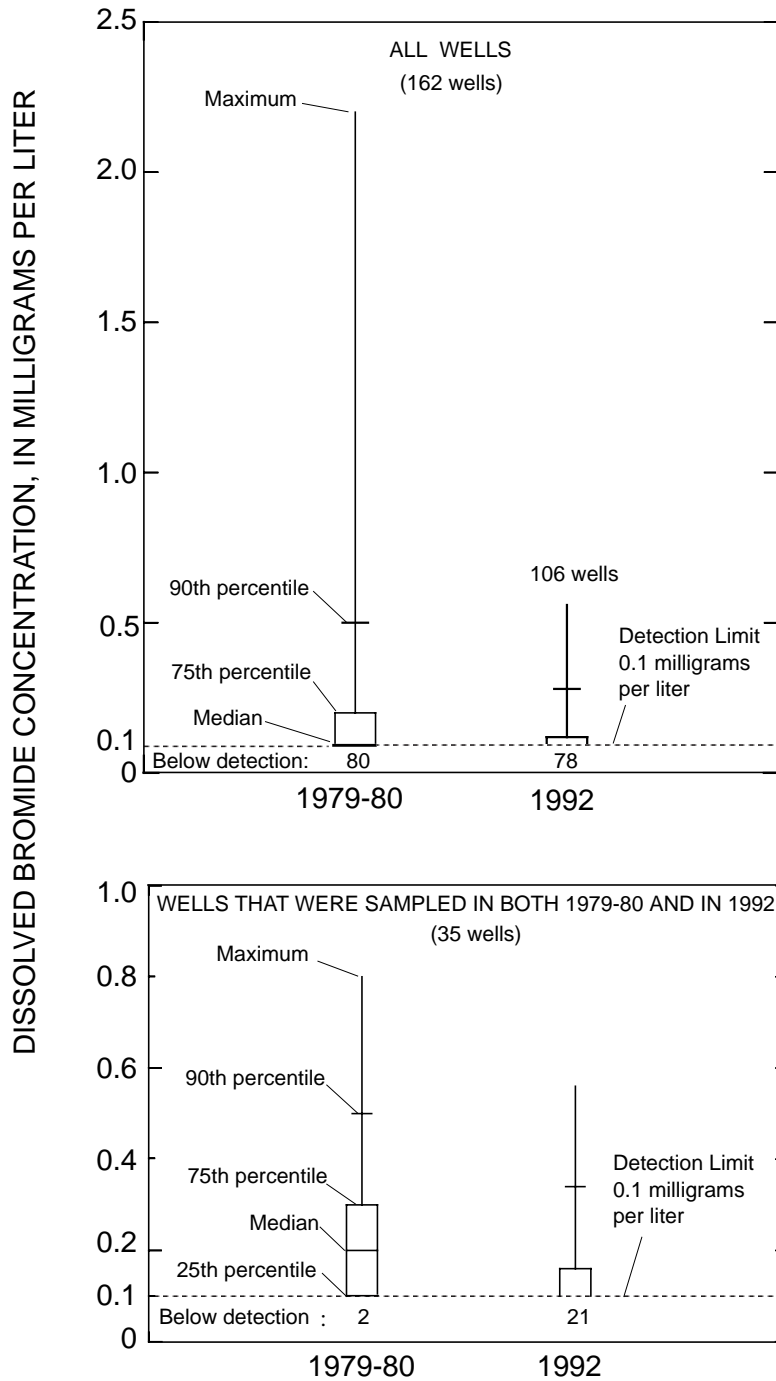


Figure 4. Summary of bromide concentration in water from wells tapping the Floridan aquifer system, 1979-80 and 1992, Duval County, Florida.

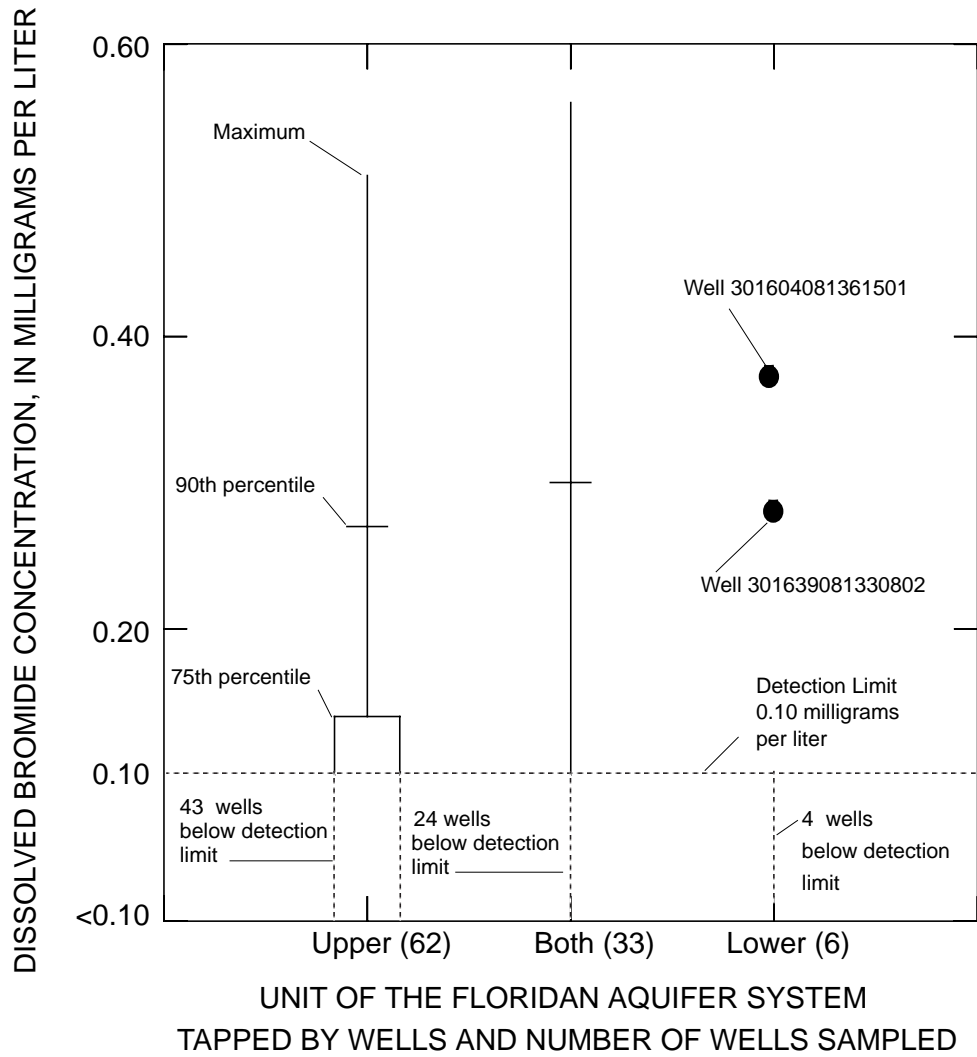


Figure 5. Summary of bromide concentration in water from wells tapping the Upper Floridan aquifer, both Upper and Lower Floridan aquifers, and the Lower Floridan aquifer, Duval County, Florida.

Table 1. Results of the Spearman correlation analysis of the relation of dissolved-bromide concentration to other chemical characteristics and to well properties

[The coefficients of determination indicate the fraction of the variation in rank of bromide concentration that is explained by variation in rank of the other chemical characteristics or well properties. The p-value is a probability representing the significance of the analysis. A p-value of 0.05 or less indicates a statistically significant relation. <, less than]

Chemical characteristic or well property	All samples		Only samples with detectable bromide	
	Coefficient of determination	p-value	Coefficient of determination	p-value
Calcium	0.04	0.03	0.23	<0.01
Magnesium	.02	.14	.18	.01
Sodium	<.01	.69	.16	.02
Potassium	.21	<.01	.15	.03
Alkalinity, total	.08	<.01	.04	.27
Sulfate	.03	.11	.04	.31
Chloride	.01	.22	.19	.01
Well depth	-.01	.28	.01	.54
Casing depth	-.01	.66	.03	.43

The correlation analysis using all samples, including those in which bromide was not detectable, indicates only relatively weak relations of bromide concentration to any of the independent variables. Bromide concentrations are significantly related (p-value <0.05) only to concentrations of calcium, potassium, and alkalinity. Of these, the relation between bromide and potassium explains most variation in bromide concentration, with a coefficient of determination of 0.21.

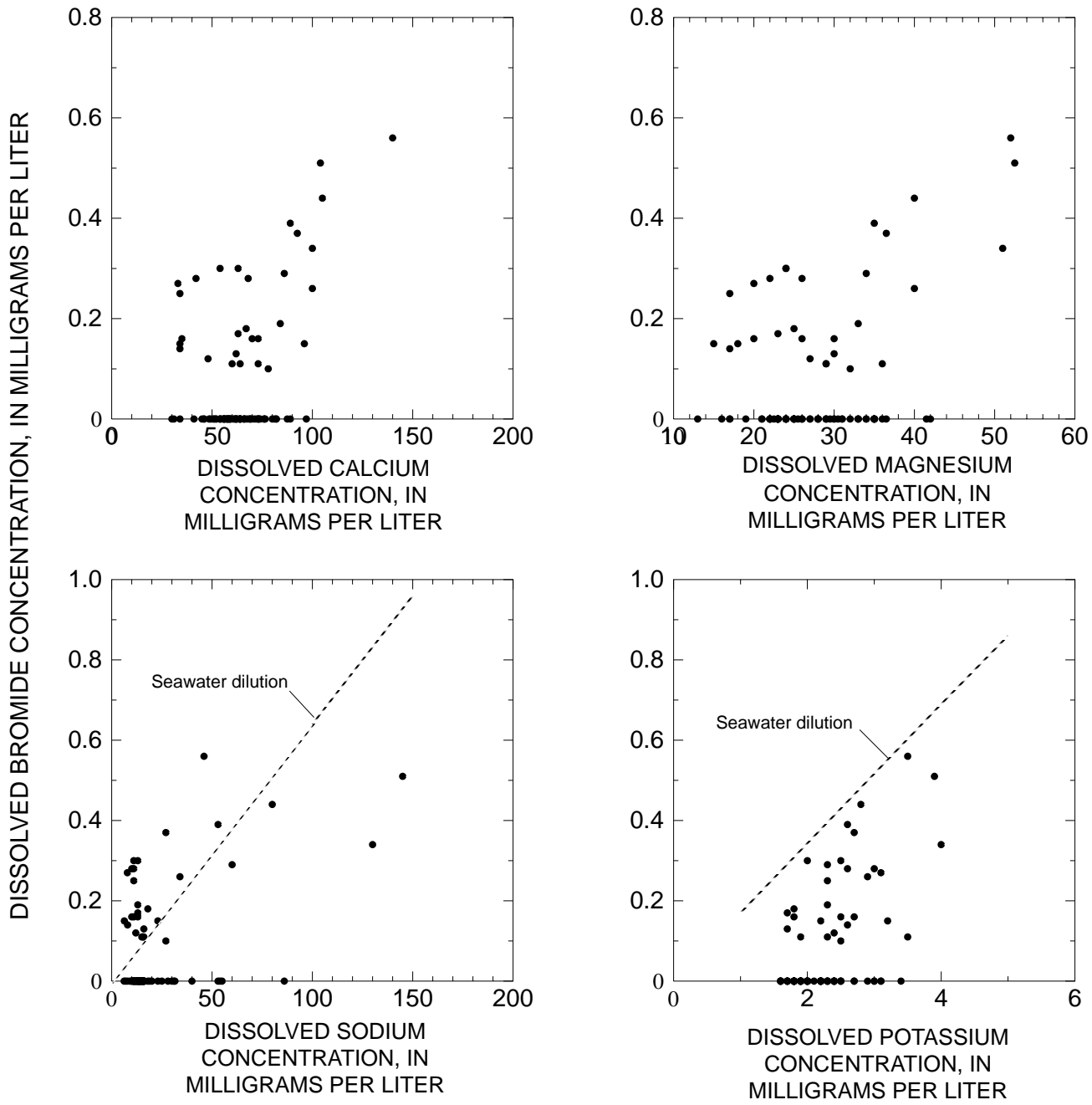
Excluding all samples with undetectable bromide concentration, the relation of bromide concentrations to the independent variables is still relatively weak. However, there are more statistically significant relations in this data set than in the data set that includes the wells with undetectable bromide. The relation of bromide concentration to calcium concentration accounts for the most variation in bromide concentration, with a coefficient of determination of 0.23.

Scatter-plots of bromide with concentrations of major cations (fig. 6), anions, and well depth (fig. 7) show the lack of a strong relation between bromide and the other characteristics. The plots indicate that waters containing high concentrations of sodium (>50 mg/L) or chloride (>100 mg/L) generally have bromide concentrations that are lower than would be expected if the waters were simple dilutions of seawater with rainwater (indicated by seawater dilution curve). Also, bromide concentrations are always lower in relation to the potassium content than would be expected based on dilutions of seawater. This indicates that the waters of the Floridan aquifer system are not always simple mixtures of seawater and freshwater

that are in contact with limestone, but may contain sodium, potassium, and chloride from other sources. Alternatively, sodium, potassium, and chloride from seawater are preferentially concentrated in the solid phase relative to bromide during precipitation of halite from seawater. Subsequent dissolution of the halite may result in waters with a lower ratio of bromide to chloride than is present in seawater. Regardless of the exact processes involved, the end result is that the relation of bromide to other dissolved constituents in the Floridan aquifer system is so variable that little relation is evident at the low concentrations of bromide in the aquifer system underlying the study area.

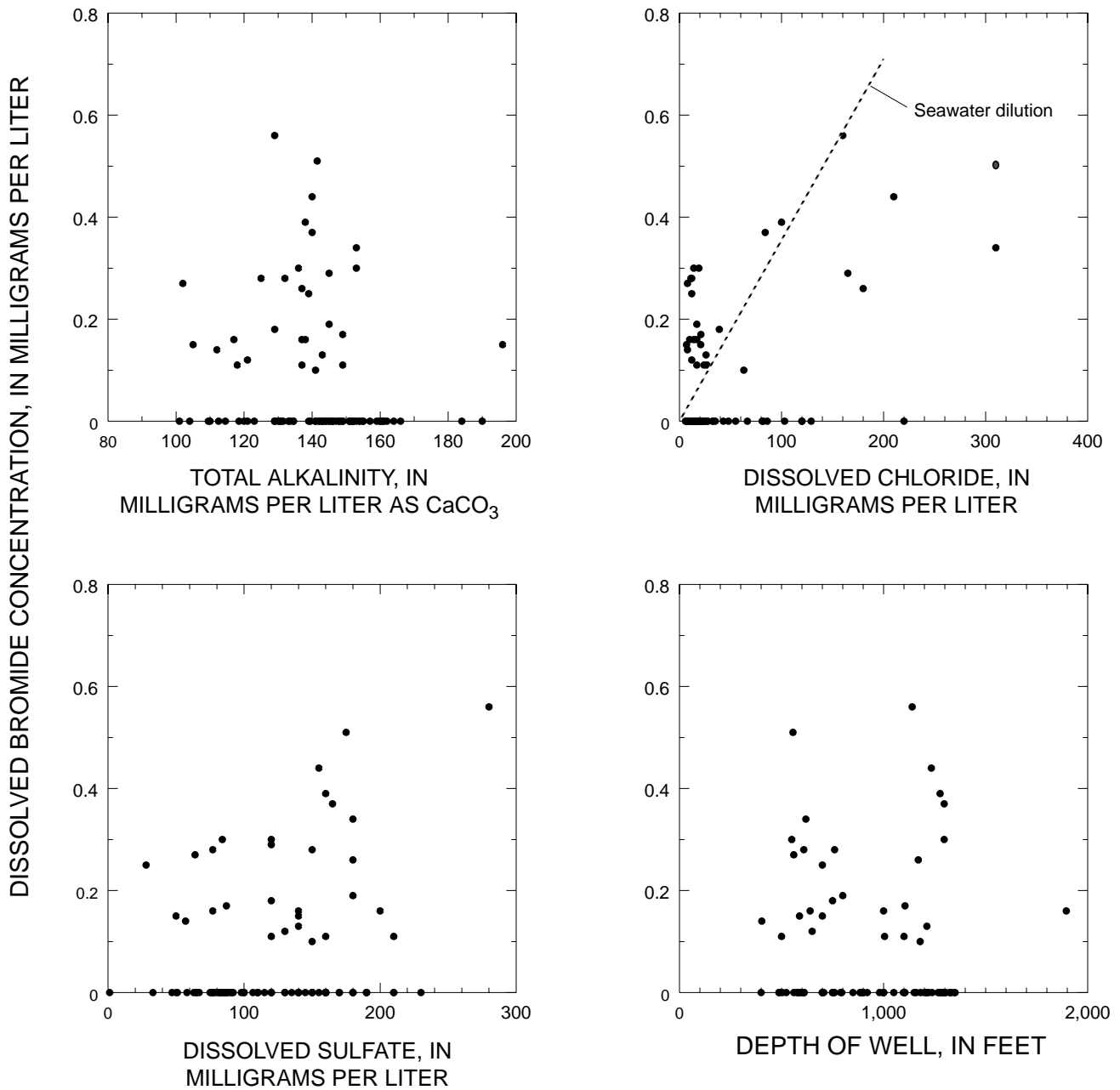
The major-ion diagrams of water samples containing detectable concentrations of bromide (fig. 8) indicate that waters where sodium plus potassium make up about 20 percent or more of the cations present, and chloride makes up about 30 percent or more of the anions present tend to have higher bromide concentrations (>0.25 mg/L). However, other waters with no detectable bromide concentrations may also have similar sodium plus potassium and chloride compositions (fig. 9). Therefore, a water type with relative high concentration of sodium plus potassium and chloride will not necessarily have detectable concentrations of bromide.

Multiple-regression analysis was used to determine if bromide concentrations were a function of the concentrations of two or more other constituents. The theory and use of multiple regression is discussed in many books on statistical analysis, for example, Draper and Smith (1981). Much more of the variation in bromide concentration was explained by application



[For clarity, bromide concentrations less than the detection limit (0.10 milligrams per liter) are plotted at 0.]

Figure 6. Relation of concentrations of bromide to calcium, magnesium, sodium, and potassium in water from 86 wells tapping the Floridan aquifer system, Duval County, Florida.



[For clarity, bromide concentrations less than the detection limit (0.10 milligrams per liter) are plotted at 0.]

Figure 7. Relation of concentrations of bromide to alkalinity, chloride, sulfate, and depth of well in water from 86 wells tapping the Floridan aquifer system, Duval County, Florida.

of a multivariable regression model than application of the single-variable correlation analysis. Using only samples with detectable bromide concentrations, modeling results indicated that including all of the major constituents as independent variables explained 75 percent of the variation in bromide concentration with a standard error of estimate of 0.068 mg/L. A plot of measured and simulated bromide concentrations indicates an acceptable fit between model simulated

and measured bromide-concentration data, but concentrations above 0.4 mg/L were overestimated in model simulation (fig. 10).

Although the multivariable model fits the samples with detectable bromide concentrations moderately well, it is not applicable to water with non-detectable concentrations of bromide (fig. 10). Bromide concentrations as high as 0.34 mg/L were simulated for samples with no detectable concentrations.

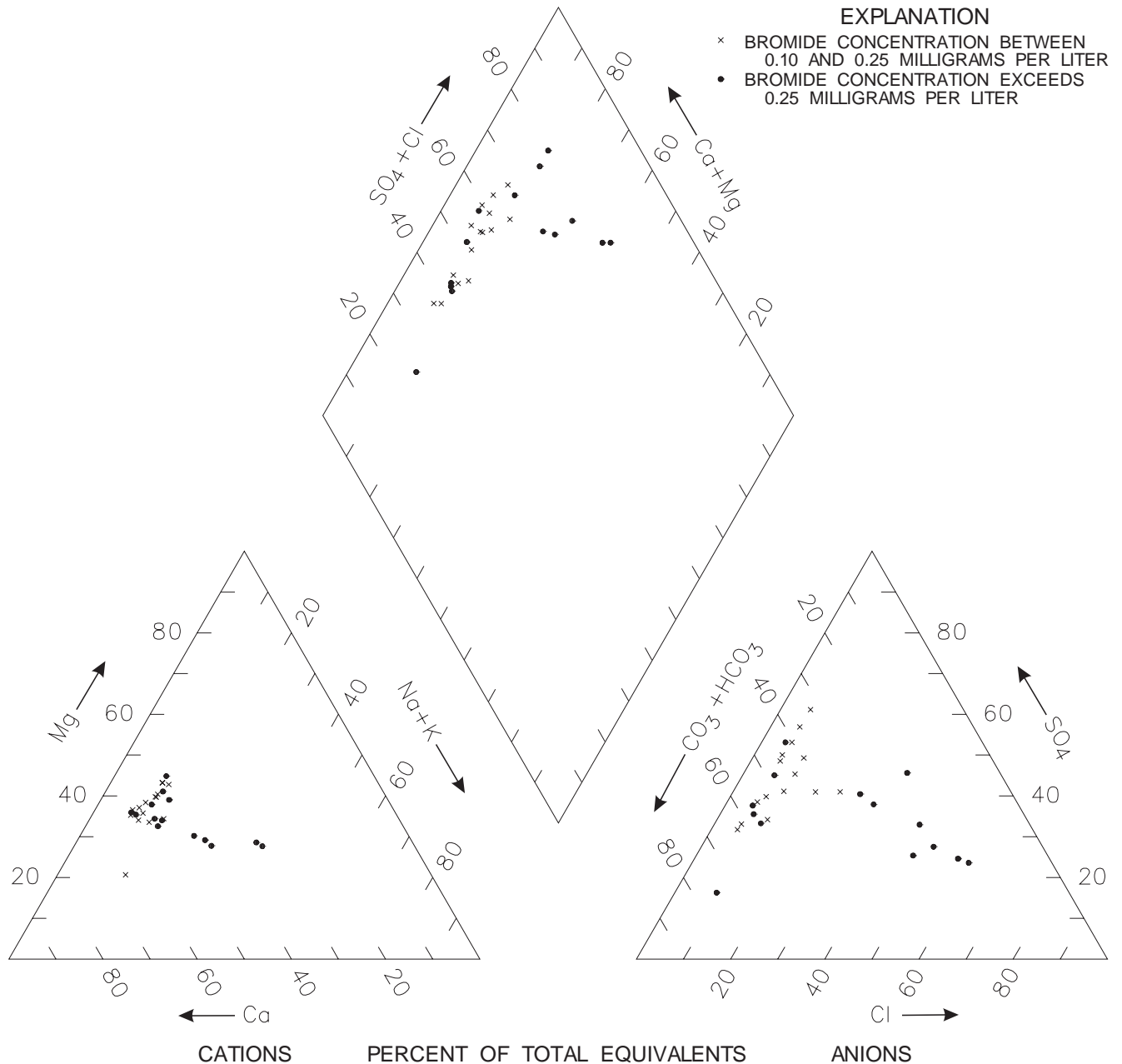


Figure 8. Major-ion composition of water samples from wells tapping the Floridan aquifer system with detectable dissolved-bromide concentrations, Duval County, Florida.

However, the agreement between simulated and measured bromide concentrations was good for simulated bromide concentrations exceeding 0.34 mg/L, though there is possibly a bias towards higher simulated concentrations. Thus, the model may be useful for simulating high concentrations (>0.34 mg/L) of bromide.

Logistic regression is a statistical technique for relating binary responses for a variable (such as detection or nondetection of bromide) to values of

independent variables, such as water-quality characteristics. The technique is discussed in many books on statistical analysis, for example, Hosmer and Lemeshow (1989). The logistic models evaluated for bromide give the probability of finding detectable concentration of bromide (>0.1 mg/L) as a function of concentrations of other constituents, using data for all wells sampled in 1992. In evaluating the logistic models, a simulated probability of 0.5 or higher was accepted as positive for detectable bromide.

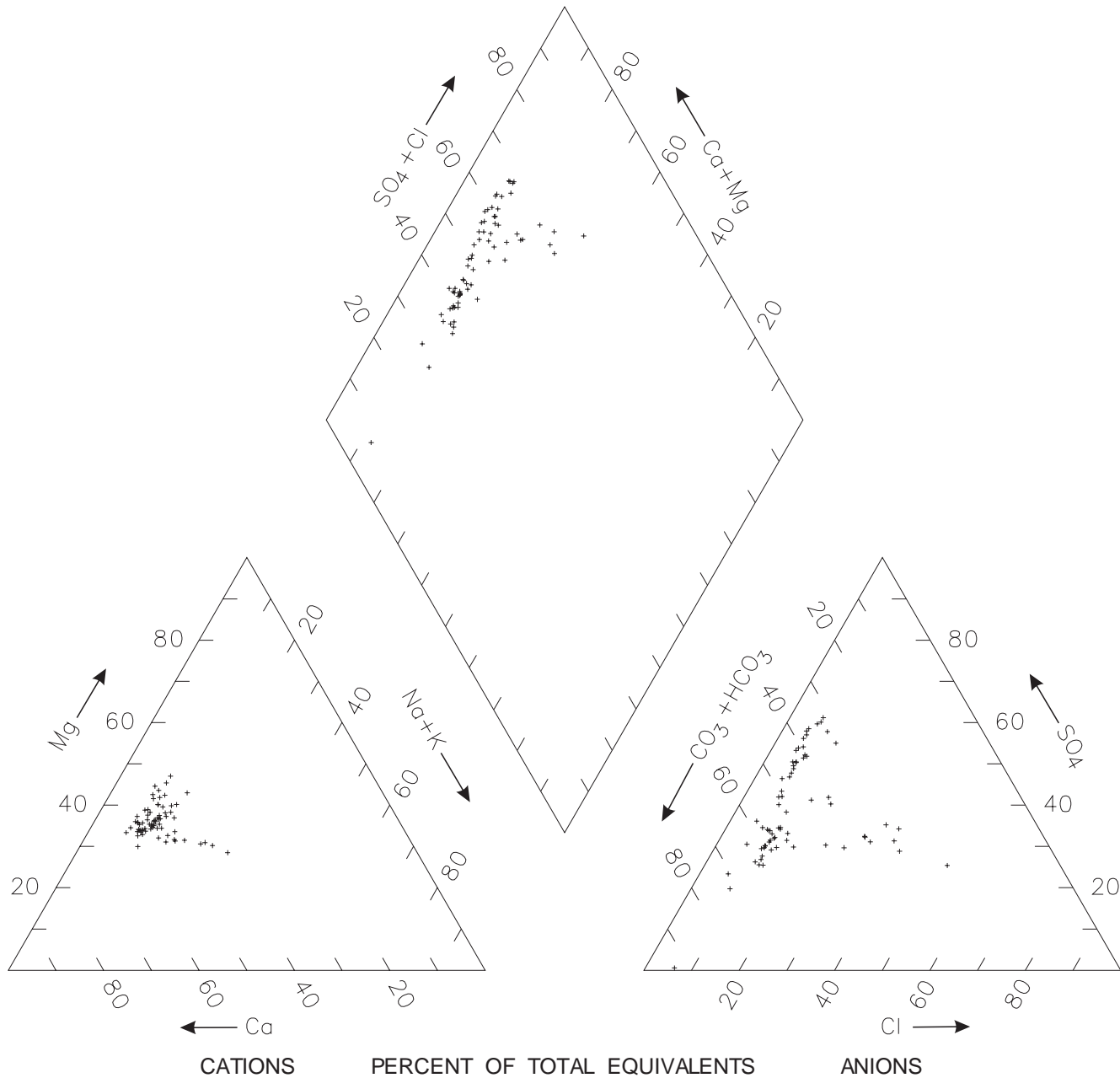
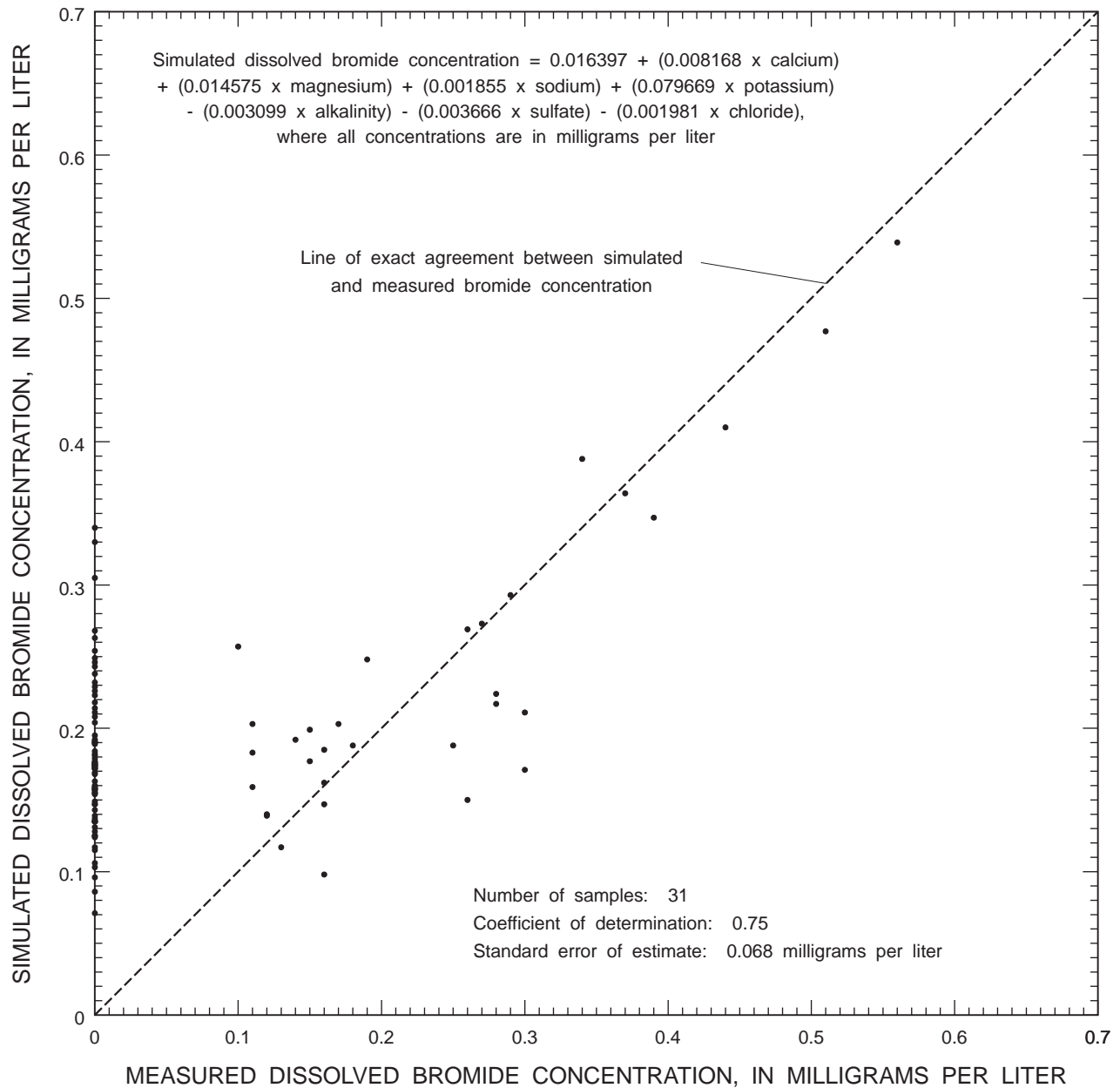


Figure 9. Major-ion composition of water samples from wells tapping the Floridan aquifer system with no detectable dissolved-bromide concentrations, Duval County, Florida.



(The model was developed using only samples with detectable concentrations of bromide, though all samples are plotted. For clarity, measured bromide concentrations less than the detection limit (0.10 milligrams per liter) are plotted at 0.)

Figure 10. Measured and model simulated bromide concentration.

Determining the wells with detectable concentrations of bromide by simulation with logistic models was not successful. A single-variable model with potassium concentration as the independent variable simulated detectable bromide concentrations in water from only 31 percent of the wells with measured detectable concentrations of bromide. Including all

cations and anions as independent variables (calcium, magnesium, sodium, potassium, alkalinity, chloride, and sulfate) in the logistic model improved the simulation accuracy somewhat, however detectable bromide concentration was simulated in water from only 41 percent of the wells with measured detectable bromide concentration.

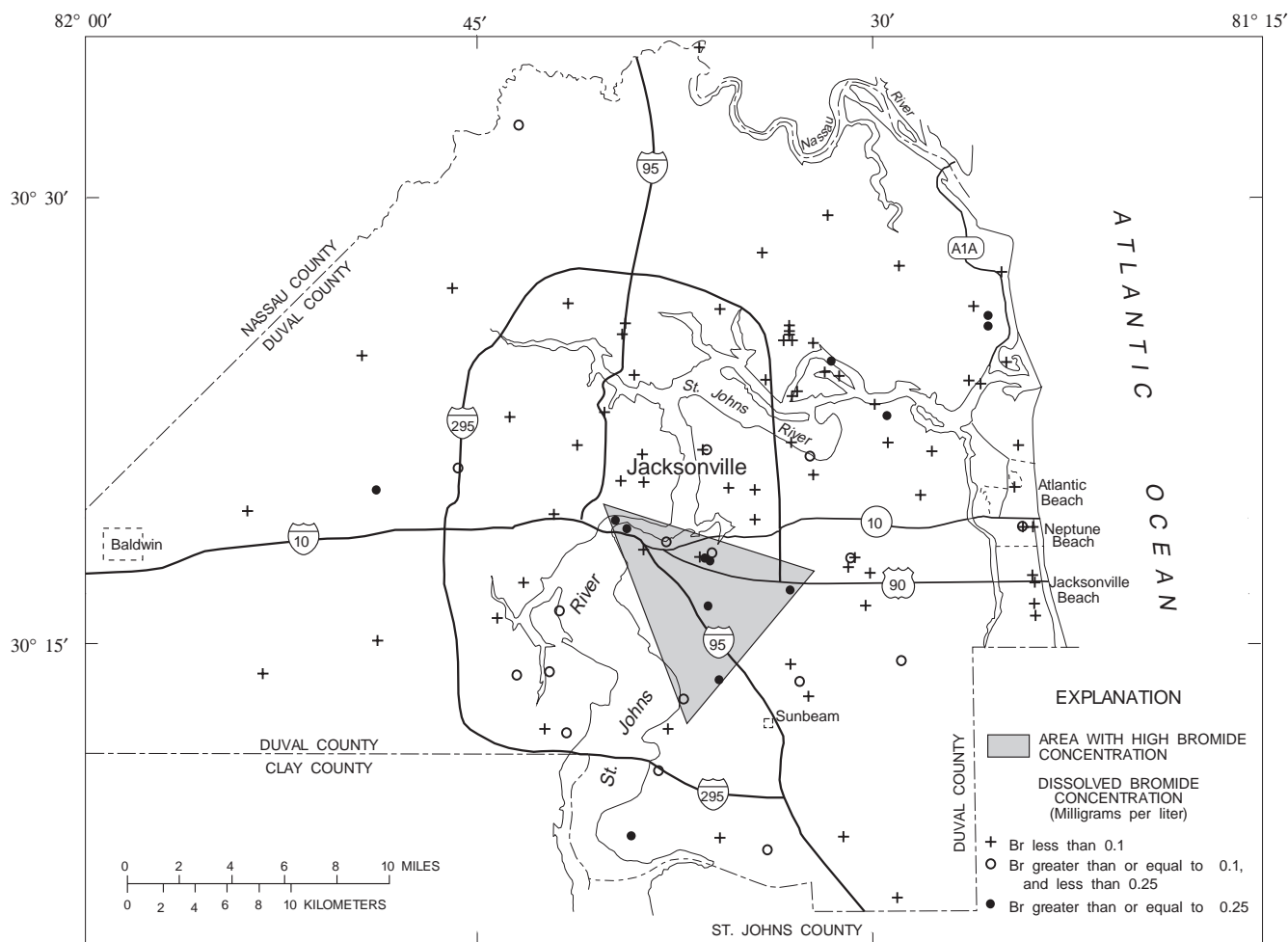


Figure 11. Areal distribution of bromide concentration in water in the Floridan aquifer system, July–August 1992, Duval County, Florida.

Areal Distribution of Bromide in Ground Water

Though the areal pattern of bromide concentrations in water in the Floridan aquifer system is not clearly defined, there are some indications of geographic areas with relatively high-bromide concentrations (fig. 11). A triangular area in which bromide concentrations generally were greater than 0.25 mg/L is located near the central part of the study area near Sunbeam. The area contains 13 wells, 8 of which yielded water containing more than 0.25 mg/L bromide, and 3 others which had detectable concentrations of bromide. Bromide concentrations were less than 0.1 mg/L in water from only two wells in the triangular area. Many of the wells along the St. Johns River also yielded water with detectable concentrations of bromide. Reasons for these areal patterns of bromide concentration are not obvious—they may be

related to faulting associated with the river channel or other features which could allow intrusion of higher-bromide water to the sampled wells.

SUMMARY AND CONCLUSIONS

Water of good quality for public supply generally is available in Duval County, northeastern Florida. However, the potential exists for a problem with the formation of excessive disinfectant by-products in finished water, resulting from the treatment of raw water containing low concentrations of naturally occurring organic compounds. Brominated disinfectant by-products, which may form in water containing trace quantities of bromide, are of particular significance because the brominated species may be assigned maximum contaminant levels that are even lower than those currently set for chloroform. In 1992, the USGS,

in cooperation with the city of Jacksonville, sampled selected wells in Duval County in an investigation to delineate the distribution of bromide in water in the Floridan aquifer system.

Two aquifer systems are present in the study area. They are, in the order in which they would be penetrated by a well, the surficial aquifer system and the Floridan aquifer system. Separating the two aquifers are the clays, silts, and sands of the intermediate confining unit, which includes most of the Hawthorn Formation. The Floridan aquifer system, which consists mostly of highly permeable carbonate rock, is the principal source of ground water in Duval County.

A total of 106 wells tapping the Floridan aquifer system were sampled and the concentrations of bromide and major dissolved characteristics were determined. A comparison of bromide concentrations from the 1992 sampling and from earlier studies in 1979-80 indicated that the earlier data had higher concentrations of bromide. The difference in the earlier and later data likely is because of a change in analytical methodology, but the reason for the differences is unknown.

In 1992, bromide concentrations exceeded the detection limit (0.10 milligrams per liter) in water from 28 of the 106 wells (26 percent) with the maximum concentration of 0.56 milligrams per liter. No indication is evident of a difference in bromide concentrations between wells open only to the Upper Floridan aquifer and those open to both the Upper and Lower Floridan aquifers.

Bromide concentration is related only weakly to well depth and concentrations of other constituents. There were no single-variable relations between bromide and major dissolved constituents, well depth, or aquifer that would be useful for predicting bromide concentrations. Much more of the variation in bromide concentration was simulated with a multivariate regression model than with the single-variable models, and may be useful for simulating relatively high concentrations of bromide (>0.34 milligrams per liter).

The areal distribution of bromide in waters of the Floridan aquifer system is not clearly defined, but higher than common concentrations were observed along the St. Johns River and in a triangular area near the community of Sunbeam.

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APPENDIX

Appendix--Chemical characteristics of water from wells in Duval County, Florida that were sampled in July--August 1992

[Well locations are shown in figure 3. All dissolved constituent concentrations are in milligrams per liter, except as indicated. Specific conductance is in microsiemens per centimeter at 25 °C. Total alkalinity is in milligrams per liter as calcium carbonate. Aquifer: U, Upper Floridan aquifer; L, Lower Floridan aquifer; B, both Upper and Lower Floridan aquifers. Depths are in feet below land surface. --, no data; <, less than]

Well identifier	Well number	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Alkalinity	Chloride	Sulfate	Bromide	Aquifer	Well depth	Casing depth
300622081284701	1	662	--	--	--	--	--	19.0	--	0.00	--	--	--
300756081335001	2	703	64	36.0	16.0	3.5	118	17.0	210.0	0.11	U	500	388
300812081390801	3	364	33	20.0	7.8	3.1	102	7.8	64.0	0.27	U	560	440
300820081354001	4	580	--	--	--	--	--	18.0	--	0.00	U	487	--
300824081305401	5	610	73	33.0	15.0	3.0	145	18.7	180.0	0.00	U	--	--
301032081380401	6	418	35	20.0	10.0	2.5	117	10.0	77.0	0.16	U	640	485
301144081413801	7	366	34	17.0	7.9	2.6	112	7.8	57.0	0.14	U	403	252
301152081423001	8	348	34	17.0	7.8	1.8	110	7.4	51.0	0.00	U	400	--
301157081374301	9	712	--	--	--	--	--	23.0	--	0.00	B	1,000	484
301255081371001	10	527	48	27.0	12.0	2.4	121	12.0	130.0	0.12	U	650	--
301305081321901	11	797	80	35.0	16.0	3.1	129	35.0	210.0	0.00	U	1,000	523
301333081324101	12	719	73	30.0	13.0	2.7	137	17.0	200.0	0.16	U	1,000	--
301335081355001	13	1,390	140	52.0	46.0	3.5	129	160.0	280.0	0.56	B	1,140	372
301337081354801	14	718	83	36.0	16.0	3.1	128	35.0	--	0.26	U	750	450
301339081433401	15	334	34	15.0	6.3	2.2	105	6.9	50.0	0.15	U	588	492
301339081531203	16	296	31	13.0	6.2	1.6	104	5.9	33.0	0.00	U	887	400
301347081421801	17	378	38	17.0	7.3	2.5	111	7.6	--	0.12	--	987	--
301409081330401	18	649	58	31.0	13.0	2.9	129	18.0	160.0	0.00	U	980	555
301415081284801	19	608	84	33.0	13.0	2.3	145	17.0	180.0	0.19	U	800	--
301450081485001	20	470	51	16.0	11.0	1.6	184	8.1	1.2	0.00	U	609	505
301537081441901	21	373	--	--	--	--	--	7.0	--	0.00	L	1,295	970
301551081415701	22	360	32	19.0	8.9	2.4	104	27.0	--	0.16	U	600	470
301552081234301	23	637	61	34.0	16.0	1.9	133	17.0	160.0	0.00	U	900	400
301604081234601	24	697	62	35.0	13.0	2.2	123	12.0	190.0	0.00	U	920	402
301604081361501	25	883	--	--	--	--	--	86.0	--	0.37	L	1,297	1,100
301607081301001	26	620	71	28.0	12.0	1.7	142	15.0	160.0	0.00	U	885	404
301620081234201	27	630	58	36.0	14.0	2.0	129	12.0	180.0	0.00	U	900	400
301639081330802	28	917	84	38.0	28.0	2.8	139	98.0	170.0	0.26	L	1,170	1,080
301648081431801	29	475	--	--	--	--	--	9.7	--	0.00	B	1,332	535
301657081233301	30	955	81	35.0	53.0	2.2	149	120.0	140.0	0.00	B	1,220	372
301704081233401	31	1,275	97	42.0	86.0	2.4	147	220.0	150.0	0.00	B	1,181	357
301715081300001	32	611	59	31.0	19.0	2.5	139	14.0	150.0	0.00	U	--	--
301716081234301	33	716	67	32.0	25.0	2.0	148	48.0	140.0	0.00	B	1,212	375
301725081305002	34	684	72	29.0	18.0	1.9	141	43.0	140.0	0.00	B	1,267	416
301740081361001	35	1,255	--	--	--	--	--	220.0	--	0.44	B	1,234	515

Appendix--Chemical characteristics of water from wells in Duval County, Florida that were sampled in July–August 1992—Continued

[Well locations are shown in figure 3. All dissolved constituent concentrations are in milligrams per liter, except as indicated. Specific conductance is in microsiemens per centimeter at 25 °C. Total alkalinity is in milligrams per liter as calcium carbonate. Aquifer: U, Upper Floridan aquifer; L, Lower Floridan aquifer; B, both Upper and Lower Floridan aquifers. Depths are in feet below land surface. --, no data; <, less than]

Well identifier	Well number	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Alkalinity	Chloride	Sulfate	Bromide	Aquifer	Well depth	Casing depth
301743081303501	36	817	82	33.0	40.0	2.2	141	103.0	150.0	0.00	B	1,097	442
301743081304701	37	785	83	33.0	27.0	2.5	141	73.0	160.0	0.10	B	1,179	423
301743081362301	38	1,308	110	42.0	85.0	3.2	140	230.0	160.0	0.39	B	1,277	547
301744081363301	39	986	--	--	--	--	--	130.0	--	0.00	B	1,301	549
301752081360501	40	672	--	--	--	--	--	27.0	--	0.11	U	1,005	534
301801081384302	41	641	--	--	--	--	--	14.0	--	0.00	B	1,348	504
301817081374901	42	600	70	26.0	11.0	1.8	138	14.0	140.0	0.16	B	1,895	752
301839081392101	43	583	63	24.0	11.0	2.5	136	13.0	--	0.30	B	1,297	552
301846081240201	44	633	62	30.0	16.0	1.7	143	26.0	140.0	0.13	B	1,212	388
301852081234201	45	399	56	28.0	13.0	2.4	101	13.0	170.0	0.00	U	585	357
301852081240301	46	627	64	34.0	12.0	1.9	130	14.0	170.0	0.00	U	1,050	--
301900081342801	47	299	15	12.0	24.0	1.5	39	59.0	--	0.00	U	635	520
301902081394601	48	590	68	26.0	10.0	2.6	125	11.2	150.0	0.28	U	760	510
301907081420901	49	587	66	26.0	10.0	2.3	131	12.0	140.0	0.00	B	1,324	594
301913081534601	50	360	34	17.0	11.0	2.3	139	12.0	28.0	0.25	U	700	466
301955081280601	51	629	64	24.0	14.0	2.7	143	15.0	160.0	0.00	U	523	410
301955081485701	52	468	42	22.0	11.0	3.0	132	12.0	77.0	0.28	U	609	525
301957081342301	53	798	--	--	--	--	--	86.0	--	0.00	B	1,150	576
302007081353201	54	836	92	34.0	30.0	2.2	145	98.0	120.0	0.00	B	1,350	606
302008081242101	55	630	61	35.0	11.0	1.8	120	11.0	180.0	0.00	B	1,300	407
302015081384501	56	518	55	21.0	12.0	1.9	151	16.0	86.0	0.00	B	1,286	531
302022081393501	57	639	--	--	--	--	--	12.0	--	0.00	L	1,275	800
302032081321001	58	757	73	28.0	31.0	1.9	143	78.0	110.0	0.00	--	1,160	--
302037081455301	59	305	96	18.0	23.0	3.2	196	20.8	140.0	0.15	U	700	500
302112081384701	60	380	30	19.0	12.0	1.9	121	15.0	47.0	0.00	U	750	535
302113081322301	61	632	67	25.0	18.0	1.8	129	47.0	120.0	0.18	--	750	--
302120081361801	62	541	63	23.0	13.0	1.7	149	21.0	87.0	0.17	B	1,105	703
302120081363001	63	549	64	23.0	14.0	1.7	151	22.0	91.0	0.00	B	1,300	619
302122081274001	64	573	66	23.0	13.0	1.8	149	16.0	120.0	0.00	U	490	--
302130081411802	65	563	--	--	--	--	--	13.0	--	0.00	B	1,280	530
302137081240001	66	624	70	26.0	13.0	2.2	142	15.0	150.0	0.00	U	575	--
302138081292301	67	664	66	27.0	16.0	2.4	146	27.8	130.0	0.00	U	900	419
302142081330701	68	602	69	25.0	13.0	1.7	144	15.0	140.0	0.00	U	610	522
302227081435001	69	613	--	--	--	--	--	11.0	--	0.00	L	1,326	1,154
302232081292901	70	1,041	--	--	--	--	--	170.0	--	0.29	U	--	--

Appendix--Chemical characteristics of water from wells in Duval County, Florida that were sampled in July–August 1992—Continued

[Well locations are shown in figure 3. All dissolved constituent concentrations are in milligrams per liter, except as indicated. Specific conductance is in microsiemens per centimeter at 25 °C. Total alkalinity is in milligrams per liter as calcium carbonate. Aquifer: U, Upper Floridan aquifer; L, Lower Floridan aquifer; B, both Upper and Lower Floridan aquifers. Depths are in feet below land surface. --, no data; <, less than]

Well identifier	Well number	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Alkalinity	Chloride	Sulfate	Bromide	Aquifer	Well depth	Casing depth
302236081401501	71	497	--	--	--	--	--	13.0	--	0.00	B	1,303	520
302300081295101	72	551	63	23.0	13.0	1.6	148	16.0	110.0	0.00	U	700	--
302317081330401	73	561	57	23.0	16.0	2.2	151	26.5	90.0	0.00	U	755	560
302323081324801	74	520	55	22.0	14.0	1.9	151	16.7	86.0	0.00	U	760	555
302339081254702	75	580	--	--	--	--	--	14.0	--	0.00	U	1,000	427
302344081340101	76	525	57	23.0	14.0	2.0	152	19.0	85.0	0.00	U	790	680
302345081261301	77	532	54	24.0	14.0	2.2	154	17.7	88.0	0.00	U	--	--
302351081390201	78	564	62	23.0	12.0	2.1	143	14.0	120.0	0.00	U	700	560
302357081311101	79	536	56	24.0	14.0	2.0	152	21.0	83.0	0.00	U	580	455
302405081314301	80	530	54	23.0	14.0	2.0	154	21.0	83.0	0.00	U	--	--
302422081244401	81	568	56	22.0	20.0	2.3	154	32.6	82.0	0.00	U	600	370
302426081312801	82	948	76	33.0	55.0	2.4	151	129.0	130.0	0.00	B	1,199	460
302428081313101	83	528	54	24.0	13.0	2.0	153	19.0	84.0	0.30	U	550	450
302428081493401	84	462	46	25.0	16.0	2.5	190	14.6	50.0	0.00	U	504	399
302502081321001	85	520	52	23.0	14.0	2.3	159	19.0	77.0	0.00	U	--	--
302502081330701	86	546	64	25.0	16.0	1.9	161	25.0	80.0	0.00	U	850	--
302503081332001	87	524	60	23.0	13.0	1.9	157	20.0	82.0	0.00	B	1,104	520
302505081331001	88	552	64	26.0	15.0	1.8	155	26.0	86.0	0.00	B	1,104	520
302511081331201	89	466	45	21.0	14.0	1.8	148	20.0	58.0	0.00	B	1,104	520
302514081393701	90	516	54	22.0	14.0	1.8	160	19.0	76.0	0.00	B	1,296	570
302519081331501	91	533	52	22.0	15.0	1.8	162	23.0	77.0	0.00	B	1,104	520
302536081331301	92	699	69	29.0	28.0	1.8	152	67.0	100.0	0.00	--	750	--
302538081253101	93	1,642	100	51.0	130.0	4.0	153	310.0	180.0	0.34	U	619	448
302538081392501	94	532	--	--	--	--	--	20.0	--	0.00	B	1,209	545
302557081253101	95	1,718	--	--	--	--	--	340.0	--	0.51	U	556	435
302608081354901	96	678	73	30.0	23.0	1.7	161	55.0	100.0	0.00	L	1,237	1,163
302608081354903	97	525	59	25.0	15.0	1.6	161	18.0	75.0	0.00	U	700	--
302616081413901	98	562	51	22.0	13.0	1.8	164	18.0	65.0	0.00	U	700	601
302618081261001	99	483	46	17.0	14.0	2.0	152	18.7	63.0	0.00	U	707	--
302647081460201	100	565	59	27.0	16.0	1.9	160	23.0	98.0	0.00	U	560	486
302724081244801	101	500	--	--	--	--	--	20.0	--	0.00	U	--	--
302738081290001	102	550	55	25.0	15.0	1.9	154	22.0	--	0.00	U	--	--
302805081341701	103	545	56	25.0	16.0	1.6	166	21.0	85.0	0.00	U	795	504
302919081314601	104	553	50	24.0	15.0	1.8	152	21.0	92.0	0.00	U	590	480
303216081433301	105	598	60	29.0	15.0	1.9	149	24.0	120.0	0.11	B	1,100	512

Appendix--Chemical characteristics of water from wells in Duval County, Florida that were sampled in July–August 1992—Continued

[Well locations are shown in figure 3. All dissolved constituent concentrations are in milligrams per liter, except as indicated. Specific conductance is in microsiemens per centimeter at 25 °C. Total alkalinity is in milligrams per liter as calcium carbonate. Aquifer: U, Upper Floridan aquifer; L, Lower Floridan aquifer; B, both Upper and Lower Floridan aquifers. Depths are in feet below land surface. --, no data; <, less than]

Well identifier	Well number	Specific conductance	Calcium	Magnesium	Sodium	Potassium	Alkalinity	Chloride	Sulfate	Bromide	Aquifer	Well depth	Casing depth
303458081364001	106	586	58	29.0	16.0	1.7	153	22.0	110.0	0.00	U	1,000	--
SUMMARY:													
Number of wells		106	86	86	86	86	86	106	80	106	--	97	80
Median		580	61	25	14	2.0	144	19	115	<0.10	--	920	508
Maximum		1,718	140	52	130	4.0	196	340	280	.56	--	1,895	1,163
Minimum		185	15	12	6.2	1.5	39	5.9	1.2	<.10	--	400	252